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UNIVERSITY OF CALIFORNIA
RIVERSIDE

Membrane Performance Enhancement Using Electrically Conducting Membranes

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Wenyan Duan

August 2016

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Dedication

This dissertation is dedicated to my parents. Although the Pacific Ocean separates us, you have always been there for me. Without your support and encouragement, I would have given up long ago.

ABSTRACT OF THE DISSERTATION

Membrane Performance Enhancement Using Electrically Conducting Membranes

by

Wenyan Duan

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, August 2016
Dr. David Jassby, Chairperson

Water shortage is a pervasive problem which has plagued societies for centuries. Recently, membrane technology has offered an effective and robust water treatment method for water sustainability due to great improvements in membrane performance. Depending on the intended applications, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO) membranes can be used individually or in combination to achieve a specific water quality goal. However, a major challenge facing these technologies is membrane fouling, where particulates in the feed stream are deposited or developed on the membrane surface during the filtration process. Membrane fouling results in performance deterioration, lifetime shortening, and ultimately, increased operational costs. Therefore, membrane cleaning and fouling control or prevention are critical research topics for membrane development.

The goal of this dissertation is to demonstrate fouling prevention and foulant removal on carbon nanotube-modified (CNT) electrically conductive UF, NF and RO membranes. First, mineral scaling was prevented and removed by applying an external anodic electrical potential to an electrically conducting CNT – polyamide RO membrane.

The results demonstrate that CaCO_3 scaling was efficiently removed by the intermittent application of 2.5V and CaSO_4 scaling can be prevented by the continuous application of 1.5V with the membrane as the anode. Second, biofouling and organic fouling were prevented while treating anaerobic sequencing batch reactor effluent by using electrically conducting UF and NF membranes. The continuous application of negative 5V to the UF membrane surface prevents organic fouling and allows good membrane performance while treating complex wastewater streams for long periods of time. The application of positive potentials to the NF membranes has also been shown to increase fouling and hinder cleaning and recovery. Third, a highly conductive and anodically stable polyaniline coated UF membrane was designed and used as a flow through electrode. Results show that the polyaniline coated CNT membrane had a significantly reduced degradation rate under high anodic potentials in a pH controlled environment when compared with polyvinyl alcohol crosslinked CNT membrane. The modified membrane can be used to degrade organic compounds and perform *in situ* oxidative cleaning of the fouled membrane without any additional oxidizing chemical reagents.

Table of Contents

Acknowledgements.....	iv
Dedication	vi
List of Figures.....	xii
List of Tables	xix
Chapter 1	1
Introduction	1
1.1 Water Crisis	2
1.2 Membrane Technology.....	4
1.3 Fouling Prevention by the Application of Electricity	11
1.4 Carbon Nanotube Based Electrically Conducting Membranes.....	13
1.5 Fouling Prevention and Mitigation Mechanisms of Electrically Conductive Membrane	14
1.6 Research Objectives	20
Chapter 2	22
Electrochemical Mineral Scale Prevention and Removal on Electrically Conducting Carbon Nanotube – Polyamide Reverse Osmosis Membranes	22
2.1 Introduction.....	23
2.2. Materials and Methods	25
2.3 Results and Discussion	29
2.4 Conclusions.....	44

Chapter 3	46
Treating Anaerobic Sequencing Batch Reactor Effluent with Electrically Conducting Ultrafiltration and Nanofiltration Membranes for Fouling Control	46
3.1 Introduction.....	47
3.2 Materials and Methods	50
3.3. Results and Discussion	57
3.4 Conclusions.....	71
3.5 Acknowledgements	72
Chapter 4	73
Polyaniline-Coated Carbon Nanotube Ultrafiltration Membranes: Enhanced Anodic Stability for <i>in Situ</i> Cleaning and Electro-Oxidation Processes	73
4.1 Introduction.....	74
4.2 Experimental Section.....	78
4.3 Results and Discussion	83
4.4 Conclusions.....	104
4.5 Acknowledgments.....	105
Chapter 5	106
Summary and Conclusions.....	106
5.1 Electrochemical Mineral Scale Prevention and Removal on Electrically Conducting Carbon Nanotube-Polyamide Reverse Osmosis Membrane.....	107

5.2 Treating Anaerobic Sequencing Batch Reactor Effluent with Electrically Conducting Ultrafiltration and Nanofiltration Membranes for Fouling Control	109
5.3 Enhanced Anodic Stability of Polyaniline-Coated Carbon Nanotube Ultrafiltration Membranes and Their Applications.....	111
Appendix	114
Appendix A: Supporting Information for Chapter 2	114
Appendix B: Supporting Information for Chapter 3.....	122
Appendix C: Supporting Information for Chapter 4.....	124
Reference.....	134

List of Figures

Figure 1. Membrane cut-off characteristics	5
Figure 2 Schematic of electrical double layer in a liquid in contact with a negatively charged surface (borrowed from Rodrigo F.V. Romo and M. Michael Pitts[55])	15
Figure 3. (Left) SEM image of surface of PA-CNT RO membrane; (Right) AFM map shows roughness according to the software RMS is 91nm on 2.5 by 2.5 μ m spot.	30
Figure 4. ATR-FTIR spectra of the electrically conducting RO membrane	31
Figure 5. CaCO ₃ scaling experiment; flux declined as CaCO ₃ scale developed on the membrane surface. When a 2.5V potential (designated by a red circle) was applied (membrane as anode), and the membrane was flushed at high velocities, flux was fully recovered.	32
Figure 6. A) Electrically conducting RO membrane surface area after the application of 2.5V; the white area, corresponding to areas still covered by CaCO ₃ is greatly reduced; B) Membrane area fully covered by CaCO ₃ scale; C) SEM of membrane surface after the application of 2.5V displaying few CaCO ₃ crystals; D) Thick CaCO ₃ deposits on fouled membrane surface (no voltage applied).	34
Figure 7. Flux decline due to CaSO ₄ scaling with no in-line filter; membrane was used as an anode with a cross-flow velocity of 4.5 cm s ⁻¹	36
Figure 8. Flux decline due to CaSO ₄ scaling with in-line 0.5 μ m filter and a cross-flow velocity of 3.4 cm s ⁻¹	36

Figure 9. SEM images of the membrane surface covered by CaSO_4 crystals; CaSO_4 scale morphology changes as a function of the applied potential. Top images are from the “transition” zone and bottom images are from the main part of the membrane (see Figure A-8 in the Appendix for a detailed description of membrane zones).	37
Figure 10. MPB model results; A) potential drop as a function of membrane surface potential and distance from the membrane surface; B) Concentrations of SO_4^{2-} ions as a function of membrane surface potential and distance from membrane surface. C) Concentration of Ca^{2+} ions as a function of membrane surface potential and distance from membrane; D) ratios between SO_4^{2-} and Ca^{2+} ions as a function of surface potential and distance from the membrane surface	42
Figure 11. As the applied surface potential increases, the region near the membrane where only SO_4^{2-} ions exist expands out into the solution, which pushes the nucleation zone away from the membrane surface.	43
Figure 12. System schematic and process diagram for an aSBR coupled to a UF and NF membrane process.	53
Figure 13. SEM images of (a) UF membrane surface, and (b) NF membrane surface. AFM images of (c) UF membrane surface, and (d) NF membrane surface. AFM images were used to calculate the surface roughness of the membranes.	59
Figure 14. (a) aSBR performance in terms of COD removal, TSS and turbidity of decanted effluent. Data is presented from day 180 onward; prior to this time, reactor performance was highly variable, and the data is not displayed. (b) SEM	

image of fouled UF membrane, which was used to filter anaerobic reactor effluent. Red circles indicate bacteria; inset: bare (clean) PVA-CNT UF membrane (c) HPLC analysis at different experimental points with identifiable peaks. The black line corresponds to the reactor feed, the red line corresponds to the reactor contents after 5 hours of operations, and the blue line corresponds to the decanted reactor effluent. Peak identities were confirmed by injecting pure standards.61

Figure 15. HPLC analysis of benzyl alcohol and benzoic acid concentrations measured at different experimental points. HPLC measurements were done in triplicate with error bars representing 95% confidence intervals.62

Figure 16. Impact of applied electrical potential on the required pressure to maintain a steady flux with (a) constant feed concentrations, and (b) system operated at 90% recovery. Experimental conditions were: aSBR effluent as feed, cross flow velocity of 20 cm/s, constant flux of 30 LMH (a) and 40 LMH (b). Electrical potentials in the figure represent the whole cell potential (potential difference between membrane (used as cathode) and counter electrode (anode)). In (a), blue (triangle) and red (cycle) lines represent the case where the membrane was used as a cathode with 5 V and 3 V applied to the membrane and counter electrode, respectively; the black (square) line corresponds to the control (0 V). In (b), the red (cycle) line corresponds to the case where the membrane was used as a cathode (5 V) and the black (square) line represents the control (0 V). All

experiments were done in triplicate, with error bars representing 95% confidence intervals.64

Figure 17. Treating aSBR effluent with electrically conducting UF membranes. (a) Flux as a function of feed concentration (up to 90% recovery). (b) Pressure required to maintain a given flux under different electrical conditions when system was operated at 90% recovery. Experimental conditions were: aSBR effluent as feed, cross flow velocity of 20 cm/s, membrane was backwashed with permeate every 30 minutes for 1 minute. Red (cycle) line represents conditions when membrane was used as cathode with 5 V applied to the membrane/counter electrode; blue (triangle) line represents conditions when the membrane was used as a cathode (5 V) and as an anode (1.5 V) during backwashing events; black (square) line represents the control (0 V).66

Figure 18. COD concentrations measured in the different UF streams. Measurements were triplicated, with error bars representing 95% confidence intervals.67

Figure 19. Fouling of electrically conducting NF membranes under different applied potentials. Experimental conditions: feed water was UF permeate, cross flow velocity was 20 cm/s, pressure was 180 psi. The red (cycle) line corresponds to conditions when the membrane was used as an anode (1.5 V); the blue (triangle) line represents conditions when the membrane was used as a cathode (5 V); the black (square) line represents the control (0 V).69

Figure 20. NF membrane recovery. Recovery was performed by flowing DIW over the membrane at 20 cm/s at a pressure of 180 psi while measuring flux. Red

(cycle) line represents conditions when membrane was used as anode (1.5 V); blue (triangle) line represents conditions when membrane was used as cathode (5 V); black (square) line represents the control (0 V). Experiments were duplicated with error bars representing 95% confidence intervals.	70
Figure 21: ECM structure and surface morphology. (Top) Cross-sectional images of ECMs. (Middle) Top-view of ECM surface. (Bottom) ECM surface topography by atomic force microscopy. Scale bars for all SEM images are 2 μm	87
Figure 22: Representative FTIR scans of PVA-CNT and PANI-CNT ECMs. Arrows indicate the 2° amine (1035-1095 cm^{-1}) and the nitrogen carbon double bond ($\sim 1650 \text{ cm}^{-1}$) typical of the emeraldine form of PANI; the chemical structure of the emeraldine form of PANI can be seen in the upper right corner of the figure.	89
Figure 23: Representative images of PANI-CNT ECMs surfaces fabricated using different current densities. Membranes were electropolymerized using sulfuric acid as the acid dopant. Scale bars for all SEM images are 500 nm. (A) Bare CNT; (B) PANI-CNT 0.25 mA cm^{-2} ; (C) PANI-CNT 0.9 mA cm^{-2} ; (D) PANI-CNT 1.5 mA cm^{-2}	90
Figure 24: Rejection of polymers by different ECMs ; Rejection data of PEG 20 kDa, PVA 50 kDa, PVA 100 kDa and PVA 150 kDa for PANI-CNT ECMs made in H_2SO_4 (black), HCl (red), oxalic acid (blue), and PVA-CNT (green) ECMs. ...	92
Figure 25: Stability of ECMs in response to chlorine exposure (500 ppm sodium hypochlorite solution), expressed as normalized changes in membrane electrical	

resistance over exposure time. Color bars represent membrane resistivity of each membrane type. Error bars represent 95% confidence intervals.94

Figure 26: PANI-CNT membrane stability under anodic conditions. (A) CV scans of PANI-CNT and PVA-CNT membranes (20 cycles); scan rate was 0.01 V/s in a 10 mM NaClO₄ solution. PVA-CNT voltammogram is shown in red, PANI-CNT in black. The total surface area of the anode was 4 cm². (B) Normalized current changes when a constant anodic potential of 2, 2.5, 2.8, 3 and 5 V (vs. Ag/AgCl reference electrode) was applied to PANI-CNT ECMs and constant anodic potentials of 3 and 5 V (vs. Ag/AgCl reference electrode) were applied to PVA-CNT ECMs; the reaction time was 10 min in a PBS buffer (10 mM Na₂HPO₄, 1.8 mM KH₂PO₄). The total surface area of the membrane anode was 8 cm². (C) Normalized current changes when a constant anodic potential of 2.5, 2.8 V (vs. Ag/AgCl reference electrode) was applied to PANI-CNT ECMs and constant anodic potentials of 2.8 V (vs. Ag/AgCl reference electrode) was applied to PVA-CNT ECMs; the reaction time was 180 min in a PBS buffer (10 mM Na₂HPO₄, 1.8 mM KH₂PO₄). The total surface area of the membrane anode was 8 cm². (D) Changes in resistance for PVA-CNT (black line) and PANI-CNT (red line) ECMs after applying 1, 2 and 3 V (vs Ag/AgCl) to the membrane's surface for 10 min in 80 ml of in PBS buffer (10 mM Na₂HPO₄, 1.8 mM KH₂PO₄). (E) Images of the ECMs after exposure to 3.5 V (vs. Ag/AgCl) for 20 min. (F) TOC and TN_b degradation percentage of PVA-CNT and PANI-CNT

ECMs after applying 1, 2 and 3V (vs. Ag/AgCl) to the membrane's surface for 20 min in 40 ml of PBS buffer (10 mM Na₂HPO₄, 1.8 mM KH₂PO₄).99

Figure 27: Electrochemical cleaning of fouled membranes (A) PANI-CNT ECM flux recovery under different flow condition. The blue line represents the initial flux of the unfouled membrane, the gray line represents the fouled membrane flux at crossflow conditions and the black line represents membrane flux after 5 min backwashing cycles with permeate (orange circles mark the backwashing events) (B) Flux recovery at three cycles of continues BSA fouling and electrochemical cleaning 3V for PANI-CNT ECMs (black) and PVA-CNT ECMs (red), initially membranes were fouled until flux reached about 30% of initial flux; (C) SEM images of membrane surface (1) Membrane fouled by 100 ppm BSA (2) BSA fouled ECM cleaned by back washing, (3) BSA fouled ECM cleaned by applying 3V (membrane as anode) to the membrane surface. Scale bars for SEM images are 2 μm 103

List of Tables

Table 1. Overview of membrane processes and their characteristics [11].	6
Table 2. CaSO_4 scaling experiments salt composition.....	28
Table 3. CaCO_3 scaling experiments salt composition	29
Table 4. UF and NF membrane properties	57
Table 5. Water quality parameters	60
Table 6: ECM physical characterization	87

Chapter 1

Introduction

1.1 Water Crisis

Water is an essential source of life. Because of the presence of water, the world thrives. The earth, aptly named the Blue Planet, is 97% covered by water, but fresh water for most living creatures is extremely limited. Less than 3% percent of the water is freshwater [1,2]. Unfortunately, this 3% are mostly stored as glaciers in the south and north poles. Therefore, less than 1% of water is realistically accessible as fresh surface water and groundwater.

These water resources are not only limited by scarcity, but also extremely unequally distributed [1,2]. Water management to reduce the disparity is necessary and has been discussed and implemented over centuries. In the past, the inadequate water supply was often solved by major infrastructure projects, such as the aqueducts of ancient Rome and modern day California State Water Project (SWP). These projects are implemented for allocating water resources to reduce water stress in high population density areas. However, these big water projects have been found to have detrimental effects on local ecosystems and are expensive. Therefore, local water resource management can play a crucial role in sustainable global development [3].

Water shortages are being exacerbated by global warming, rapid population growth, and environmental contamination; these are the leading contributors in a continuous downward spiral toward a strained biosphere [2,4]. Global warming leads to extreme weather, such as drought in arid areas. Growing populations increase the water demand, which can lead to overdrawn groundwater aquifers. In coastal areas, the over-pumping of groundwater can cause seawater intrusion, which significantly reduces the groundwater

quality [5]. Surface water and groundwater contamination also burden water infrastructure and further reduces water supplies. To further expand the water supply, it is crucial to look beyond the traditional hydrological cycle towards unconventional water sources, such as seawater and wastewater. However, compared to fresh water sources, seawater and wastewater have much higher salinity and organic loading. With those contaminants present in water, conventional drinking water treatment facilities will struggle to deliver their products in the same amount and with the same quality. In order to gain access to these problematic water sources, new technologies such as desalination and membrane separation are often required.

Desalination technology including thermal desalination (multi-stage flash distillation, multi-effect distillation and vapour compression distillation) and membrane based desalination (reverse osmosis, nanofiltration and electrodialysis) are two major technologies for seawater purification. Thermal desalination is much more energy intensive compared with membrane based desalination, but it can deal with more saline water and results in better permeate water quality [6]. Membrane based desalinations, especially reverse osmosis (RO), which already operate near the thermodynamic limit, have been widely implemented around the world [7]. However, seawater desalination is still a location-dependent technology, which is preferably built near the ocean. Inland brackish water desalination faces a significant technological hurdle in brine disposal [8,9].

Wastewater as another alternative water source in populated areas has been discussed and practiced in the past decade [10]. The quantity and quality of wastewater is predictable and relatively stable compared with natural water sources, which allows for simpler

management. However, there are still several important concerns restricting wastewater recycling and reuse. Current challenges include antibiotic resistant bacteria [10], viruses and other microorganisms, emerging organic contaminants, high transportation costs due to separate pipeline infrastructure, unclear regulations and limited public acceptance. In order to reduce the risks of antibiotic resistant microorganisms and emerging organic contaminants in drinking water, decentralized water treatment facilities at the end user level have more advantages. Membrane technology, due to having very few maintenance requirements, has become a promising decentralized water treatment choice. However, for membrane treatment of wastewater, the biggest challenge is membrane fouling [10–16].

Despite all these challenges, membrane technologies are still promising for new water source purification beyond the traditional hydrological cycle. Further reducing membrane operational costs and extending membrane lifetime will enable this technology to serve our community even better.

1.2 Membrane Technology

1.2.1 Membranes Classification and Applications

Due to membrane technology's rapid growth in the past 3-4 decades, it has become a very important and unique method used for a variety of applications. Currently, commercially available membranes include reverse osmosis membranes (RO), nanofiltration membranes (NF), ultrafiltration membranes (UF) and microfiltration membranes (MF). The main differences between these membranes are their pore size properties and removal mechanisms. MF membranes have the largest pore size and use

sieving as their major removal mechanism. RO membranes have no pores, which allows only water molecules and, occasionally, small uncharged molecules to diffuse through (Figure 1).

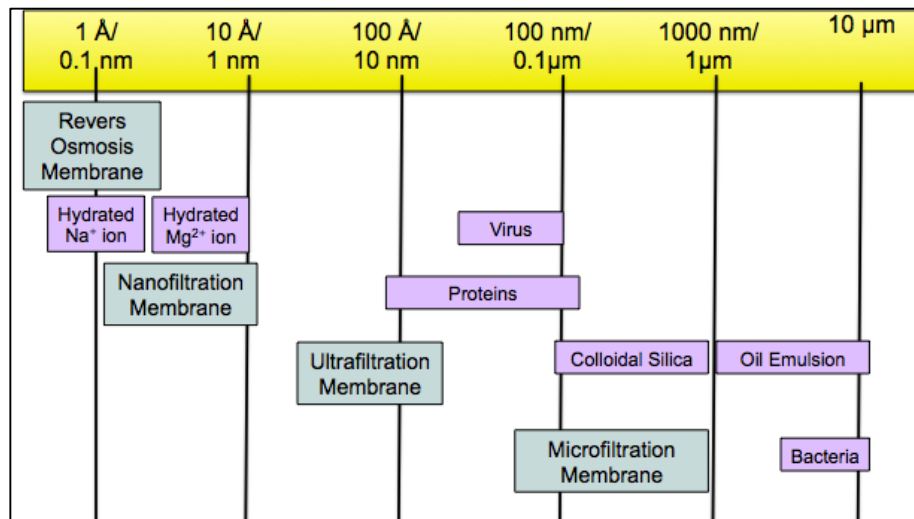


Figure 1. Membrane cut-off characteristics

1.2.1.1 Reverse Osmosis Membranes

RO membranes are semi-permeable membranes used to remove monovalent ions (i.e. NaCl) and small charged organic molecules. The typical rejection of NaCl is usually more than 99% (Table 1) [9,11,17]. In the RO process, an external pressure is applied to overcome the osmotic pressure caused by the concentration difference of the solute on both sides of the membrane. The typical pressure for driving seawater desalination ranges from 100-1300 psi [7,8,18]. There are two types of RO membranes on the market: asymmetric cellulose acetate (CA) RO membranes and thin film composite (TFC) polyamide (PA) membranes. The PA membranes dominate the RO membrane market sales with 91% share, with CA membrane representing most of the remaining sales. Although the CA based RO

membranes are mildly chlorine resistant, which allows for chemical cleaning, the PA based RO membranes have higher salt rejection and higher pressure tolerance which serve the practical needs of seawater desalination better [9].

Table 1. Overview of membrane processes and their characteristics [11].

Membrane Type	Operation Pressure (psi)	Salt Rejection (%)	MWCO (Da)	Permeability ($\text{Lh}^{-1}\text{m}^{-2}\text{psi}^{-1}$)
Reverse Osmosis Membrane	100-1800	>99 (NaCl)	100	0.003-0.1
Nanofiltration Membrane	40-300	>60 (NaCl)	>200	0.1-2
Ultrafiltration Membrane	1.5-72.5	0	>10K	0.7-70
Microfiltration Membrane	1.5-30	0	>1000K	>70

1.2.1.2 Nanofiltration Membranes

NF membranes are also semi-permeable membranes with the pore sizes (0.1 nm to 10 nm, Figure 1) in between UF and RO. Unlike RO membranes which remove all the ions in the water, these membranes only remove divalent ions, and let the majority of monovalent ions pass through, leading to several advantages for NF membranes: low operational pressure, high flux and greater than 90% divalent ion rejection (Table 1) [19]. NF membranes are fabricated via an interfacial polymerization (IP) technique like RO membranes with a less compact thin film composition structure. They are often used for

groundwater softening, RO feed pretreatment and removal of small organic dyes from textile wastewater [11].

1.2.1.3 Ultrafiltration Membranes

UF membranes are membranes with a pore size of 10-100 nm (Figure 1). Due to this large pore size, UF membranes typically cannot reject salts, but operate with a significantly lower operational pressure. UF membranes are commonly made by a phase inversion technique. The commonly used polymers include polyvinylidene fluoride (PVDF), polysulfone (PS), polyethersulfone (PES) and polyacrylonitrile (PAN). These polymer are chemically and mechanically robust as well as easy to process [20]. UF membranes are an alternative method for integrating coagulation, sedimentation, clarification, disinfection and sand filtration processes [21–23], because they can remove suspended particles, colloids, turbidity, algae, bacteria and viruses [24]. They are also used as pretreatment for other advanced membrane applications to reduce membrane fouling in following stages (*e.g.* NF and RO).

1.2.1.4 Microfiltration Membranes

MF membranes are membranes with a pore size of 100 nm to 10 μ m. These membranes operate similarly to UF membranes, but with the highest permeability among four types of pressure driven membranes. The most commonly used materials are hydrophobic materials, polytetrafluoroethylene (PTFE), poly (vinylidene flouride) (PVDF) polypropylene (PP), polyethylene (PE), and hydrophilic materials, cellulose esters, polysulfone (PS) polycarbonate (PC) [11]. Microfiltration membranes are prepared by

sintering, track-etching, stretching, or phase inversion techniques. Due to the robust materials used to manufacture the membranes, MF membranes have fairly good chemical stability and excellent mechanical strength. They are often used as feed pretreatment to reduce fouling for other smaller pore membranes [11].

1.2.2 Membrane Fouling and Conventional Control Technologies

Unfortunately, membranes are plagued by several issues, the principal amongst them being fouling [25–27]. In membrane fouling, materials present in the feed stream (e.g. bacteria, organic molecules, precipitated salts) deposit or develop on the membrane surface or clog the pores, obstructing the flow of water. Once the membrane is fouled, the membrane system will experience a significant flux drop, which will dramatically increase the energy consumption, operational cost and shorten the membrane's lifetime. There are four types of membrane fouling, which are classified based on the foulant: (1) mineral scaling, (2) organic fouling (3) colloidal fouling and (4) biofouling.

1.2.2.1 Scaling

Mineral scaling is a significant issue in membrane e desalination. The most common fouling species are calcium sulfate and calcium carbonate [28,29]. Fouling in the form of scaling is the result of inorganic crystal formation on the membrane surface. Crystal nucleation occurs when the solubility limit for a mineral is exceeded at the membrane surface due to salt ion accumulation [30–32]. The phenomenon in which a layer of ions accumulates along the membrane surface is known as concentration polarization (CP) [33].

The two main types of scale formation in membrane systems are homogeneous and heterogeneous crystal growth. Homogeneous crystal growth occurs in solution, while heterogeneous crystal growth occurs on an existing surface (*e.g.* membrane surface, spacer) in the membrane system, and has a much faster growth rate [31,32,34]. The crystal formation growth rate also depends on the degree of super-saturation (expressed as the saturation index), temperature, as well as the local molar ratio of cations to anions [35].

Depending on the salt crystal species, mineral scaling can be controlled in membrane systems by using turbulent flow conditions that enhance mixing in the feed solution and reduce concentration polarization along the membrane surface, through the addition of antiscalant chemicals, by adjusting the solution pH, or by some combination of the above [7,8,36].

Dosing antiscalant in the feed water is a commonly used strategy to prevent inorganic fouling in RO membrane systems. Antiscalants are mixtures of various molecular weight polycarboxylates and polyacrylates [37]. The exact mechanism of scale inhibition is not clearly understood, but it is generally accepted the anti-scaling agents absorb on both the membrane surface and formed crystals or incipient crystals, which leads to the reduction of scale formation and crystal growth on the membrane surface [38]. However, identifying a cost-effective dosage is usually a tedious task, with the dosage highly dependent on different water constituents [37]. Overdosing the system not only increases the operation cost, but results in increased organic fouling [37]. To reduce the use of antiscalants, an *in situ* scaling prevention method would be highly beneficial.

1.2.2.2 Organic and Colloidal Fouling

Colloidal or organic fouling usually happens when a membrane is used to treat surface water or treated secondary effluent due to its high organic loading [25,39]. Depending on the membrane pore size, two different colloidal fouling mechanisms have been identified. For RO, NF and tight UF membranes, the colloidal fouling is caused by an accumulation of colloidal material on the membrane surface, which leads to a cake/gel layer formation. For MF membranes, the colloids can clog the membrane pores first and then develop a layer on top of the membrane surface [39–41]. The attachment of colloids to the membrane surface depends on colloidal surface charge, solution ionic strength, membrane surface roughness, and membrane surface charge [39].

Colloidal and organic fouling is typically controlled by air scrubbing, backwashing and chemical cleaning procedures [42]. Backwashing and air scrubbing are used to remove the cake/gel layer deposited on the membrane surface. Chemical cleaning (e.g. soaking in bleach) can be used to remove adhered organic matter on the membrane surface and clean the clogged pores, but requires system down-time and is not compatible with PA-based RO membranes, which rapidly degrade in the presence of even minute (<1 ppm) concentrations of chlorine [43,44].

1.2.2.3 Biofouling

Biofouling is another major problem in membrane technology that occurs when membranes are used to treat water containing bacteria [14,45]. It is initiated by irreversible bacterial attachment on the membrane surface, followed by the growth of the attached

bacteria and the formation of a biofilm. Biofilms will significantly reduce the flux and increase the trans-membrane pressure [42,46], are nearly impossible to effectively remove and significantly increase membrane operational costs [32,47]. This is because bacteria generate extracellular polymeric substance (EPS), which not only firmly glues bacteria onto the membrane and protects the attached bacteria from chemical disinfection and membrane cleaning procedures [42,48].

Biofouling occurs on all types of membranes, and despite extensive use of pretreatment as well as the addition of biocides and disinfectants, it remains a major hindrance for widespread membrane application [49–52]. Bacteria have been found to attach and multiply on nearly all surfaces under a wide range of living conditions [49]. When combined with passive foulant accumulation (e.g. colloidal fouling and cake layer formation), bacteria can not only speed up the formation of gel/cake layers, but also build up a protective coating (e.g. EPS) to prevent removal by shear forces and disinfectants, which are typical cleaning methods [26,53]. The most efficient way to remove biofouling is chemical cleaning, which requires system down time and is difficult to implement in RO systems, due to the susceptibility of polyamide to oxidizing agents, such as chlorine [53].

1.3 Fouling Prevention by the Application of Electricity

The application of an electric field to enhance membrane filtration and prevent organic and colloidal fouling has been widely implemented [37] and is known as electrofiltration [38]. Typically, the electric field is applied across the membrane via two electrodes placed on either side of the membrane [39,40]. Electrofiltration is distinct from

electrodialysis, where ion movement is driven by electrophoretic forces, and which is an energy intensive process [41]. One of the major obstacles to the commercial implementation of electrofiltration is lack of stable and economical electrode material as well as the high energy demand associated with the standard process. Very high electrical potentials must be applied to the electrode pair, which results in greatly increased energy demands and can promote electrode corrosion [42].

Electrical methods for controlling bacterial adhesion on conductive surfaces can be divided into current-driven and potential-driven applications, and each application can be further divided into cathodic, anodic, and alternating modes [43]. Due to the nature of negatively charged bacteria [13], a cathodically-charged surface can prevent bacterial attachment and detach bacteria [54–56]. The application of cathodic potentials to a membrane surface has been reported to kill bacteria by the production of low concentrations of hydrogen peroxide near the membrane through the electro-reduction of oxygen [44]. Alternatively, direct electron transfer between bacteria and an anode surface can inactivate the adhered bacteria, which has been widely used to control marine biofouling [45]. However, when anodic potentials are applied, the dead bacteria tend to remain on the surface, severely and irreversibly fouling the membrane and making the method ineffective [57–60]. To overcome the complications caused by anodic potential or current, the use of alternating voltage has been implemented as an effective approach for biofouling prevention [46].

1.4 Carbon Nanotube Based Electrically Conducting Membranes

Carbon nanotubes (CNTs) are 3D tube-like structures, resembling seamlessly rolled 2D graphene sheets. CNTs are a very promising possible electrode material due to their nano-size, high electric conductivity [47], and large specific surface areas ($50\text{--}1000\text{ m}^2\text{g}^{-1}$) [48]. They have been used in a wide array of applications [49–51]. Due to a large specific surface area, they have been widely used as adsorbents for organic chemicals via van der Waals interactions [52,53] and for heavy metals via carboxylate surface group interactions [54]. The high electrical conductivity of CNTs have led to them being viewed as a feasible material for conductive membranes [44,55–58]. Having an electrically conductive membrane provides the benefits of electrofiltration while increasing the working area far above that of a solid electrode. The 3D conductive structure also can serve as a flow through electrode to significantly increase the mass transfer and convection-enhanced mass transfer to the electrode surface, which has been shown to be the primary limitation for electrochemical transformation [59].

However, CNTs still face a universal anode problem when using as anode: corrosion and water oxidation. The water oxidation can substantially reduce the current efficiency for the intended reactions [61,62]. This issue of low oxygen evolution potential (OEP) is usually solved by doping catalytic metallic nano-particles. Liu and Vecitis et. al. have successfully utilized bismuth-doped tin oxide (BTO) to increase the OEP of BTO-CNTs composite to 1.71 V (vs. Ag/AgCl) [61]. Anodic stability is a major obstacle for CNTs used as electrochemical reaction anode material [63]. CNT anode corrosion has been reported as $>1.7\text{ V}$ for multiwall CNTs and >1.0 for single wall CNTs (vs. Ag/AgCl) [61].

Unfortunately, in order to degrade many environmental contaminants, the required anodic potential can go up to 3.4 V (vs. Ag/AgCl) [61,64]. Therefore, developing stable CNTs composite material as anode at high potential is crucial for broader applications in the future.

1.5 Fouling Prevention and Mitigation Mechanisms of Electrically Conductive Membrane

1.5.1 Scaling Prevention Using Electrically Conductive Membrane

Scaling on the membrane surface is mainly due to irreversible crystal nucleation on the membrane surface. This leads to crystal cake layer formation that covers the pores of the membrane, as briefly discussed in Section 1.2.2.1. As a result, reducing nucleation rates on the membrane surface can significantly slow down scaling. Previous works by Alimi and Gadri have demonstrated that changing the lattice cation/anion stoichiometry molar ratio seriously impacts the induction time, which is the time period between the achievement of supersaturation conditions and the appearance of the first crystal [35,65]. The cations/anions molar ratio can be determined by bulk solution or changes in the region near a charged surface. The change of ion distribution near a charged surface is well explained using electrical double layer theory (EDL).

Electrical double layer theory describes the ion distribution near a charged surface. EDL theory states that for negatively charged surfaces (Figure 2), positive ions (i.e. counter-ions) form a layer near the charged surface known as the Stern layer. In this Stern layer the charge and potential distribution are determined primarily by the geometrical

restrictions of the ions and molecular size and short range interaction between ions, surface and adjoining dipoles. Additional positive ions attracted by the negatively charged surface face a repulsion force from the counter-ions in the Stern layer, known as the diffusive layer. The density of this layer gradually decreases with the distance from the colloidal particle until it reaches equilibrium with the rest of the ions in the solution [66].

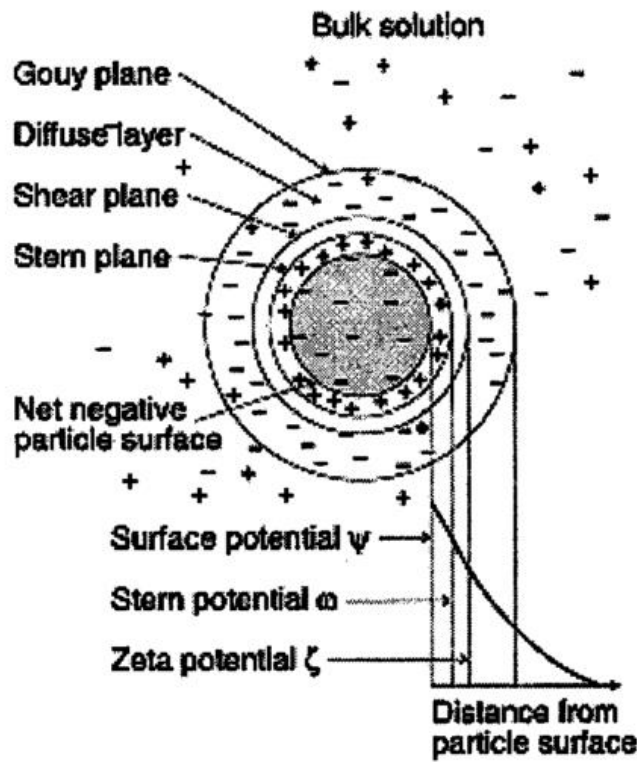


Figure 2. Schematic of electrical double layer in a liquid in contact with a negatively charged surface (borrowed from Rodrigo F.V. Romo and M. Michael Pitts[67])

The potential distribution in the EDL structure has been described by Gouy [68] and Chapman [69]. The Poisson-Boltzmann equation gives a potential distribution as a function of distance from the charged surface. In one dimension this can be written as follows [70]:

$$\epsilon_e \frac{d^2 \Psi}{dx^2} = - e N_A \sum_{i=1}^m z_i c_i^{\infty} \exp\left(-\frac{z_i e \Psi}{kT}\right) \quad (1)$$

where ψ is the electrical potential, z is the valence of ions, e is the elementary charge, N_A is Avogadro's number, c_i^{∞} is the bulk ion concentration, ϵ_e is the permittivity of the electrolyte solution (varies with ion concentration), k is Boltzmann's constant, and T is temperature.

It is important to note that in eq. 1 shown above, it assumes point like ions and constant solution permittivity throughout the system. Although this approach is applied successfully in predicting ionic profiles close to planar surfaces in symmetrical electrolyte solutions, it is known to strongly overestimate ionic concentration near highly charged surfaces and for multivalent ions [66,70]. Stern was the first person to introduce the Stern layer conception to overcome the limitations of PB theory. Since then, several attempts have been proposed to overcome the hydration ion size effect, surface adsorption problems and other issues in Stern layer theory better fit the experimental results [67].

The method I proposed to use for CaSO_4 scaling prevention uses the EDL and the Stern layer theory to design a new antiscaling strategy. Specifically, I applied an external potential to the membrane surface. The increased surface potential leads to changes in the anion and cation distribution ratio near the membrane surface [71] as a result of the formation of a thick EDL, whose thickness is highly dependent on the applied electrical potential [72]. Inside the EDL, and in particular, in the Stern layer, the stoichiometric ratio of cations and anions is significantly altered (Figure 2). The non-stoichiometric ratio significantly decreases the CaSO_4 nucleation rate near the surface [35]. Nucleated crystal

clusters form mainly in the stoichiometrically balanced bulk solution [70], where they can be washed away by crossflow instead of depositing on the membrane surface.

1.5.2 Organic Fouling Reduction on Electrically Charged Membrane

To understand the interactions between bacteria, organic matter and the membrane surface, it is very important to identify the forces involved in this system. There are many important interactions affecting particle deposition including electrostatic interaction, van der Waals attraction, Brownian motion, hydration and steric forces. Among these, the electrostatic interaction and van der Waal attraction play significant roles. The relation of these two interaction forces has been originally introduced and discussed by DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek) [73]. Electrostatic interaction was calculated using the EDL theory. The electrostatic force F_e can be calculated through the surface elementary integration method (Eq. 2) shown below.

$$F_e = 2\pi \int_0^r \left[-\frac{\delta f_F(x)}{\delta x} \left(x + a - a\sqrt{1 - \left(\frac{r}{a}\right)^2} \right) + \frac{\delta f_F(x)}{\delta x} \left(x + a + a\sqrt{1 - \left(\frac{r}{a}\right)^2} \right) \right] r dr \quad (2)$$

where $\frac{\delta f_F(x)}{\delta x}$ is the derivation of the Free energy, a is a constant partial radius and r is the variable radius [74].

Van der Waals interaction energy is the total sum of the dipole-dipole interaction, dipole-induced dipole interaction and dispersion energy, which can be calculated using Eq. 3 showing as follow:

$$F_{vw} = -\frac{A}{12} \left[\frac{2}{x} - \frac{1}{x^2} + \frac{1}{x+1} - \frac{1}{(x+1)^2} \right] \quad (3)$$

where A is the Hamaker constant, r is the particle diameter and x is the ratio of separation distance to particle diameter [75].

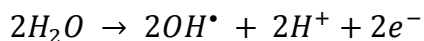
In a flow system, especially in a membrane filtration system, besides DLVO interaction forces, the flow dynamic has a significant influence on the particle movements and deposition including particle diffusion, drag force, lifting force and system pressure. These dynamic forces can be impacted by the particle size and solution physical properties. When an external potential is added to the system, electrophoretic force should also be considered.

The mechanism I propose to use with electrically conductive membranes to prevent organic fouling, colloidal fouling and biofouling is electrostatic interaction. The effectiveness of this method can be explained by comparing the possible existing opposing forces that determine particle deposition. Most organic colloidal particles and bacteria are negatively charged in an aqueous environment [67,76]. In these cases, an additional electrical field applied by the membrane can provide a strong electrostatic repulsive force and electrophoretic force, which pushes the negatively charged particles away from the membrane surface.

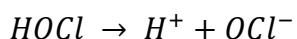
1.5.2 Electrochemical Oxidation to Mitigate Organic Fouling Layer

The feasibility of electrochemical destruction of organic compounds in wastewater has attracted much attention for almost half a century [77,78]. Electrochemical oxidation is performed through the electro-generation of strong oxidants on the electrode surface. The process of electrooxidation includes both direct and indirect oxidation. Direct

oxidation is the electrochemical oxidation of compounds which can happen directly at anodes surface through the generation of hydroxyl radicals. Indirect oxidation is electrochemical oxidation pollutants occur via oxidants (e.g. chlorine (Cl_2), hypochlorite (OCl^-) and persulfate ($\text{S}_2\text{O}_8^{2-}$)) which are generated by electrochemical reactions [79]. Direct oxidation is achieved through the production of hydroxyl radicals ($\text{OH}^\cdot$), which are very active chemical oxidation agents which are generated on the anode surface that can lead to complete mineralization of organic contaminants [80]. Efficient electrochemical generation of hydroxyl radicals requires that the electrode has a high oxygen evolution over-potential; otherwise, water, the most abundant molecule in an aqueous solution, could be oxidized to oxygen instead of hydroxyl radicals [81]. Common anode materials used for hydroxyl radical generation include doped- SnO_2 [82], doped- PbO_2 [83,84] and boron-doped diamond (BDD) [85–87,62]. The hydroxyl radical generation reaction occurs as follows[80]:



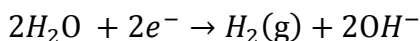
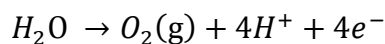
Indirect oxidation is defined as the *in situ* generation of oxidant chemical reactants (i.e. Cl_2 and $\text{S}_2\text{O}_8^{2-}$) that can oxidize organic compounds to less complex compounds [79,88]. Typically, the main oxidizing agent responsible for indirect electrochemical oxidation is chlorine, which is generated through the electrooxidation of chloride ions [79,89,90]. These chlorine molecules can react with water to form hypochlorous acid (HOCl) or hypochlorite ions which are responsible for the organic chemical degradation.



The toxicity of the byproducts and their fouling potential on the membrane surface for this indirect chlorination process still remain a big challenge that needs further exploration. Therefore, direct oxidation by hydroxyl radical is preferred.

1.5.3 Direct Electrolysis

When the potential applied to the electrode is higher than the water splitting potential, electrolysis of water molecules occurs. In this process, oxygen and protons are generated on the anode, and hydrogen and hydroxide ions are generated on the cathode [91].



Although these reactions are not ideal for organic oxidation purposes, they are useful when foulants are pH sensitive, e.g. $CaCO_3$ scales dissolving rapidly under acidic conditions.

1.6 Research Objectives

The overall objectives of this dissertation were to use CNT-based electrically conducting membranes to solve many of the problems plaguing membrane-based water treatment processes.

In Chapter 2, electrochemical mineral scale prevention on electrically conductive CNT – PA RO membranes was investigated. The objective of this project was to find the optimal potential to apply on the membrane in order to prevent and remove $CaCO_3$ and $CaSO_4$ mineral scaling on the surface. Membrane fouling development and recovery was

evaluated by monitoring permeate flux change. Scanning electron microscopy (SEM) was used to image the membrane surface before and after the experiment to verify the efficiency of the cleaning. A modified Poisson-Boltzmann equation was used to help explain the CaSO_4 fouling prevention mechanism.

In Chapter 3, the use of electrically charged UF and NF membranes to reduce fouling while treating water from an anaerobic reactor treating industrial wastewater was discussed. The purpose of this study was to determine the flow rate and electrical conditions that minimize organic fouling and biofouling, and to evaluate membrane cleaning procedures in UF and NF modules.

In Chapter 4, highly electrically conductive and anodically stable composite polyaniline/CNT ultrafiltration membranes formed via electropolymerization under acidic conditions was explored. The objective of the study was to evaluate membrane anodic stabilities via cyclic voltammetry and chronoamperometry and their effect on organic molecule oxidation and *in situ* membrane cleaning without additional cleaning reagents.

In Chapter 5, conclusions from the doctoral work are given as well as discussion on the application of electrical conducting membranes to prevent or mitigate different fouling among different membranes applications in light of the experimental evidence from preceding chapters.

Chapter 2

Electrochemical Mineral Scale Prevention and Removal on Electrically Conducting Carbon Nanotube – Polyamide Reverse Osmosis Membranes

Previously Published in *Environmental Science: Processes & Impacts*

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2.1 Introduction

Desalination is an increasingly used method to provide potable water to areas with limited fresh water resources [6,88,92]. However, this technology is still plagued by several issues, principal amongst them is membrane fouling [17,27,93]. State-of-the-art commercial reverse osmosis (RO) membranes operate near the thermodynamic limit [94]. Therefore, to improve membrane performance and reduce process energy consumption, pretreatment and membrane fouling reduction must be achieved [6]. One type of membrane fouling process is mineral scaling, where salt crystals precipitate out of the solution, forming a dense layer on the membrane surface that obstructs the flow of water through the membrane. Mineral scaling occurs when the concentration of rejected ions along the membrane surface exceeds the solubility limit for a particular mineral, resulting in the nucleation and growth of inorganic crystals on the membrane surface [30–32]. The phenomenon where a layer of ions accumulates along the membrane surface is known as concentration polarization (CP). Once scaling occurs, the RO system will experience a significant decrease in water flux and could be physically damaged, which could lead to a drop in salt rejection [76]. Additionally, the nucleated salt crystals can physically harm the membrane surface. Depending on salt crystal species, mineral scaling can be controlled in RO membrane systems by using turbulent flow conditions that enhance mixing in the feed solution and reduce solute concentrations along the membrane surface, through the addition of anti-scaling chemicals, by adjusting the solution pH [7,8,36], or by some combination of the above. Two of the most common salt species responsible for mineral scale formation in membrane applications are CaCO_3 and CaSO_4 [8,36]. CaCO_3 scale can

be controlled by adjusting solution pH, as CaCO_3 dissolves readily under acidic conditions [36]. In contrast, CaSO_4 is pH insensitive, and requires the addition of anti-scaling agents [95].

Mineral scaling formation has been studied for decades, with two main mechanisms identified: homogeneous crystal growth occurs when salt crystals form and grow in the solution and heterogeneous crystal growth on a solid surface (such as a membrane surface) [31,32,34]. In general, the heterogeneous route causes more rapid crystal formation and growth. The growth rate of crystal depends on degree of super-saturation (expressed as the saturation index) as well as the local ratio of cations to anions [35].

The accumulation of ions on the membrane surface and the formation of the CP layer are associated with diffusion and advection of ion toward, away from, and along the membrane surface. However, the application of an electric charge to a surface leads to the formation of an electrical double layer (EDL) along the surface [96]. In the EDL structure, the concentrations of co-ions and counter ions are non-stoichiometric, with counter ion concentrations decreasing and co-ions concentrations increasing as the distance from the charged surface grows, until bulk concentrations are achieved. The distance from the electrically charged surface where bulk concentrations exist is a function of the surface charge and solution ionic strength [97–99]. Several reports have demonstrated that excess concentrations of either anions or cations lead to delayed nucleation and crystal growth, with the most rapid crystal growth observed when stoichiometric conditions exist [35,99].

Several reports have demonstrated that the application of an electric field during cross-flow filtration reduces the impact of various fouling mechanisms, including CP

formation and organic material deposition [100–103]. We have developed an electrically conducting RO membrane that maintains the transport properties needed in desalination processes, with the added benefit of high electrical conductivity [60]. Electrical conductivity is imparted through the combination of functionalized carbon nanotubes (CNTs) that are cross-linked to the polyamide (PA) membrane matrix, forming a true nano-composite.

In this paper we describe how the application of an electrical potential to the surface of an electrically conducting RO membrane can significantly delay the formation of CaSO_4 crystals near on membrane and dissolve CaCO_3 crystals growing on the membrane surface. Furthermore, we develop a model that predicts the concentrations of ions as a function of applied membrane potential and distance from the membrane surface. We use this model to qualitatively explain the observed decline in CaSO_4 fouling.

2.2. Materials and Methods

2.2.1 Materials

Carboxylated multiwall carbon nanotubes (CNT-COOH) were purchase from Cheap Tubes (Cheaptubes Inc., Brattleboro, VT). Polysulfone (PSF) ultrafiltration (UF) supports were purchased from Sepro Membranes (Sepro Membranes Inc., Oceanside, CA). *m*-Phenylenediamine (MPD), trimesoyl chloride (TMC), CaCl_2 , NaSO_4 , MgSO_4 , sodium dodecylbenzenesulfonate (NaDDBS), and NaHCO_3 were purchased from Sigma-Aldrich and used as received.

2.2.2. Membrane Fabrication

The RO membrane fabrication process followed our previously reported method [60]. In short, CNT-COOH suspensions were created by sonicating the CNT-COOH in a solution containing the surfactant NaDDBS for 30 minutes. Then, a certain volume of CNT-COOH suspension was deposited onto a PSF UF support, rinsed with deionized water (DIW), and allowed to dry. Then the support was immersed in a 2% aqueous solution of MPD for two hours, slightly dried, and immersed into a 0.15% solution of TMC in hexane for two minutes. The membranes were then cured for 10 minutes at 90°C and stored in DIW at 4°C until use.

2.2.3. Membrane Characterization

Scanning electron microscopy (SEM, JEOL Akishima-Shi, Tokyo) was used to image the surface morphology as well as the salt crystals growing on the membranes. For SEM images, the conducting nature of the membrane negated the need to sputter-coat the membrane with a metal layer. Attenuated total reflectance – Fourier transformed infrared spectroscopy (ATR-FTIR, Thermo Scientific, Franklin, MA) was used to verify the formation of ester bonds between CNT-COOH and the PA polymer matrix [104]. A four-point conductivity probe was used to characterize membrane sheet resistance. The open-circuit potential of the membrane, representing the “true” potential on the membrane surface, was measured in reference to a Ag/AgCl reference electrode using a potentiostat (Gamry Instruments, Warminster, PA) [105]. Atomic force microscopy (AFM; Bruker Biosciences, Billerica, MA) was used to measure membrane surface roughness.

2.2.4. Experimental Procedure

A modified cross-flow RO module was used in all scaling experiments; the module incorporates electrodes designed to deliver an external charge to the membrane surface and a counter electrode (316 stainless steel sheet) seated 3 mm above the membrane surface. The electrodes delivering the external charge are positioned outside of the inner O-ring, and do not come into contact with the solution. The active membrane area in this setup was 20 cm² (4.8 cm × 4.2 cm).

The feed solution was continuously re-circulated through the system (Appendix Figure A-1), and the permeate was weighed periodically to determine flux. The system was operated in a constant pressure mode, with the initial pressure adjusted so as to maintain identical initial flux values for all experiments. Pressure was controlled by adjusting a needle valve on the retentate line, and a diaphragm pump was used to provide flow and pressure to the system (Wanner Engineering, Minneapolis, MN). External electrical potentials were applied to the membrane surface by connecting the membrane to an arbitrary waveform generator (Rigol, Oakwood Willage, OH). Permeate quality was continuously monitored by measuring its conductivity.

2.2.5. *CaSO₄ Scaling Experiments*

In these experiments, we used a scaling solution meant to simulate brackish groundwater (Table 2) [29].

Table 2. CaSO₄ scaling experiments salt composition

Salt	Concentration (M)
Na ₂ SO ₄	0.0105
MgSO ₄	0.0145
CaCl ₂	0.0164

A large volume (4 L) of the scaling solution (saturation index of 1.01 with respect for CaSO₄) was continuously recycled through the system with no crystal formation observed in the bulk. In some of the CaSO₄ scaling experiments, an in-line 0.5 μm polycarbonate filter was used on the retentate line to trap any crystals formed during the filtration experiments [29]. In these experiments the cross-flow velocity in the RO module was maintained at either 3.4 cm s^{-1} , when the in-line filter was used, or 4.5 cm s^{-1} when no in-line filter was present. The increased flow rate associated with the higher velocities resulted in a transmembrane pressure across the in-line filter that exceeded the filter housing's capacity and led to leaks. A DC voltage was continuously supplied to the membrane surface, with the membrane acting as an anode with an applied potential of 1.5 V (approximately 1 V vs. a Ag/AgCl reference electrode).

2.2.6 CaCO_3 Scaling Experiments

In these experiments, we used a scaling solution described in Table 3 [106].

Table 3. CaCO_3 scaling experiments salt composition

Salt	Concentration (M)
Na_2CO_3	0.0094
KCl	0.0107
CaCl_2	0.0072
MgCl_2	0.0047

The scaling solution (saturation index of 4.38 with respect for CaCO_3) was continuously recycled through the system without filtration. No crystal formation was observed in the bulk. In these experiments, the cross-flow velocity in the RO module was maintained at 4.5 cm s^{-1} . The membranes were allowed to scale for a period of several hours, and then a 2.5 V potential (membrane as anode) was applied for 15 minutes. After that, the voltage was shut off and the system was allowed to continue operating.

2.3 Results and Discussion

2.3.1 Membrane Characterization

The electrically conducting RO membrane achieved a NaCl rejection rate of 98% (tested using an 8 g L^{-1} NaCl solution). Pure water flux was determined to be $2 \pm 0.53 \text{ LMH}$ per bar. This value is somewhat lower than that reported from commercial RO membranes (typical values of pure water flux ranging between 3.2 and 3.96 LMH per bar), but hardly surprising as we did not subject our membranes to any post-fabrication processing steps used to enhance membrane flux. It is important to note that the application of an electrical potential did not change salt rejection or pure water flux through the membrane. SEM

images of the membrane surface show the typical “noodle” structure associated with PA RO membranes (Figure 3 Left).

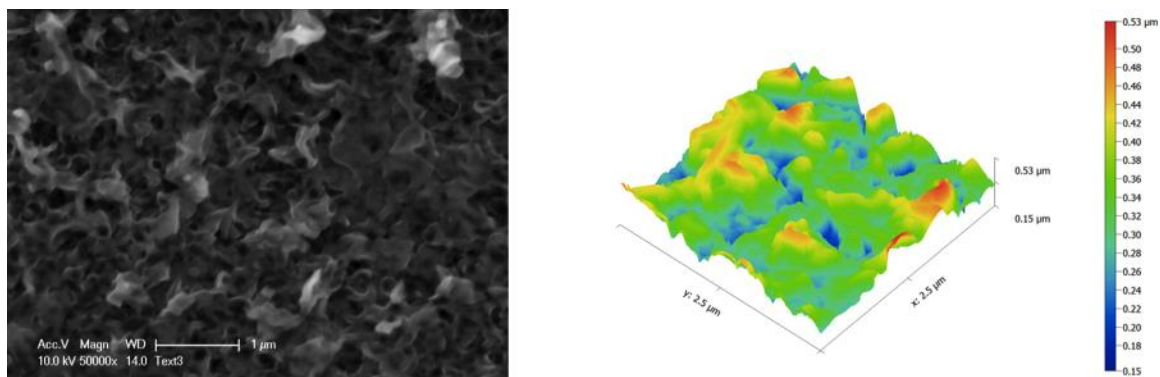


Figure 3. (Left) SEM image of surface of PA-CNT RO membrane; (Right) AFM map shows roughness according to the software RMS is 91nm on 2.5 by 2.5μm spot.

Sheet resistance was measured to be $2.56 \pm 0.71 \text{ k}\Omega$. An AFM image of the membrane surface can be seen in Figure 3 (Right). AFM image analysis indicated that membrane surface roughness was 91 nm. This roughness value is similar to values reported in previous studies of RO membrane surface [107,108]. ATR-FTIR analysis of the membrane surface revealed the presence of an ester bond (1728 cm^{-1}) linking the hydroxyl group on the CNTs to the TOC monomer in the PA, as well as the characteristic peaks corresponding to the amide bonds linking the TMC and MPD monomers (1643 cm^{-1} , 1610 cm^{-1} , and 1543 cm^{-1} ; Figure 4) [60].

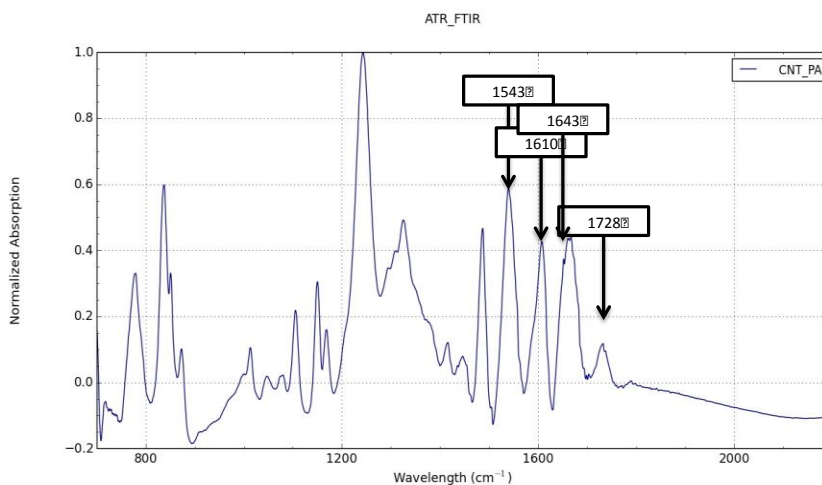


Figure 4. ATR-FTIR spectra of the electrically conducting RO membrane

The open circuit potential of the membrane as a function of the applied potential can be seen in appendix Figure A-2; this potential represents the approximate potential (as there will be some potential drop between the membrane and reference electrode), with reference to the Ag/AgCl electrode, that the solution around the membrane experiences. The ionic strength of the solution was 164 mM and the distance between the working and reference electrode was 5 mm. Thus, when a potential of 2.5 V is applied to the membrane/counter electrode pair and the membrane is used as an anode, the “true” potential on the membrane surface will be approximately 1.8 V vs. the Ag/AgCl reference; this potential (which is 1.23 V for the water-splitting reaction vs. the hydrogen standard electrode) is sufficient to split water and produce protons along the membrane surface [109].

2.3.2 CaCO_3 Scaling Removal

In this portion of the study we demonstrate the ability of the electrically conducting RO membrane to remove CaCO_3 scale that grew on the membrane surface during the treatment of brackish water with a high saturation index with respect to CaCO_3 (Table 3). The growth of CaCO_3 scale on the membrane surface results in a significant drop in flux (Figure 5). Flux recovery was consistently demonstrated upon the application of an external potential to the membrane surface, when the membrane was used as an anode.

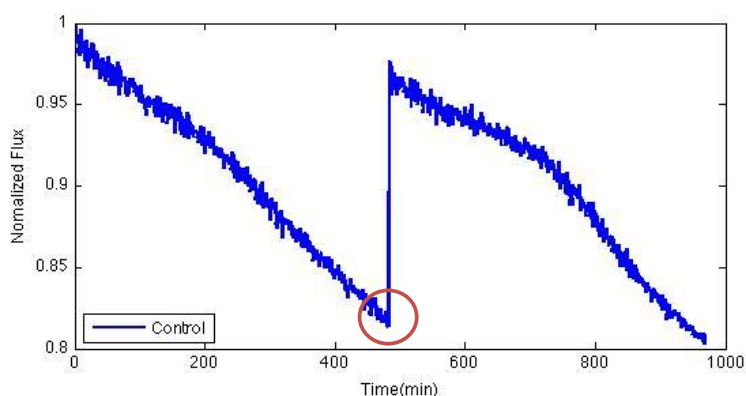


Figure 5. CaCO_3 scaling experiment; flux declined as CaCO_3 scale developed on the membrane surface. When a 2.5V potential (designated by a red circle) was applied (membrane as anode), and the membrane was flushed at high velocities, flux was fully recovered.

As shown in Figure 5, when no electrical potential was applied to the membrane surface the flux through the membrane experienced a persistent drop as a result of the growth of CaCO_3 scale, with water fluxes declining by over 18% over a period of 460 minutes. After ~460 minutes, the pressure was shut off and a 2.5 V potential was applied to the membrane/counter electrode pair for 30 minutes (5 min on/5 min off). As can be seen, the water flux quickly recovered to near (98% recovery) the initial value, indicating

that the CaCO_3 scale was effectively removed from the membrane surface. After 30 minutes, the potential was shut off and the pressure resumed, and the system experienced resumed fouling due to CaCO_3 scaling. These results were observed in multiple experiments, and can be seen in the Appendix (Figure A-5 to A-7). Simple flushing of the membrane (with no potential applied) did not result in any flux recovery. The reason the pressure was turned off during the application of the potential was the need to increase cross-flow velocities during the descaling process. The diaphragm pump used during the pressurized mode could only deliver a velocity of 4.5 cm/s; at these flow velocities, any detached CaCO_3 scale quickly re-deposited on the membrane surface. To avoid this, we used a peristaltic pump, which delivered a flow velocity of 8.6 cm/s, during the de-scaling stage. At this velocity, the detached CaCO_3 was quickly removed from the system and flux was rapidly restored [32]. While the flow velocities provided by the peristaltic pump were higher, they were still very low and in line with flow velocities used in many RO processes. Visual inspection of the membrane before and after the electrical de-scaling treatment clearly demonstrated the impact of the applied voltage, with the electrified membrane exhibiting a significantly reduced white area corresponding to the presence of CaCO_3 crystals (Figure. 6).

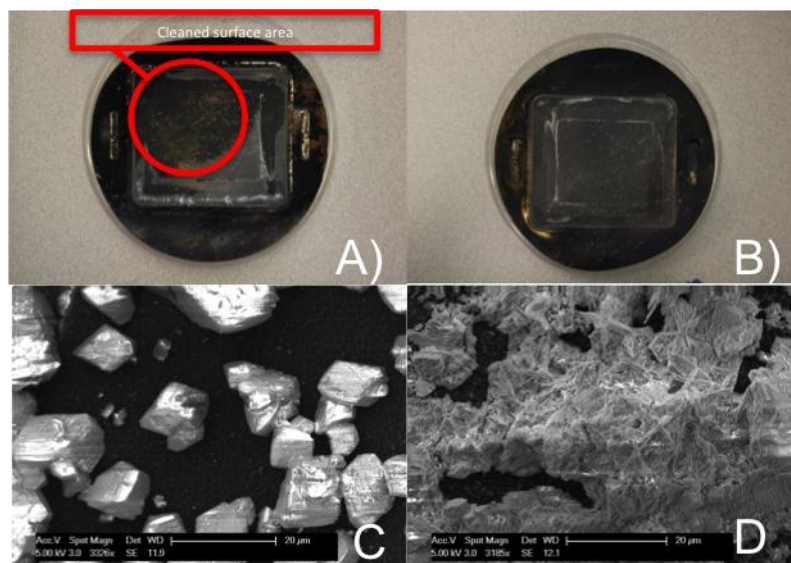
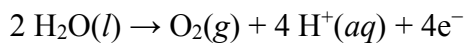
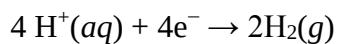


Figure 6. A) Electrically conducting RO membrane surface area after the application of 2.5V; the white area, corresponding to areas still covered by CaCO_3 is greatly reduced; B) Membrane area fully covered by CaCO_3 scale; C) SEM of membrane surface after the application of 2.5V displaying few CaCO_3 crystals; D) Thick CaCO_3 deposits on fouled membrane surface (no voltage applied).

As displayed in Appendix Figure A-2, the “true” potential on the membrane when 2.5V are applied to the membrane/counter electrode pair (when the membrane is used as an anode) is 1.8V vs. the Ag/AgCl reference electrode. At this potential water oxidation occurs, and results in the formation of H^+ along the membrane surface (membrane as anode) [110].



The corresponding half reaction takes place on the cathode



CaCO₃ crystals are very pH sensitive, and dissolve rapidly in low pH conditions [36,110]. Thus, when the electrical potential is applied to the scaled membrane surface local pH values are reduced due to the formation of H⁺, and the deposited CaCO₃ crystals dissolve/detach from the membrane surface, resulting in flux restoration.

2.3.3 CaSO₄ Scale Prevention

Here we demonstrate the ability of the electrically charged membrane to significantly delay the onset of CaSO₄ scale formation. In contrast to CaCO₃, CaSO₄ scale is pH insensitive, and cannot be removed through pH adjustments. As in the case of CaCO₃ scaling, the growth of CaSO₄ scale on the membrane surface is associated with flux decline and performance loss. We investigated two scenarios in this portion of the study; in the first scenario, the CaSO₄ scaling solution was recycled through the RO module with no filtering and in the second scenario we added an in-line 0.5µm microfilter designed to remove any particulate CaSO₄ formed during the experiment and carried along the feed stream.

When no in-line filter was used, the continuous application of 1.5V to the membrane/counter electrode pair (membrane as anode) led to a slight decline in the rate of flux decay (Figure 7). These results were done in duplicate and can be seen in the Appendix Figure A-3 and Figure A-4.

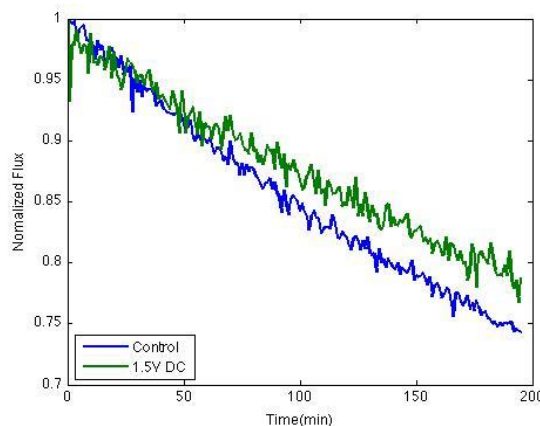


Figure 7 Flux decline due to CaSO_4 scaling with no in-line filter; membrane was used as an anode with a cross-flow velocity of 4.5 cm s^{-1} .

When no potential was applied, the rate of flux decline was 30% greater than the flux decline rate experienced by the electrically charged membrane. When an in-line filter was used, the rate of flux decline experienced by the non-charged membrane was more than twice that experienced by the electrically charged membrane (1.5V as anode) (Figure 8). Duplicates of these experiments can be seen in the supporting information.

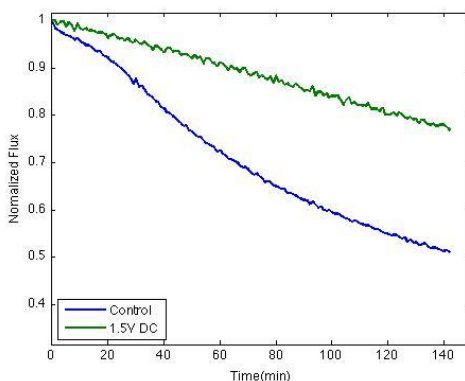


Figure 8. Flux decline due to CaSO_4 scaling with in-line $0.5 \mu\text{m}$ filter and a cross-flow velocity of 3.4 cm s^{-1} .

This would indicate that a large amount of flux decline observed when no in-line filter was used could be associated with secondary deposition of CaSO_4 crystals formed during the RO process. Indeed, after prolonged use, the in-line filter developed a coarse yellowish coating, which we assumed to be trapped CaSO_4 crystals formed during the RO process. In a typical RO system, the feed stream would not be recycled. Therefore, the in-line filtration conditions are more representative of realistic conditions one would encounter in field applications of RO technology. Membrane fouling rates in the absence of the inline filter are similar to the flux decline observed when an in-line filter was used and the membrane was electrically charged. However, flow velocities used when the in-line filter was present were significantly lower than those used when the filter was absent, which would lead to more challenging fouling conditions.

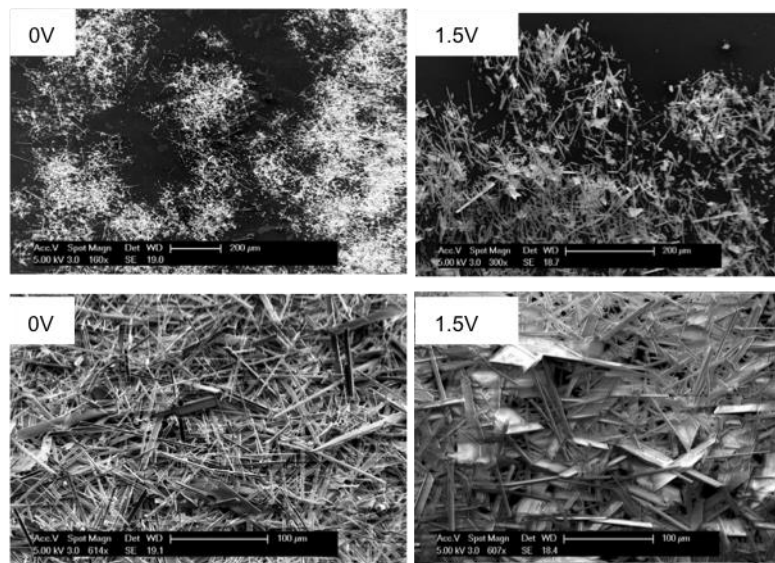


Figure 9. SEM images of the membrane surface covered by CaSO_4 crystals; CaSO_4 scale morphology changes as a function of the applied potential. Top images are from the “transition” zone and bottom images are from the main part of the membrane (see Figure A-8 in the Appendix for a detailed description of membrane zones).

Applying a positive external charge to the membrane surface also had a significant impact on the deposited crystal morphology. When no voltage was applied, the CaSO_4 exhibited the typical needle-like morphology, and the crystals were tightly packed (Figure 9). In contrast, when the membrane is used as an anode with 1.5 V applied, we can see that the crystals are much larger, and not as tightly packed, which would explain why the flux decline was not as severe, as water can flow through the scale structure.

When an electrically charged surface is placed in contact with an ionic solution, ions will redistribute themselves to maintain system electroneutrality, forming an EDL [96,98]. Thus, when the membrane is positively charged (membrane as anode), negative counter ions will flock to the membrane surface, while positive co-ions will be repelled away from the membrane; along the counter electrode (cathode) the situation is reversed. The number of counter-ion associated charges (negative charges when membrane is used as anode) along the membrane surface will equal the number of positive charges on the membrane surface; the number of positive charges on the membrane surface is proportional to the membrane electrical potential. Thus, by applying high external potentials to the electrically conducting RO membrane surface, large numbers of negative counter ions are needed along the membrane surface to maintain electroneutrality.

Due to the hydrated volume of counter-ions, when a sufficiently charged membrane surface is brought into contact with an ionic solution, a single layer of ions will not be sufficient to ensure charge neutrality. Thus, multiple layers of counter-ions accumulate along the membrane surface [97,111]. In these layers, the concentration of co-ions are near zero. For rapid nucleation to occur, both positive and negative ions need to be present in

near-equal concentrations [35,99]. Therefore, in the presence of a highly charged surface, the nucleation of sparingly soluble salts, such as CaSO_4 , is discouraged near the charged surface. Away from the charged membrane surface the concentrations of co- and counter-ions equalize, and rapid nucleation can take place. However, the crystal nuclei are formed away from the membrane surface, and can be carried away by the cross-flow.

2.3.4 Modelling Ion Concentrations along an Electrically Charged RO Membrane Surface

The standard Poisson-Boltzmann (SPB) model can be used to predict ion concentrations near a charged surface when surface potentials do not exceed ~ 200 mV. However, when surface potentials exceed 200 mV, the basic assumption on which the SPB model is based is violated, namely that the ions are in an infinitely dilute solution. The SPB model does not take into account the finite volume of ions, and therefore has no limit to the number of counter ions in the Stern layer, which is physically impossible. One result of this over-simplification is that the SPB over predicts the potential drop as one moves away from the charged surface. A useful modification to the SPB model, known as the modified PB model (MPB), considers the volume of ions when calculating the number of counter-ions attracted to an oppositely charged surface. As a result, the MPB equation predicts a region along the membrane surface that is more than one molecule thick, where only counter ions exist; this layer is significantly thicker than the single layer of counter ions in the Stern layer used by in the SPB model.

We used the MPB model to predict the potential as a function of distance from the membrane surface [70]:

$$\varepsilon_e \frac{d^2 \Psi}{dx^2} = \frac{-e N_A \sum_{i=1}^m z_i c_i^\infty \exp\left(-\frac{z_i e \Psi}{kT}\right)}{1 + \sum_{i=1}^m \frac{c_i^\infty}{c_i^{\max}} \left[\exp\left(-\frac{z_i e \Psi}{kT}\right) - 1 \right]}$$

We then used the predicted potential to calculate the local ion concentrations as a function of distance from the membrane [70]:

$$c_i = \frac{c_i^\infty \exp\left(-\frac{z_i e \Psi}{kT}\right)}{1 + \sum_{i=1}^m \frac{c_i^\infty}{c_i^{\max}} \left[\exp\left(-\frac{z_i e \Psi}{kT}\right) - 1 \right]}$$

where ψ is the electrical potential, z is the valence of ions, e is the elementary charge, N_A is Avogadro's number, c_i^∞ is the bulk ion concentration, $c_i^{\max}$ is the maximum ion concentrations in a given space given ionic steric effects, ε_e is the permittivity of the electrolyte solution (changes with ion concentration), k is Boltzmann's constant, and T is temperature. The boundary conditions for this problem are $\psi_{x=0} = \psi_{\text{applied}}$ and $\psi_{\text{bulk}} = 0$. $c_i^{\max}$ can be calculated using the following equation [70]:

$$c_i^{\max} = \frac{p}{\frac{4}{3} \rho R_i^3 N_A}$$

where p is a packing coefficient, R_i is the ionic radius, and N_A is Avogadro's number.

We used these equations to predict the concentrations of Ca^{2+} and SO_4^{2-} ions as a function of distance from the membrane surface. In this model, we used the Ca^{2+} and SO_4^{2-} concentrations found in our model CaSO_4 scaling solution (Table 2). As expected, the

model predicted that by increasing the applied electrical potential to the membranes surface (membrane as anode) the layer of SO_4^{2-} counter-ions extends further away from the membrane surface (Figure 10 B). When modelling the system, we did not consider the concentration polarization (CP) layer formed along the membrane surface. As can be seen in Figure 10 B and C, the concentrations of counter-ions (SO_4^{2-}) along the membrane surface reached a maximum of approximately 4.6 M. This maximum concentration is a function of the volume of the hydrated ions, and as can be seen, this value is reached when 250 mV are applied to the membrane surface; increasing the applied surface potential simply expands the counter-ion exclusive zone but does not increase the maximum ion concentration, which is physically bound. Beyond the exclusive counter-ion zone, the concentrations of counter- and co-ions begin to converge, eventually reaching the concentration within the CP layer. We do not consider ion concentration change from the bulk to the CP in this model, as it does not impact ion concentrations within the first few nm away from the membrane, which are wholly dependent on the surface potential.

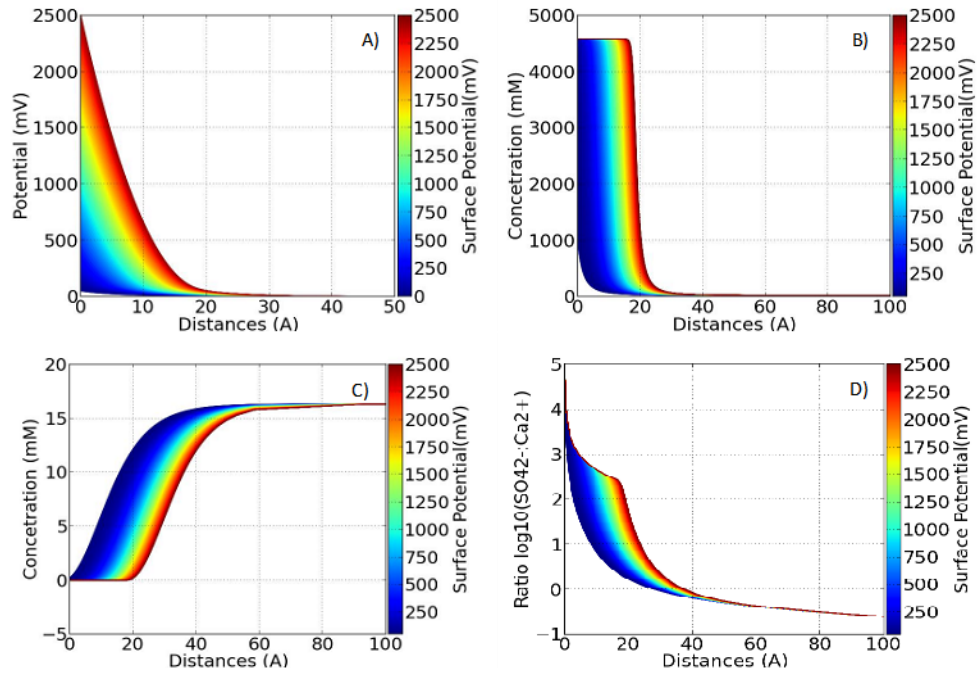


Figure 10. MPB model results; A) potential drop as a function of membrane surface potential and distance from the membrane surface; B) Concentrations of SO_4^{2-} ions as a function of membrane surface potential and distance from membrane surface. C) Concentration of Ca^{2+} ions as a function of membrane surface potential and distance from membrane; D) ratios between SO_4^{2-} and Ca^{2+} ions as a function of surface potential and distance from the membrane surface

Correspondingly, the distance away from the membrane where Ca^{2+} ions are excluded grows (Figure 10C). The ratio between Ca^{2+} and SO_4^{2-} ion concentrations, which determines the nucleation rate of CaSO_4 , demonstrates that as the membrane electrical potential increases from zero to 2.5V, the distance from the membrane where stoichiometric concentrations exist more than doubles, from below 2 nm to more than 4 nm (Figure 10D). Thus, the region where nucleation can actually take place is pushed out away from the membrane surface, which would reduce the ability of the formed CaSO_4 nuclei to attach and grow on the membrane surface (Figure 11). While these distances are very small, it is important to remember that the size of a CaSO_4 crystal nucleus is approximately 1.5 nm. Therefore, the nucleus does not form directly near the membrane surface, and can be carried away by the cross flow.

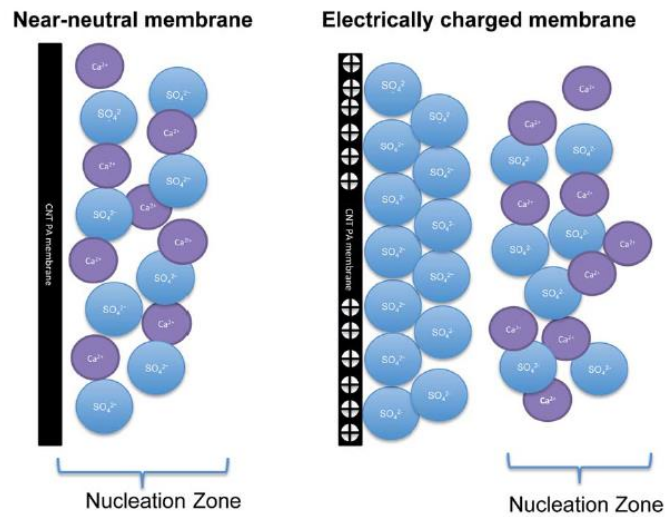


Figure 11. As the applied surface potential increases, the region near the membrane where only SO_4^{2-} ions exist expands out into the solution, which pushes the nucleation zone away from the membrane surface.

The surface roughness of the electrically conduction RO membrane used in this study was determined to be 91 nm (Figure 3). Thus, in our experimental system, when a crystal is formed in a membrane “crevice” it is less likely to be carried away by the cross-flow as opposed to a crystal formed on a “hill” where the cross-flow is more likely to remove the crystal. The model qualitatively explains our experimental observations: the application of an external potential to the membrane surface leads to a decrease (but not outright prevention) in membrane scaling rates. We hypothesize that by reducing membrane surface roughness we will be able to eliminate membrane areas that are likely to “trap” crystal nuclei, thus improving membrane performance.

2.4 Conclusion

In this paper we describe how the application of an electrical potential to the surface of an electrically conducting CNT-PA composite RO membrane can remove CaCO_3 scale and significantly slow the formation of CaSO_4 scale. When the membrane is used as an anode, the application of 2.5V leads to the formation of localized H^+ due to the oxidation of water, which cause the dissolution and removal of CaCO_3 scale deposited on the membrane surface. CaSO_4 scale growth, which is pH-insensitive, was significantly delayed through the application of relatively low electrical potentials to the membrane surface (1.5V, which is below the water splitting point). We used as MPB model to predict ion concentrations along the membrane surface as a function of the applied electrical potential; when sufficient electrical potential was applied, the ratio between anions and cations was altered, which has been shown to lead to a drop in crystal nucleation rates. Crystals that

did form did so away from the membrane surface and were carried away by the cross-flow, which we hypothesize is the reason for the observed drop in CaSO_4 fouling rates. The results of this study illustrate the potential benefits of using electrically conducting membranes in RO water treatment processes. Widespread adoption of this technology could significantly reduce the use of anti-scaling chemicals and acids in the treatment of brackish groundwater and recycled wastewater.

Chapter 3

Treating Anaerobic Sequencing Batch Reactor Effluent with Electrically Conducting Ultrafiltration and Nanofiltration Membranes for Fouling Control

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3.1 Introduction

Anaerobic bioreactors are an attractive treatment option for high-strength wastewater[12]. Several advantages associated with anaerobic processes include the generation of methane gas that can be harvested for energy production, reduced sludge production, and no aeration requirements, which reduces process energy demands[112–114]. Anaerobic bioreactors have been demonstrated to be effective at degrading a range of organic contaminants found in industrial wastewater, including benzyl alcohol, a chemical used as a paint stripper [115,116]. The use of benzyl alcohol in industrial activities, such as airplane depainting, produces large intermittent flows of high organic strength wastewater. Frequently, the flowrate of industrial wastewater depends on the schedule and activity of the industry in question, i.e. flowrates can go to zero on weekends and holidays, unless large flow equalization tanks are used. The option of idling the reactor during low flowrate conditions, as well as their ability to treat high intermittent concentrations, make anaerobic sequencing batch reactors (aSBRs) an attractive option for industrial wastewater treatment when nutrient removal is not a critical issue.

Membranes as a tertiary wastewater treatment technology have been widely applied in areas such as wastewater reuse, desalination pretreatment, and in membrane bioreactors [24]. As a physical separation barrier, ultrafiltration (UF) membranes can effectively retain particulate matter and microorganisms resulting in high quality permeate suitable for further treatment by nanofiltration (NF) [117]. Importantly, membrane modules can be coupled directly to a conventional wastewater treatment processes, and can be easily integrated into existing wastewater treatment trains. Thus, using UF and NF membranes to

treat the effluent from aSBR offers the potential of producing extremely high quality water that can be safely discharged or reused.

The water quality of a treatment train incorporating membrane treatment can be tailored by the choice of membranes used in the process. For pressure-driven membranes, better separation and higher quality effluent is typically achieved by using denser membranes that require higher operating pressures, such as NF and reverse osmosis (RO). Typically, feed water to NF and RO membranes requires pretreatment to remove foulants; this pretreatment is often done through the use of less restrictive membranes such as microfiltration (MF) and UF[7]. The use of UF and NF membranes in series to treat bioreactor effluent has been demonstrated to produce excellent water quality, with near complete removal of small organic molecules such as pharmaceuticals and endocrine disruptors[118]. A significant advantage of NF processes over RO is that they operate at lower pressures and do not lead to monovalent salt buildup (e.g. NaCl) in the reactor, which can damage the bacteria responsible for the biological process [119].

Fouling prevention is one of the most challenging aspects of tertiary wastewater treatment with membranes [120–122]. During filtration, suspended and dissolved materials in the water deposit on the membrane surface, which leads to decreased process performance, increased energy demand, and reduced membrane lifetime [15,123]. In aerobic membrane bioreactors (MBRs) with submerged membranes, vigorous air scouring is used for the dual purpose of providing oxygen to aerobic bacteria and physically cleaning fouled membrane surfaces [124,125]. However, air scouring is not advisable during anaerobic processes due to the need for low oxygen concentrations. Several strategies have

been proposed to mitigate membrane fouling when scouring is not possible, including: scouring with biogas[126], operating at below a so called “critical flux” value (although this does not prevent fouling over the long term)[121], and using electrical fields to repel charged foulants and bacteria from the membrane surface [60,127–130].

Electrically conducting membranes have been demonstrated to be effective at solving many of the fouling problems associated with membrane processes, as well as endowing membranes with new functionalities. These membranes have been demonstrated to prevent membrane fouling when used as cathodes during the filtration of high concentrations of organic molecules [129]. Electrically conducting NF and RO membranes demonstrated excellent anti-biofouling and anti-scaling properties when an electrical potential was applied to the membrane surface [60,71,130]. In addition, electrically charged membranes have been used as electrocatalytic platforms for the purpose of electrochemically transforming various aqueous contaminants [131,132]. The use of electroactive membranes for fouling prevention during aerobic MBR processes has been previously explored, but to the best of our knowledge, no one has explored the use of electrically active UF and NF membranes in series for the treatment of anaerobic reactor effluent [128]. Additionally, while the effectiveness of electrically charged membranes in preventing fouling has been demonstrated using simple, single component systems, few studies have demonstrated the use of this class of membranes in the treatment of complex waste streams containing multiple foulants. Importantly, in studies of most membrane treatment systems, permeate water is recirculated to maintain constant organic concentration, or the systems operate in single pass mode, which means both permeate and feed stream are discarded

after passing through membrane. Therefore, there is still a need to investigate the fouling behavior of UF and NF membrane systems in series when treating industrial wastewater at higher recovery rates (90%) while returning membrane concentrate back to the reactor for further treatment, a situation more similar to real applications of this technology.

This study demonstrates the use of an aSBR coupled to an electrically conducting UF and NF membrane system for the treatment of high-strength industrial wastewater containing large concentrations of industrial paint stripper. The ultimate goals of this study were: 1) to evaluate the anaerobic degradation of benzyl alcohol using an aSBR; 2) to prevent fouling of the electrically charged UF membrane (used as a cathode) when treating effluent from the aSBR operating at 90% recovery without any chemical cleaning; and, 3) to study the downstream influence of this treated waste stream on the fouling and subsequent cleaning of an electrically conducting NF membrane system.

3.2 Materials and Methods

3.2.1 Materials

Carboxylated multiwall carbon nanotubes (CNT-COOH) were purchased from Cheap Tubes (Cheaptubes Inc. Brattleboro, VT). Polysulfone (PSF) UF supports were purchased from Sepro Membranes (Sepro Membranes Inc., Oceanside, CA); the membranes have a reported molecular weight cut off of 65 kDa. ACS grade trimesoyl chloride (TMC), MgSO_4 , piperazine (PiP), and polyvinyl alcohol (PVA) were purchased from Fisher Scientific. A surrogate wastewater containing dilute commercial paint-stripper (B&B Trittech 9095, kindly provided by the Air Force Civil Engineering Center) was used as the

feed solution for the aSBR. B&B Tritech 9095 contains mainly benzyl alcohol and hydrogen peroxide.

3.2.2 Conductive Membrane Fabrication

Electrically conducting UF membranes were fabricated based on a previously described process[133]. To summarize, 75 ml of 0.01 mg/ml CNT-COOH in DIW were pressure deposited onto the PSF support. Then, a solution of PVA in DIW was pressure deposited onto the support for a final weight ratio of 3:1 PVA to CNTs. The PVA layer was then cross-linked to the membrane support by submerging in a 90°C solution of 1 g/l glutaraldehyde and 0.37 g/L of hydrochloric acid in DIW for 1 hour. Once complete, the UF materials were stored at 4°C.

The fabrication of electrically conducting NF membranes has also been described in a previous paper[60,71]. Some modifications were made: 50 ml of 0.01 mg/ml CNT-COOH in DIW were pressure deposited onto the PSF support. The support was then soaked in an aqueous PiP (2%) solution for 2 minutes. A rubber roller was used to remove excess water prior to immersing the membrane in a 0.15% TMC solution in hexane. After 1 minute, the membrane was removed from the hexane, dried in an oven at 90°C for 10 minutes and stored at 4°C.

3.2.3 Membrane and Water Characterization

The electrically conducting UF and NF membranes were characterized using a range of instruments. Images of the membrane surface were obtained using scanning electron

microscopy (SEM; FEI XL30 SEM-FEG; Hillsboro, OR) with no sputter-coating. Membrane roughness was measured using atomic force microscopy (AFM; Bruker, Billerica, MA). Contact angle measurements were performed using a contact angle goniometer (Attension, Linthicum Heights, MD). Membrane conductivity was measured using a 4-point conductivity probe (Veeco, Plainview, NY).

Multiple analytical tools were used to characterize the water quality throughout the treatment process. Total organic carbon (TOC; OI Analytical, College Station, TX) and chemical oxygen demand (COD; Hach, Loveland, CO) were used to evaluate aSBR and membrane performance by sampling the feed, effluent and permeate at different treatment stages. Total suspended solids (TSS) were analyzed following Standard Methods procedures[134]. The turbidity of the different water samples was measured using a turbidity meter (Hach, Loveland, CO). Water conductivity was measured using a conductivity probe (Thermo Scientific, Waltham, MA). High pressure liquid chromatography (HPLC; Agilent, Santa Clara, CA) was used to determine the concentration and identities of the different organic compounds in the reactor, reactor effluent, and UF permeate. HPLC calibration curves were prepared for benzyl alcohol and benzoic acid for analysis on an XDB-C-18 column. HPLC operating conditions were: flow rate = 1 ml min⁻¹, injection volume = 100 μ l, detector wavelength = 254nm. The mobile phase was 3:97 of acetonitrile:10mM formic acid at 0 – 4.5 min, 70:30 of acetonitrile:10mM formic acid at 4.5 – 7 min and 3:97 of acetonitrile:10mM formic acid at 7 – 9 min.

3.2.4 Feed Water Source for aSBR and Membrane

The feed solution for the aSBR was created by diluting B&B Tritech 9095 into dechlorinated tap water to produce a COD of 2000 mg/L. In addition, a commercial fertilizer (Vigoro All Purpose Liquid Plant Food) was added to the reactor (1 g/L) to provide nitrogen and phosphorous to the bacteria. The effluent of the aSBR was fed directly to the UF system, and the UF permeate was used as the feed solution for the NF system.

3.2.5 Anaerobic Sequencing Batch Reactor and Membrane Treatment Operational Procedures

A water treatment train coupling the aSBR to the UF and NF membrane systems was used in these experiments (Figure 12). When the membrane systems were operated at 90% recovery, the final retentate from the UF and NF systems (10% of the original feed volume) was returned to the aSBR.

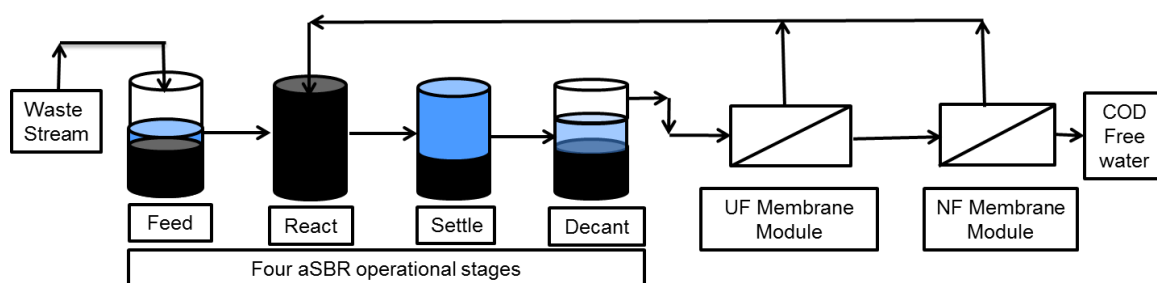


Figure 12. System schematic and process diagram for an aSBR coupled to a UF and NF membrane process.

The reactor (3 L) was operated on a 24 hour cycle (Figure 12). At the beginning of each cycle, the reactor was fed 1 L of feed solution and allowed to react for 21 hours. During the reaction phase, the reactor was continuously stirred at a constant 35°C. Any gases produced during the degradation process were allowed to escape the system. After 21 hours, stirring was stopped, and the reactor was allowed to settle for 3 hours. Following the settling step, 1 L of the reactor content was decanted from the top, analyzed, and used as the feed solution for the UF system. The electrically conducting UF membrane was placed in a custom-built flat sheet membrane module that allows an external electrical potential to be applied to the membrane surface and contains a titanium counter electrode situated 4 mm above the membrane surface (Appendix B-1). A 3 mm thick polypropylene mesh spacer was placed between the membrane and counter electrode. The effective area of the membrane was 40 cm².

Prior to the start of the experiment, the UF membrane was compressed at 90 psi with DIW for at least 48 hours until the flux stabilized. Flow and pressure to the UF system was provided by a rotary vane pump (McMaster-Carr, Santa Fe, CA), with cross-flow velocity of 20 cm/s. Electrical potentials were applied to the membrane surface and counter electrode by connecting the system to an arbitrary waveform generator operating in DC mode (Rigol, Oakwood Village, OH). The UF system was operated at constant flux unless otherwise specified, which was maintained by adjusting the pressure in the UF membrane module. The optimal electrical potential was determined by comparing the effect of 0 V, 3 V, and 5 V of negative surface potential on membrane fouling using aSBR effluent under constant feed concentrations; under constant feed concentrations, aSBR effluent was

introduced to the UF membrane, with both the feed and permeate returning to the feed reservoir (no recovery).

To test the UF membrane's ability to withstand fouling while operating at 90% recovery, we compared membrane performance as a function of applied potential (0 V vs. 5 V as cathode) while not recycling the membrane permeate. In these experiments, the membrane was operated at a constant flux of 40 LMH, with no backwashing. To test the long-term performance of the UF system at 90% recovery, the UF membrane system was run with the optimal electrical potentials identified previously. Here, three batches of decanted aSBR effluent were run consecutively through the system at 90% recovery with different electrical conditions (-5 V, -5 V/+1.5 V, and 0 V) with no physical or chemical cleaning between each batch. During these experiments, the membrane was backwashed every 30 minutes for 1 minute with permeate.

An Arduino-based control system was used to monitor, maintain and record the operating conditions, including flow rate and velocity, membrane flux, and pressure[129]. Membrane flux was determined by collecting and weighing the membrane permeate. Automatic backwashing was controlled through the Arduino system, and was performed using a peristaltic pump (Cole Parmer, Vernon Hills, IL), which used UF permeate as the backwashing fluid. During backwashing events, different electrical potentials were applied to the membrane surface (0 V, -5 V, and +1.5 V). The UF permeate was characterized in terms of TOC, COD, TSS, turbidity, and conductivity, and used as feed solution for the NF system.

The electrically conducting NF membrane was used in a similar flow module in flat-sheet configuration as described above, except that this module was reinforced with steel plates to withstand the higher pressures used during the NF process. Additionally, the NF module did not contain a mesh spacer (Appendix Figure B-1). The effective area of the membrane was 40 cm². Prior to the start of the experiments, the NF membranes were compressed at 200 psi for at least 48 hours in DIW until the flux stabilized. Flow and pressure for the NF system were provided by a diaphragm pump (Wanner Engineering, Minneapolis, MN), with a cross-flow velocity of 20 cm/s.

Feed water for the NF membrane was UF permeate. The NF membrane was tested under three electrical conditions (0 V, -5 V, and +1.5 V); in all cases, the potential was applied as DC, and the membrane was used to recover 90% of the NF feed. All NF experiments were done in duplicate. An Arduino-based control and data acquisition system was used for the NF process, similar to the one described above for the UF system. The electrical potential was applied to the NF membrane by an arbitrary waveform generator, and the system was operated at a constant pressure (180 psi). Membrane cleaning was conducted immediately after the fouling experiments using DI water at a crossflow velocity of 20 cm/s. NF permeate was characterized in terms of TOC, COD, TSS, Turbidity, and conductivity.

3.3. Results and Discussion

3.3.1 Membrane Fabrication and Characterization

The electrically conducting UF membranes used in this study have been extensively characterized in a previous study [56,129]. A summary of the UF membrane characteristics can be seen in Table 1. Briefly, the PVA-CNT-COOH network deposited on the surface of the PS35 PSF support creates a smooth (46 ± 2 nm), electrically conducting (1132 ± 32 Ω /square) robust layer that can be backwashed without experiencing delamination from the PSF support (Figure 13a, c). The CNT-COOH and PVA molecules are covalently bound through ester and ether bonds between the hydroxyl and carboxyl groups on the molecules using glutaraldehyde as the cross-linking agent[129]. Due to the very porous network of CNTs, the rejection properties of the composite structure are governed by the underlying PS35 PSF support (MWCO = 65 kDa)[129]. The use of the highly hydroxylated PVA molecule in the electrically conducting layer renders the surface very hydrophilic, with a water contact angle of $32 \pm 3^\circ$ (Table 4, Appendix Figure B-2).

Table 4. UF and NF membrane properties

Membrane Characterization ^o	UF Membrane ^o	NF Membrane ^o
Root Mean Squared Roughness (nm) ^o	46.37 ± 2.37 ^o	13.84 ± 0.99 ^o
Resistivity (Ω/sq) ^o	1132 ± 32 ^o	1191.3 ± 16.2 ^o
Contact Angle ($^\circ$) ^o	32 ± 2.8 ^o	37.1 ± 0.08 ^o
<u>MgSO₄</u> Rejection ^o	0% ^o	96 ± 2 % ^o
Permeability (LMH/psi)* ^o	34.6 ± 0.77 ^o	0.19 ± 0.02 ^o

* LMH (Liter m^{-2} hr^{-1})^o

The electrically conducting NF membranes used in this study are a slightly modified version of the membrane material described previously [60,71]. The only significant difference was the use of PiP instead of m-phenylenediamine, which modified ion rejection and surface roughness. NF membrane properties are summarized in Table 4. When challenged with MgSO₄ or NaCl solution (1.5 g/L) the NF membranes used in this study exhibited a 96±2% and 60±6% rejection, respectively. In these membranes, the polyamide is covalently bound to the surface of the CNTs through ester bonds formed between the TMC molecule and hydroxyl groups on the CNTs [60,71]. SEM images of the membrane surface can be seen in Figure 13b; AFM image analysis of the NF membrane surface yielded a surface roughness of 14±1 nm, which is similar to the roughness of commercially available NF membrane materials (Figure 13d) [107,135]. SEM images of the membrane surface reveal a structure that is similar in appearance to commercially available NF membranes made with PiP (Figure 13b) [136]. The electrical resistivity of the NF membrane was determined to be 1,191 Ω/square, and the contact angle was found to be 37±0.1° (Appendix Figure B-2).

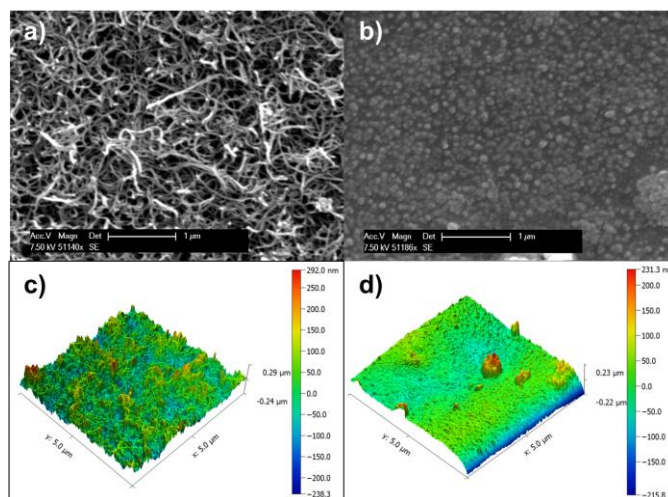


Figure 13. SEM images of (a) UF membrane surface, and (b) NF membrane surface. AFM images of (c) UF membrane surface, and (d) NF membrane surface. AFM images were used to calculate the surface roughness of the membranes.

3.3.2 Anaerobic Reactor Performance and Reactor Effluent Quality

The decanted effluent characteristics (COD removal, TSS, and turbidity) from the aSBR are plotted over time in Figure 14a. It took approximately 6 months for the reactors to achieve stable operating conditions. However, once these conditions were achieved, the reactor maintained excellent COD removal capacity, with COD removal ranging between 80-90% after 24 hours (Figure 14a). TSS and turbidity levels in the decanted water showed some variability that was attributed to the handling of the decanting process, with TSS values generally maintained below 65 mg/L and turbidity below 80 NTUs. However, most days had values that were significantly below these values (Figure 14a). Reactor effluent used during the membrane experiments was taken during days when the turbidity was below 20 NTUs. The reactor effluent contained 16 ± 2 mg/l of TSS and 13.7 ± 1.8 mg/l of VSS, with a ratio of 0.86 VSS/TSS (Table 5). VSS in wastewater is typically associated with the presence of bacteria, microbial degradation products, and other cellular products,

such as extracellular polymeric substances[13]. Thus, the majority of TSS in the decanted reactor effluent is organic on nature. An SEM image of a fouled UF membrane demonstrates the complex nature of the decanted reactor effluent; the SEM image shows multiple bacteria and an abundance of amorphous organic matter covering the membrane surface, demonstrating the complex nature of the membrane feed stream (Figure 14b).

Table 5. Water quality parameters

Parameter	Reactor Effluent	UF Permeate	NF Permeate
Total Organic Carbon (ppm)	26.5±4	22.5±5	4.8±0.4
Chemical Oxygen Demand (ppm)	96.5±12	60±10	3±3
Turbidity (NTU)	16±2	0.9±0.5	< 0.1
Conductivity (µS/cm)	1260±461	1111±314	129±31
Volatile Suspended Solid (VSS) (ppm)	13.7±1.8	ND*	ND*
Total Suspended Solid (TSS) (ppm)	16.2±2.4	4±4	ND*
VSS/TSS (%)	86 ± 4	ND*	ND*

*ND means the parameter is not detectable

HPLC analysis of water taken at different time points from the reactor shows the changes associated with the microbial transformation of the organic content of the reactor feed (Figure 14c). Here, the original organic compound (benzyl alcohol, $t=3.63$ min) is rapidly transformed to benzoic acid ($t=4.06$ min). A minor component of the feed (benzaldehyde, $t=4.53$ min) is not detected in the reactor effluent. Another small peak, detected at 0.56 min, grows with time; we were unable to identify this peak, but speculate it is a small organic acid due to its short elution time.

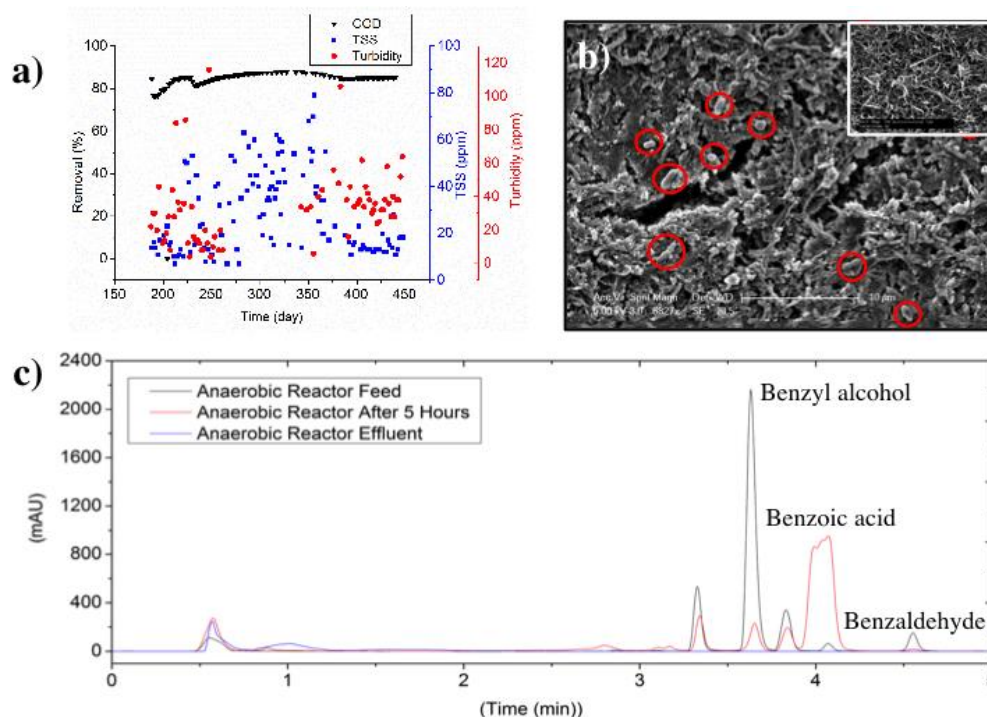


Figure 14. (a) aSBR performance in terms of COD removal, TSS and turbidity of decanted effluent. Data is presented from day 180 onward; prior to this time, reactor performance was highly variable, and the data is not displayed. (b) SEM image of fouled UF membrane, which was used to filter anaerobic reactor effluent. Red circles indicate bacteria; inset: bare (clean) PVA-CNT UF membrane (c) HPLC analysis at different experimental points with identifiable peaks. The black line corresponds to the reactor feed, the red line corresponds to the reactor contents after 5 hours of operations, and the blue line corresponds to the decanted reactor effluent. Peak identities were confirmed by injecting pure standards.

HPLC analysis of the aSBR content after 5 hours of reaction, as well as the decanted effluent, demonstrate the temporal changes in the concentration and speciation of the organic molecules in the reactor (Figure 15). The main intermediate transformation product of benzyl alcohol was identified as benzoic acid, which is in agreement with previously reported work on the anaerobic degradation pathways of benzyl alcohol [115,116]. Furthermore, it has been reported that during the anaerobic degradation of benzyl alcohol, benzoic acid forms and then disappears, with methane and very small concentrations of

volatile fatty acids as the final degradation products [115]. In the aSBR, the concentration of benzyl alcohol rapidly drops over the reaction time, with the primary degradation product, benzoic acid, emerging and then declining as the bacteria in the reactor continue the degradation process (Figure 15). After 5 hours, the concentration of benzyl alcohol in the aSBR drops by 84%, and after 21 hours of reaction, we could not detect any benzyl alcohol in the reactor (Figure 15). The concentration of the main transformation product, benzoic acid, rapidly increases to a concentration of 284 ppm after 5 hours, and then declines to zero in the aSBR effluent (after 21 hour). As mentioned before, the overall COD removal stabilized at approximately 86% in the aSBR (Figure 14a).

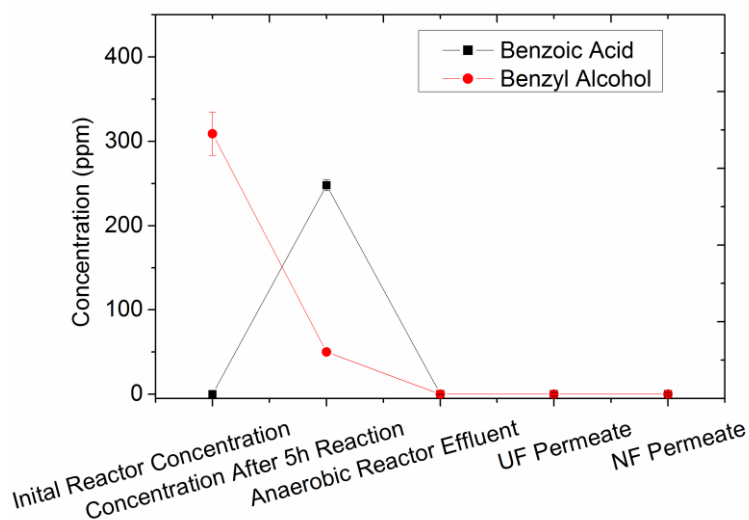


Figure 15. HPLC analysis of benzyl alcohol and benzoic acid concentrations measured at different experimental points. HPLC measurements were done in triplicate with error bars representing 95% confidence intervals.

3.3.3 UF Membrane Performance - Determining Optimal Operating Conditions

The decanted effluent from the aSBR was used as the feed for the UF membrane system. Since the main degradation products of the anaerobic processes (other than methane, hydrogen and carbon dioxide) have been identified as negatively charged small molecules, it was expected that the application of a negative potential to the membrane surface would reduce the extent of membrane fouling during the treatment of the aSBR effluent [137–139]. The application of a negative potential to the surface of the electrically conducting UF membranes had a significant impact on membrane fouling during the filtration of aSBR effluent (Figure 16a); here, the system was operated at a constant flux of $30 \text{ liter m}^{-2} \text{ hr}^{-1}$ (LMH), with an increase in pressure corresponding to membrane fouling. As can be seen, when no potential was applied, the pressure required to maintain the constant flux increased from 1.5 to 3.1 psi over the course of 5 hours. In contrast, when the membrane was used as a cathode the pressure increased to 2.4 and 2.2 psi when the whole cell potential was 3 V and 5 V, respectively. The UF feed (reactor effluent) water quality in all UF experiments can be seen in Table 5. In these experiments, water quality properties were maintained constant by recycling the membrane permeate back to the feed. To ensure reproducibility, the membranes were cleaned between each run to ensure that the DI water permeability was similar to the initial conditions.

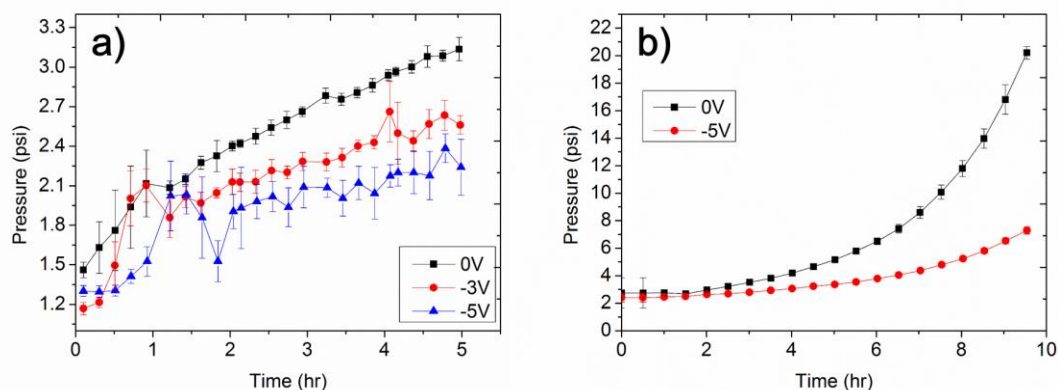


Figure 16. Impact of applied electrical potential on the required pressure to maintain a steady flux with (a) constant feed concentrations, and (b) system operated at 90% recovery. Experimental conditions were: aSBR effluent as feed, cross flow velocity of 20 cm/s, constant flux of 30 LMH (a) and 40 LMH (b). Electrical potentials in the figure represent the whole cell potential (potential difference between membrane (used as cathode) and counter electrode (anode)). In (a), blue (triangle) and red (cycle) lines represent the case where the membrane was used as a cathode with 5 V and 3 V applied to the membrane and counter electrode, respectively; the black (square) line corresponds to the control (0 V). In (b), the red (cycle) line corresponds to the case where the membrane was used as a cathode (5 V) and the black (square) line represents the control (0 V). All experiments were done in triplicate, with error bars representing 95% confidence intervals.

In an attempt to simulate real-world conditions, a second set of experiments were performed where the membrane permeate was not recirculated, which resulted in the increased concentration of the feed solution over time. Here, the membrane was operated at a constant flux of 40 LMH, and the pressure was monitored over time when the membrane was used as a cathode (5 V cell potential) or under no potential conditions (0 V) (Figure 16b). The system was operated at 90% recovery, i.e. until the feed volume reached 10% of its initial value. As can be seen, the application of 5 V to the system (membrane as cathode) resulted in significantly better performance. When no potential was applied, the system reached a final pressure of 17 psi in order to maintain a constant flux

of 40 LMH. In contrast, when an electrical potential was applied, the system only required 7 psi to maintain that flux.

3.3.4 Treating aSBR Effluent with Electrically Charged UF Membranes

Based on the results seen in Figure 16, it was decided that to effectively treat the aSBR effluent with the UF membrane while maintaining minimal fouling, the membrane would operate in a decreasing flux mode. In this mode, the system was run at 90% recovery, where membrane permeate was collected and not returned to the feed. Additionally, the flux was adjusted to the feed concentration, such that the initial flux (30 LMH) was reduced by 2 LMH for every 20% recovery. Thus, the final flux (when the system is approaching 90% recovery) would be 22 LMH (Figure 17a). In addition, the membrane was backwashed with UF permeate for one minute every half hour; no further cleaning of the membrane was performed. In this series of experiments, three decanted volumes from the aSBR were treated consecutively under each set of experimental conditions. The application of 5 V to the membrane and counter electrode (membrane as a cathode) had a significant impact on membrane fouling, with the pressure increasing from 1.5 psi to 2.2 psi over the course 65 hours, which was the length of time needed to treat three decanted volumes with 90% recovery (Figure 17b). In contrast, when no potential was applied, the final pressure was nearly 7 psi, which is over three times higher than the case where the membrane was used as a cathode (Figure 17b). Interestingly, when the membrane was used as a cathode (5 V), but switched to an anode (1.5 V) during backflushing events, the membrane experienced very rapid fouling (Figure 17b). In fact, the fouling was so rapid (and irreversible) that the

experiment was aborted at the end of the second round of aSBR effluent treatment. This result confirmed that the majority of foulants in the aSBR decanted effluent were negatively charged since they rapidly and irreversibly attached to the membrane surface when it was positively charged; it is possible that in addition to electrostatic adsorption, oxidizing conditions generated by the membrane anode could lead to electropolymerization of the organic molecules on the membrane surface, which could lead to irreversible membrane fouling.

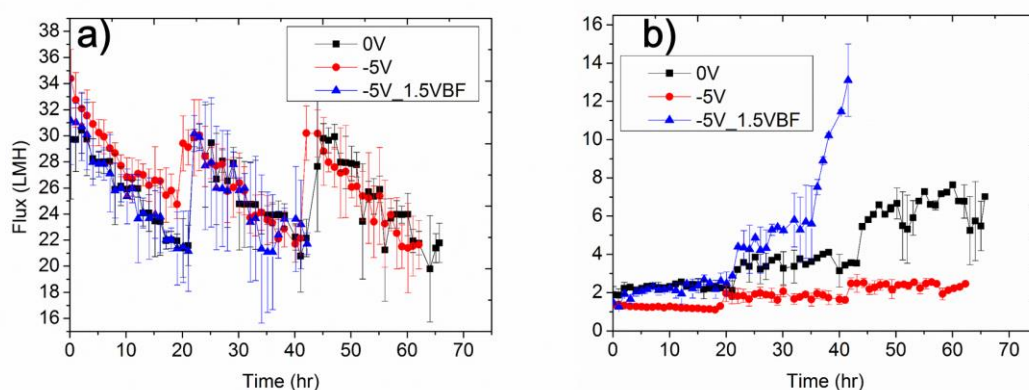


Figure 17. Treating aSBR effluent with electrically conducting UF membranes. (a) Flux as a function of feed concentration (up to 90% recovery). (b) Pressure required to maintain a given flux under different electrical conditions when system was operated at 90% recovery. Experimental conditions were: aSBR effluent as feed, cross flow velocity of 20 cm/s, membrane was backwashed with permeate every 30 minutes for 1 minute. Red (cycle) line represents conditions when membrane was used as cathode with 5 V applied to the membrane/counter electrode; blue (triangle) line represents conditions when the membrane was used as a cathode (5 V) and as an anode (1.5 V) during backwashing events; black (square) line represents the control (0 V).

UF permeate water quality parameters are summarized in Table 5. Not surprisingly, the UF membrane treatment had a modest impact on TOC levels, which decreased from 26.5 ± 4 to 22.5 ± 5 ppm. Based on previous literature and our HPLC analysis, it is expected

that the majority of the organic compounds in the aSBR effluent are small organic molecules, which would pass through a UF membrane[115]. However, the UF membrane treatment did have a dramatic impact on TSS and turbidity levels, reducing them from 16.2 ± 2.4 ppm to 4 ± 4 ppm, and from 16 ± 2 NTUs to 0.9 ± 0.5 NTUs, respectively (Table 5). COD levels in the UF permeate were 37% lower than in the feed. No statistical significance was found in COD levels between the UF permeate or retentate generated from the charged and uncharged membranes (Figure 18). Thus, this water is suitable as NF feed due to its low TSS and turbidity levels.

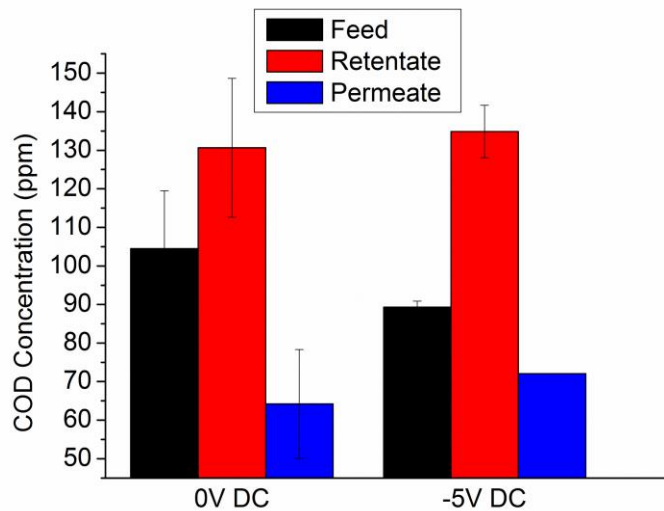


Figure 18. COD concentrations measured in the different UF streams. Measurements were triplicated, with error bars representing 95% confidence intervals.

3.3.5 NF Membrane Performance – NF Fouling

UF permeate was used as feed water for the NF membranes. In these experiments, the system was operating in concentration mode, where membrane permeate was not returned to the feed, and the feed was allowed to concentrate over time (90% recovery). NF

membranes were operated at a constant pressure (180 psi), with flux decline indicating membrane fouling. Interestingly, fouling in the NF system was not sensitive to the application of an electrical potential to the membrane surface, with nearly identical fouling rates observed when the membrane was charged with 5 V (as cathode), 0 V, or 1.5 V (as anode) (Figure 19). NF permeate had excellent water quality, with non-detectable TSS and turbidity levels, and near zero TOC and COD values (4.8 ± 0.4 and 3 ± 3 ppm, respectively) (Table 5). We speculate that the negligible impact of the electrical potential on membrane fouling is caused by the nature of the foulants that pass through the UF membrane. Since the majority of organic molecules found in the aSBR effluent (which is used as UF feed) are negatively charged, they are repelled by the negatively charged UF membranes. Thus, molecules that do pass through the UF membrane are likely to be neutral or positively charged, which would make them immune to the enhanced electrostatic forces generated during the application of an electrical charge on the NF surface [24].

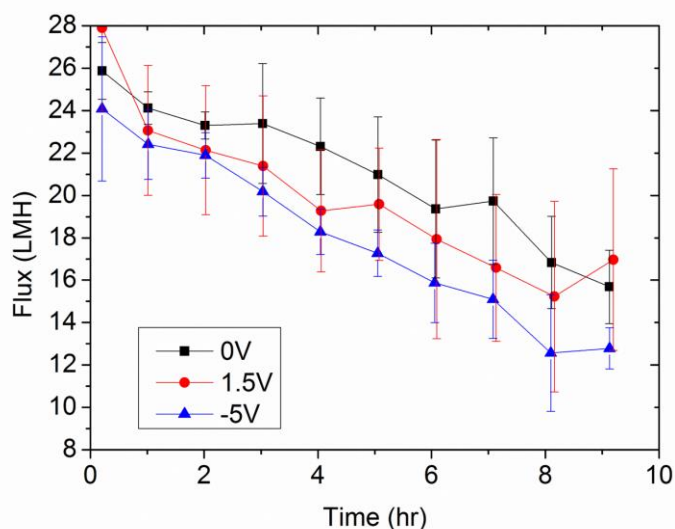


Figure 19. Fouling of electrically conducting NF membranes under different applied potentials. Experimental conditions: feed water was UF permeate, cross flow velocity was 20 cm/s, pressure was 180 psi. The red (cycle) line corresponds to conditions when the membrane was used as an anode (1.5 V); the blue (triangle) line represents conditions when the membrane was used as a cathode (5 V); the black (square) line represents the control (0 V).

3.3.6 NF Recovery

After the fouling experiments, an attempt was made to recover membrane performance by flowing DIW across the fouled membrane surface at a cross-flow velocity of 20 cm/s; the DIW was continuously recycled. Interestingly, when the membrane was used as an anode during cleaning (1.5 V), the cleaning process was not successful in restoring membrane flux to its original value, with the flux recovering to only 16 LMH, only 57% of its initial value (28 LMH) (Figure 20). In contrast, when the membrane was used as a cathode (5 V), or when no potential was applied, nearly full flux recovery was observed, with the flux returning to its original value. It is possible that under anodic

conditions some of the deposited organic matter underwent polymerization, which led to irreversible membrane fouling [28, 38].

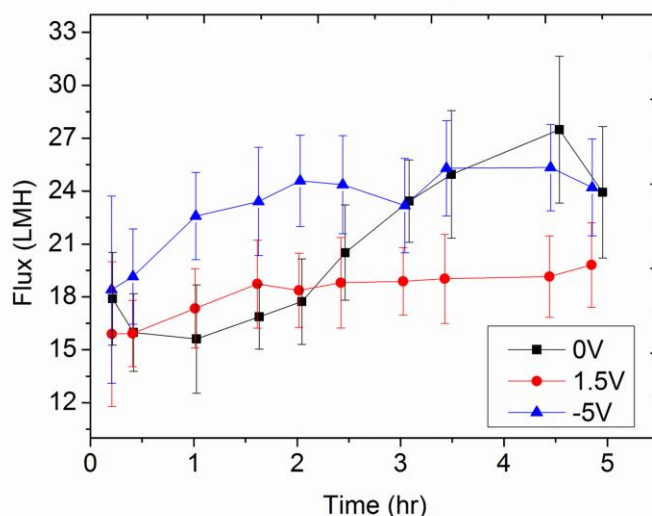


Figure 20. NF membrane recovery. Recovery was performed by flowing DIW over the membrane at 20 cm/s at a pressure of 180 psi while measuring flux. Red (cycle) line represents conditions when membrane was used as anode (1.5 V); blue (triangle) line represents conditions when membrane was used as cathode (5 V); black (square) line represents the control (0 V). Experiments were duplicated with error bars representing 95% confidence intervals.

3.3.7 Economic Analysis

Energy consumption associated with the application of 5 V to the UF membrane system was determined to be 0.01 kWh/m². This was calculated by measuring the current density on the membrane (0.2 mA/cm²) and multiplying this value by the potential (5 V) to get the power density (10 W/m²). During the UF treatment, the average flux of the system was 26 LMH. Based on this value, it was calculated that the energy consumption per cubic meter of UF permeate was 0.4 kWh/m³. Assuming average commercial energy costs in CA

(averaged over winter and summer - \$0.2/kWh), the additional cost associated with the application of the electrical potential is \$0.076/m³ of treated water.

3.4 Conclusions

In this paper we demonstrate the use of an aSBR coupled to a UF and NF membrane system for the purpose of treating high-strength industrial wastewater with intermittent flow containing benzyl alcohol – a commonly used paint stripper. The aSBR is demonstrated to be able to effectively degrade the organic contaminant (80-90%) over a 24-hour period, producing effluent that is relatively low in COD. Furthermore, we demonstrate the advantages associated with the use of electrically charged membranes for the treatment of anaerobic reactor effluent. When the UF membrane is used as a cathode (5 V), long-term experiments show that the membrane experiences very little fouling while continuously producing high quality effluent. In contrast, if the UF membrane is uncharged, significant fouling occurs and system performance is compromised, which could lead to an increase in chemical cleaning events. In contrast to the UF membranes, NF membrane fouling was not impacted by the application of an electrical potential. However, when attempting to recover the lost flux on the NF membranes, positively charged NF membranes were not completely recovered, which is likely due to polymerization of fouling molecules on the NF surface. The negatively charged and uncharged NF membrane's flux was recoverable after a simple rinse with DIW. The water treatment system described here yielded treated water with an excellent quality that can be readily discharged or reused. Importantly, the enhanced anti-fouling capabilities of the

electrically charged UF membranes will significantly reduce the need for chemical cleaning, as well as the cost of the overall process.

3.5 Acknowledgements

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Chapter 4

Polyaniline-Coated Carbon Nanotube Ultrafiltration Membranes: Enhanced Anodic Stability for *in Situ* Cleaning and Electro-Oxidation Processes

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4.1 Introduction

Membranes are used in the water treatment industry for seawater desalination, wastewater reclamation, and the treatment of surface water or groundwater for drinking water production [27]. A major impediment to membrane processes is membrane fouling, which results in a decline in system performance, reduced rejection, and requires additional cleaning steps needed to restore the membrane's flux [140]. Regardless of its cause (i.e. particulate, inorganic, organic and biological fouling) [15,141,142], the restoration of membrane performance results in operational disruptions and additional costs in terms of energy and chemicals. In addition, the removal of small, uncharged contaminants from municipal and industrial wastewater is difficult to achieve using low pressure membranes, requiring additional treatment steps, such as advanced oxidation processes [143], which add additional costs due to chemicals, transportation and storage of reactants [144].

Electrically conducting membranes (ECMs) synthesized through the deposition and cross-linking of a carbon nanotubes (CNT) network on a porous support, have been demonstrated to decrease multiple forms of fouling through the application of electrical potentials to the membrane surface. The mechanism for fouling prevention was found to be influenced by electrochemical reactions and electrostatic force [60,71,128–130,145,146]. Electrochemical flux recovery (i.e. electro-cleaning) has been demonstrated by applying cathodic potentials on the ECM's, with the cleaning mechanism described by the dual effect of hydrogen peroxide and oxygen gas micro-bubbles electro-generated at the membrane surface [147]. In addition, CNT-based filters and membranes have demonstrated the potential of coupling filtration with electrochemical reactions

(electrooxidation and electro-reduction [145,147–149]) showing improved reaction rates in comparison to non-porous configurations (*i.e.* stirred reactors) due to the increased advective mass transport of the target molecules to the electrode surface and overall surface area [87,105,150].

Although CNT-based ECMs show promising abilities, they have been found to be unstable under elevated anodic potentials in aqueous environments due to the oxidation of the CNTs and their breakdown when exposed to hydroxyl radicals generated on the CNT surface [151,152]. Therefore, development of anode materials with high anodic stability is of great importance, in particular for organic oxidation processes, which require relatively high potentials. Attempts to increase the resistance of CNT-based ECMs to anodic potentials have been centered on anchoring or coating metal nanoparticles (cobalt oxide, bismuth-doped tin oxide) on the surface of the CNTs; while results demonstrated some stability at potentials up to 2.2 V [61,153] (vs. a Ag/AgCl reference electrode), these ECMs were still unstable at higher anodic potentials.

Polyaniline (PANI) is a conjugated polymer with properties such as environmental stability, low toxicity and high electrical conductivity [154], which has been used in many applications including sensors, electronics, and fuel cells [155–158]. Composite membranes based on CNT-conjugated polymers (*i.e.* PANI, polypyrrole) have been previously fabricated through several methods including flash welding [159,160], non-solvent induced phase separation [161,162] and polymer blending [163,164] showing enhanced mechanical stability and high electrical conductivity. Furthermore, PANI based

composite structures were found to be more hydrophilic, which increases their resistance to organic and biological fouling [165–167].

Another approach, fabrication through electrochemical polymerization has demonstrated improved mechanical properties and higher electrical and ionic conductivity [168–171]. Electrochemical polymerization under acidic conditions produces PANI in the ‘emeraldine’ form, which is the electrically conducting form of PANI [172–175]. The acidic dopant has been demonstrated to influence the electropolymerized material in terms of structure and rate. Examples include Desilvestro et al (1993) who observed that polymerization rates of PANI from aqueous acidic solutions were influenced by the acid dopant in which they were fabricated, with the electropolymerization reaction occurring faster from an aqueous solution of sulfuric acid than from an aqueous solution of hydrochloric acid. In addition, the polymerization rate influenced the morphology of the PANI Films; PANI polymerized in sulfuric acid appeared in short fibrous stumps (typical length $<0.5\ \mu\text{m}$) while PANI from hydrochloric acid was found to be in a loosely packed network of fibrils with diameters of $0.2\text{--}0.3\ \mu\text{m}$ [176]. Benson et al. (2013) used aqueous solutions containing hydrochloric acid to fabricate highly dense PANI coatings on a CNT template [177]. Wu et al. fabricated PANI-CNT films from acidic aqueous solutions and deposited them on CNT electrodes. The film had a PANI layer coated on the CNTs with diameters between 100 nm and 130 nm as measured by SEM. Additional SEM observations confirmed that the PANI coated individual CNTs and formed a nanoporous structure [178].

PANI has been demonstrated to be sensitive to electrooxidation at low pH conditions. Yang et al. (2004) showed first order rate constants for degradation, with rates of $7 \cdot 10^{-3} \text{ sec}^{-1}$ at pH 0 (sulfuric acid 1M) and $1.4 \cdot 10^{-3} \text{ sec}^{-1}$ (sulfuric acid 0.1 M), respectively [179]. Mazeikiene et al. measured similar first-order rate constants ($\sim 10^{-3} \text{ sec}^{-1}$) for PANI degradation under acidic conditions (sulfuric acid 0.5M) [180]. However, to the best of our knowledge, PANI electrooxidation at neutral pH values has not been extensively explored. Furthermore, since most water treatment applications operate at near neutral pH values, we have concentrated our efforts on testing PANI-coated membranes at these pH values

In the current work, highly conductive composite PANI-CNT ultrafiltration (UF) ECMs were fabricated *via* electrochemical polymerization. A CNT network deposited on a porous polysulfone support was used as a template for PANI electrochemical deposition under acidic conditions. Membranes were characterized in terms of hydrophilicity, surface and electrical properties, filtration performance (i.e. flux and molecular weight cut off) and stability under oxidative anodic electrical potentials. Results revealed good separation properties with greatly improved stability under anodic conditions compared to a control poly(vinyl alcohol)-CNT (PVA-CNT) ECMs. PANI-CNT ECMs were studied for their ability to electrochemically oxidize a water soluble model compound (methylene blue (MB)) using relatively low potentials with remarkably high transformation efficiency. In addition, *in situ* membrane cleaning was explored by applying anodic potentials to a PANI-CNT ECM fouled by bovine serum albumin (BSA), and the results were compared to the results obtained using a PVA-CNT ECM as well as to standard physical cleaning methods.

4.2 Experimental Section

4.2.1 Materials

PS-35 polysulfone UF membranes were purchased from Nanostone (Nanostone Inc., Oceanside, CA). Multi-walled CNT functionalized with carboxylic groups via plasma treatment were purchased from CheapTubes (Cheaptubes Inc., Brattleboro, VT), and had the reported parameters: outer diameter of 13–18 nm, length of 3–30 μm , purity of >99 wt%, and functional group content of 7.0%. 50 wt. % glutaraldehyde solution, sulfuric acid (98%), hydrochloric acid (40%), and oxalic acid (>99%) were purchased from Fisher Scientific (Pittsburg, PA) and used as received. Dodecylbenzenesulfonic acid (DDBS), aniline, MB solution (0.05 wt. % in H_2O), BSA, polyethylene glycol 20,000 (PEG 20K), polyvinyl alcohol 150,000 (PVA 150K) and polyvinyl alcohol 100,000 (PVA 100K) were purchased from Sigma Aldrich (St. Louis, MO) and used as received.

4.2.2 Membrane Fabrication

4.2.2.1 Fabrication of Polyvinyl Alcohol-Carbon Nanotubes Membranes

PVA-CNT ECMs were prepared as previously described by Dudchenko et al. [129] and Ronen et al. [130] Briefly, CNT powder was suspended using a horn sonicator in deionized (DI) water at 0.01 wt. % with 1:10 ratio of CNT:DDBS. 1 wt. % 150K PVA in DI water was dissolved at 100 °C by stirring for 1 h. A 1:3 ratio of PVA:CNT (w/w) suspension was pressure deposited onto a PS-35 membrane support. The prepared membranes were then immersed into a crosslinking solution consisting of glutaraldehyde

(cross linker) and hydrochloric acid (catalyst), heated at 90 °C for 1 h, then dried at 90 °C for 5 min, and stored at room temperature.

4.2.2.2 Fabrication of Polyaniline-Coated Carbon Nanotube Membranes

PANI-CNT composite ECMs were prepared *via* electrochemical polymerization. To prepare the aniline electro-polymerization reaction solution, an acid dopant (sulfuric/hydrochloric/oxalic acid, 0.5 M) was added to DI water and mixed at room temperature for 15 minutes, and then aniline (0.1 M) was added to the acid solution and vigorously mixed for 15 minutes. 150 ml of the CNT suspension was pressure deposited (50 psi) onto a 150 mm diameter PS-35 membrane, and this deposited CNT network (2 μm thick) was used as the substrate for electro-polymerization (Appendix Figure C-2 presents a cross section of the deposited CNT layer on the UF support). For the electropolymerization reaction, the deposited CNT network was submerged in the aniline solution and connected to an external power source (Korad KA3005P DC power supply), with the CNT network used as an anode while a titanium wire was used as a cathode. Electropolymerization of polyaniline was done by applying a constant current (10 mA) for 60 min, followed by a thorough washing of the membrane with DI water. The PANI-CNT membranes were stored at room temperature until used.

4.2.3 Membrane Characterization

ECM surfaces were imaged using scanning electron microscopy (SEM; FEI XL30 SEM-FEG; Hillsboro, OR). The samples were sputter coated with Pt/Pb target for 40s

(Sputter coater 108 Auto, Cressington, UK). For cross-sectional images, the membranes were frozen in liquid nitrogen and fractured, then affixed onto SEM stubs with copper tape. Contact angle measurements were performed with a contact angle goniometer (Attension, Linthicum Heights, MD) using the captive bubble method in DI water. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR; Thermo Scientific; Waltham, MA) was performed on PANI-CNT and PVA-CNT ECMs to identify chemical bonds in the membrane structure. Membrane conductivity was measured with a four-point conductivity probe (Veeco; Plainview, NY) in sheet resistance mode. ECM surface roughness measurements were performed using atomic force microscopy (AFM, Asylum Research MFP-3D). All AFM measurements were performed in air, at room temperature and constant 30% relative humidity. An estimation of pore sizes through the membrane's conducting network was performed using image processing software (ImageJ version 1.46r) analyzing SEM images of the ECM surface.

4.2.4 Membrane Stability under Anodic Conditions

The ECM's stability under anodic electro-oxidation was evaluated for both PANI-CNT and PVA-CNT materials using cyclic voltammetry (CV) and linear sweep voltammetry on an electrochemical workstation (CHI600E, Austin, TX). An Ag/AgCl electrode was used as the reference electrode with a titanium sheet used as counter electrode, and the ECM used as the working electrode. For the stability experiments, either 10 mM KCl solution or 10 mM phosphate-buffered saline was used as the supporting electrolyte. During linear sweep experiments the anode potential was step increased by 1

V from 0 to 3.0 V at 10 min intervals and during CV a scan rate of 10 mV s⁻¹ was used at a potential range of 0 to 3.5 V (vs. Ag/AgCl). To evaluate stability, steady state currents were recorded at set time intervals and total organic carbon (TOC) and total nitrogen bound (TN_b) readings were taken from of the solution in which the ECMs were immersed while applying steady state current (TOC; OI Analytical, College Station, TX).

4.2.5 Membrane Chlorine Stability

The PANI-CNT ECMs tolerance to chlorine exposure was evaluated by changes of membrane electrical conductivity. Membrane sections were immersed into a solution of 500 ppm sodium hypochlorite. Samples were removed at 3, 6, 12, 24 and 36 hours, washed with DI water, dried at room temperature for at least 72 hours and stored dry for resistance measurement using a four-point conductivity probe. In addition, samples were tested using FT-IR (Thermo Scientific; Waltham, MA) to evaluate any changes in the chemical structure of PANI over time.

4.2.6 PANI-CNT Membrane Performance Evaluation

A custom-built flat sheet cross-flow membrane module (Appendix Figure C-1A), which was designed to apply an external electrical potential to the membrane surface, was used to evaluate the ECMs. A titanium counter electrode (flat sheet) was situated 4 mm above the membrane surface. The active area of the membrane was 40 cm². Molecular weight cut off (MWCO) measurements were taken for four solutions, 50 ppm each of PEG 20 K, PVA 50 K, PVA 100 K, and PVA 150 K. The feed and permeate samples were taken

after 150 ml of permeate had been collected for each MWCO experiment. Rejection data for each membrane was calculated based on TOC measurements of feed and permeate samples (TOC; OI Analytical, College Station, TX).

4.2.7 Methylene Blue Electrooxidation

MB transformation was measured in batch and continuous flow-through system. In the batch system, MB was added to 40 mL of DI water (final MB concentration of 5 ppm). A flat sheet ECM (PVA-CNT or PANI-CNT) and a titanium sheet were used as an anode and cathode, respectively. The size of the membrane was about 4 cm² and a range of electrical potentials (0-3 V) were applied on the whole cell. Samples of the solution were taken at several time points and the MB concentration was measured using a spectrophotometer (Beckman Coulter DU 800) and measuring absorption at a wavelength of 665 nm [150,181]. Prior to the application of the electrical potential, the ECMs were soaked in the MB solution for one hour. In the flow-through experiments (Appendix Figure C-1B), an ECM was placed in the flow cell with a titanium sheet counter electrode, with 3 V applied to the membrane and counter electrode (membrane as anode). Experiments were done at a constant flux of 70 LMH with a pressure of 1.5 psi. MB concentrations in the permeate were evaluated as described in the batch experiment.

4.2.8 Electrochemical In situ Membrane Cleaning

ECMs (PANI-CNT and PVA-CNT) were placed in the crossflow cell and compressed with DI water at 10 PSI overnight (Appendix Figure C-1C). Initially, each membrane was

fouled by 100 ppm of BSA (in a 10 ppm sodium chloride solution) until reaching approximately 30 % of the initial flux (35 LMH to 10 LMH at about 1 psi). Fouled membranes were imaged using SEM. Next, several different cleaning scenarios were investigated:

- (1) Cleaning by cross-flushing with a 10 ppm NaCl solution.
- (2) Repeatedly back washing of the membrane with permeate (10 ppm NaCl) for 5 minutes.
- (3) Applying an anodic potential (3 V whole cell potential) to the membrane (either PANI-CNT or PVA-CNT) under a cross flow regime (10 ppm NaCl solution); this process was repeated three times (i.e. membrane fouling followed by electrochemical cleaning). The ECM's conductivity was measured after each cleaning cycle. All cleaning experiments were followed by washing with DI water and drying for 24 hours at room temperature before imaging by SEM.

4.3 Results and Discussion

PANI-CNT ECMs were compared to PVA-CNT based membranes in terms of physical properties, separation properties and anodic stability [60,129,130]. PVA-CNT membranes were previously prepared in our lab and serve as a reference ECM. However, their stability under oxidative anodic conditions was not previously investigated. In terms of visual difference (Appendix Figure C-3), the fabricated PANI-CNT ECMs had a greenish hue as a result of the electropolymerization reaction, while the reference membranes (PVA-CNT) were black due to the CNT layer (results are similar to previously

reported data concerning the fabrication of PANI on conductive layers under similar conditions (i.e. acidic conditions and anodic electrical potential [182,183].)

4.3.1 Impact of Acidic Dopant

The acid dopant mixed with aniline influences the PANI electropolymerization process [184,185]. PANI-CNT ECMs were evaluated for the influence of the dopant on the electropolymerization process in terms of surface properties, membrane separation and electrical properties.

4.3.1.1 Surface Characterization and Physical Properties

Following fabrication, ECMs were imaged by SEM (Figure 21, top and middle images) and characterized by AFM for surface roughness (Figure 21, lower image). Cross-sectional images of the ECMs (Figure 21, top row) reveal the composite nature of the membrane structure, with the polysulfone support layer on the bottom, and a CNT-polymer composite resting on top. The electropolymerized PANI coating can clearly be seen in the top-view images of the PANI-CNT ECMs, when compared to the PVA-CNT ECM (Figure 21, middle row); in these images, the spacing between the CNTs is reduced through the addition of the PANI layer coating the CNT network. Our SEM results agree with previous observations made of PANI-coated CNTs, where the PANI can be seen forming a continuous layer coating the CNT network [177,178,186]. The choice of the acid dopant impacts the overall porosity of the PANI-CNT network; using image analysis (Appendix Figure C-4) it was observed that while sulfuric acid PANI-CNT and PVA-CNT demonstrated very similar porosity values (25.52 ± 0.45 % and 27.67 ± 1.10 %, respectively,

$p < 0.05$), oxalic and hydrochloric acid doped PANI-CNT showed significantly lower porosity values (17.33 ± 1.31 % and 18.41 ± 0.73 %, respectively, $p < 0.05$). The porosity measurements are in agreement with measured permeate flux values (Table 1), with PANI-CNT ECMs based on the sulfuric acid dopant showing the highest flux (43 ± 8 liters $\text{m}^{-2} \text{hr}^{-1}$ (LMH)), which is similar to the PVA-CNT ECM (40 ± 4 LMH), while the ECMs fabricated using the hydrochloric and oxalic acid dopant exhibiting very low flux (4 ± 2 LMH and 2 ± 0.5 LMH, respectively). High magnification SEM images of the membranes surface (Appendix Figure C-5) indicate that the oxalic and hydrochloric acid based ECMs have a denser looking surface, which corresponds to the lower calculated porosity values for these membranes. While the observed drop in porosity for the oxalic and hydrochloric acid doped PANI is not as dramatic as the drop in flux, we speculate that the low fluxes observed in these ECMs is a result of a dense PANI layer growing within the CNT network, which reduced the membrane's permeability. Our results are in agreement with the trend described in the literature indicating that using sulfuric acid dopant results in a less dense PANI layer over the CNT network with higher permeation rates [176,177]. However, an exact reason for the observed differences in PANI morphology is unclear, and a detailed investigation into this issue is beyond the scope of this research.

Membrane roughness measured using AFM showed that the root mean squared roughness was also acidic dopant dependent. PANI-CNT ECMs fabricated with sulfuric acid proved to be the least rough (20 ± 2 nm), demonstrating a decrease of 56% in comparison to PVA-CNT ECMs (46.37 ± 2.37 nm) (Table 6 and Figure 21 lower panel). PANI-CNT ECMs based on oxalic acid also showed a significant decrease in roughness

(25 ± 2.5 nm), while hydrochloric acid-based ECMs were very similar to the PVA-CNT ECMs (43 ± 4 nm). Contact angle measurements showed an increase in hydrophilicity for all PANI-CNT ECMs in comparison to the reference PVA-CNT ECM, with the highest improvement measured for PANI-CNT membrane fabricated using sulfuric acid ($19.4^\circ \pm 1.2$ for PANI-CNT vs. $32^\circ \pm 2.8$ for PVA-CNT) (Table 6). These results are in line with previous reports describing PANI-CNT networks [187,188]. The increased hydrophilicity of membranes has been shown to reduce the attachment of bacteria, proteins, and other organic foulants due to the hydration layer formed at the membrane-water interface, and is a critical aspect of anti-fouling surfaces. [165–167]

The electrical resistance of the PANI-CNT ECMs was significantly reduced in comparison to the PVA-CNT ECM (Table 6). The largest decrease in electrical resistance was detected for PANI-CNT ECMs fabricated using sulfuric acid ($56 \pm 2 \Omega \text{ cm}^{-2}$ for PANI-CNT vs. $1132 \pm 32 \Omega \text{ cm}^{-2}$ for PVA-CNT). Overall, all of the PANI-CNT membranes exhibited excellent electrical conductivity, with the highest electrical conductivity being $8928 \pm 307 \text{ S m}^{-1}$ for the sulfuric acid doped ECMs. As PANI has low electrical resistance when it is in the emeraldine form [182,189] (typical electrical conductivity of 10^2 S m^{-1}), we speculate that the drop in electrical resistance observed after the PANI is electropolymerized onto the CNT network is a result of the PANI effectively bridging the gap between neighboring CNTs, leading to a more efficient percolation network. Due to the thinness of the PANI layer (Figure 21), we do not believe that the additional thickness provided by the electropolymerized PANI significantly adds to the overall conductivity of the PANI-CNT network.

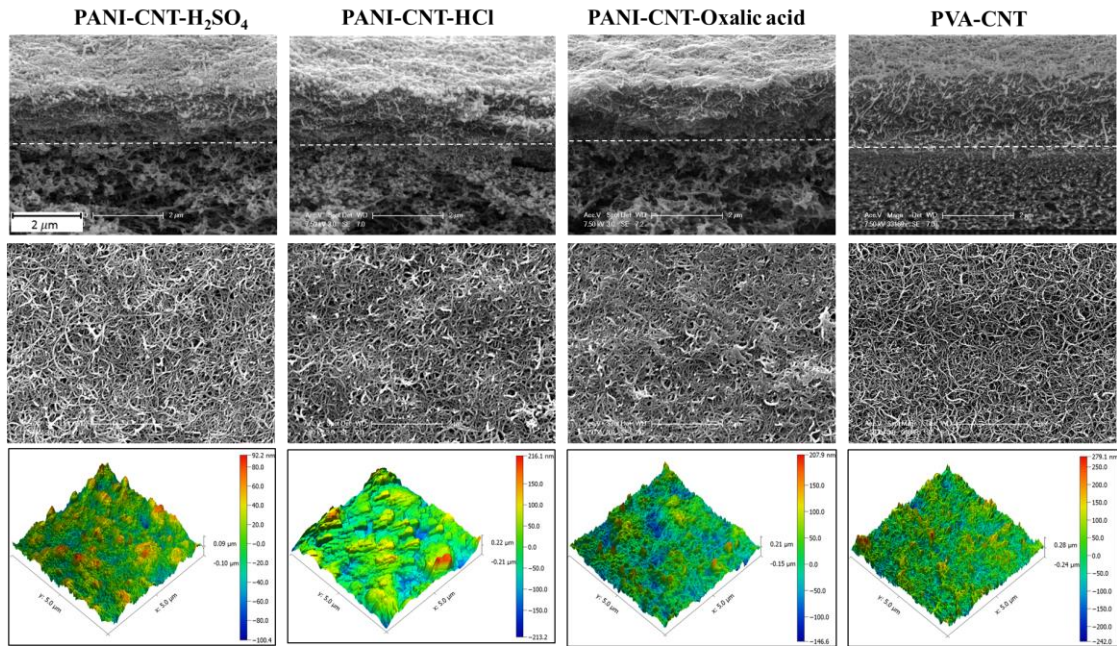


Figure 21: ECM structure and surface morphology. (Top) Cross-sectional images of ECMs. (Middle) Top-view of ECM surface. (Bottom) ECM surface topography by atomic force microscopy. Scale bars for all SEM images are 2 μm

Table 6: ECM physical characterization

ECM Characteristic	PVA-CNT	PANI-CNT-Sulfuric acid	PANI-CNT-Hydrochloric acid	PANI-CNT-Oxalic acid
Root Mean Squared Roughness (nm)	46.3 ± 2.4	20 ± 2	43 ± 4	25 ± 2.5
Resistivity ($\Omega \text{ sq}^{-1}$)	1132 ± 32	56 ± 2	92 ± 3	77 ± 4
Conductivity (S m^{-1})	883 ± 24	8928 ± 307	5434 ± 171	6493 ± 320
Contact Angle ($^\circ$)	32 ± 2.8	19.4 ± 1.2	21.1 ± 1.9	27.1 ± 2.2
Flux (LMH/psi)	40 ± 4	43 ± 8	4 ± 2	2 ± 0.5

Based on their physical characterization, MWCO, flux and electrical resistance results, it was decided that the PANI-CNT ECMs fabricated from the sulfuric acid solution were the best candidates for water treatment applications, and therefore, all further experiments were performed on these and compared to PVA-CNT ECMs.

Figure 22 shows representative FTIR spectra of PVA-CNT and PANI-CNT (sulfuric acid dopant) ECMs. The FTIR spectrum of all PANI-CNT ECMs showed the presence of similar chemical bonds regardless to the dopant used for fabrication (Appendix Figure C-6). The characteristic peaks at 1557 and 1455 cm^{-1} are associated with the stretching vibration of the quinoid ring and benzenoid ring, respectively. The bands at 1200-1300 cm^{-1} correspond to C-N stretching vibration of aromatic amines. In addition, two bonds, which indicate the presence of the “emeraldine” form of PANI when they appear simultaneously, were detected - the nitrogen-hydrogen bond (2° amine) at 1035-1095 cm^{-1} and the nitrogen-carbon double bond at 1650 cm^{-1} (Figure 22) [188]. Thus, the FTIR spectrum confirms the formation of the conducting emeraldine form of PANI on the surface of the CNT network.

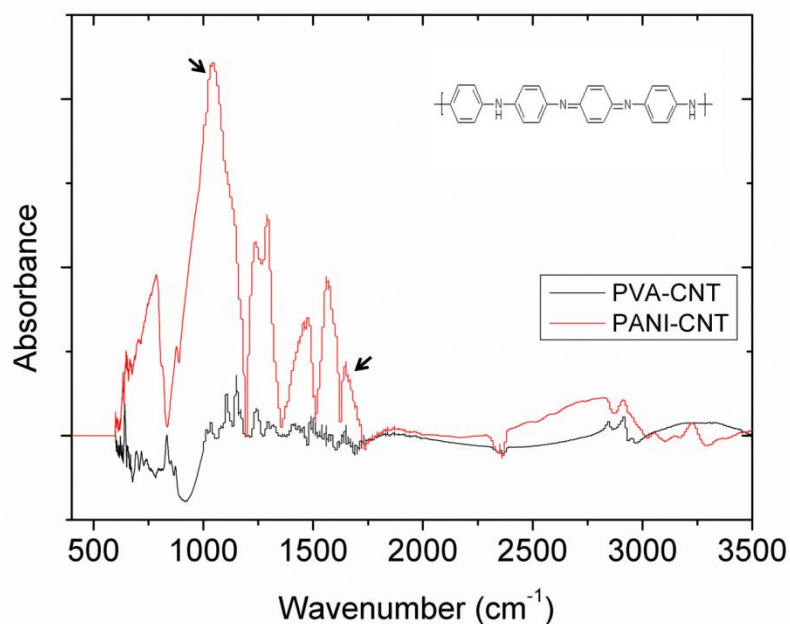


Figure 22: Representative FTIR scans of PVA-CNT and PANI-CNT ECMs. Arrows indicate the 2° amine (1035-1095 cm⁻¹) and the nitrogen carbon double bond (~1650 cm⁻¹) typical of the emeraldine form of PANI; the chemical structure of the emeraldine form of PANI can be seen in the upper right corner of the figure.

4.3.1.2 Impacts of Current Density on Structure of Electropolymerized Membrane

The influence of the applied current on the structure of the PANI coating during its electropolymerization on the CNT network (with sulfuric acid dopant) was evaluated by electropolymerizing PANI using three current densities (Figure 23A-D). In these experiments, the total deposition time, membrane area, and acid dopant (sulfuric acid) were kept constant. The lowest current density of 0.25 mA cm⁻² (Figure 25B) yielded a thin, homogeneous and smooth PANI coating without any significant decrease in the CNT network porosity, as determined by SEM image analysis. However, increasing the current density resulted in a thicker PANI layer and a reduction of the CNT network porosity by

up to 24% (27.67 ± 1.10 % for PVA-CNT and 28.52 ± 1.08 %, 25.52 ± 0.45 %, and 21.77 ± 4.1 % for PANI-CNT with applied currents of 0.25, 0.9, and 1.5 mA cm^{-2} , respectively). Additional images and image analysis examples are presented in Figure Appendix Figure C-7. A similar trend was described by Benson et al. (2013) who electropolymerized PANI on CNTs in a hydrochloric acid medium, and reported that higher current densities increased PANI thickness and decreased surface porosity [177]. Furthermore, Gloukhovski et al. was able to fabricate dense nanofiltration membranes by electropolymerizing a PANI coating on an electrically conductive support layer at high current densities (3.78 mA cm^{-2}) [175].

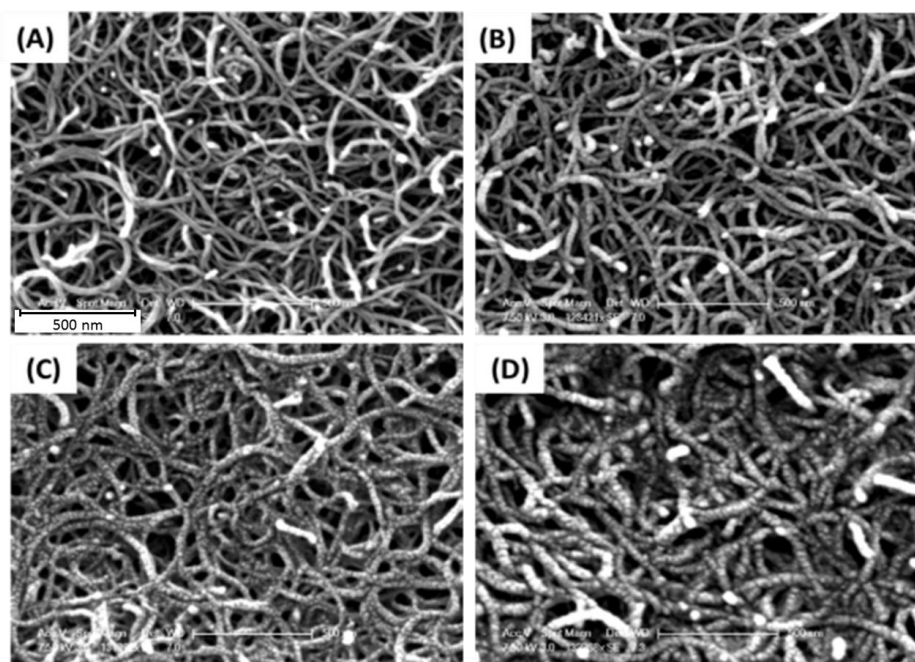


Figure 23: Representative images of PANI-CNT ECMs surfaces fabricated using different current densities. Membranes were electropolymerized using sulfuric acid as the acid dopant. Scale bars for all SEM images are 500 nm. (A) Bare CNT; (B) PANI-CNT 0.25 mA cm^{-2} ; (C) PANI-CNT 0.9 mA cm^{-2} ; (D) PANI-CNT 1.5 mA cm^{-2}

4.3.1.3 Membrane Rejection Proper

The ECMs rejection properties (i.e. the MWCO) were evaluated by testing the membrane's rejection of a range of polymers with different molecular weights (Figure 24). Membranes showed low rejection to small molecules up to 50 kDa and 70-90 % rejection of larger (100 kDa) molecules; at this size range, the highest rejection was for the sulfuric acid based ECMs and the lowest was for the PVA-CNT based ECMs ($89\pm6\%$ and $70\pm5\%$ rejection, respectively). All membranes rejected the larger molecules (150 kDa). The MWCO is defined as the MW at which 90% of the molecules are rejected by a membrane. Therefore, the MWCO for all membranes was determined to be somewhere between 100-150 kDa (approximately 18-21 nm assuming spherical particles) [190]. Based on image analysis of SEM images of the ECMs surface (Appendix Figure C-8) the typical pore sizes of the CNT network (assuming circular pores) were 125 nm, 120 nm, 90 nm and 73 nm for PVA-CNT, sulfuric, hydrochloric and oxalic acid dopants, respectively. All results indicate that the pore sizes are larger than the detected MWCO. Therefore, it can be assumed that the separation properties of the membranes (i.e. the MWCO) are defined by the supporting UF membrane (made from polysulfone) used for the CNT deposition and not by the PANI-CNT or PVA-CNT layers.

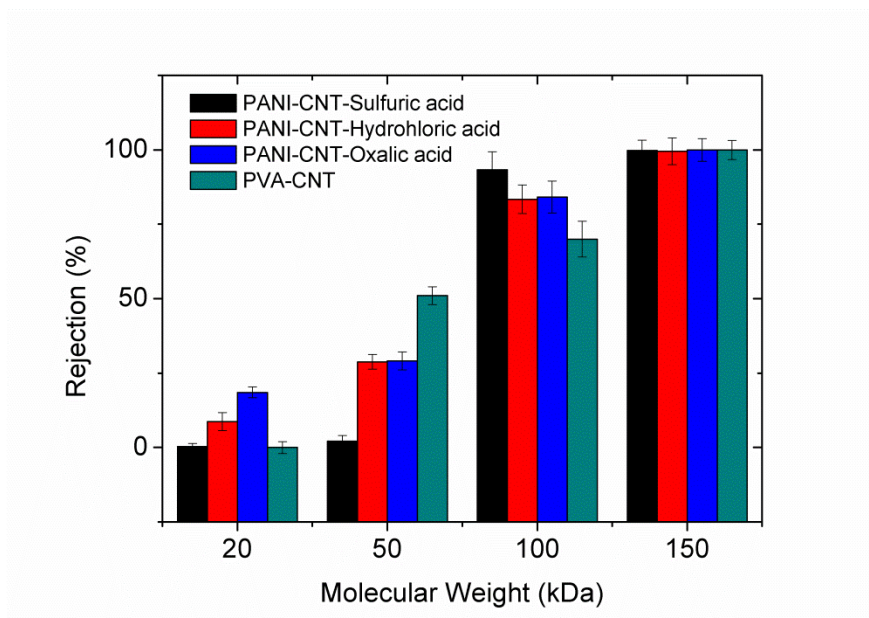


Figure 24: Rejection of polymers by different ECMs ; Rejection data of PEG 20 kDa, PVA 50 kDa, PVA 100 kDa and PVA 150 kDa for PANI-CNT ECMs made in H₂SO₄ (black), HCl (red), oxalic acid (blue), and PVA-CNT (green) ECMs.

4.3.2 Membrane Stability

4.3.2.1 Chlorine Tolerance

A membrane's tolerance to chlorine exposure is of critical importance, as commercial membranes are typically cleaned by chlorine solutions for organic and biofilm removal [49]. Commercial membranes manufacturer's cleaning manuals recommend a cleaning process for UF membranes that includes a daily 30 minute rinse with a chlorine solution (150 ppm) [191]. Membrane chlorine cleaning typically occurs at relatively high pH (pH > 8) to assist in the degradation of deposited organic matter [192]. In our experiment, the initial pH of the solution containing the membrane coupon upon the addition of NaOCl was 10.6, which declined to pH 8 after 36 hours of exposure. CNT-based materials (*i.e.* composite membranes) are prone to damage from exposure to chlorine containing

solutions, leading to functionalization of the CNTs and changes in their physical and chemical properties [193–195]. Tolerance to chlorine was evaluated by measuring any changes in the ECM's conductivity and chemical structure [196]. Figure 25 shows results from chlorine tolerance experiments. Overall, ECMs doped with sulfuric acid showed the best stability, with an electrical resistance increase of 27 ± 2.3 % after 18,000 ppm-hr of exposure. However, there was some variability in the electrical resistance of these membranes over time, with no clear trend visible. The same was true for other ECMs, with only the PVA-CNT and the hydrochloric acid doped ECMs showing a consistent trend (47 ± 1.06 and 62 ± 1.06 % increase in resistance, respectively), with electrical resistance increasing throughout the exposure period. Huang et al. demonstrated that PANI membranes fabricated by chemical oxidation are sensitive to chlorine exposure [197] (250 ppm for 2 hours) and suffer from a decrease in rejection. Although our method did not evaluate rejection, we speculate that changes in the mechanical structure of the membranes would influence the electrical conductivity significantly. Thus, based on the relatively small changes in electrical resistivity experienced by the sulfuric acid doped ECMs, we can assume that these membranes will be stable under the significantly lower chlorine concentrations and exposure times used during membrane cleaning activities.

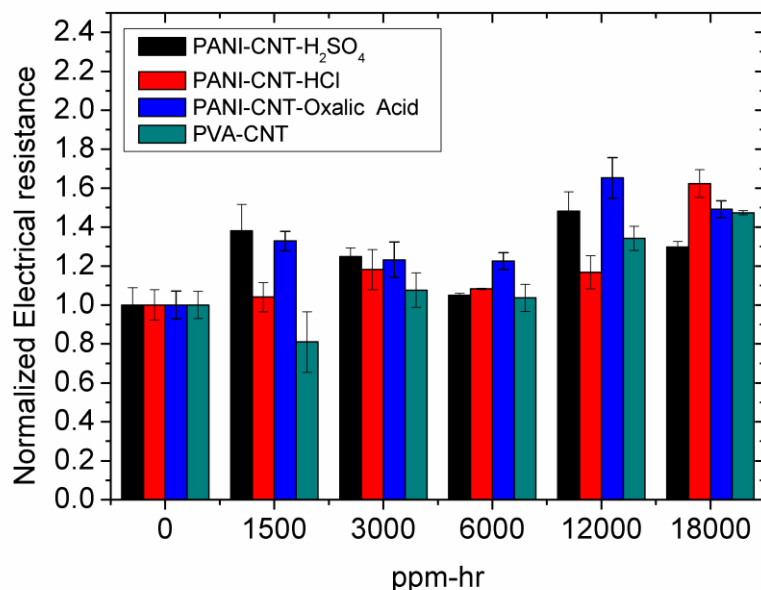


Figure 25: Stability of ECMs in response to chlorine exposure (500 ppm sodium hypochlorite solution), expressed as normalized changes in membrane electrical resistance over exposure time. Color bars represent membrane resistivity of each membrane type. Error bars represent 95% confidence intervals.

In addition to electrical conductivity changes, the influence of chlorine on sulfuric acid doped PANI-CNT membranes was evaluated using FT-IR (Appendix Figure C-9). Results indicate that both peaks which represent the Emeraldine structure (a nitrogen hydrogen bond (2° amine) at 1035-1095 cm⁻¹ and a nitrogen carbon, double bond at 1650 cm⁻¹) are still visible after exposure to chlorine, even after exposure to 18000 ppm-hr which is equivalent to 240 recommended cleaning cycles.

4.3.2.2 Membrane Stability under Anodic Potentials

One of the concerns arising from using CNT-based membranes for electrooxidation reactions is the degradation of the CNTs under anodic conditions, which leads to the loss of electrical conductivity and eventually to membrane breakdown [151]. PANI-CNT ECMs were evaluated for electrochemical stability by measuring changes in current and the material's electrical conductivity under a range of anodic conditions. Figure 26A shows representative CV scans of PANI-CNT and PVA-CNT ECMs at anodic potentials ranging between 0 and 3.5 V vs. Ag/AgCl. Each CV test consisted of twenty cycles at a scan rate of 10 mV s^{-1} in a 10 mM NaClO₄ solution. As can be seen, the PVA-CNT ECM showed a significant and rapid decrease in current with increasing CV cycles, with the final CV cycles displaying virtually no current; this finding indicates a drop in the electrical conductivity of the membrane, which is likely a result of CNT oxidation and breakdown. In contrast, PANI-CNT ECM showed enhanced current stability over time, with the current dropping by 0.27 mA ($\sim 6.3\%$ decline) over the 20 cycle period. The higher currents measured using the PANI-CNT ECM in comparison to PVA-CNT ECM when similar potentials were applied are a result of the higher conductivity of the PANI-CNT material. To further probe the material's ability to withstand anodic conditions, a constant potential was applied to the membrane surface for 10 minutes, with the current continuously measured (the ECMs were immersed in a PBS buffer at pH 7.2); the potentials applied were 3 and 5 V vs. a Ag/AgCl reference electrode for PVA-CNT ECMs and 2, 2.5, 2.8, 3 and 5 V vs. a Ag/AgCl reference electrode for PANI-CNT ECMs (Figure 26 B). PBS buffer was used to control the pH of the solution as low pH values impact the PANI structure,

making it more susceptible to electrooxidation [184]. When a continuous anodic potential of 5 V (vs. Ag/AgCl) was applied to the ECMs, a rapid drop in current was observed on the PVA-CNT material, while the decline in current on the PANI-CNT material was significantly lower, with the total current decline for PANI-CNT and PVA-CNT at 5 V being 16 % and 52 %, respectively. When a 3 V potential was applied, the PANI-CNT material displayed a relatively stable current (5% decline), while the current measured from the PVA-CNT material continuously declined over time (overall a 14.4 % decline). Additional measurements at lower potentials showed lower decline rates (a decline of 1.1 ± 1.4 , 1.73 ± 2.1 and 2.87 ± 1.6 %, for the 2, 2.5, 2.8 V vs. Ag/AgCl, respectively). However, the minor decline in current for the 2.8, 2.5, and 2 V cases were not statistically significant, as determined by the average rate of current decline (slope of the fitted line, Figure 26 B, Appendix Table C-1). Therefore, it can be concluded that PANI-CNT ECMs are far less prone to degradation by anodic oxidation at neutral pH values, and may be completely stable at potentials as high as 2.8 V vs. Ag/AgCl at neutral pH. Additional long term experiments (3 hours) at 2.5 and 2.8 V vs. Ag/AgCl indicate that the PANI-CNT ECMs are stable with a negligible decrease in current (<5 %) in comparison to PVA-CNT ECMs, which lost all current (Figure 26C). In addition to changes in current, changes to the electrical resistance of the ECMs in response to the application of anodic potentials were evaluated. The electrical resistance of the ECMs was measured after they were exposed to a range of anodic potentials for 10 minutes. Results show a rapid increase in resistance for PVA-CNT ECMs, with resistance increasing from $1132 \pm 32.7 \text{ } \Omega \text{ sq}^{-1}$ at 0 V to $2556 \pm 42.2 \text{ } \Omega \text{ sq}^{-1}$ at 3 V vs. Ag/AgCl (a 125 % increase) (Figure 26D). In contrast,

PANI-CNT ECMs exhibited a mild increase in resistance, with resistance increasing from $98.8 \pm 12.2 \, \Omega \, \text{sq}^{-1}$ at 0 V to $159 \pm 6.1 \, \Omega \, \text{sq}^{-1}$ at 3 V vs. Ag/AgCl (a 60.8 % increase) (Figure 26D). At a low anodic potential of 1 V, the electrical resistance of PANI-CNT ECMs was constant in contrast to an increase in electrical resistance of PVA-CNT ECMs (3% and 63% increase in PANI-CNT and PVA-CNT, respectively). Figure 26E shows digital camera images of the membranes after 20 minutes of applied anodic potential (3.5 V vs. Ag/AgCl) in PBS buffer; results reveal that PVA-CNT membranes suffer from CNT degradation expressed as a removal of a CNT section from the membrane's surface (the white area indicates the absence of CNT), while the PANI-CNT membrane showed no visual difference when subjected to similar conditions. Importantly, the degradation of the PVA-CNT material seems to occur at the water/air interface, suggesting that oxygen plays a role in CNT degradation.

The degradation of the membranes was also evaluated by measuring the TOC and TN_b values of solutions containing PVA-CNT and PANI-CNT ECMs after applying 1, 2, and 3 V (vs. Ag/AgCl) to the membranes' surface; in these experiments, the membranes were subjected to an electrical potential for 20 minutes in 40 ml of PBS (Figure 26E). Results were calculated as the percentage of mass electro-degraded in relation to the initial deposited mass (as CNT or PANI). The percentage of mass degraded increased with increased applied potential for PVA-CNT membranes (3.07, 3.47 and 4.41 % for 1, 2 and 3 V vs Ag/AgCl, relatively) while staying almost constant for the PANI-CNT membrane (0.5, 0.47 and 0.41 % for 1,2 and 3 V vs Ag/AgCl, relatively) indicating a higher stability for the PANI-CNT membrane. When comparing the TN_b values, both membranes revealed

an increase in the degraded percentage with increasing potential, although a lower percentage was detected with the PANI-CNT membrane. The presence of nitrogen in the PVA-CNT is assumed to be a result of the CNT Functionalization process which involves the use of nitric acid [198]. These results are expected as the degradation rate of PVA-CNT ECMs was rapid in comparison to PANI-CNT ECMs. Overall, the concentrations of TOC and TN_b detected from the PANI-CNT ECMs were extremely low.

SEM images of the membrane's surface after applying anodic potentials of 1 V, 2 V and 3 V (vs Ag/AgCl) for 10 min in a PBS buffer solution (Appendix Figure C-10 and C-11) revealed a difference between the membranes as a function of the applied potential. PVA-CNT ECMs appeared to become more porous and less dense with thinner CNTs when higher potentials are applied, with porosity increasing from 28.66 ± 1.74 % at 0 V to 32.54 ± 1.72 % when 3 V were applied. PANI-CNT ECMs showed little change in porosity, with values increasing from 28.73 ± 1.33 % at 0 V to 29.26 ± 1.02 % at 3 V. Based on the observed enhanced resistance to anodic oxidation of the PANI-CNT membranes, it was determined that these ECMs are promising materials capable of enhancing membrane-based water treatment processes.

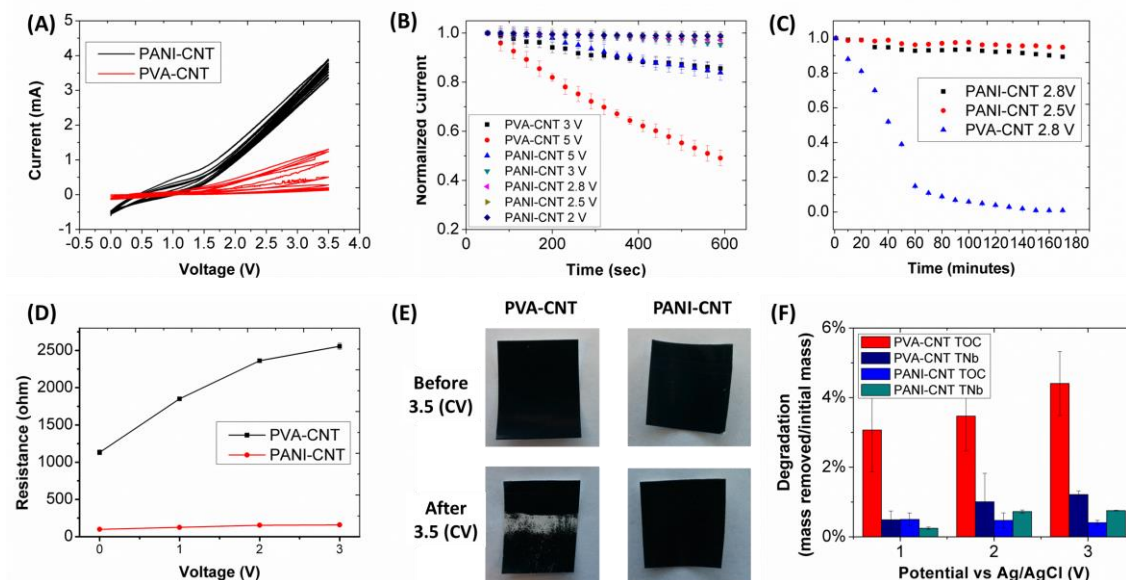


Figure 26: PANI-CNT membrane stability under anodic conditions. (A) CV scans of PANI-CNT and PVA-CNT membranes (20 cycles); scan rate was 0.01 V/s in a 10 mM NaClO₄ solution. PVA-CNT voltammogram is shown in red, PANI-CNT in black. The total surface area of the anode was 4 cm². (B) Normalized current changes when a constant anodic potential of 2, 2.5, 2.8, 3 and 5 V (vs. Ag/AgCl reference electrode) was applied to PANI-CNT ECs and constant anodic potentials of 3 and 5 V (vs. Ag/AgCl reference electrode) were applied to PVA-CNT ECs; the reaction time was 10 min in a PBS buffer (10 mM Na₂HPO₄, 1.8 mM KH₂PO₄). The total surface area of the membrane anode was 8 cm². (C) Normalized current changes when a constant anodic potential of 2.5, 2.8 V (vs. Ag/AgCl reference electrode) was applied to PANI-CNT ECs and constant anodic potentials of 2.8 V (vs. Ag/AgCl reference electrode) was applied to PVA-CNT ECs; the reaction time was 180 min in a PBS buffer (10 mM Na₂HPO₄, 1.8 mM KH₂PO₄). The total surface area of the membrane anode was 8 cm². (D) Changes in resistance for PVA-CNT (black line) and PANI-CNT (red line) ECs after applying 1, 2 and 3 V (vs Ag/AgCl) to the membrane's surface for 10 min in 80 ml of in PBS buffer (10 mM Na₂HPO₄, 1.8 mM KH₂PO₄). (E) Images of the ECs after exposure to 3.5 V (vs. Ag/AgCl) for 20 min. (F) TOC and TN_b degradation percentage of PVA-CNT and PANI-CNT ECs after applying 1, 2 and 3 V (vs. Ag/AgCl) to the membrane's surface for 20 min in 40 ml of PBS buffer (10 mM Na₂HPO₄, 1.8 mM KH₂PO₄).

4.3.4 Membrane Cleaning

As PANI-CNT ECMs prepared in sulfuric acid proved to be more stable under anodic oxidative conditions, and due to their high electrical conductivity, two possible future applications were explored; in all cases, PANI-CNT ECM's performance was compared to PVA-CNT ECMs. In the first application, the ECMs were tested for their ability to perform *in situ* electrochemical membrane cleaning after the membrane was fouled with a protein (BSA). The ECM's ability to restore flux was evaluated and compared to traditional cleaning methods. In the second application, ECMs were studied for their ability to electrochemically oxidize a model water soluble organic molecule (MB) at relatively low potentials (up to 3 V on the whole flow cell or 1.7 V vs. Ag/AgCl on the ECM's surface see Appendix Figure C-12).

4.3.4.1 Electrochemical Cleaning of Fouled Membranes

While typical membrane cleaning processes involve some form of chemical addition (e.g. chlorine, sodium hydroxide) to the feed solution[199], PANI-CNT ECMs cleaning experiments were designed to evaluate their capacity for *in situ* electrochemical cleaning *via* electrooxidation, without any external chemical addition. To induce fouling, PANI-CNT ECMs were exposed to 100 ppm of BSA (in 10 mM NaCl) to reduce the initial flux from 35 to 10 LMH (Figure 27A).

No change in permeate flux was observed when the ECMs were washed with permeate in the cross-flow configuration (linear velocity of 10 cm s^{-1}) or when backwashed for 1 hour with permeate (Figure 27A). In addition, no flux recovery was observed when

1.5 V were applied to the PANI-CNT ECM (data not shown). In contrast, excellent flux recovery (93%) was observed when 3 V of anodic potential (whole cell) were applied to the freshly fouled PANI-CNT ECM surface for 20 min (Figure 27B). Once cleaned, the membrane was re-fouled with BSA and a second electrochemical cleaning was applied (20 minutes at 3 V). However, only 84% of the flux was recovered in the second round of cleaning; a third round of fouling/cleaning yielded an 81% flux recovery (Figure 27B); membrane electrical resistance remained unchanged throughout the experiment. We speculate that small organic fragments resulting from BSA breakdown were lodged in the polysulfone support pores, and the membrane would require more extensive cleaning to fully recover. A similar fouling-cleaning cycle with a PVA-CNT ECM resulted in significantly lower flux recovery (62% in the first fouling cycle). Importantly, the membrane electrical resistance spiked to $5\text{k}\Omega\text{ sq}^{-1}$ after the first cleaning cycle, resulting in a negligible electrical current, which led to the membrane losing its electrochemical properties and its ability to be self-cleaned (Figure 27B). It should also be noted that to achieve a recovery value of 62% for the PVA-CNT ECM, the membranes had to be subjected to anodic potentials for 60 min (in comparison to 20 minutes for the PANI-CNT ECM). Critically, when electrochemical cleaning was attempted in the absence of NaCl, no flux recovery was observed (data not shown). Based on the fact that no cleaning was observed in the absence of chloride, we conclude that indirect oxidation (driven by the electrochemical oxidation of chloride to chlorine) of the BSA-fouled surface is responsible for the observed cleaning results (Equations 2-4). SEM images of the fouled membrane surface at different steps of the experiment (Figure 27C) indicate that backwashing was

able to partly remove the BSA layer from the membrane surface, although the corresponding permeate flux did not change, as BSA fouling in UF membranes is initially dominated by pore blocking and/or pore constriction, followed by cake formation on the membrane surface during long-term fouling [200]. When anodic electrical potentials were applied, flux recovery results are in correlation with SEM images, which show a completely clean ECM surface (Figure 27C). Thus, it is likely that the electrochemical cleaning of the PANI-CNT ECMs led to BSA removal from the membrane's pores. These results support the theory of indirect oxidation (through Cl_2 generation) as the primary foulant removal mechanism. As the selectivity of the membrane has been shown to be determined by the polysulfone support membrane and not the PANI-CNT deposited above, the observed flux decline is likely a result of polysulfone pore fouling. Therefore, if the cleaning mechanism involved direct oxidation, it would produce hydroxyl radicals, which have a very short lifetime (approximately 10^{-9} seconds [201]) and a low probability of reaching the polysulfone layer. In contrast, active chlorine, which was electro-generated as a result of indirect oxidation, has a longer life span and could reach the UF support layer based on the calculated residence time (0.2 s). Thus, *in situ* membrane cleaning via electrooxidation processes is a viable cleaning method that has the potential of significantly simplifying membrane-based water treatment processes.

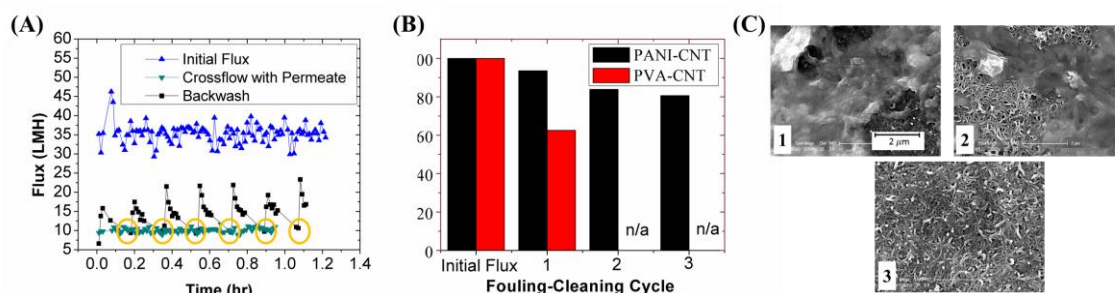


Figure 27: Electrochemical cleaning of fouled membranes (A) PANI-CNT ECM flux recovery under different flow condition. The blue line represents the initial flux of the unfouled membrane, the gray line represents the fouled membrane flux at crossflow conditions and the black line represents membrane flux after 5 min backwashing cycles with permeate (orange circles mark the backwashing events) (B) Flux recovery at three cycles of continues BSA fouling and electrochemical cleaning 3V for PANI-CNT ECMs (black) and PVA-CNT ECMs (red), initially membranes were fouled until flux reached about 30% of initial flux; (C) SEM images of membrane surface (1) Membrane fouled by 100 ppm BSA (2) BSA fouled ECM cleaned by back washing, (3) BSA fouled ECM cleaned by applying 3V (membrane as anode) to the membrane surface. Scale bars for SEM images are 2 μm

4.3.4.2 Electrooxidation of a Model Organic Compound – Methylene Blue

Oxidation of organic compounds from the feed solution was evaluated using MB as a model compound. The current work did not investigate the transformation pathways of MB, instead focusing on whether an ECM is capable of electrochemically transforming the MB, which was detected through changes in the UV-vis absorption spectrum of the molecule [202]. A detailed description of the theory behind the electrooxidation process as well as a detailed description of our experimental results can be found in the Appendix (Appendix Figure C-13). In short, we demonstrate that the PANI-CNT ECM out performs the PVA-CNT ECM in both batch, and effectively transforms MB in single pass flow-through (filtration) experiments. In batch mode, PANI-CNT material transformed 32% of the MB after 60 minutes, compared to 20% for the PVA-CNT material, when 3 V were

applied to the membrane/counter electrode (Appendix Figure C-13). In the flow-through experiments, the PANI-CNT ECM transformed 84.1 ± 1.7 % of MB in a single pass through the membrane (3 V, 1 μm thick membrane, <0.2 S membrane residence time).

4.4 Conclusions

PANI-CNT ECMs were fabricated through a process of electropolymerization of aniline monomers using different acidic dopants, with CNT networks deposited on a polymeric membrane support serving as an electrically conducting substrate for the electropolymerization process. After the electropolymerization process, the electrical resistance of the material decreased significantly in comparison to electrically conducting PVA-CNT ECMs previously used in different membrane applications [129,203]. It was determined that PANI-CNT ECMs fabricated using sulfuric acid as the dopant exhibited the best transport, electrical, and stability characteristics, making them ideal for water treatment applications. PANI-CNT ECMs were found to have enhanced resistance to anodic oxidation, with little degradation observed up to an anodic potential of 3 V (vs. Ag/AgCl) under neutral pH conditions. Thus, these membrane materials are promising candidates for electroactive membrane materials suitable to participate in electrooxidation reactions.

The application of electrical potentials to the ECMs coupled with the advective transport characteristic of membrane separation processes offers a promising enhancement to existing membrane-based water treatment processes. We tested the PANI-CNT membrane's ability to degrade a model organic contaminant (MB) as well as facilitate the

in-situ cleaning of a fouled membrane surface (with BSA). Results demonstrate that the application of an anodic potential to the ECM surface facilitated the electrochemical transformation of MB (90% transformation in a single pass) as well as resulted in the almost complete removal of the organic foulant (obviating the need for additional chemical cleaning agents).

In terms of power consumption, the electrooxidation of 5 ppm of MB on PANI-CNT ECMs required only 2.5 kW m^{-3} , with a contact time $<1 \text{ s}$. In contrast, photocatalytic treatment processes used for MB degradation have been reported to consume 40 kW m^{-3} , and require a contact time ranging between 30-60 minutes [204,205]. Thus, PANI-CNT based membranes have promising properties that make them attractive candidates for multiple water treatment applications such as wastewater treatment and pre-treatment membranes for RO.

4.5 Acknowledgments

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Chapter 5

Summary and Conclusions

The overall goal of this research was to investigate the electrical and operational conditions of need for fouling prevention using CNT-based electrically conductive membranes. To that end, we explored how electrically conducting CNT – polyamide RO membranes prevent and remove CaSO_4 and CaCO_3 mineral scaling (Chapter 2), how electrically conducting UF and NF membranes implemented in series prevent fouling while treating anaerobic sequencing batch reactor effluent (Chapter 3), and how anodically stable polyaniline coated CNT UF membranes remove aqueous dyes and recover through *in situ* membrane cleaning (Chapter 4).

5.1 Electrochemical Mineral Scale Prevention and Removal on Electrically Conducting Carbon Nanotube-Polyamide Reverse Osmosis Membrane

In Chapter 2, various electrical potentials were applied to the membrane surface while filtering model scaling solutions with high saturation indices. A fully automatic RO system was built and controlled using the Python program platform. Scaling progression was monitored through flux measurements and was evaluated by SEM after each experiment.

Several key findings can be drawn from the work presented in Chapter 2. First, the pH sensitive CaCO_3 scale was efficiently removed from the membrane surface through the intermittent application of 2.5 V to the membrane surface when the membrane acted as an anode. At such high voltage, water oxidation occurred at the anode, leading to proton formation and resulted in the dissolution of deposited CaCO_3 crystals. During the descaling stage, it is important to reduce the pressure in the flow cell to minimize crystal re-deposition. Second, pH insensitive CaSO_4 scale formation was significantly retarded

through the continuous application of 1.5 V, below the water splitting potential, to the membrane surface when the membrane was operated as an anode. The continuous application of a sufficient electrical potential to the membrane surface leads to the formation of a thick layer of counter ions along the membrane surface. This forced CaSO_4 crystal formation away from the membrane surface, allowing the newly formed crystals to be carried away by the cross-flow.

Third, a simple model was developed, based on a modified Poisson–Boltzmann equation, to sufficiently explain our observations. The thickness of the EDL increased when sufficient electrical potential was applied to the membrane surface, resulting in a significantly higher stoichiometric anion and cation ratio. As a result, the crystal nucleation rate in EDL layer is significantly slower near the membrane than in the saturated bulk solution.

Overall, the results in chapter 2 illustrate potential benefits that electrically conducting membrane offer to RO treatment of high saturation index brackish inland groundwater. Results indicate that the implementation of this technology could significantly reduce the use of anti-scalants and acid in the treatment of brackish groundwater. These changes would also lengthen membrane lifetime and significant reduce system down time, resulting in reduced costs for the entire RO water treatment process.

Although these conclusions offer significant potential improvement for RO treatment, several future research questions arise from the work presented in Chapter 2. In order to fully characterize the usability of this technology, further studies could be done to determine the effects of negative potential on scaling behavior, the effects of membrane

surface potential on anti-scaling chemicals, and the effects of interfering ions on scale prevention.

5.2 Treating Anaerobic Sequencing Batch Reactor Effluent with Electrically Conducting Ultrafiltration and Nanofiltration Membranes for Fouling Control

In Chapter 3, an anaerobic sequencing batch reactor coupled to electrically conducting UF and NF membranes in order to treat high-strength industrial wastewater containing high concentrations of benzyl alcohol, a commercial paint stripper, was studied. Anaerobic wastewater reclamation is very challenging due to limited membrane fouling prevention methods. This work has offered a robust way to reduce membrane organic fouling while treating anaerobic effluent.

The results presented in Chapter 3 contain four key findings. First, the HPLC results demonstrated that an anaerobic process can be used to successfully degrade benzyl alcohol, and identified that the major degradation product is benzoic acid. After 21 hours in the aSBR, an overall COD removal of approximately 86% was achieved.

Second, these results indicated that the application of negative 5V to the ultrafiltration membrane surface results in the best fouling prevention, compared with 0 and negative 3V. In order to achieve 90% fresh water recovery, 1 minute of back washing with UF membrane permeate was necessary every half hour in order to efficiently prevent membrane fouling and allow for longer and higher operational fluxes during the treatment of complex wastewater streams.

Third, the application of 1.5V positive potential to the membrane surface during back washing, which was originally intended to kill bacteria [44,202], increased membrane fouling dramatically. This may be due to the remaining aromatic organic benzoic acid polymerizing on the membrane CNT structure and restricting the passage of water. Similar observations have been reported for other aromatic organic compounds [112].

Fourth, negative electrical potential applied to the NF membrane surface had no impact on fouling prevention, while positive potential applied to the membrane made the fouling worse in addition to hindering the cleaning and recovery of the NF membranes.

Overall, in Chapter 3, the feasibility of using electrically conducting membranes to prevent membrane fouling during the treatment of anaerobic reactor effluent at high operational fluxes was investigated. These observations have significant implications for the future treatment of complex anaerobic wastewater streams that are not suitable for traditional membrane treatment. Water supplies that were previously considered inaccessible due to a lack of treatment options may become usable through this new technology.

In this research, a bench scale anaerobic batch reactor which only treated benzyl alcohol has been specifically investigated. However, there are a wide variety of emerging contaminants of significant concern for wastewater reclamation whose removal might be improved by using electrically conducting NF membranes. The conclusions in Chapter 3 have relatively limited implications for the removal of contaminants in general, but the technology may be generalizable. Future studies could determine the effectiveness of this technique on a variety of similar contaminants to determine if they can be degraded

similarly to benzyl alcohol. In addition, using electrically conducting UF may offer a method for deactivating antibiotic resistance bacteria during treatment.

5.3 Enhanced Anodic Stability of Polyaniline-Coated Carbon Nanotube

Ultrafiltration Membranes and Their Applications

Electrically conducting membranes (ECMs) have been reported to be efficient in fouling prevention and the destruction of aqueous chemical compounds. In Chapter 4, we reported a fabrication method for highly conductive and anodically stable composite polyaniline-carbon nanotubes (PANI-CNT) ultrafiltration (UF) ECMs. PANI-CNT UF membranes were made through a process of electropolymerization of aniline on a CNT substrate under acidic conditions. The resulting PANI-CNT UF ECMs were characterized by scanning electron microscopy, atomic force microscopy, a four-point conductivity probe, cyclic voltammetry, and contact angle goniometry.

The analysis of the membranes in Chapter 4 revealed three key findings. First, the coating of polyaniline on the CNTs significantly increased the electrical conductivity of the membrane. The PANI coating works like a conductive glue to firmly bridge CNTs together, enhancing the electron transfer between CNTs. The PANI coating also increased membrane surface hydrophilicity without sacrificing membrane selectivity or permeability.

Second, the anodic stability of the CNT membrane was greatly improved by the PANI coating. The membrane's anodic stability was evaluated in a pH controlled aqueous environment under a wide range of anodic potentials using a three-electrode cell. The

results indicate a significantly reduced degradation rate for the PANI CNT ECM in comparison to a CNT-poly (vinyl alcohol) ECM under 2.5V anodic potentials.

Third, this anodically stable membrane can be used as a flow through electrode to oxidize organic compounds. A model organic compound (methylene blue) was electrochemically transformed at high efficiency (90%) in a single pass through the anodically charged ECM. It also served as an *in situ* self-cleaning membrane via the application of indirect oxidation. A positive 3V potential was applied to efficiently clean membranes fouled with bovine serum albumin.

Overall in Chapter 4, a robust anodically stable electrically conducting PANI-CNT UF membrane via an electro-polymerization technique has been successfully developed. The membranes are highly conducting and stable in a large range of anodic potentials. These observations have significant implications for the future of water treatment for wastewater reuse. It offers a possible new treatment technology which can integrate membrane separation and advanced oxidation. This can significantly reduce current water treatment footprints. Optimally, this hybrid system could change current centralized water treatment strategies to more remote and decentralized water treatment systems to fulfill the requirements of our future sustainable development.

Although these conclusions offer significant potential improvement for water treatment, one question arises from the work presented in Chapter 4. The PANI-CNT ECM membrane is sensitive to pH. At low pH, PANI can lose its conductivity dramatically. When the membrane is operating above the water splitting potential or oxidizing chemical compounds, which usually involves proton generation, it is critical to have a proton

acceptor present to control pH. In this research, we used a PBS buffer to control pH, but ultimately a pH insensitive material is preferred. In the future, it is important to develop a new material with high conductivity, inert to pH change, which has a high oxygen revolution potential.

Appendix

Appendix A: Supporting Information for Chapter 2

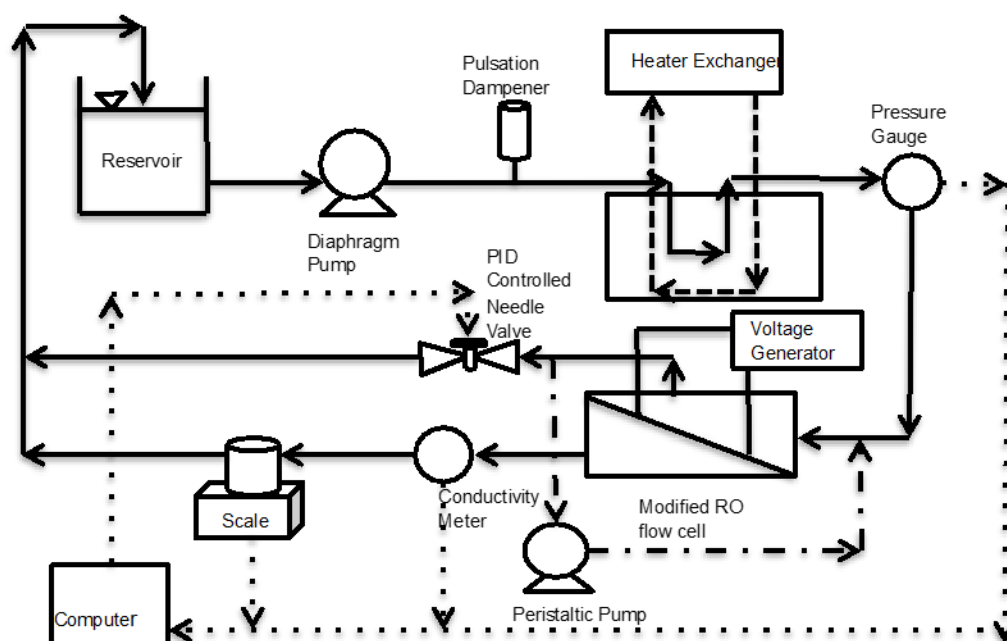


Figure A-1. System diagram: solid lines represent water flow; dotted lines represent computer data flow; dashed line represent membrane flushing flows.

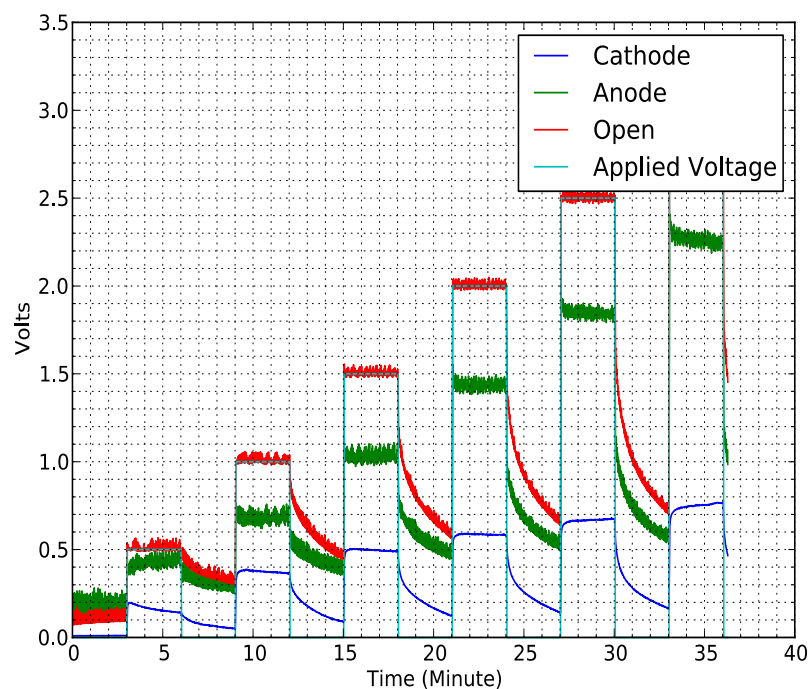


Figure A-2. Membrane surface potential (as anode or cathode) vs. a Ag/AgCl reference electrode as a function of applied electrical potential; the red line represents the applied potential; the green line represents the surface potential when the membranes is an anode; the red line represents the surface potential when the membrane is used as a cathode.

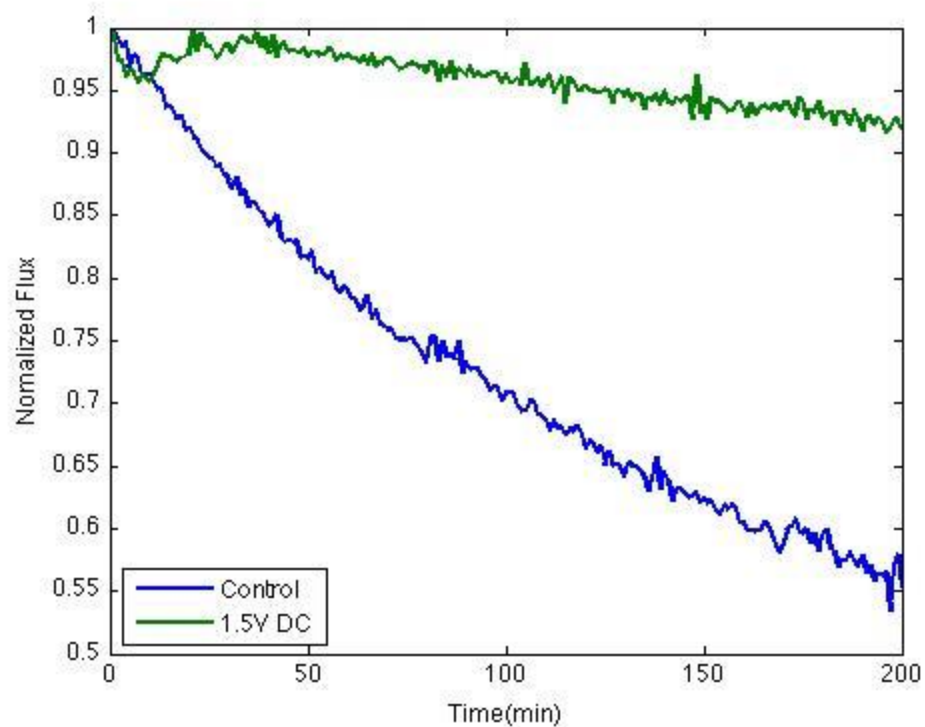


Figure A-3. Impact of electrical potential on CaSO_4 scale formation, when an in-line $0.5\ \mu\text{m}$ filter was used to remove suspended particulate matter from the recirculated retentate.

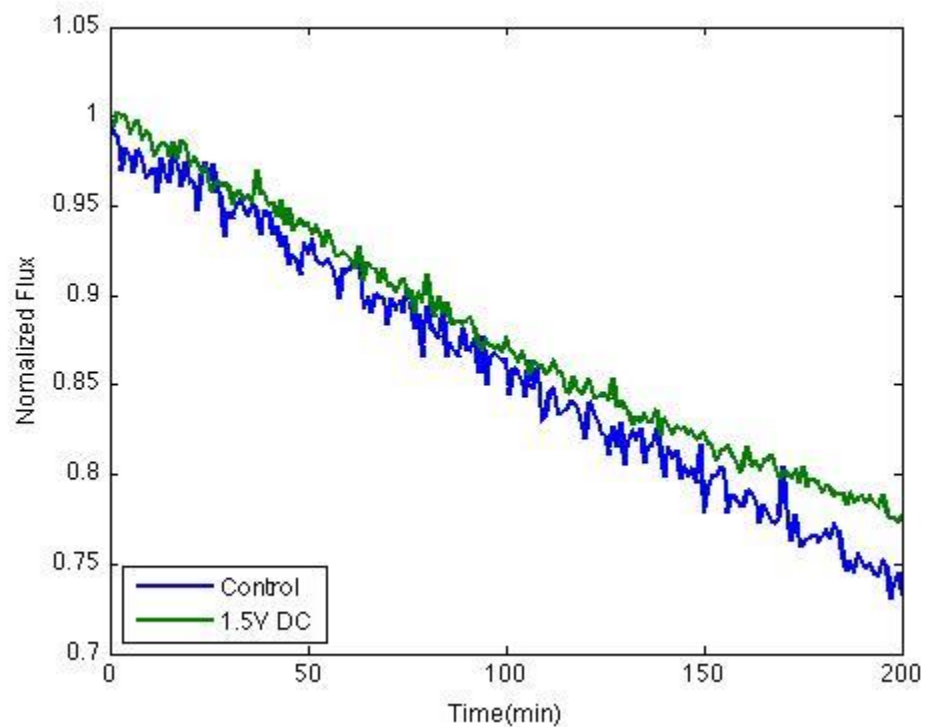


Figure A-4. Impact of electrical potential on CaSO_4 scale formation, when no in-line 0.5 μm filter was used.

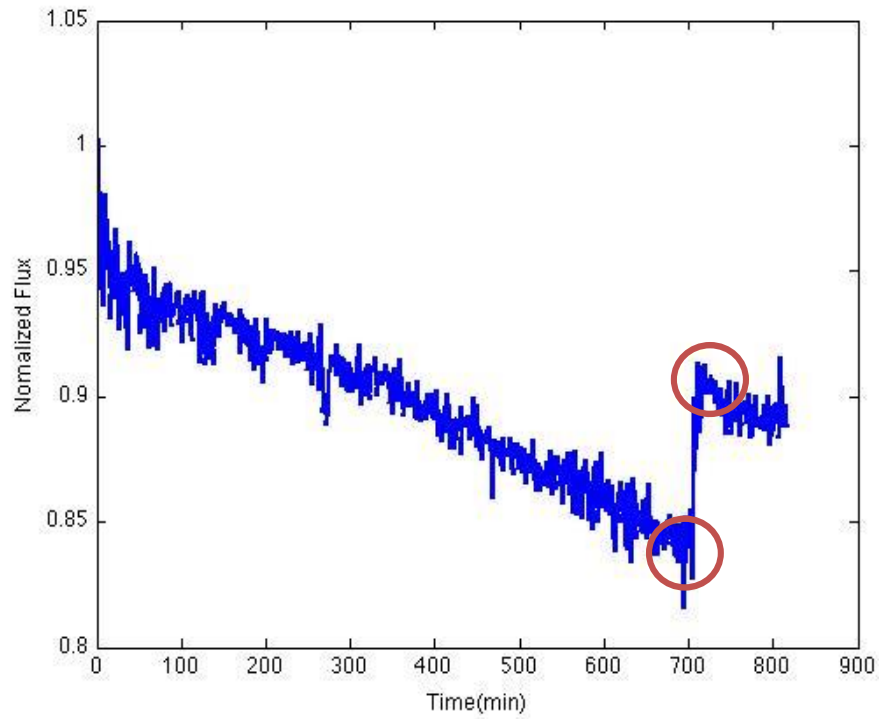


Figure A-5. CaCO_3 Scaling experiment: the first red cycle indicates when 2.5 V DC were applied for 10 minutes; the second red circle indicates when the voltage was turned off.

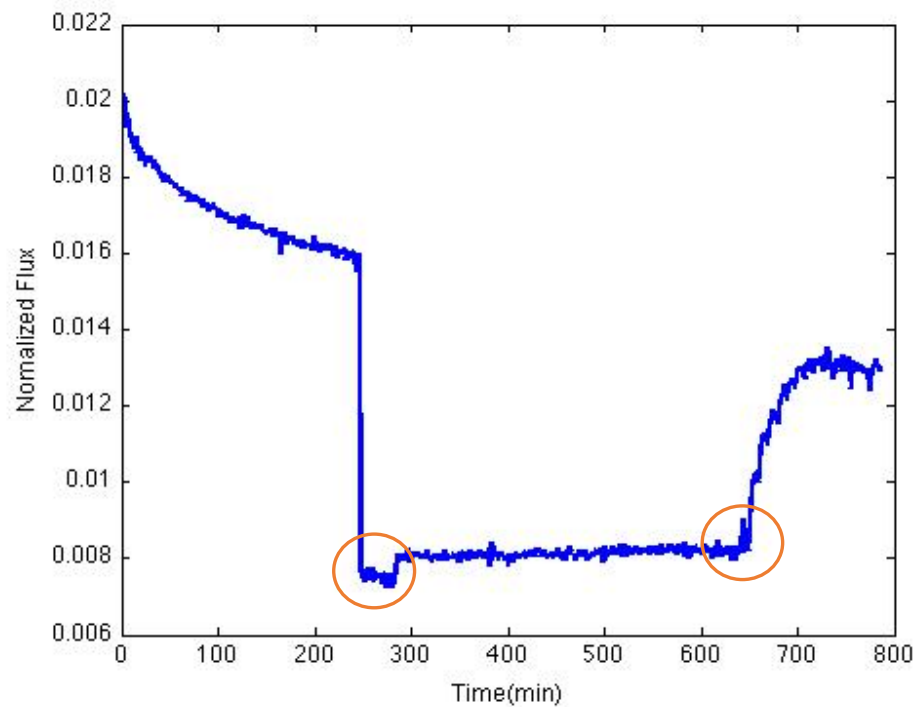


Figure A-6. CaCO_3 scaling experiment: the first red cycle indicates decrease pressure to 400 psi (operation pressure of scaling experiment is 550 psi in the beginning of the experiment, up to approximately 240 min.) together with rinsing with deionized water, which resulted in very little flux recovery. The second circle indicates the point where 2.5 V DC were applied to the membrane surface for 10 minutes (membrane as anode).

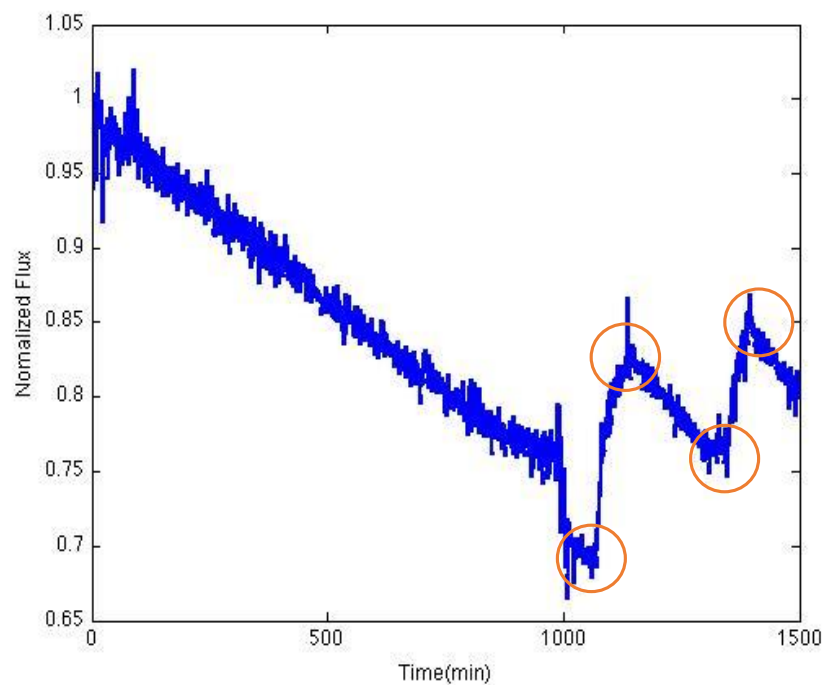


Figure A-7 CaCO_3 scaling experiment: the 1st and 3rd red cycle indicated applied 2.5V DC on the membrane surface, the 2nd and 4th stop applied the voltage. The cross flow is 4 cm/s in cell and pressure is 400 psi.



Figure A-8. Three different zones were evident after CaSO_4 scaling experiment; an area near the inlet where no scaling were evident, likely due to turbulent conditions, a transition zone, and a heavy scaling zone. The image above was taken from one of the control experiments, where no electrical potential was applied to the membrane surface.

Appendix B: Supporting Information for Chapter 3

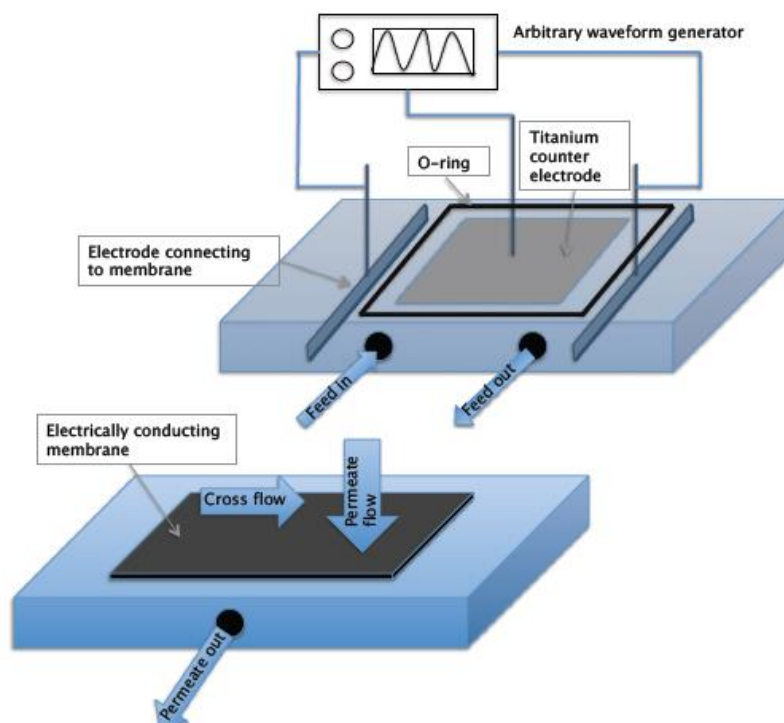


Figure B-1. Membrane module used in experiments; modules were constructed from acetylplastic. The Figure depicts the two halves of the module with the membrane resting on the bottom half. A buna O-ring isolates the feed stream from the side electrodes that provide the electric charge to the membrane surface. The membrane coupon used in the cell is large enough to allow contact with the side electrodes beyond the borders of the O-ring. A titanium counter electrode sits 4 mm above the membrane surface, and is in contact with the feed stream. The counter electrode has a surface area nearly as large as the membrane surface. Feed water flows in to the module, with some of the feed passing through the membrane to generate the permeate; the retentate flows out of the module.

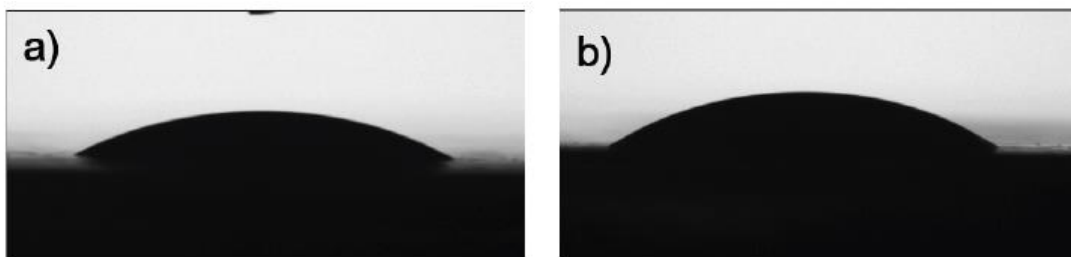


Figure B-2. Images generated using the contact angle goniometer of (a) a water drop in contact with the UF membrane, and (b) a water drop in contact with the NF membrane surface. In these experiments, 6 μ l of DIW was dropped onto the membrane surface and allowed to equilibrate for 1 minute before the contact angle was measured. All measurements were done in triplicate.

Appendix C: Supporting Informations for Chapter 4

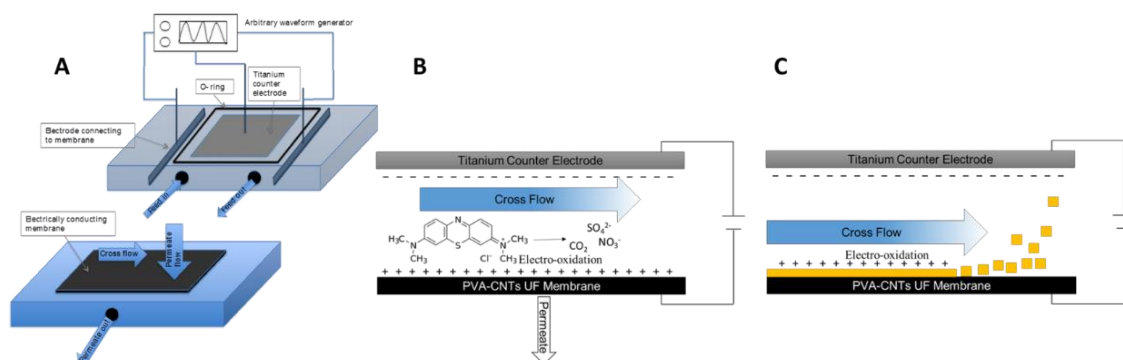


Figure C-1. Experimental systems; (A) Flow through membrane module used in advanced application experiments; (B) Methylene blue degradation in flow-through filtration PANI-CNTs system; (C) Electrochemical *in situ* membrane cleaning

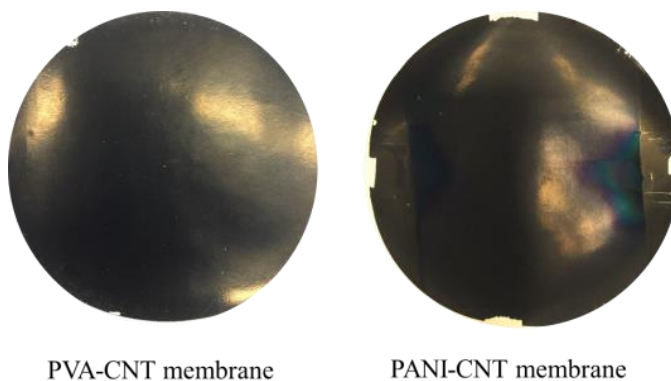


Figure C-2: Digital camera images of the fabricated membranes, (Left) PVA-CNT membrane (Right) PANI-CNT membrane. The lines on the PANI-CNT membrane are a result of the electrical connector between the membrane and the power source.

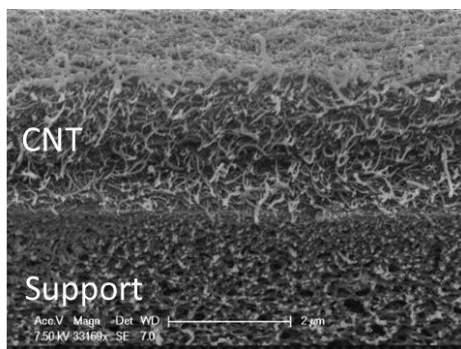


Figure C-3: Cross section of CNT layer deposited on a polysulfone UF support. Typical thickness of the CNT layer was about 2 μm . The average permeability of the CNT membrane was about 40 LMH/psi. Scale is 2 μm .

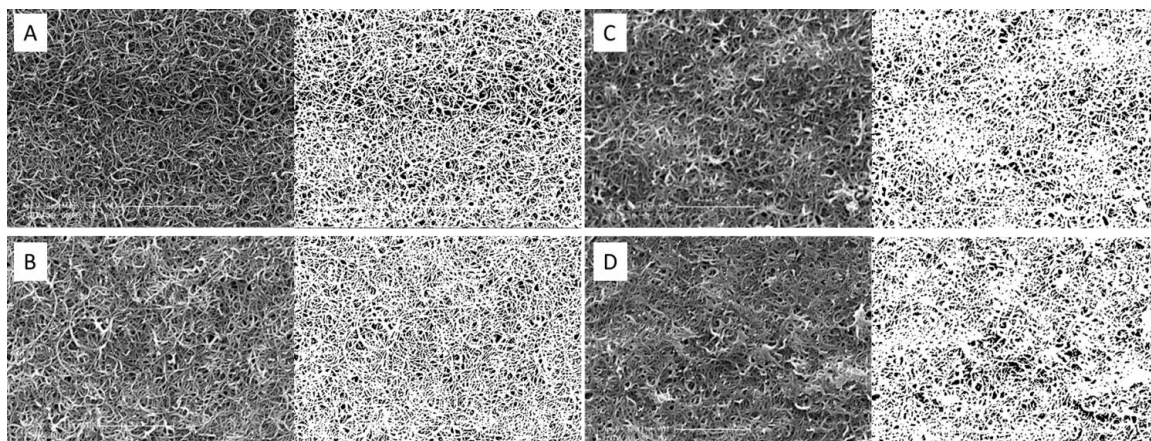


Figure C-4: Porosity analysis using imageJ. (A) PVA-CNT membrane; (B) PANI-CNT sulfuric acid dopant; (C) PANI-CNT hydrochloric acid dopant; (D) PANI-CNT oxalic acid dopant. Scale bars for all SEM images are 2 μm

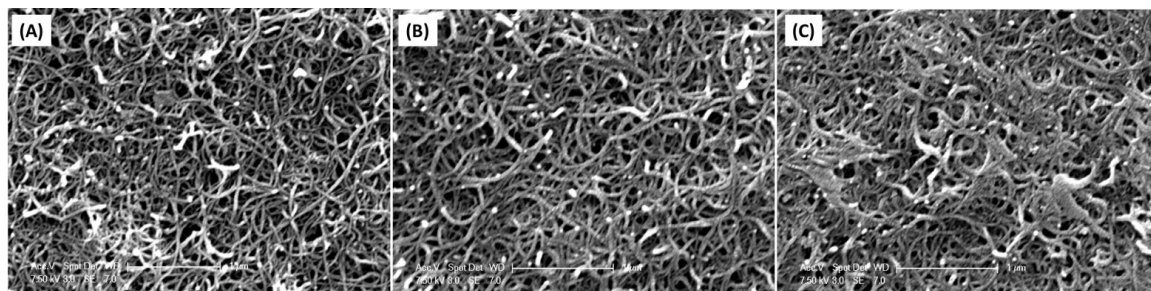


Figure C-5: High magnification SEM images of the PANI-CNT membranes. (A) Sulfuric acid based PANI-CNT; (B) Hydrochloric acid based PANI-CNT; (C) Oxalic acid based PANI-CNT. Scale bars for all SEM images are 1 μm

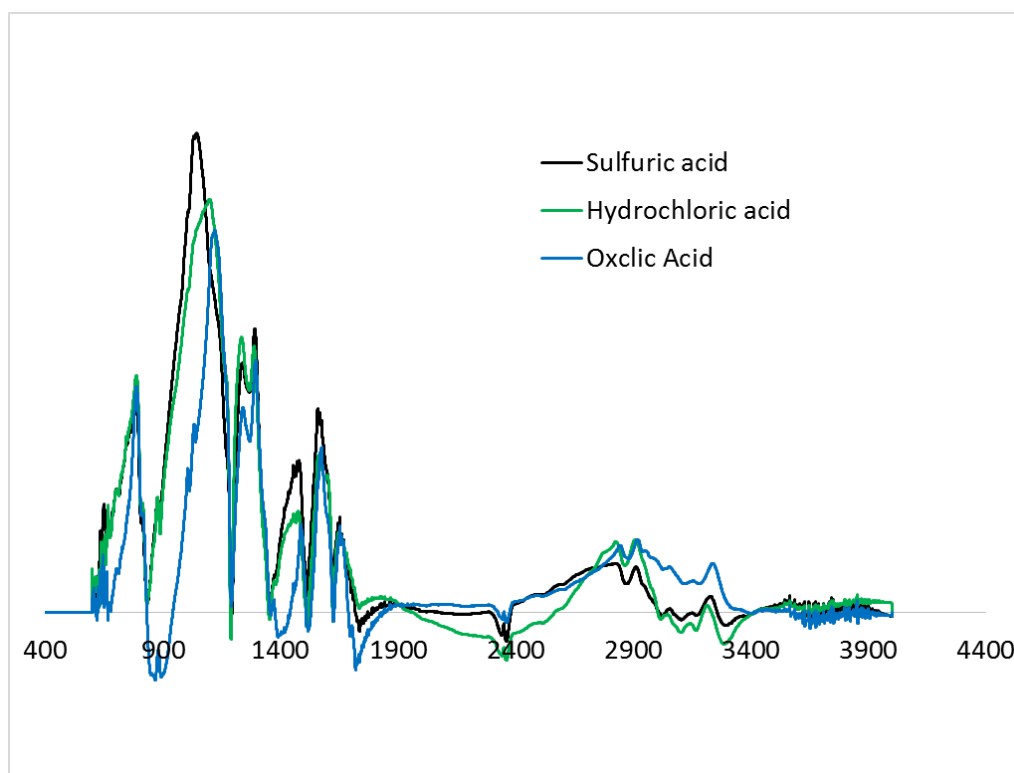


Figure C-6. Representative FTIR scans of PANI-CNTs membranes based on all acidic dopants.

All membranes show a nitrogen hydrogen bond (2° amine) at $1035\text{--}1095\text{ cm}^{-1}$ and a nitrogen carbon, double bond at 1650 cm^{-1} . [188,206] Thus, indicating the presence of the conductive form of PANI, “emeraldine” on the CNTs network.

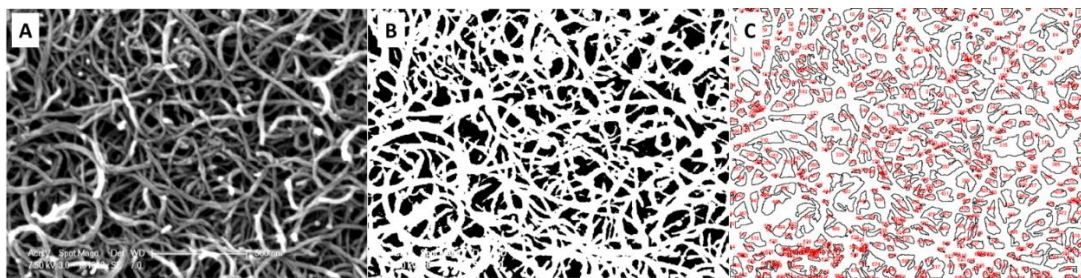


Figure C-7. Porosity and pore size analysis using imageJ. (A) Original membrane surface image; (B) Binary Image; (C) Output of imageJ drawing of pores used for calculation of pores area. Scale bar is 500 nm.

Average pore size:

According to image analysis the average pore area for sulfuric acid based membranes was about 14396 nm^2 , assuming round pores (i.e. average roundness coefficient of 0.75), the typical pore diameter is about 120 nm.

Average Porosity:

According to images analysis the typical porosity was calculated by dividing the sum of pore areas by the total area in the image.

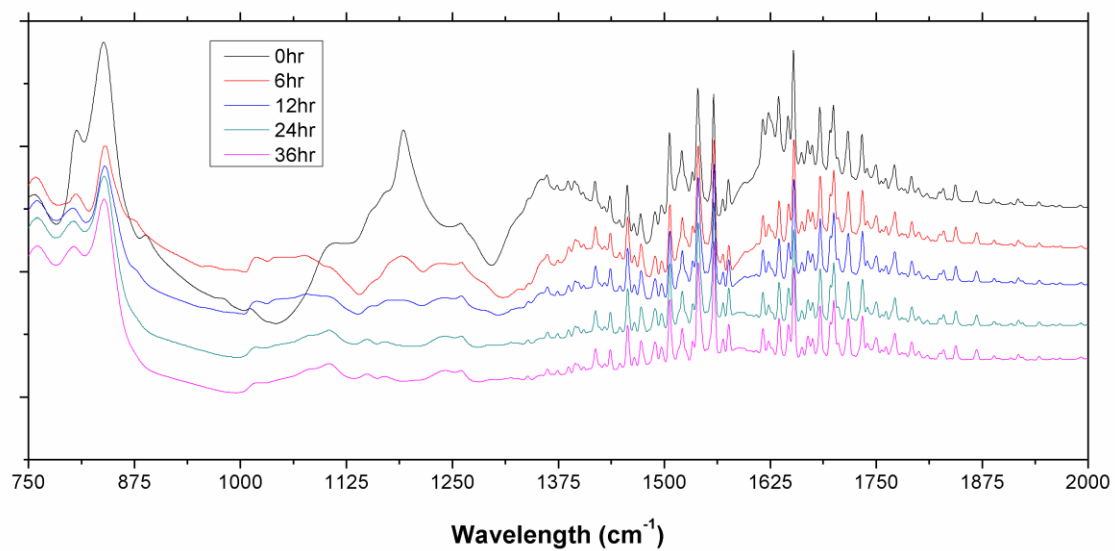


Figure C-8: FTIR scans of PANI-CNTs membranes after exposure to chlorine (500 ppm-hr). Even after exposure to chlorine, membranes show a nitrogen hydrogen bond (2° amine) at 1035-1095 cm^{-1} and a nitrogen carbon, double bond at 1650 cm^{-1} (both peaks are marked).

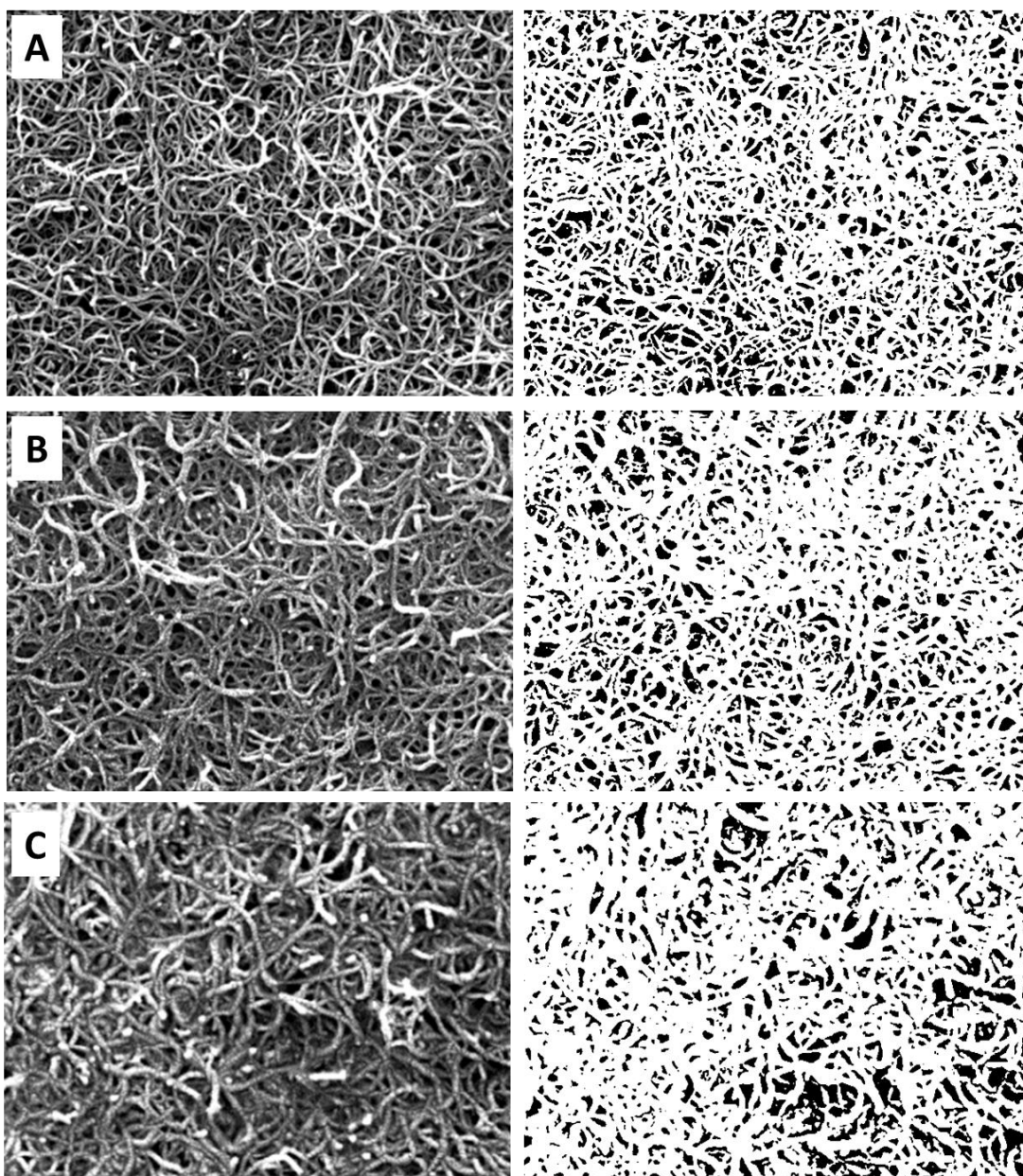


Figure C-9. PANI-CNTs porosity as a function of applied current density quantified using imageJ. Left panel: original SEM images; right panel: binary output of imageJ. (A) PANI-CNTs 2.5 mA cm^{-2} ; (B) PANI-CNTs 9 mA cm^{-2} ; (C) PANI-CNTs 15 mA cm^{-2}

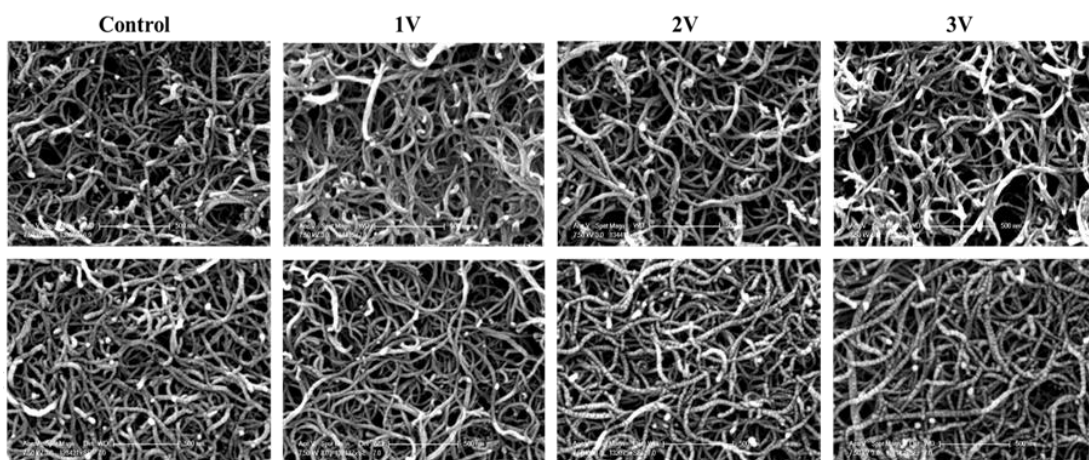


Figure C-10. SEM images of PVA-CNT and PANI-CNT membranes after applying 1 V, 2 V and 3 V (vs Ag/AgCl) for 10 min in a PBS buffer solution; Top panel: PVA-CNT membrane; Lower panel; PANI-CNT membrane. Scale bars for all SEM images are 500 nm.

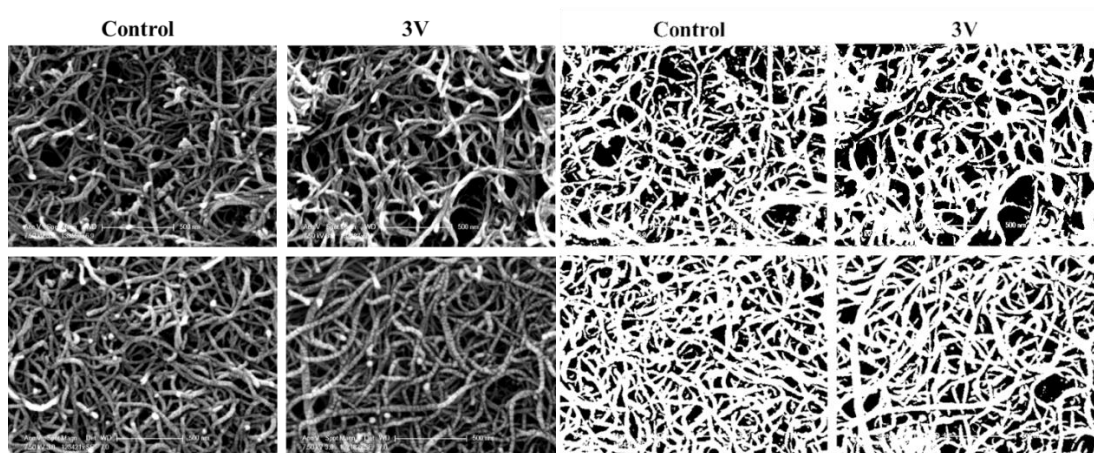


Figure C-11. SEM images of PVA-CNT and PANI-CNT membranes after applying 1 V, 2 V and 3 V (vs Ag/AgCl) for 10 min in a PBS buffer solution; Top panel: PVA-CNT membrane; Lower panel; PANI-CNT membrane. Scale bars for all SEM images are 500 nm.

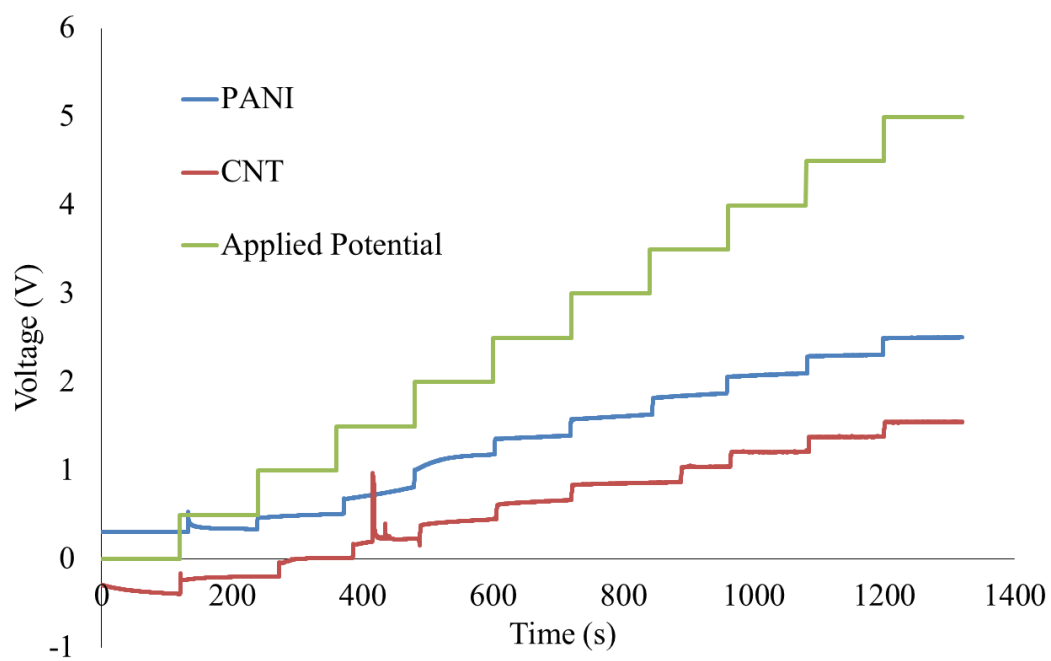


Figure C-12. Applied electrical potential compared to the real potential on the membrane versus a Ag/AgCl reference electrode.

Table C-1. Normalized current decline slopes - first order rate constants (corresponding to Figure 7 B)

Applied anodic potential (V)	slope (sec ⁻¹)
2.0	$-2 \pm 4.5 \cdot 10^{-5}$
2.5	$-3 \pm 4.5 \cdot 10^{-5}$
2.8	$-4 \pm 3.5 \cdot 10^{-5}$
3.0	$-6 \pm 5 \cdot 10^{-5}$

Reference

- [1] F. Resources, Global Hydrological Cycles and, Science (80-.). 313 (2006) 1068–1072.
- [2] C.J. Vorosmarty, Global Water Resources: Vulnerability from Climate Change and Population Growth, Science (80-.). 289 (2000) 284–288. doi:10.1126/science.289.5477.284.
- [3] J.G. Hering, T.D. Waite, R.G. Luthy, J.E. Drewes, D.L. Sedlak, A changing framework for urban water systems, Environ. Sci. Technol. 47 (2013) 10721–10726. doi:10.1021/es4007096.
- [4] J. Yeston, R. Coontz, J. Smith, C. Ash, A thirsty world, Science (80-.). (2006) 2006. <http://www.sciencemag.org/content/313/5790/1067.short> (accessed January 14, 2014).
- [5] J. Bear, A.H.-D. Cheng, S. Sorek, D. Ouazar, I. Herrera, Seawater intrusion in coastal aquifers: concepts, methods and practices, Springer Science & Business Media, 1999.
- [6] M. Elimelech, W. Phillip, The Future of Seawater Desalination: Energy, Technology, and the Environment, Science (80-.). 333 (2011) 712–717. <http://www.sciencemag.org/content/333/6043/712.short> (accessed October 13, 2013).
- [7] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, Desalination. 216 (2007) 1–76. doi:10.1016/j.desal.2006.12.009.
- [8] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges., Water Res. 43 (2009) 2317–48. doi:10.1016/j.watres.2009.03.010.
- [9] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—Development to date and future potential, J. Memb. Sci. 370 (2011) 1–22. doi:10.1016/j.memsci.2010.12.036.
- [10] D. Fatta-kassinos, Wastewater Reuse and Current Challenges, n.d. doi:10.1007/978-3-319-23892-0.
- [11] B. Van Der Bruggen, A Review of Pressure-Driven Membrane Processes in Wastewater Treatment and Drinking Water Production, Environ. Prog. (2003). <http://onlinelibrary.wiley.com/doi/10.1002/ep.670220116/abstract> (accessed

November 15, 2013).

- [12] Y.J. Chan, M.F. Chong, C.L. Law, D.G. Hassell, A review on anaerobic-aerobic treatment of industrial and municipal wastewater, *Chem. Eng. J.* 155 (2009) 1–18. doi:10.1016/j.cej.2009.06.041.
- [13] M. & Eddy, *Wastewater Engineering: Treatment and Resource Recovery*, McGraw-Hill international ed., 2014.
- [14] Y. Miura, Y. Watanabe, S. Okabe, Membrane biofouling in pilot-scale membrane bioreactors (MBRs) treating municipal wastewater: impact of biofilm formation., *Environ. Sci. Technol.* 41 (2007) 632–8.
- [15] W. Guo, H.H. Ngo, J. Li, A mini-review on membrane fouling, *Bioresour. Technol.* 122 (2012) 27–34. doi:10.1016/j.biortech.2012.04.089.
- [16] A.A. Alturki, N. Tadkaew, J. a. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications, *J. Memb. Sci.* 365 (2010) 206–215. doi:10.1016/j.memsci.2010.09.008.
- [17] H.K. Lonsdale, The growth of membrane technology, *J. Memb. Sci.* 10 (1982) 81–181. doi:http://dx.doi.org/10.1016/S0376-7388(00)81408-8.
- [18] M. Kurihara, H. Yamamura, T. Nakanishi, High recovery/high pressure membranes for brine conversion SWRO process development and its performance data, *Desalination.* 125 (1999) 9–15. doi:10.1016/S0011-9164(99)00119-8.
- [19] N. Hilal, H. Al-Zoubi, N.A. Darwish, A.W. Mohammad, M. Abu Arabi, A comprehensive review of nanofiltration membranes: Treatment, pretreatment, modelling, and atomic force microscopy, *Desalination.* 170 (2004) 281–308. doi:10.1016/j.desal.2004.01.007.
- [20] J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, *Nat. Rev. Mater.* 1 (2016) 1–15. doi:10.1038/natrevmats.2016.18.
- [21] P.H. Wolf, S. Sivers, S. Monti, UF membranes for RO desalination pretreatment, *Desalination.* 182 (2005) 293–300. doi:10.1016/j.desal.2005.05.006.
- [22] J. Arévalo, G. Garralón, F. Plazab, B. Moreno, J. Pérez, M.Á. Gómez*, Wastewater reuse after treatment by tertiary ultrafiltration and a membrane bioreactor (MBR): a comparative study, *Desalination.* 243 (2009) 32–41. doi:10.1016/j.desal.200.

- [23] C.-W. Jung, L.-S. Kang, Application of combined coagulation-ultrafiltration membrane process for water treatment, *Korean J. Chem. Eng.* 20 (2003) 855–861. doi:10.1007/BF02697288.
- [24] G. Tchobanoglous, J. Darby, K. Bourgeois, J. McArdle, P. Genest, M. Tylla, Ultrafiltration as an advanced tertiary treatment process for municipal wastewater, *Desalination*. 119 (1998) 315–322. doi:10.1016/S0011-9164(98)00175-1.
- [25] Q. Li, M. Elimelech, Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms., *Environ. Sci. Technol.* 38 (2004) 4683–93. <http://www.ncbi.nlm.nih.gov/pubmed/15461180>.
- [26] M. Herzberg, M. Elimelech, Biofouling of reverse osmosis membranes: Role of biofilm-enhanced osmotic pressure, *J. Memb. Sci.* 295 (2007) 11–20. doi:10.1016/j.memsci.2007.02.024.
- [27] B. Van Der Bruggen, C. Vandecasteele, T. Van Gestel, W. Doyen, R. Leysen, A review of pressure-driven membrane processes in wastewater treatment and drinking water production, *Environ. Prog.* 22 (2003) 46–56. doi:10.1002/ep.670220116.
- [28] Y. Cohen, B. McCool, A. Rahardianto, M. Kim, J. Faria, Membrane desalination of agricultural drainage water, in: *Salin. Drain. San Joaquin Val. Calif.*, Springer, 2014: pp. 303–341.
- [29] W.-Y. Shih, A. Rahardianto, R.-W. Lee, Y. Cohen, Morphometric characterization of calcium sulfate dihydrate (gypsum) scale on reverse osmosis membranes, *J. Memb. Sci.* 252 (2005) 253–263. doi:10.1016/j.memsci.2004.12.023.
- [30] S. Sablani, M. Goosen, R. Al-Belushi, M. Wilf, Concentration polarization in ultrafiltration and reverse osmosis: a critical review, *Desalination*. 141 (2001) 269–289. <http://www.sciencedirect.com/science/article/pii/S0011916401850050> (accessed November 15, 2013).
- [31] M. Brusilovsky, J. Borden, D. Hasson, Flux decline due to gypsum precipitation on RO membranes, *Desalination*. 86 (1992) 187–222. <http://www.sciencedirect.com/science/article/pii/0011916492800336> (accessed October 13, 2013).
- [32] S. Lee, C. Lee, Effect of operating conditions on CaSO_4 scale formation mechanism in nanofiltration for water softening, *Water Res.* 34 (2000) 3854–3866. <http://www.sciencedirect.com/science/article/pii/S0043135400001421> (accessed October 15, 2013).

- [33] V. Gekas, B. Hallström, Mass transfer in the membrane concentration polarization layer under turbulent cross flow : I. Critical literature review and adaptation of existing sherwood correlations to membrane operations, *J. Memb. Sci.* 30 (1987) 153–170. <http://www.sciencedirect.com/science/article/pii/S0376738800813496> (accessed October 15, 2013).
- [34] M. OKAZAKI, S. KIMURA, SCALE FORMATION ON REVERSE-OSMOSIS MEMBRANES, *J. Chem. Eng. Japan.* 17 (1984) 145–151.
- [35] F. Ahmi, A. Gadri, Kinetics and morphology of formed gypsum, *Desalination.* 166 (2004) 427–434. <http://www.sciencedirect.com/science/article/pii/S001191640400325X> (accessed November 13, 2013).
- [36] C. Tzotzi, T. Pahiadaki, A study of CaCO₃ scale formation and inhibition in RO and NF membrane processes, *J. Memb. Sci.* 296 (2007) 171–184. doi:10.1016/j.memsci.2007.03.031.
- [37] M. Al-Shammiri, M. Safar, M. Al-Dawas, Evaluation of two different antiscalants in real operation at the Doha research plant, *Desalination.* 128 (2000) 1–16. <http://www.sciencedirect.com/science/article/pii/S0011916400000199> (accessed August 16, 2014).
- [38] M. Öner, Ö. Doğan, G. Öner, The influence of polyelectrolytes architecture on calcium sulfate dihydrate growth retardation, *J. Cryst. Growth.* 186 (1998) 427–437. <http://www.sciencedirect.com/science/article/pii/S0022024897005186> (accessed August 16, 2014).
- [39] X. Zhu, M. Elimelech, Colloidal Fouling of Reverse Osmosis Membranes: Measurements and Fouling Mechanisms, *Environ. Sci. Technol.* 31 (1997) 3654–3662. doi:10.1021/es970400v.
- [40] G. Amy, Fundamental understanding of organic matter fouling of membranes, *Desalination.* 231 (2008) 44–51. doi:10.1016/j.desal.2007.11.037.
- [41] S.T. Kelly, A.L. Zydney, Mechanisms for BSA fouling during microfiltration, *J. Memb. Sci.* 107 (1995) 115–127. doi:10.1016/0376-7388(95)00108-O.
- [42] N. Hilal, O.O. Ogunbiyi, N.J. Miles, R. Nigmatullin, Methods Employed for Control of Fouling in MF and UF Membranes: A Comprehensive Review, *Sep. Sci. Technol.* 40 (2005) 1957–2005. doi:10.1081/SS-200068409.

- [43] V.T. Do, C.Y. Tang, M. Reinhard, J.O. Leckie, Degradation of polyamide nanofiltration and reverse osmosis membranes by hypochlorite., *Environ. Sci. Technol.* 46 (2012) 852–9. doi:10.1021/es203090y.
- [44] S. Avlonitis, W.T. Hanbury, T. Hodgkiess, Chlorine degradation of aromatic polyamides, *Desalination*. 85 (1992) 321–334. doi:10.1016/0011-9164(92)80014-Z.
- [45] R.M. Donlan, Biofilms: microbial life on surfaces., *Emerg. Infect. Dis.* 8 (2002) 881–90. doi:10.3201/eid0809.020063.
- [46] Y.-L. Jin, W.-N. Lee, C.-H. Lee, I.-S. Chang, X. Huang, T. Swaminathan, Effect of DO concentration on biofilm structure and membrane filterability in submerged membrane bioreactor., *Water Res.* 40 (2006) 2829–36. doi:10.1016/j.watres.2006.05.040.
- [47] W.-N. Lee, I.-S. Chang, B.-K. Hwang, P.-K. Park, C.-H. Lee, X. Huang, Changes in biofilm architecture with addition of membrane fouling reducer in a membrane bioreactor, *Process Biochem.* 42 (2007) 655–661. doi:10.1016/j.procbio.2006.12.003.
- [48] X.Y. Li, S.F. Yang, Influence of loosely bound extracellular polymeric substances (EPS) on the flocculation, sedimentation and dewaterability of activated sludge., *Water Res.* 41 (2007) 1022–30. doi:10.1016/j.watres.2006.06.037.
- [49] J.S. Baker, L.Y. Dudley, Biofouling in membrane systems – a review, *Desalination*. 118 (1998) 81–89.
- [50] Y. Cohen, B. Mccool, A. Rahardianto, M. Kim, J. Faria, *Salinity and Drainage in San Joaquin Valley, California*, Springer Netherlands, Dordrecht, 2014. doi:10.1007/978-94-007-6851-2.
- [51] S.E. Coetser, T.E. Cloete, Biofouling and biocorrosion in industrial water systems., *Crit. Rev. Microbiol.* 31 (2005) 213–32. doi:10.1080/10408410500304074.
- [52] H.C. Flemming, Biofouling in water systems-cases, causes and countermeasures., *Appl. Microbiol. Biotechnol.* 59 (2002) 629–640. doi:10.1007/s00253-002-1066-9.
- [53] H.-C. Flemming, Reverse osmosis membrane biofouling, *Exp. Therm. Fluid Sci.* 14 (1997) 382–391. doi:10.1016/S0894-1777(96)00140-9.
- [54] W. Kulcke, G. Brunner, Use of alternating electrical fields as anti-fouling strategy in ultra filtration of biological suspensions - Introduction of a new experimental procedure for crossflow filtration, *J. Memb. Sci.* 142 (1998) 75–86. <http://www.sciencedirect.com/science/article/pii/S0376738897003104> (accessed July 19, 2014).

- [55] A. Ronen, W. Duan, I. Wheeldon, S.L. Walker, D. Jassby, Low Voltage Electrochemical Microbial Attachment Inhibition on Electrically Conducting Surfaces, *Environ. Sci. Technol.* (2015). doi:10.1021/acs.est.5b01281.
- [56] C.F. de Lannoy, D. Jassby, D.D. Davis, M.R. Wiesner, A highly electrically conductive polymer-multiwalled carbon nanotube nanocomposite membrane, *J. Memb. Sci.* 415-416 (2012) 718–724. doi:10.1016/j.memsci.2012.05.061.
- [57] S.H. Hong, J. Jeong, S. Shim, H. Kang, S. Kwon, K.H. Ahn, et al., Effect of electric currents on bacterial detachment and inactivation, *Biotechnol. Bioeng.* 100 (2008) 379–386. doi:10.1002/bit.21760.
- [58] J.R. Pan, Y. Su, C. Huang, Characteristics of soluble microbial products in membrane bioreactor and its effect on membrane fouling, *Desalination.* 250 (2010) 778–780. doi:10.1016/j.desal.2008.11.040.
- [59] J. Huang, Z. Wang, J. Zhang, X. Zhang, J. Ma, Z. Wu, A novel composite conductive microfiltration membrane and its anti-fouling performance with an external electric field in membrane bioreactors, *Sci. Rep.* 5 (2015) 9268. doi:10.1038/srep09268.
- [60] C.-F. de Lannoy, D. Jassby, K. Gloe, A.D. Gordon, M.R. Wiesner, Aquatic biofouling prevention by electrically charged nanocomposite polymer thin film membranes., *Environ. Sci. Technol.* 47 (2013) 2760–8. doi:10.1021/es3045168.
- [61] H. Liu, A. Vajpayee, C.D. Vecitis, Bismuth-doped tin oxide-coated carbon nanotube network: Improved anode stability and efficiency for flow-through organic electrooxidation, *ACS Appl. Mater. Interfaces.* 5 (2013) 10054–10066. doi:10.1021/am402621v.
- [62] P.A. Michaud, M. Panizza, L. Ouattara, T. Diaco, G. Foti, C. Comninellis, Electrochemical oxidation of water on synthetic boron-doped diamond thin film anodes, *J. Appl. Electrochem.* 33 (2003) 151–154. doi:10.1023/A:1024084924058.
- [63] R.H. Baughman, A.A. Zakhidov, W.A. De Heer, Carbon Nanotubes — the Route Toward Applications, 297 (2002) 787–793.
- [64] Q. Zhuo, S. Deng, B. Yang, J. Huang, G. Yu, Efficient Electrochemical Oxidation of Perfluorooctanoate Using a Ti / SnO₂ -Sb-Bi Anode, (2011) 2973–2979.
- [65] P.G. Klepetsanis, E. Dalas, P.G. Koutsoukos, Role of Temperature in the Spontaneous Precipitation of Calcium Sulfate Dihydrate, (1999) 1534–1540.
- [66] M. Elimelech, J. Gregory, X. Jia, R.A. Williams, Particle Deposition and

Aggregation Measurement , Modelling and Simulation, (n.d.).

- [67] R.F. Romo, M.M. Pitts., Application of electrotechnology for removal and prevention of reverse osmosis biofouling, *Environ. Prog.* 18 (1998) 107–112.
- [68] M. Gouy, Sur la constitution de la charge electrique a la surface d'un electrolyte, *J. Phys. Theor. Appl.* 9 (1910) 457–468.
- [69] D.L. Chapman, *Philosophical Magazine Series 6 LI* . A contribution to the theory of electrocapillarity, 5982 (2016). doi:10.1080/14786440408634187.
- [70] J.J. López-García, J. Horno, C. Grosse, Poisson-Boltzmann description of the electrical double layer including ion size effects., *Langmuir*. 27 (2011) 13970–4. doi:10.1021/la2025445.
- [71] W. Duan, A. Dudchenko, E. Mende, C. Flyer, X. Zhu, D. Jassby, Electrochemical mineral scale prevention and removal on electrically conducting carbon nanotube--polyamide reverse osmosis membranes, *Environ. Sci. Process. Impacts*. 16 (2014) 1300–1308.
- [72] M. Lochhead, S. Letellier, V. Vogel, Assessing the Role of Interfacial Electrostatics in Oriented Mineral Nucleation at Charged Organic Monolayers, *J. Phys.* 5647 (1997) 10821–10827. <http://pubs.acs.org/doi/abs/10.1021/jp972283w> (accessed October 13, 2013).
- [73] M. Elimelech, J. Gregory, X. Jia, Particle deposition and aggregation: measurement, modelling and simulation, Butterworth-Heinemann, 2013.
- [74] S. Bhattacharjee, M. Elimelech, Surface Element Integration : A Novel Technique for Evaluation of DLVO Interaction between a Particle and a Flat Plate, 285 (1997) 273–285.
- [75] N. Laboratorium, G. Eindhoven-holland, THE LONDON--VAN DER WAALS ATTRACTION BETWEEN SPHERICAL PARTICLES by H. C. H A M A K E R, (1937).
- [76] J. Crittenden, M.W. Harza, Water treatment: principles and design, John Wiley & Sons, 2005.
- [77] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.* 38 (2004) 11–41. doi:10.1016/j.seppur.2003.10.006.
- [78] K. Jüttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, *Electrochim. Acta*. 45 (2000) 2575–2594.

doi:10.1016/S0013-4686(00)00339-X.

- [79] C.A. Marti, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes { }, (2006) 1324–1340. doi:10.1039/b517632h.
- [80] B.P. Chaplin, Critical review of electrochemical advanced oxidation processes for water treatment applications, *Environ. Sci. Process. Impacts*. 16 (2014) 1182–1203. doi:10.1039/C3EM00679D.
- [81] B. Marselli, J. Garcia-Gomez, P. -a. Michaud, M. a. Rodrigo, C. Comninellis, Electrogenation of Hydroxyl Radicals on Boron-Doped Diamond Electrodes, *J. Electrochem. Soc.* 150 (2003) D79. doi:10.1149/1.1553790.
- [82] C. Comninellis, C. Pulgarin, Electrochemical oxidation of phenol for wastewater treatment using SnO₂, anodes, *J. Appl. Electrochem.* 23 (1993) 108–112.
- [83] a. M. Polcaro, S. Palmas, F. Renoldi, M. Mascia, On the performance of Ti/SnO₂ and Ti/PbO₂ anodes in electrochemical degradation of 2-chlorophenol for wastewater treatment, *J. Appl. Electrochem.* 29 (1999) 147–151. doi:10.1023/A:1003411906212.
- [84] H. Sharifian, Electrochemical Oxidation of Phenol, *J. Electrochem. Soc.* 133 (1986) 921. doi:10.1149/1.2108763.
- [85] J. Iniesta, Electrochemical oxidation of phenol at boron-doped diamond electrode, *Electrochim. Acta*. 46 (2001) 3573–3578. doi:10.1016/S0013-4686(01)00630-2.
- [86] R.B.A. Souza, L.A.M. Ruotolo, Electrochemical treatment of oil refinery effluent using boron-doped diamond anodes, *J. Environ. Chem. Eng.* 1 (2013) 544–551. doi:10.1016/j.jece.2013.06.020.
- [87] B.P. Chaplin, G. Schrader, J. Farrell, Electrochemical destruction of N-nitrosodimethylamine in reverse osmosis concentrates using Boron-doped diamond film electrodes., *Environ. Sci. Technol.* 44 (2010) 4264–4269. doi:10.1021/Es903872p.
- [88] M. a Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas, A.M. Mayes, Science and technology for water purification in the coming decades., *Nature*. 452 (2008) 301–10. doi:10.1038/nature06599.
- [89] M. Panizza, a Barbucci, R. Ricotti, G. Cerisola, Electrochemical degradation of methylene blue, *Sep. Purif. Technol.* 54 (2007) 382–387. doi:10.1016/j.seppur.2006.10.010.

- [90] O. Scialdone, S. Randazzo, A. Galia, G. Silvestri, Electrochemical oxidation of organics in water: role of operative parameters in the absence and in the presence of NaCl, *Water Res.* 43 (2009) 2260–72. doi:10.1016/j.watres.2009.02.014.
- [91] K. Rajeshwar, J.G. Ibanez, G.M. Swain, Electrochemistry and the environment, *J. Appl. Electrochem.* 24 (1994) 1077–1091. doi:10.1007/BF00241305.
- [92] J. Yeston, R. Coontz, J. Smith, C. Ash, A Thirsty World, *Sci.* 313 (2006) 1067. doi:10.1126/science.313.5790.1067.
- [93] K.L. Chen, L. Song, S.L. Ong, W.J. Ng, The development of membrane fouling in full-scale RO processes, *J. Memb. Sci.* 232 (2004) 63–72. doi:10.1016/j.memsci.2003.11.028.
- [94] A. Zhu, A. Rahardianto, P.D. Christofides, Y. Cohen, Reverse osmosis desalination with high permeability membranes—cost optimization and research needs, *Desalin. Water Treat.* 15 (2010) 256–266.
- [95] A.G. Pervov, Scale formation prognosis and cleaning procedure schedules in reverse osmosis systems operation, *Desalination.* 83 (1991) 77–118. doi:10.1016/0011-9164(91)85087-B.
- [96] A. Soffer, M. Folman, The electrical double layer of high surface porous carbon electrode, *J. Electroanal. Chem. Interfacial Electrochem.* 38 (1972) 25–43. doi:http://dx.doi.org/10.1016/S0022-0728(72)80087-1.
- [97] J. Wu, T. Jiang, D. Jiang, Z. Jin, D. Henderson, A classical density functional theory for interfacial layering of ionic liquids, *Soft Matter.* 7 (2011) 11222–11231. doi:10.1039/C1SM06089A.
- [98] D. Henderson, D. Boda, Insights from theory and simulation on the electrical double layer., *Phys. Chem. Chem. Phys.* 11 (2009) 3822–30. doi:10.1039/b815946g.
- [99] M.J. Lochhead, S.R. Letellier, V. Vogel, Assessing the Role of Interfacial Electrostatics in Oriented Mineral Nucleation at Charged Organic Monolayers, *J. Phys. Chem. B.* 101 (1997) 10821–10827. doi:10.1021/jp972283w.
- [100] a. D. Enevoldsen, E.B. Hansen, G. Jonsson, Electro-ultrafiltration of industrial enzyme solutions, *J. Memb. Sci.* 299 (2007) 28–37. doi:10.1016/j.memsci.2007.04.021.
- [101] Z. Lazarova, W. Serro, Electromembrane separation of mineral suspensions: Influence of process parameters, *Sep. Sci. Technol.* 37 (2002) 515–534.

doi:10.1081/SS-120001445.

- [102] W. Bowen, R. Kingdon, H. Sabuni, ELECTRICALLY ENHANCED SEPARATION PROCESSES: THE BASIS OF IN SITU INTERMITTENT ELECTROLYTIC MEMBRANE CLEANING (IEMC) AND IN SITU ELECTROLYTIC MEMBRANE RESTORATION (IEMR)*, *J. Memb. Sci.* 40 (1989) 219–229. (accessed November 15, 2013).
- [103] I. Loh, R. Moody, J. Huang, ELECTRICALLY CONDUCTIVE MEMBRANES: SYNTHESIS AND APPLICATIONS, *J. Memb. Sci.* 50 (1990) 31–49. <http://www.sciencedirect.com/science/article/pii/S0376738800808844> (accessed November 15, 2013).
- [104] C. de Lannoy, D. Jassby, D.D. Davis, M.R. Wiesner, A highly electrically conductive polymer–multiwalled carbon nanotube nanocomposite membrane, *J. Memb. Sci.* 415–416 (2012) 718–724. doi:10.1016/j.memsci.2012.05.061.
- [105] G. Gao, C.D. Vecitis, Electrochemical carbon nanotube filter oxidative performance as a function of surface chemistry., *Environ. Sci. Technol.* 45 (2011) 9726–34. doi:10.1021/es202271z.
- [106] N. Cifuentes-Araya, G. Pourcelly, L. Bazinet, Water splitting proton-barriers for mineral membrane fouling control and their optimization by accurate pulsed modes of electrodialysis, *J. Memb. Sci.* 447 (2013) 433–441. doi:10.1016/j.memsci.2013.06.055.
- [107] E.M. Vrijenhoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, *J. Memb. Sci.* 188 (2001) 115–128. doi:10.1016/S0376-7388(01)00376-3.
- [108] A.K. Ghosh, B.-H. Jeong, X. Huang, E.M.V. Hoek, Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties, *J. Memb. Sci.* 311 (2008) 34–45. doi:10.1016/j.memsci.2007.11.038.
- [109] S. Khan, M. Al-Shahry, W. Ingler, Efficient Photochemical Water Splitting by a Chemically modified n-TiO₂, *Science* (80-.). 297 (2002) 2243–2245. <http://www.sciencemag.org/content/297/5590/2243.short> (accessed November 19, 2013).
- [110] M.M. Tlili, M. Benamor, C. Gabrielli, H. Perrot, B. Tribollet, Influence of the Interfacial pH on Electrochemical CaCO₃ Precipitation, *J. Electrochem. Soc.* 150 (2003) C765. doi:10.1149/1.1613294.
- [111] D. Jiang, D. Meng, J. Wu, Density functional theory for differential capacitance of

- planar electric double layers in ionic liquids, *Chem. Phys. Lett.* 504 (2011) 153–158. doi:10.1016/j.cplett.2011.01.072.
- [112] R.E. Speece, Anaerobic biotechnology for industrial wastewater treatment a description of several installations, *Environ. Sci. Technol.* 17 (1983) 416A–427A. doi:10.1139/196-121.
- [113] L.T. Angenent, K. Karim, M.H. Al-Dahhan, B. a Wrenn, R. Domínguez-Espinosa, Production of bioenergy and biochemicals from industrial and agricultural wastewater., *Trends Biotechnol.* 22 (2004) 477–85. doi:10.1016/j.tibtech.2004.07.001.
- [114] F.Y. Cakir, M.K. Stenstrom, Greenhouse gas production: A comparison between aerobic and anaerobic wastewater treatment technology, *Water Res.* 39 (2005) 4197–4203. doi:10.1016/j.watres.2005.07.042.
- [115] O. Todini, L.W. Hulshoff Pol, Anaerobic degradation of benzaldehyde in methanogenic granular sludge: The influence of additional substrates, *Appl. Microbiol. Biotechnol.* 38 (1992) 417–420.
- [116] G. Fuchs, Anaerobic metabolism of aromatic compounds, *Ann. N. Y. Acad. Sci.* 1125 (2008) 82–99. doi:10.1196/annals.1419.010.
- [117] M. Gómez, a. de la Rua, G. Garralón, F. Plaza, E. Hontoria, M. a. Gómez, Urban wastewater disinfection by filtration technologies, *Desalination.* 190 (2006) 16–28. doi:10.1016/j.desal.2005.07.014.
- [118] T. Wintgens, M. Gallenkemper, T. Melin, Endocrine disrupter removal from wastewater using membrane bioreactor and nanofiltration technology, *Desalination.* 146 (2002) 387–391. doi:10.1016/S0011-9164(02)00519-2.
- [119] J.-H. Choi, S. Dockko, K. Fukushi, K. Yamamoto, A novel application of a submerged nanofiltration membrane bioreactor (NF MBR) for wastewater treatment, *Desalination.* 146 (2002) 413–420. doi:10.1016/S0011-9164(02)00524-6.
- [120] KWANG-HO CHOO, CHUNG-HAK LEE, MEMBRANE FOULING MECHANISMS IN THE MEMBRANE-COUPLED ANAEROBIC BIOREACTOR, *Water Res.* 30 (1996) 1771–1780.
- [121] B.. Cho, a. . Fane, Fouling transients in nominally sub-critical flux operation of a membrane bioreactor, *J. Memb. Sci.* 209 (2002) 391–403. doi:10.1016/S0376-7388(02)00321-6.

- [122] I.-S. Chang, P. Le Clech, B. Jefferson, S. Judd, Membrane Fouling in Membrane Bioreactors for Wastewater Treatment, *J. Environ. Eng.* 128 (2002). [http://ascelibrary.org/doi/abs/10.1061/\(ASCE\)0733-9372\(2002\)128:11\(1018\)](http://ascelibrary.org/doi/abs/10.1061/(ASCE)0733-9372(2002)128:11(1018)) (accessed September 4, 2014).
- [123] S.K. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, *J. Memb. Sci.* 132 (1997) 159–181. doi:10.1016/s0376-7388(97)00060-4.
- [124] S.P. Hong, T.H. Bae, T.M. Tak, S. Hong, A. Randall, Fouling control in activated sludge submerged hollow fiber membrane bioreactors, *Desalination*. 143 (2002) 219–228. doi:10.1016/S0011-9164(02)00260-6.
- [125] A. Sofia, W.J. Ng, S.L. Ong, Engineering design approaches for minimum fouling in submerged MBR, *Desalination*. 160 (2004) 67–74. doi:10.1016/S0011-9164(04)90018-5.
- [126] Z. Huang, S.L. Ong, H.Y. Ng, Submerged anaerobic membrane bioreactor for low-strength wastewater treatment: Effect of HRT and SRT on treatment performance and membrane fouling, *Water Res.* 45 (2011) 705–713. doi:10.1016/j.watres.2010.08.035.
- [127] L. Liu, J. Liu, B. Gao, F. Yang, Minute electric field reduced membrane fouling and improved performance of membrane bioreactor, *Sep. Purif. Technol.* 86 (2012) 106–112. doi:10.1016/j.seppur.2011.10.030.
- [128] L. Liu, J. Liu, B. Gao, F. Yang, S. Chellam, Fouling reductions in a membrane bioreactor using an intermittent electric field and cathodic membrane modified by vapor phase polymerized pyrrole, *J. Memb. Sci.* 394-395 (2012) 202–208. doi:10.1016/j.memsci.2011.12.042.
- [129] A. V. Dudchenko, J. Rolf, K. Russell, W. Duan, D. Jassby, Organic fouling inhibition on electrically conducting carbon nanotube – polyvinyl alcohol composite ultra filtration membranes, *J. Memb. Sci.* 468 (2014) 1–10. doi:10.1016/j.memsci.2014.05.041.
- [130] A. Ronen, W. Duan, I. Wheeldon, S.L. Walker, D. Jassby, Microbial attachment inhibition through low voltage electrochemical reactions on electrically conducting membranes., *Environ. Sci. Technol.* (2015). doi:10.1021/acs.est.5b01281.
- [131] G. Gao, C.D. Vecitis, Electrocatalysis aqueous phenol with carbon nanotubes networks as anodes: Electrodes passivation and regeneration and prevention, *Electrochim. Acta.* 98 (2013) 131–138. doi:10.1016/j.electacta.2013.02.127.

- [132] A.M. Zaky, B.P. Chaplin, Porous substoichiometric TiO₂ anodes as reactive electrochemical membranes for water treatment., *Environ. Sci. Technol.* 47 (2013) 6554–63. doi:10.1021/es401287e.
- [133] A. V. Dudchenko, J. Rolf, K. Russell, W. Duan, D. Jassby, Organic fouling inhibition on electrically conducting carbon nanotube–polyvinyl alcohol composite ultrafiltration membranes, *J. Memb. Sci.* 468 (2014) 1–10. doi:10.1016/j.memsci.2014.05.041.
- [134] A.P.H. Association, A.W.W. Association, W.P.C. Federation, W.E. Federation, Standard methods for the examination of water and wastewater, American Public Health Association., 1915.
- [135] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes, *Desalination*. 242 (2009) 168–182. doi:10.1016/j.desal.2008.04.004.
- [136] M. Jahanshahi, A. Rahimpour, M. Peyravi, Developing thin film composite poly(piperazine-amide) and poly(vinyl-alcohol) nanofiltration membranes, *Desalination*. 257 (2010) 129–136. doi:10.1016/j.desal.2010.02.034.
- [137] A. Ramesh, D.J. Lee, S.G. Hong, Soluble microbial products (SMP) and soluble extracellular polymeric substances (EPS) from wastewater sludge, *Appl. Microbiol. Biotechnol.* 73 (2006) 219–225. doi:10.1007/s00253-006-0446-y.
- [138] Y. He, P. Xu, C. Li, B. Zhang, High-concentration food wastewater treatment by an anaerobic membrane bioreactor., *Water Res.* 39 (2005) 4110–8. doi:10.1016/j.watres.2005.07.030.
- [139] J.H. Shin, S.M. Lee, J.Y. Jung, Y.C. Chung, S.H. Noh, Enhanced COD and nitrogen removals for the treatment of swine wastewater by combining submerged membrane bioreactor (MBR) and anaerobic upflow bed filter (AUBF) reactor, *Process Biochem.* 40 (2005) 3769–3776. doi:10.1016/j.procbio.2005.06.012.
- [140] M.F. a. Goosen, S.S. Sablani, H. Al-Hinai, S. Al-Obeidani, R. Al-Belushi, D. Jackson, Fouling of Reverse Osmosis and Ultrafiltration Membranes: A Critical Review, *Sep. Sci. Technol.* 39 (2005) 2261–2297. doi:10.1081/SS-120039343.
- [141] R. Field, Fundamentals of Fouling in Membrane Technology, in: Peinemann Klaus-Viktor, Pereira Nunes Suzana (Eds.), *Membr. Water Treat.*, WILEY-VCH Verlag GmbH & Co, 2010: pp. 1–23. doi:10.1002/9783527631407.ch1.
- [142] S. Shirazi, C.J. Lin, D. Chen, Inorganic fouling of pressure-driven membrane processes - A critical review, *Desalination*. 250 (2010) 236–248.

doi:10.1016/j.desal.2009.02.056.

- [143] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, et al., A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, *Sci. Total Environ.* 473-474 (2014) 619–641. doi:10.1016/j.scitotenv.2013.12.065.
- [144] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84. doi:10.1080/10643380500326564.
- [145] G. Gao, Q. Zhang, C.D. Vecitis, CNT–PVDF composite flow-through electrode for single-pass sequential reduction–oxidation, *J. Mater. Chem. A.* 2 (2014) 6185. doi:10.1039/c3ta14080f.
- [146] C.D. Vecitis, M.H. Schnoor, M.S. Rahaman, J.D. Schiffman, M. Elimelech, Electrochemical multiwalled carbon nanotube filter for viral and bacterial removal and inactivation, *Environ. Sci. Technol.* 45 (2011) 3672–3679. doi:10.1021/es2000062.
- [147] R. Hashaiekh, B.S. Lalia, V. Kochkodan, N. Hilal, A novel in situ membrane cleaning method using periodic electrolysis, *J. Memb. Sci.* 471 (2014) 149–154. doi:10.1016/j.memsci.2014.08.017.
- [148] G. Gao, C.D. Vecitis, Reactive depth and performance of an electrochemical carbon nanotube network as a function of mass transport, *ACS Appl. Mater. Interfaces.* 4 (2012) 6096–6103. doi:10.1021/am301724n.
- [149] B. Singh, F. Ejaz, T. Shah, N. Hilal, R. Hashaiekh, Electrically conductive membranes based on carbon nanostructures for self-cleaning of biofouling, 360 (2015) 8–12.
- [150] C.D. Vecitis, G. Gao, H. Liu, Electrochemical carbon nanotube filter for adsorption, desorption, and oxidation of aqueous dyes and anions, *J. Phys. Chem. C.* 115 (2011) 3621–3629. doi:10.1021/jp111844j.
- [151] S. Ohmori, T. Saito, Electrochemical durability of single-wall carbon nanotube electrode against anodic oxidation in water, *Carbon N. Y.* 50 (2012) 4932–4938. doi:10.1016/j.carbon.2012.06.023.
- [152] M. Tominaga, Y. Yatsugi, N. Watanabe, Oxidative corrosion potential vs. pH diagram for single-walled carbon nanotubes, *RSC Adv.* 4 (2014) 27224. doi:10.1039/c4ra02875a.

- [153] X. Lu, C. Zhao, Highly efficient and robust oxygen evolution catalysts achieved by anchoring nanocrystalline cobalt oxides onto mildly oxidized multiwalled carbon nanotubes, *J. Mater. Chem. A*. 1 (2013) 12053. doi:10.1039/c3ta12912h.
- [154] B. Wang, J. Tang, F. Wang, Electrochemical polymerization of aniline, *Synth. Met.* 18 (1987) 323–328. doi:10.1016/0379-6779(87)90899-X.
- [155] Y. Qiao, C.M. Li, S.-J. Bao, Q.-L. Bao, Carbon nanotube/polyaniline composite as anode material for microbial fuel cells, *J. Power Sources*. 170 (2007) 79–84. doi:10.1016/j.jpowsour.2007.03.048.
- [156] Y.C. Yong, X.C. Dong, M.B. Chan-Park, H. Song, P. Chen, Macroporous and monolithic anode based on polyaniline hybridized three-dimensional Graphene for high-performance microbial fuel cells, *ACS Nano*. 6 (2012) 2394–2400. doi:10.1021/nn204656d.
- [157] J. Huang, S. Virji, B.H. Weiller, R.B. Kaner, Nanostructured Polyaniline Sensors, *Chem. - A Eur. J.* 10 (2004) 1314–1319. doi:10.1002/chem.200305211.
- [158] Y.F. Shen, J. Tang, Z.H. Nie, Y.D. Wang, Y. Ren, L. Zuo, Preparation and application of magnetic Fe₃O₄ nanoparticles for wastewater purification, *Sep. Purif. Technol.* 68 (2009) 312–319. doi:10.1016/j.seppur.2009.05.020.
- [159] Y. Liao, D.-G. Yu, X. Wang, W. Chain, X.-G. Li, E.M. V Hoek, et al., Carbon nanotube-templated polyaniline nanofibers: synthesis, flash welding and ultrafiltration membranes., *Nanoscale*. 5 (2013) 3856–62. doi:10.1039/c3nr00441d.
- [160] Y. Liao, X. Li, E.M. V Hoek, R.B. Kaner, Carbon nanotube/polyaniline nanofiber ultrafiltration membranes, *J. Mater. Chem. A*. 1 (2013) 15390. doi:10.1039/c3ta13902f.
- [161] Y. Liao, T.P. Farrell, G.R. Guillen, M. Li, J.A.T. Temple, X.-G. Li, et al., Highly dispersible polypyrrole nanospheres for advanced nanocomposite ultrafiltration membranes, *Mater. Horiz.* 1 (2014) 58–64. doi:10.1039/C3MH00049D.
- [162] G.R. Guillen, T.P. Farrell, R.B. Kaner, E.M. V. Hoek, Pore-structure, hydrophilicity, and particle filtration characteristics of polyaniline–polysulfone ultrafiltration membranes, *J. Mater. Chem.* 20 (2010) 4621. doi:10.1039/b925269j.
- [163] Y. Liao, X. Wang, W. Qian, Y. Li, X. Li, D.G. Yu, Bulk synthesis, optimization, and characterization of highly dispersible polypyrrole nanoparticles toward protein separation using nanocomposite membranes, *J. Colloid Interface Sci.* 386 (2012) 148–157. doi:10.1016/j.jcis.2012.07.039.

- [164] B.T. McVerry, J.A.T. Temple, X. Huang, K.L. Marsh, E.M. V Hoek, R.B. Kaner, Fabrication of low-fouling ultrafiltration membranes using a hydrophilic, self-doping polyaniline additive, *Chem. Mater.* 25 (2013) 3597–3602. doi:10.1021/cm401288r.
- [165] S. Chen, L. Li, C. Zhao, J. Zheng, Surface hydration: Principles and applications toward low-fouling/nonfouling biomaterials, *Polymer (Guildf)*. 51 (2010) 5283–5293. doi:10.1016/j.polymer.2010.08.022.
- [166] J. Mansouri, S. Harrisson, V. Chen, Strategies for controlling biofouling in membrane filtration systems: challenges and opportunities, *J. Mater. Chem.* 20 (2010) 4567. doi:10.1039/b926440j.
- [167] S. Krishnan, C.J. Weinman, C.K. Ober, Advances in polymers for anti-biofouling surfaces, *J. Mater. Chem.* 18 (2008) 3405. doi:10.1039/b801491d.
- [168] G. Zotti, S. Cattarin, N. Comisso, Cyclic potential sweep electropolymerization of aniline, *J. Electroanal. Chem. Interfacial Electrochem.* 239 (1988) 387–396. doi:10.1016/0022-0728(88)80293-6.
- [169] H. Lu, Y. Zhou, S. Vongehr, K. Hu, X. Meng, Electropolymerization of PANI coating in nitric acid for corrosion protection of 430 SS, *Synth. Met.* 161 (2011) 1368–1376. doi:10.1016/j.synthmet.2011.05.003.
- [170] M.H. Pournaghi-Azar, B. Habibi, Electropolymerization of aniline in acid media on the bare and chemically pre-treated aluminum electrodes. A comparative characterization of the polyaniline deposited electrodes, *Electrochim. Acta.* 52 (2007) 4222–4230. doi:10.1016/j.electacta.2006.11.050.
- [171] R. Mažeikienappproaches the limit, a. Malinauskas, Electrochemical stability of polyaniline, *Eur. Polym. J.* 38 (2002) 1947–1952. doi:10.1016/S0014-3057(02)00103-9.
- [172] J.L. Camalet, J.C. Lacroix, S. Aeiych, K. Chane-Ching, P.C. Lacaze, Electrosynthesis of adherent polyaniline films on iron and mild steel in aqueous oxalic acid medium, *Synth. Met.* 93 (1998) 133–142. doi:10.1016/S0379-6779(97)04099-X.
- [173] C. Rebelo, U. De Coimbra, Properties of polyaniline formed at tin dioxide electrodes in weak acid solution : effect of the counterion, 23 (1993) 332–338.
- [174] R. Murugesan, E. Subramanian, Effect of organic dopants on electrodeposition and characteristics of polyaniline under the varying influence of H₂SO₄ and HClO₄

- electrolyte media, *Mater. Chem. Phys.* 80 (2003) 731–739. doi:10.1016/S0254-0584(03)00127-5.
- [175] R. Gloukhovski, Y. Oren, C. Linder, V. Freger, Thin-film composite nanofiltration membranes prepared by electropolymerization, *J. Appl. Electrochem.* 38 (2008) 759–766. doi:10.1007/s10800-008-9505-7.
- [176] J. Desilvestro, W. Scheifele, Morphology of electrochemically prepared polyaniline. Influence of polymerization parameters, *J. Mater. Chem.* 3 (1993) 263. doi:10.1039/jm9930300263.
- [177] J. Benson, I. Kovalenko, S. Boukhalfa, D. Lashmore, M. Sanghadasa, G. Yushin, Multifunctional CNT-Polymer Composites for Ultra-Tough Structural Supercapacitors and Desalination Devices, *Adv. Mater.* 25 (2013) 6625–6632. doi:10.1002/adma.201301317.
- [178] M. Wu, G.A. Snook, V. Gupta, M. Shaffer, D.J. Fray, G.Z. Chen, Electrochemical fabrication and capacitance of composite films of carbon nanotubes and polyaniline, *J. Mater. Sci.* 15 (2005) 2297–2303. doi:10.1002/sia.3387.
- [179] X. Yang, Q. Xie, S. Yao, A comparative study on polyaniline degradation by an electrochemical quartz crystal impedance system: Electrode and solution effects, *Synth. Met.* 143 (2004) 119–128. doi:10.1016/j.synthmet.2003.10.027.
- [180] A. Malinauskas, R. Mazeikiene, Kinetic study of the electrochemical degradation of polyaniline, *Synthetic Met.* 123 (2001) 349–354.
- [181] M. a Hassan, M.M. El Jamal, Kinetic Study of the Electrochemical Oxidation of Methylene Blue with Pt Electrode, *Port. Electrochim. Acta.* 30 (2012) 351–359. doi:10.4152/pea.201205351.
- [182] J. Stejskal, P. Kratochvíl, A.D. Jenkins, The formation of polyaniline and the nature of its structures, *Polymer (Guildf).* 37 (1996) 367–369. doi:10.1016/0032-3861(96)81113-X.
- [183] R.K. Yuan, Z.P. Gu, H. Yuan, Studies of controllable colour change properties of polyaniline film, *Synth. Met.* 69 (1995) 233–234. doi:10.1016/0379-6779(94)02430-7.
- [184] Y. Wang, K. Levon, Influence of dopant on electroactivity of polyaniline, *Macromol. Symp.* 317-318 (2012) 240–247. doi:10.1002/masy.201200008.
- [185] R. Prakash, Electrochemistry of polyaniline: Study of the pH effect and electrochromism, *J. Appl. Polym. Sci.* 83 (2002) 378–385. doi:10.1002/app.10025.

- [186] F. Qu, M. Yang, J. Jiang, G. Shen, R. Yu, Amperometric biosensor for choline based on layer-by-layer assembled functionalized carbon nanotube and polyaniline multilayer film., *Anal. Biochem.* 344 (2005) 108–114. doi:10.1016/j.ab.2005.06.007.
- [187] E.N. Konyushenko, J. Stejskal, M. Trchová, J. Hradil, J. Kovářová, J. Prokeš, et al., Multi-wall carbon nanotubes coated with polyaniline, *Polymer (Guildf)*. 47 (2006) 5715–5723. doi:10.1016/j.polymer.2006.05.059.
- [188] Z. Zhang, Z. Wei, M. Wan, Nanostructures of polyaniline doped with inorganic acids, *Macromolecules*. 35 (2002) 5937–5942. doi:10.1021/ma020199v.
- [189] N.K. Guimard, N. Gomez, C.E. Schmidt, Conducting polymers in biomedical engineering, *Prog. Polym. Sci.* 32 (2007) 876–921. doi:10.1016/j.progpolymsci.2007.05.012.
- [190] H.P. Erickson, Size and shape of protein molecules at the nanometer level determined by sedimentation, gel filtration, and electron microscopy, *Biol. Proced. Online*. 11 (2009) 32–51. doi:10.1007/s12575-009-9008-x.
- [191] Koch Membranes, SPIRAPRO™ HFK™ Pharmaceutical grade UF elements product specification, n.d.
- [192] C. Regula, E. Carretier, Y. Wyart, G. Gésan-Guiziou, A. Vincent, D. Boudot, et al., Chemical cleaning/disinfection and ageing of organic UF membranes: A review, *Water Res.* 56 (2014) 325–365. doi:10.1016/j.watres.2014.02.050.
- [193] J.M. Yuan, X.H. Chen, X.H. Chen, Z.F. Fan, X.G. Yang, Z.H. Chen, An easy method for purifying multi-walled carbon nanotubes by chlorine oxidation, *Carbon N. Y.* 46 (2008) 1266–1269. doi:10.1016/j.carbon.2008.05.003.
- [194] E. Unger, A. Graham, F. Kreupl, M. Liebau, W. Hoenlein, Electrochemical functionalization of multi-walled carbon nanotubes for solvation and purification, *Curr. Appl. Phys.* 2 (2002) 107–111. doi:10.1016/S1567-1739(01)00072-4.
- [195] U. Dettlaff-Weglikowska, J.-M. Benoit, P.-W. Chiu, R. Graupner, S. Lebedkin, S. Roth, Chemical functionalization of single walled carbon nanotubes, *Curr. Appl. Phys.* 2 (2002) 497–501. doi:10.1016/S1567-1739(02)00164-5.
- [196] a. Malinauskas, Chemical deposition of conducting polymers, *Polymer (Guildf)*. 42 (2001) 3957–3972. doi:10.1016/S0032-3861(00)00800-4.
- [197] X. Huang, B.T. McVerry, C. Marambio-Jones, M.C.Y. Wong, E.M. V. Hoek, R.B. Kaner, Novel chlorine resistant low-fouling ultrafiltration membrane based on a

- hydrophilic polyaniline derivative, *J. Mater. Chem. A* 3 (2015) 8725–8733. doi:10.1039/C5TA00900F.
- [198] P. Kar, A. Choudhury, Sensors and Actuators B: Chemical Carboxylic acid functionalized multi-walled carbon nanotube doped polyaniline for chloroform sensors, *Sensors Actuators B. Chem.* 183 (2013) 25–33. doi:10.1016/j.snb.2013.03.093.
- [199] C. Liu, S. Caothien, J. Hayes, T. Caothuy, Membrane Chemical Cleaning : From Art to Science, n.d.
- [200] W.S. Ang, M. Elimelech, Protein (BSA) fouling of reverse osmosis membranes: Implications for wastewater reclamation, *J. Memb. Sci.* 296 (2007) 83–92. doi:10.1016/j.memsci.2007.03.018.
- [201] W.A. Pryor, OXY-RADICALS AND RELATED SPECIES: Their Formation, Lifetimes, and Reactions, *Annu. Rev. Physiol.* 347 (1986) 3953–3962. doi:10.1002/2014WR015857. Received.
- [202] K. Wang, M.-C. Wei, T.-H. Peng, H.-C. Li, S.-J. Chao, T.-F. Hsu, et al., Treatment and toxicity evaluation of methylene blue using electrochemical oxidation, fly ash adsorption and combined electrochemical oxidation-fly ash adsorption, *J. Environ. Manage.* 91 (2010) 1778–1784. doi:10.1016/j.jenvman.2010.03.022.
- [203] A. Ronen, S.L. Walker, D. Jassby, Electroconductive and electroresponsive membranes for water treatment, *Rev. Chem. Eng.* 0 (2016). doi:10.1515/revce-2015-0060.
- [204] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, et al., Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania, *Appl. Catal. B Environ.* 39 (2002) 75–90. doi:10.1016/S0926-3373(02)00078-4.
- [205] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671–698. doi:10.1021/cr00018a003.
- [206] J. Tang, X. Jing, B. Wang, F. Wang, Infrared spectra of soluble polyaniline, *Synth. Met.* 24 (1988) 231–238. doi:10.1016/0379-6779(88)90261-5.