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CATALYZED DEGRADATION OF HYDROGEN PEROXIDE: A REVIEW OF WATER
TREATMENT MEMBRANE FOULING, CONCENTRATION POLARIZATION, AND
PROPOSED SOLUTIONS

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ABSTRACT

Efficient water treatment, a process that has been revolutionized in recent decades, is in high demand as population growth and climate change create worsening global water scarcity. As a result, developments in nanofiltration and reverse osmosis filtration membranes have allowed for water treatment capabilities for challenging streams with high salinities and dissolved contaminants. However, persistent and ubiquitous issues of fouling and concentration polarization (CP) reduce efficiency and increase operational costs within treatment facilities. Thus, an entire field of research has been developed in order to determine long-term, holistic solutions to these issues to be implemented in future water treatment systems. This thesis discusses the current and predicted future state of global water scarcity and the current capabilities, applications, and limitations of membrane water treatment systems as well as some common implementations and practices used to mitigate the persistent issues of fouling and concentration polarization. This thesis also discusses in detail a study conducted by several researchers in the Penn State University Department of Chemical Engineering, which finds definitive conclusion for *in-situ* metallic salt nanoparticle catalytic coatings as a solution to energy losses due to fouling and CP. Finally, the catalase enzyme will be discussed as a possible catalytic coating in future reactive micromixing experiments.

TABLE OF CONTENTS

LIST OF FIGURES	iii
LIST OF TABLES	iv
ACKNOWLEDGEMENTS	v
Chapter 1: Background Information	1
1.1 Clean Water on a Global Scale	1
1.2 Water Treatment Systems: Capabilities, Materials, and Configurations	2
1.3 Water Treatment Systems: Current Applications, Issues and Solutions	6
1.4 Membrane Biofouling; Causes and Current Solutions.....	10
1.5 Concentration Polarization; Causes and Current Solutions	16
Chapter 2: Copper Oxide Nanoparticles; a Proposed Solution to Fouling and Concentration Polarization	19
2.1 A Conceptual Background and Proposed Solution	19
2.2 Methods and Materials	23
2.3 Results and Discussion.....	25
2.4 Study Conclusions.....	33
Chapter 3: Catalase; an Enzymatic Approach	34
3.1 A Conceptual Background and Proposed Solution	34
3.2 Notes for Potential Coating Procedures	36
3.3 Catalase-Coated Oil Emulsion Experiment.....	38
3.4 Catalase Reactive Micromixing Conclusions	41
Chapter 4: Conclusion.....	43
BIBLIOGRAPHY	45

LIST OF FIGURES

Figure 1. Water filtration common contaminants and rejection	3
Figure 2. DOW FILMTEC TFC polyamide spiral-wound membrane module	6
Figure 3. Fouling disruption via (a) increasing hydrophilicity, (b) inducing surface charge, (c) long-chain hydrophilic molecule brushes	9
Figure 4. Biofilm growth with respect to time.....	11
Figure 5. Biofilm growth within the matrix of the feed spacer	12
Figure 6. Flow and pressure drop of the cross-flow membrane units that were air sparged	16
Figure 7. Solute concentration vs. position at the membrane surface.. ..	17
Figure 8. TEM imaging of CuO nanoparticles	20
Figure 9. Schematic of the theoretical fouling and CP mitigation.....	23
Figure 10. SEM images with inset TEM images of 8 ppm CuO/PDA and 80 ppm CuO/PDA ..	26
Figure 11. Rate constant of hydrogen peroxide degradation with respect to the concentration of CuO solution used to coat the membranes	27
Figure 12. Oxygen bubble formation on the membrane surface.	27
Figure 13. Normalized flux decline in a cross flow CuO/PDA coated RO membrane system	29
Figure 14. Biofilm formation on the surface of an NF90 membrane	31
Figure 15. Molecular structure of catalase found in H. Pylori.....	36
Figure 16. Dead-end stirred cell unit for testing catalase-coated BW30 RO membranes	40
Figure 17. Total mass of permeate vs. time for catalase-coated BW30 membranes charged with various feeds in a dead-end stirred cell unit	41

LIST OF TABLES

Table 1: Activity and deactivation constant of several types of catalase. At similar activities, the catalase from *Aspergillus niger* has a significantly slower rate of deactivation.³² 38

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Chapter 1: Background Information

1.1 Clean Water on a Global Scale

Increasing global development places increased stress on the natural resources available to us. A large issue that humanity will face is the diminishing access to clean drinking water. As the global population grows so does the demand for clean water and with that the requirement for sustainable approaches to providing clean water for drinking and sanitation needs. 2,000 years ago, the population was less than 3% of its current size, yet the total amount of water on Earth was the exact same.¹ During the 20th century, the global human population tripled, yet the usage of water per capita grew six times.² Moreover, with global populations estimated to hit 8.2 billion people by 2050, the issue of water scarcity is only going to increase.³

Water scarcity is roughly defined as a population where individuals do not have affordable access to enough safe, clean water to satisfy his or her needs of drinking, washing, and general sanitation. When individuals lack said access, they are said to be water insecure.² If enough people in a region are water insecure, the region is said to be water scarce. It is generally agreed that the minimum requirement of clean water for drinking, washing, and sanitation is 50 liters per person per day.² For a city like Mumbai, India, this would mean the requirement to clean 240 million gallons of water per day in order to meet the minimum requirements for drinking water security. It is also important to note that this does not take into account water for agricultural needs, which, although it requires a lower standard of sanitation, has a minimum

security requirement of 1000 liters per person per day, a value 20 times greater than that for drinking water.¹

In 2016, some of the world's foremost global water scarcity researchers conservatively estimated that 1.6 billion people globally (15% of the world's population) are living with water insecurity.³ Upwards of 5 million people die annually due directly to water-related diseases.⁴ Even in the absence of climate change effects, it is projected that by 2050, 3.1 billion people (37%) will fall into the category of water insecure.³ There is no perfect solution to this issue, nor will it ever be completely solved. However, with the coordinated efforts of scientists, engineers, policy makers, community developers, and many others, a comprehensive plan can and should be made to provide affordable access to clean water for our world's growing population in the midst of a changing climate and a depletion of natural resources. One integral piece of this puzzle, and the subject of this thesis, is the need for efficient and effective membrane filtration systems.

1.2 Water Treatment Systems: Capabilities, Materials, and Configurations

Clean drinking water is a necessity for a healthy population, yet it is not an easy feat to provide said clean drinking water on the scale of millions of gallons per day. Before surface water or groundwater can be sold to the public, it must be filtered and conform to the standards of the Safe Drinking Water Act, a federal law that allows for the regulation of drinking water by the EPA.⁵ This act states the maximum concentrations of pollutants and organisms that can be present in drinking water after treatment⁵. Said contaminants include (from largest to smallest) suspended solids, bacteria, colloids, viruses, macromolecules, small organic compounds, ionic

compounds, salts, and heavy metals.⁶ The level of filtration of these species depends on the type of membrane used in the treatment system. The four main categories of treatment membranes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).⁶ These membrane categories and their associated rejection sizes and filtration capabilities can be seen in Figure 1 below.

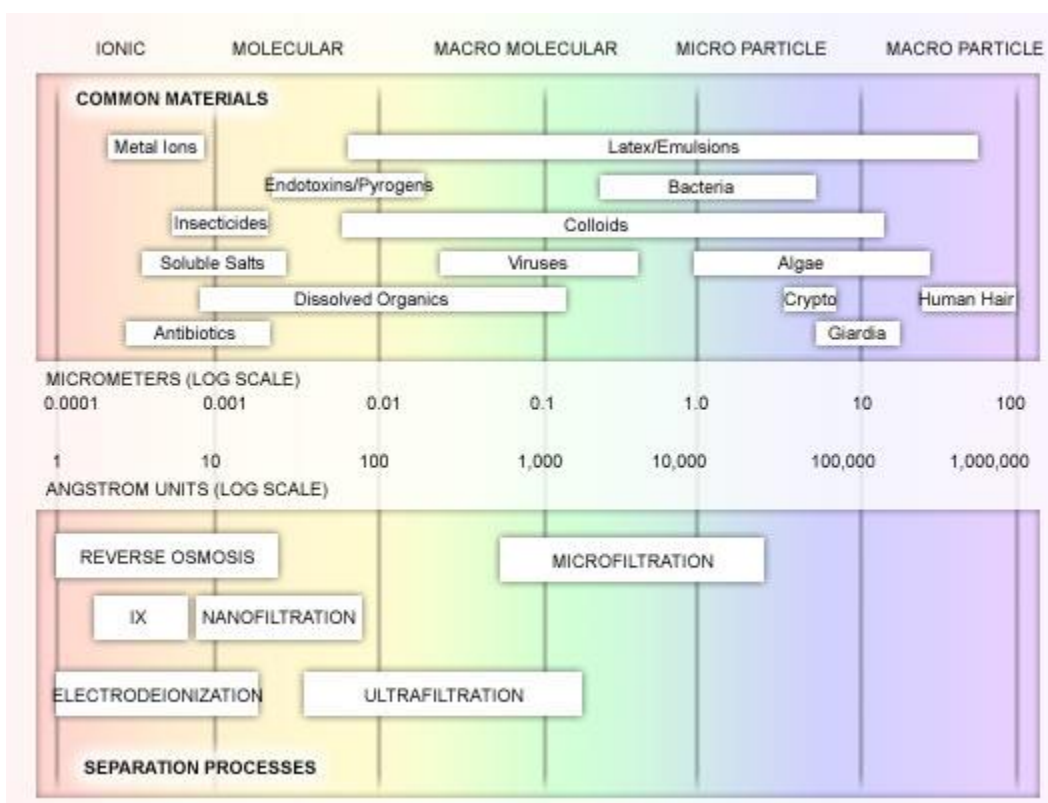


Figure 1. Water filtration common contaminants and rejection⁷

Although the official title of ‘reverse osmosis membrane’ is reserved for the treatment membranes with the largest rejection of small solutes, all water filtration membranes operate by method of reverse osmosis. The water is forced through the semi-permeable membrane from high to low contaminant concentration, against the natural concentration gradient and therefore opposite the direction of natural flow created by osmosis, hence ‘reverse osmosis’.⁸

Assuming equal permeate flow rates, larger pressures must be applied to the feed-side of membrane systems with smaller pore-size. This is due to both an increase in the total contaminants being filtered (causing larger osmotic pressures) and the increased pressure from trying to force the same quantity of water through smaller passages (effectively frictional pressure).⁹ Higher operational pressures require larger pumps and therefore an increase in operational energy input and cost.⁹ This will be discussed further in the applications section.

The most widely used membranes in water filtration systems are thin film composite (TFC) polyamide membranes.¹⁰ These membranes consist of three layers: an ultra-thin (0.2 μm) barrier layer on the outside surface, a micro-porous interlayer (40 μm), and a polyester web (~140 μm) on the backside.¹⁰ The polyester web provides structural support to the membrane while the barrier layer on the surface provides the actual filtration functions. The interlayer provides support for the barrier layer, which needs to withstand high-pressure compression. The pore-size of the membrane depends on the level of filtration required. It is the ultra-thin barrier layer that is often made of aromatic polyamides, which are structurally robust and chemically resistive, allowing for durability when filtering contaminants and during cleaning procedures.¹⁰ For the remainder of this paper I will focus on TFC polyamide membranes.

TFC polyamide membranes can be modularly configured in two common ways: hollow fiber and spiral-wound. The former is valued for its high packing density and larger permeate production rates.¹¹ However, hollow fiber membrane modules are more prone to fouling (will be further discussed later) than spiral-wound membrane modules.¹¹ Thus, for the purpose of longevity, spiral-wound modules are favored to hollow fiber modules.

TFC polyamide spiral-wound membrane modules have a 91% share in NF/RO markets globally and have been the main configuration in water filtration systems for some decades

now.¹⁰ They are valued for their large ratio of membrane surface area to module volume, high filtration parameter specificity, simple scalability and inter-changeability, easy system troubleshooting, low cost of replacement, and are considered the least expensive configuration to produce from TFC membrane material.¹⁰ DOW is one of the largest producers of spiral-wound membrane modules. For the remainder of this paper, I will be referring specifically to TFC polyamide membranes made by DOW FILMTEC, as they were the provider of membranes for the study discussed here.

The configuration of spiral-wound modules is made optimal by incorporating the largest surface area of membrane per module volume. This allows for the greatest filtration capacity in the smallest space. First, a ‘sandwich’ is made of flat membrane sheets separated by alternating layers of permeate carrier material and feed spacer material.¹² The thin-film barrier layer of each piece of membrane is facing the feed spacer while the polyester web backside of the membrane is facing the permeate carrier material.¹² This sandwich is then rolled up into a tube and enclosed by an outer wrap, hence the ‘spiral-wound’. As the dirty water flows through this tube via the feed spacer, it runs parallel or in a ‘cross-flow’ fashion to the thin-film surface. A pressure difference forces the water through the pores of the membrane and into the permeate carrier material. Once in this layer of the sandwich, the clean water travels around the spiral and is collected in the permeate tube in the center of the module to be carried away (Fig. 2).¹² On an industrial scale, these modules can have diameters of up to 18 inches and lengths of several feet.¹⁰ Individual modules are combined in parallel to meet the capacity needs of a water treatment facility.

Advances in materials have been a constant provider of new technology for water treatment systems. This new technology has allowed for the efficient treatment of dirty water on

enormous scales. One treatment facility is capable of cleaning well over one hundred million gallons of water on a daily basis.¹³ With an increase in water treatment capacity also comes an increase in membrane applications. The industry of water treatment, driven by the demand for clean water, is expanding its capabilities and there is no end in sight to the current rate of innovation. Whatever the possibilities are, however, the usage and proliferation of new treatment applications firmly rests on the need for profit and the economic viability of the process.

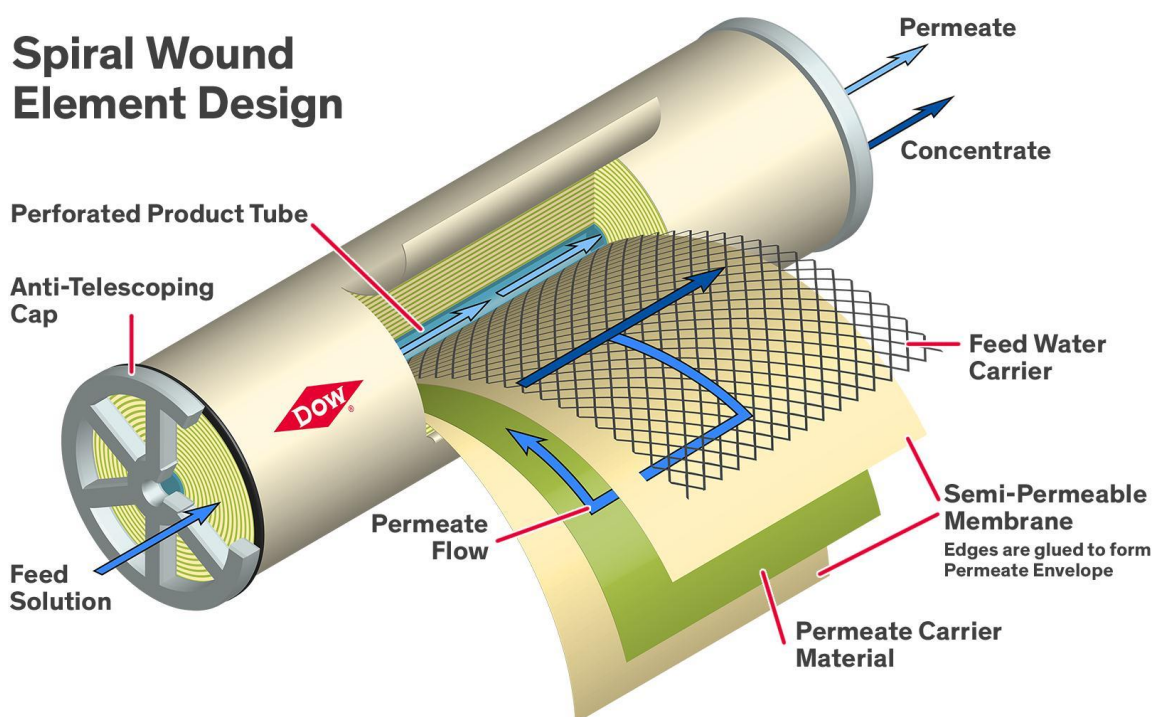


Figure 2. DOW FILMTEC TFC polyamide spiral-wound membrane module¹⁴

1.3 Water Treatment Systems: Current Applications, Issues and Solutions

As discussed, spiral-wound TFC polyamide membranes are mainly used for nanofiltration and reverse osmosis.⁶ The level of filtration required depends on two things: the conditions of the feed water and the specific requirements/usage of the treated water. Advances in materials have allowed for the creation of membranes to be used in a wide variety of

applications.¹² Some of these include the treatment of well water, surface water, brackish water, sea water, industrial process and waste water, water produced in oil field operations, and municipal wastewater for recycle.¹² All of these applications are designed to produce clean water for municipalities, industrial processes, or for the return to surface water or marine systems. In this manner, treatment by use of TFC polyamide membranes allows for the management of total water resources in a specific area, something of high value to regions that are threatened by water scarcity.¹² For the sake of brevity, this paper will continue to focus on using nanofiltration and reverse osmosis membranes in the treatment of surface water and seawater, though the issues discussed are ubiquitous to water treatment as a whole and the solutions proposed could be universally applied.

The greatest issues faced by water treatment membrane systems are fouling and concentration polarization. Both will be described with current technologies designed to mitigate their negative effects.

Fouling, in this context, is a process by which the surface of the membranes becomes physically blocked by a variety of molecular, ionic, or biological species.¹⁵ The four main types of fouling are inorganic, organic, colloidal, and biological.¹⁵ Inorganic fouling is usually characterized by the buildup of salt precipitates on the membrane surface. This is also commonly referred to as scaling. Organic fouling involves typically larger organic species, like proteins, that are hydrophobic in nature. Colloidal foulants include silica, iron, and clays and are characterized by their colloidal nature (homogeneous mixture of insoluble particles).¹⁵ Biological fouling is the growth of (typically) bacterial contaminants on the surface of the polyamide membrane. Biological fouling poses a particular issue due to the fact that simple mixing has little to no effect on the growth of bacteria.

Specifically, fouling is problematic because a blockage of the membrane surface limits the surface area that can be used for treatment and disallows the easy passage of water. This in turn decreases the flux of permeated water out of the system. In order to maintain a constant flux in a system that must treat a set amount of water, a larger pressure drop must be applied causing an increase in energy usage and therefore operational cost.⁹ As it currently stands, a new membrane module may be placed within a system and over time, fouling slowly increases and forces higher feed pressures. This continues until it becomes economically problematic and the module must be replaced. Solutions that extend the amount of time between membrane replacement are highly valued for their cost-saving capabilities. Currently, there are several universally accepted methods for disrupting or slowing fouling at the membrane surface.¹⁵

One method for reducing fouling is increasing the hydrophilicity of the membrane surface¹⁵. Many foulants are hydrophobic in nature, which adds to their fouling capabilities. A hydrophilic membrane will create a layer of pure water at the surface, thus preventing the adsorption/deposition of hydrophobic species on membrane. It should be noted that while they are a smaller proportion of overall foulants, hydrophilic foulants will actually pose a greater issue when using hydrophilic membranes.¹⁵

Surface charge is a property of RO and NF membranes that has a significant impact on fouling rates.¹⁵ Modern technology allows us to engineer membranes with specific surface charge. This practice is beneficial when the fouling of a particular system is well understood and the charge of the most problematic foulant is known. In such a case, the membrane can be designed to electrostatically repel the foulant of issue.¹⁵

A currently developing method for foulant repulsion is the installment of long-chain hydrophilic molecules on the membrane surface. These molecules create a hydrophilic layer that

provides steric repulsion to hydrophobic proteins and disallow for their adsorption into the membrane surface.¹⁵ Steric repulsion is caused by the requirement that a protein changes configuration to interact with the hydrophilic layer.¹⁵ A change in configuration would cause a decrease in configurational entropy, a naturally unfavorable outcome that the protein avoids. This method for fouling mitigation is still being developed for RO and NF systems.¹⁵ All of these membrane alterations can be viewed in Figure 3.

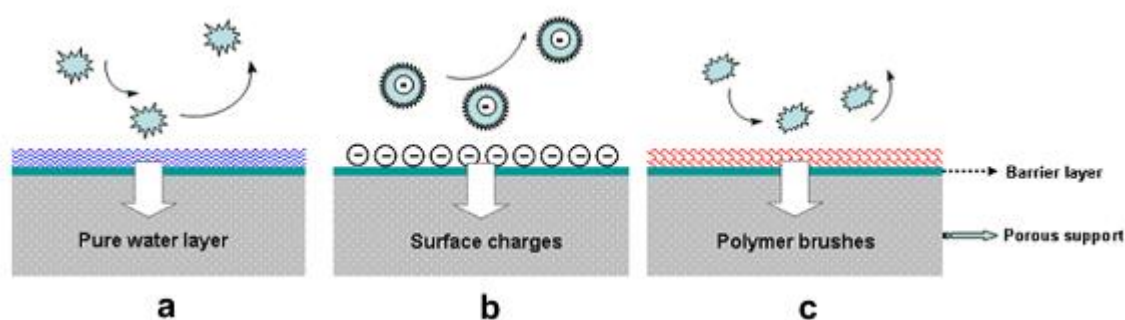


Figure 3. Fouling disruption via (a) increasing hydrophilicity, (b) inducing surface charge, (c) long-chain hydrophilic molecule brushes¹⁵

While altering the surface of the membrane is a method to slow the rate of fouling in the long-run, it has proven unable to completely stop fouling from occurring. Thus, as fouling builds over time, it is critical that cleaning measures be taken at the process level.¹⁶ If done properly, cleaning of RO and NF treatment systems can extend the time between module replacements and therefore cut down on capital cost, though it often time increases operational costs too. There exist three overarching methods for cleaning membrane systems: chemical, physical, and physiochemical.¹⁶ Chemical cleaning methods are designed to weaken the cohesion of foulants to the membrane surface and are useful for biofouling and inorganic fouling (scaling). Some methods of physical cleaning include CO₂ back permeation, air sparging, flushing, and vibrating.¹⁶

1.4 Membrane Biofouling; Causes and Current Solutions

Nearly all water sources contain microorganisms to varying degrees. They feed on the nutrients and organics within the water and proliferate uncontrollably. In wastewater treatment systems, the purposeful growth of bacteria in activated sludge tanks is a desirable outcome as the microorganisms are used to break down organic molecules into methane and carbon dioxide.¹⁷ However, bacterial growth within a process/drinking water treatment membrane system is problematic. Many types of bacteria need a surface upon which to anchor, colonize, and reproduce. TFC polyamide membranes are essentially a rough plastic surface that allow for the selective movement of water. As such the surface is varied and not smooth, a quality that makes for good filtration, but poor biofouling mitigation. Thus, microorganisms will attach themselves to the membrane surface, feed on the nutrient- and organic-rich feed water and reproduce. In doing so, they will also excrete extracellular polymeric substances (EPS), a sort of 'gel' that they are embedded in, and create a biofilm.¹⁷ It is important to note that the biofilm is mostly made up of EPS, the substance that contributes most to biofouling. This is the basis for biofouling of polyamide membranes and is what contributes heavily to efficiency losses of water treatment systems.

There are three phases to the accumulation of a biofilm on the surface of a membrane: induction, growth, and plateau.¹⁷ During the induction phase, bacterial accumulation on the membrane surface is primarily due to water-borne organisms latching onto the surface and not from cell reproduction. Accumulation is slow and fouling is negligible during this phase. These bacteria that have attached themselves to the surface then begin to reproduce. When cell growth

contributes more to biofilm formation than does the adhesion of free floating cell, the biofilm enters the logarithmic growth phase.¹⁷ During this phase, EPS is produced and the biofilm grows rapidly. At some point in this growth, the biofilm passes the threshold of interference (Fig. 4), at which point the biofilm now has a noticeable effect on filtration performance.¹⁷ As with any bacterial system, the population eventually reaches a maximum based on available resources. Thus, when the biofilm reaches a certain thickness, an equilibrium is reached between bacterial proliferation and death/detachment and the colonial growth plateaus.¹⁷ The thickness of the biofilm upon reaching this plateau is what determines the extent of biofouling.

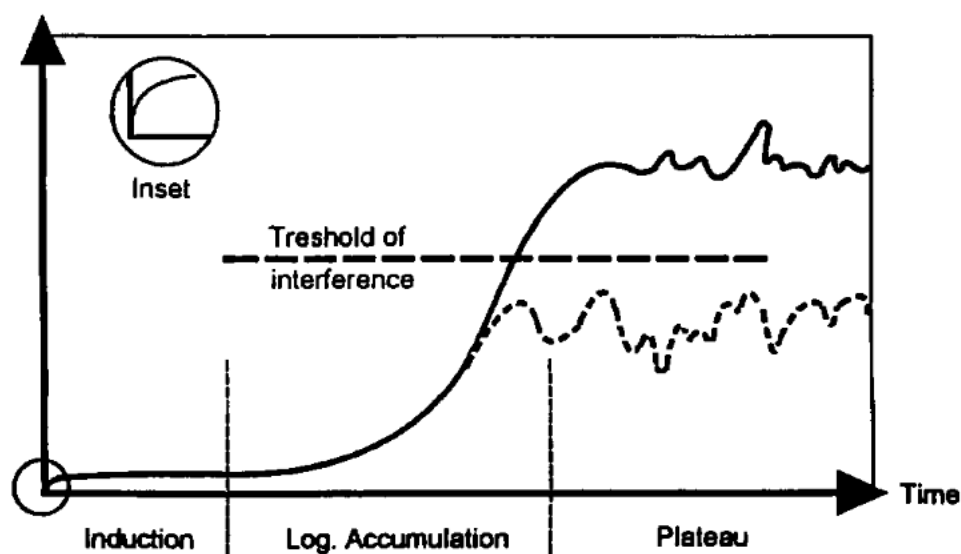


Figure 4. Biofilm growth with respect to time. The extent of fouling is determined by how far past the threshold of interference the plateau occurs¹⁷.

Within spiral-wound membrane modules, biofouling is often times made worse by the use of a feed spacer on the feed side of the membrane.¹⁸ This is due to the structure of the feed spacer, which seems to lend itself to bacterial growth. With this in mind, solutions to biofouling

need to take into account growth on both the membrane surface and within the matrix of the feed spacer (Fig. 5).



Figure 5. Biofilm growth within the matrix of the feed spacer¹⁸

The issue that comes with fouling, and more specifically biofouling, is one of pressure drops.¹⁸ Under normal operation, a large amount of feed pressure (usually around 200 pisa) must be applied in order to force clean permeated water through the semipermeable membranes at the desired rate.¹⁷ The desired rate is based on process or municipal needs and must be met. With the addition of biofouling in a spiral-wound membrane module, a greater pressure drop must be applied across the feed spacer and the membrane in order to maintain a constant flux of permeated water.¹⁸ The need for higher feed-side pressure is specifically due to the frictional

forces acting against the flow of water.¹⁹ The application of larger pressure drops requires the usage of more energy. Pumps need to work harder to force constant permeate fluxes through fouled membrane modules. With this higher energy usage comes a direct increase in operational costs, making water treatment more expensive.¹⁷ Additionally, larger pressure drops increase the possibility of tearing the membrane.

In looking specifically at the polyamide membrane surface, a physical modification that has been made in attempting to slow the growth of biofilm is the smoothening of the membrane surface.¹⁵ As stated above, the roughness of these membranes allows for the easy attachment of bacteria and the promotion of film growth.¹⁷ However, this roughness is a byproduct of the filtration mechanism. The surface of the membrane must be rough in order to allow for the transport of water across it. So, while this alteration to the surface does slow (but doesn't completely stop) the formation of biofilms, it also makes for an inefficient water-treatment system.⁶

Traditionally, two operational measures have been employed in attempting to slow/stop biofilm formation and mitigate the effects of biofouling.¹⁸ The first, physical method is the removal of bacteria by method of pre-filtering the feed water with a low-cost micro or ultrafiltration system. This is relatively effective because, for non-biological foulants, the fouling potential is based directly on the concentration of foulant in the feed.¹⁷ However, while this does slow the initial coalescence of bacteria on the membrane surface, it does not change the final outcome once a biofilm inevitably forms. The second, chemical method is the pre-treatment of feed water using a biocide (usually chlorine) in order to metabolically inactivate the bacteria.¹⁸ While intuitively this solution makes sense, in practice it has now been phased out of most systems. While chlorine in the feed may kill the bacteria in the feed, it actually has a negative

effect on those that somehow manage to plant themselves successfully on the membrane surface.¹⁹ Chlorine triggers the bacteria involved in growing the biofilm to actually release more EPS, a defense mechanism.¹⁹ EPS is the main component in the biofilm matrix and is what causes frictional pressure losses in the system. There is also the potential to inadvertently develop a biocide-resistant strain of bacteria that can withstand higher concentrations of chlorine.¹⁹ Additionally, regular chlorination treatment will damage a polyamide membrane over time.

Neither removing contaminants from the feed stream nor chemically treating the feed have proven effective in preventing or disrupting biofouling.²⁰ Using higher levels of pre-filtration would require much more energy than that which is required due to fouling. Pre-treating with higher concentrations of chlorine or stronger biocides would likely damage the membrane and put harmful chemicals into the drinking water supply. That said, it seems that one of the only ways to stop biofouling before or during biofilm formation is to physically remove or disrupt it at the membrane surface level. One such method of doing so is air sparging.²⁰ Air sparging is the sudden reversal of flow in the membrane module (much like backwashing) but upon reversing the flow, pressurized air is added to the permeate-side of the module. Basically, it is backwashing with a mixture of air and water instead of just water.

In an experiment conducted by E.R Cornelissen et al., the effects of air sparging on biofouling were studied in order to determine the best practices for industrial application.²⁰ In this study, two identical cross-flow membrane units ran constantly for about 110 days. Both units were set to change pressure in order to maintain constant flux, similar to an industrial system. The initial pressure for both modules was 200 mbar and the steady flux was about 350 L/hr. The first unit was sparged every time the feed pressure reached 400 mbar but the second unit was

sparged on a daily basis. As can be seen in Figure 6, sporadic sparging effectively removed biofouling every time the pressure reached 400 mbar. This occurred every few weeks and worked well for about four cleanings. In between cleanings, a biofilm would form and build, causing consistent exponential increases in feed-side pressure. In contrast, the unit that was sparged every day saw a slow, but steady increase in feed-side pressure in order to maintain steady flux. There was not sufficient time in between sparging for a biofilm to form. It was concluded that in terms of energy usage, the setup that saw daily cleaning is the more efficient and cost effective method for mitigating biofouling. However, in both cases, eventually other types of fouling take hold as well and it becomes impossible for the membrane to return to its initial operating parameters. It seems that, while the unit that saw daily cleanings did effectively slow down the negative effects of biofouling, it is very difficult to increase the longevity of the membrane modules. In the same study it was also concluded that, when air sparging, the time of back-flow needed in order to effectively clean the membrane is about five minutes. Any time spent sparging past that is ineffective at removing more biofilm and is thus wasting operational time. This study proves that the mechanical removal or disruption of the biofilm on the membrane surface may be the best method of mitigating biofouling on a large scale.

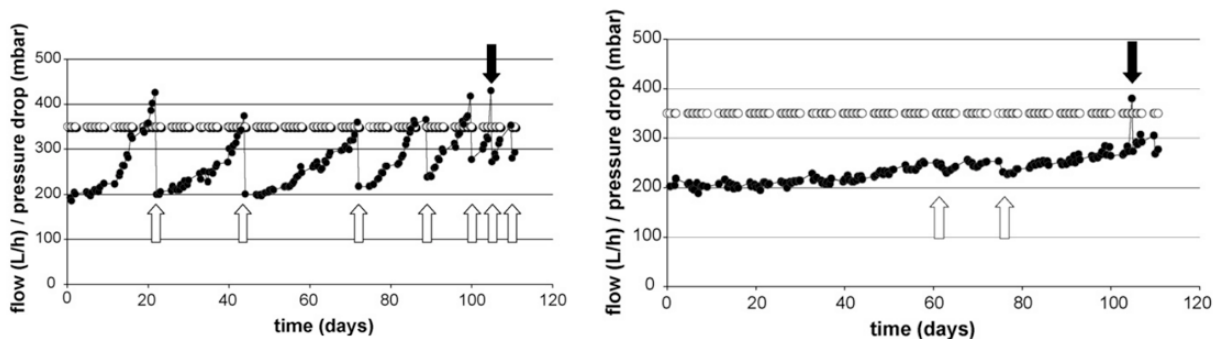


Figure 6. Flow (hollow dots) and pressure drop (black dots) of the cross-flow membrane units that were air sparged sporadically (left) and daily (right). The black arrows are likely spikes due to particulate fouling. The white arrows on the left plot indicate times of cleaning. The white arrows on the right plot represent times of intermittent chemical cleaning.²⁰

1.5 Concentration Polarization; Causes and Current Solutions

Fouling involves the clogging of a membrane by the attachment of a substance to the membrane. There is another method by which the flux of clean, permeated water becomes slowed. Concentration polarization is the accumulation of retained solute on the feed-side of the membrane.²¹ This accumulation causes solute concentrations that are much larger at the membrane surface than in the bulk feed and causes high osmotic pressures in the opposite direction of desired flow.²¹ This induced osmotic pressure is dependent on the concentration at the membrane surface and not in the bulk and thus is much larger than the osmotic pressure induced by the bulk concentration. While fouling physically blocks the flow of water through the membrane, concentration polarization induces an osmotic pressure in the opposite direction than the pressure drop being applied to the system. Similar to fouling, concentration polarization (CP)

calls for an increase in applied pressure drop across the membrane and therefore elevated energy costs.

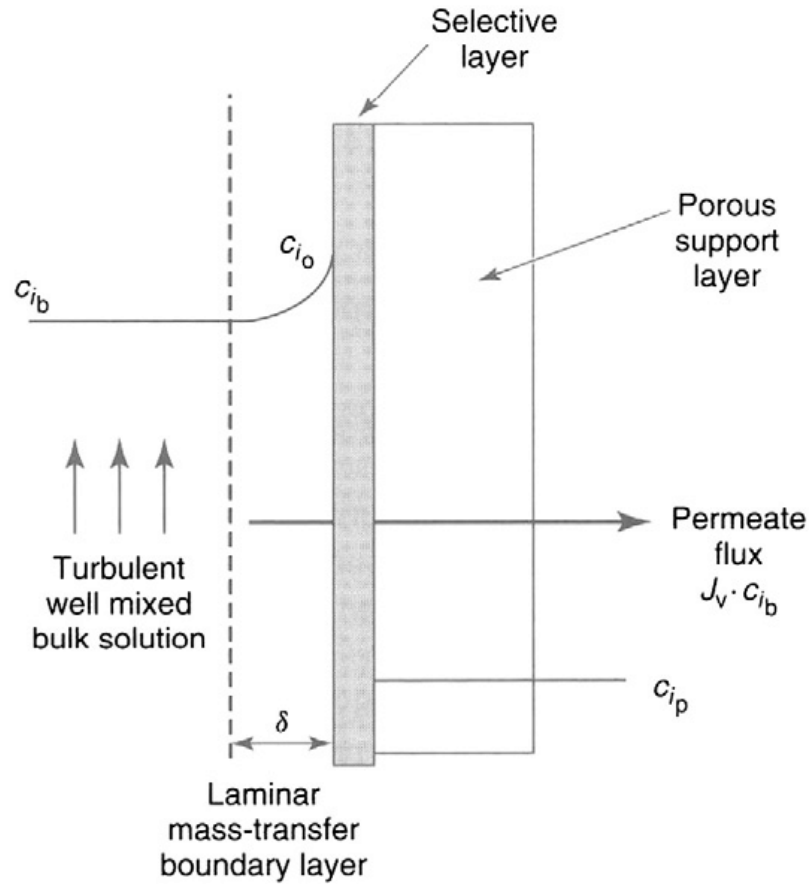


Figure 7. Solute concentration vs. position at the membrane surface. The increase in concentration at the surface causes larger osmotic pressure against the direction of permeate flow²².

Concentration polarization is characterized by the CP modulus (f_{CP}), which is a ratio of the solute concentration at the membrane surface (C_m) to that in the bulk (C_B).²³ An f_{CP} of 1 represents a system with no concentration polarization. This will be useful in later analysis (Eqn. 1).

$$f_{CP} = C_m/C_b \quad (1)$$

The main solution to CP is mixing. Steady mixing of the feed stream at the membrane surface disrupts the buildup of high concentrations at the surface. This is easily achieved in a countercurrent membrane filtration system as mechanical mixing equipment can be placed directly on top of the membrane.²⁴ However, as previously discussed, the main system used industrially is the cross-flow spiral-wound membrane system. In this setup, the mechanical mixing of the feed at the membrane surface is not so easily achieved. The fact that the membranes work on a cross-flow basis does help reduce the effects of CP to a certain extent. However, due to the existence of a hydrodynamic boundary layer above the membrane surface, excess solute buildup is inevitable (Fig. 7).²² Thus, a method for disruption of concentration polarization at the membrane surface is needed.

Chapter 2: Copper Oxide Nanoparticles; a Proposed Solution to Fouling and Concentration Polarization

2.1 A Conceptual Background and Proposed Solution

A study was conducted by Dr. Rajarshi Guha et al. at Penn State University to test the usage of copper oxide (CuO) nanoparticles as an additive to RO and NF membranes in mitigating fouling and concentration polarization.²³ This study will be summarized in the following sections for the purpose of showing the concept of catalyzed hydrogen peroxide degradation as a means of solving industrial water treatment inefficiencies. All writing in this section is in reference to this specific study unless otherwise cited. As an undergrad, I was brought on to the Kumar Research Group shortly after this study was completed.

Current solutions to fouling and CP involve expensive changes to membrane structure or surface coating, operational rotation or vibration of membrane modules, or costly backwashing procedures of a variety of forms. The idea of adding nanoparticles to the membrane surface is not a new concept.²³ Nanoparticles, an emerging field with a plethora of applications, have been studied for use in water treatment membranes for some time. Additionally, as previously covered, changes in surface charge and hydrophilicity, the smoothening of membrane surfaces, and the installment of long-chain hydrophilic molecules on the membrane surface to provide steric repulsion have been found effective but not over the long term.¹⁵ Guha et al. wished to study a new application of nanoparticles in RO and NF membranes to produce a ‘self-cleaning membrane’.²³

Since the early 1900s, nanoparticles like copper oxide, iron oxide, and gold, among others, have been used extensively for their small size yet large potential electronic, chemical, and optical properties.²³ Copper oxide is particularly useful because of its natural abundance, high stability, low production cost, and good electrical properties.²⁵ Additionally, and most importantly for this study, metal oxides act as catalysts in the degradation of hydrogen peroxide (H_2O_2) to liquid water (H_2O) and gaseous oxygen (O_2).²³

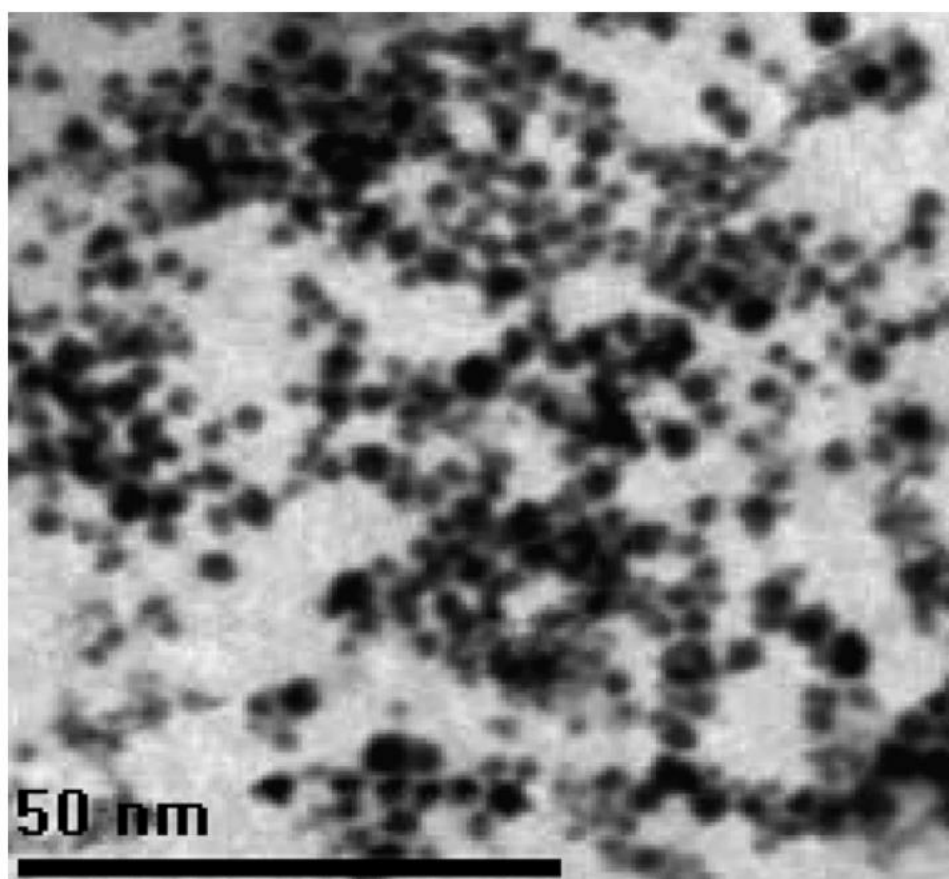


Figure 8. TEM imaging of CuO nanoparticles²⁵

It was hypothesized by Guha et al. that in cross-flow membrane filtration, like that which is implemented in spiral-bound water treatment membrane units, degradation of hydrogen

peroxide at the membrane surface would produce oxygen bubbles. These bubbles would coalesce into an effervescence that would add a sort-of mechanical 'mixing' to remove all types of foulants and disturb the hydrodynamic boundary layer that harbored the higher solute concentrations contributing to CP.²³ Theoretically, copper oxide nanoparticles could be chemically anchored *in-situ* to the membrane surface and low concentration hydrogen peroxide (0.2%, 56 mM), could be periodically charged into the treatment feed stream which would then be decomposed rapidly upon encountering the membrane-bound nanoparticles. This would create an environment of "reactive micromixing".

An intermediate byproduct of the degradation of hydrogen peroxide is hydroxyl free radicals ($\text{OH}\cdot$).²⁶ Under non-catalytic degradation rates, these radicals prove inconsequential. However, under the rapid degradation rates that are catalyzed by copper oxide, this poses both possible issues and usages. Hydroxyl free radicals, like other radicals, are very reactive due to their highly oxidative nature.²⁷ A free radical will seek out and steal single electrons from stable molecules, thus creating another free radical and initiating a domino-effect of oxidation. They are responsible for the harmful degradation of DNA and damage to cells within the body. The highly reactive nature of the hydroxyl free radical is helpful in the case of water treatment because it aids in the decomposition of stubborn organic molecules present in the feed. These molecules, if left undisturbed, would serve to foul the membranes until otherwise broken down.¹⁵ For the same reasons hydroxyl free radicals are helpful, they are also harmful as they will serve to unselectively decompose any organic molecules present, including the polyamide surface of the membrane itself.²³ Thus, the study by Guha et al. also set out to determine an method for protecting the membrane surface from attack by hydroxyl free radicals.

Polydopamine (PDA) has proven useful in a variety of applications. Previous research has proven it's worth as a membrane surface coating as it increases hydrophilicity and increases the ability to functionalize the membrane surface immensely.²⁸ By itself, a polydopamine-coated NF or RO membrane is more resistant to fouling than one that is not. Additionally, the polydopamine, when polymerizing on the membrane surface does so in a way that produces a lattice that does not significantly hinder mass transfer flux (rate of permeate flow per unit area).²⁹ A polydopamine coating can also serve to protect the polyamide membrane by scavenging the hydroxyl free radicals produced by hydrogen peroxide degradation.²³ Instead of harming the membrane, the part that is actually providing the filtration, the hydroxyl radicals will harm the PDA coating, a preferred outcome. Additionally, PDA is very resistive to removal and requires hydrogen peroxide concentrations of 30% to be removed, much larger than feed peroxide concentrations.³⁰

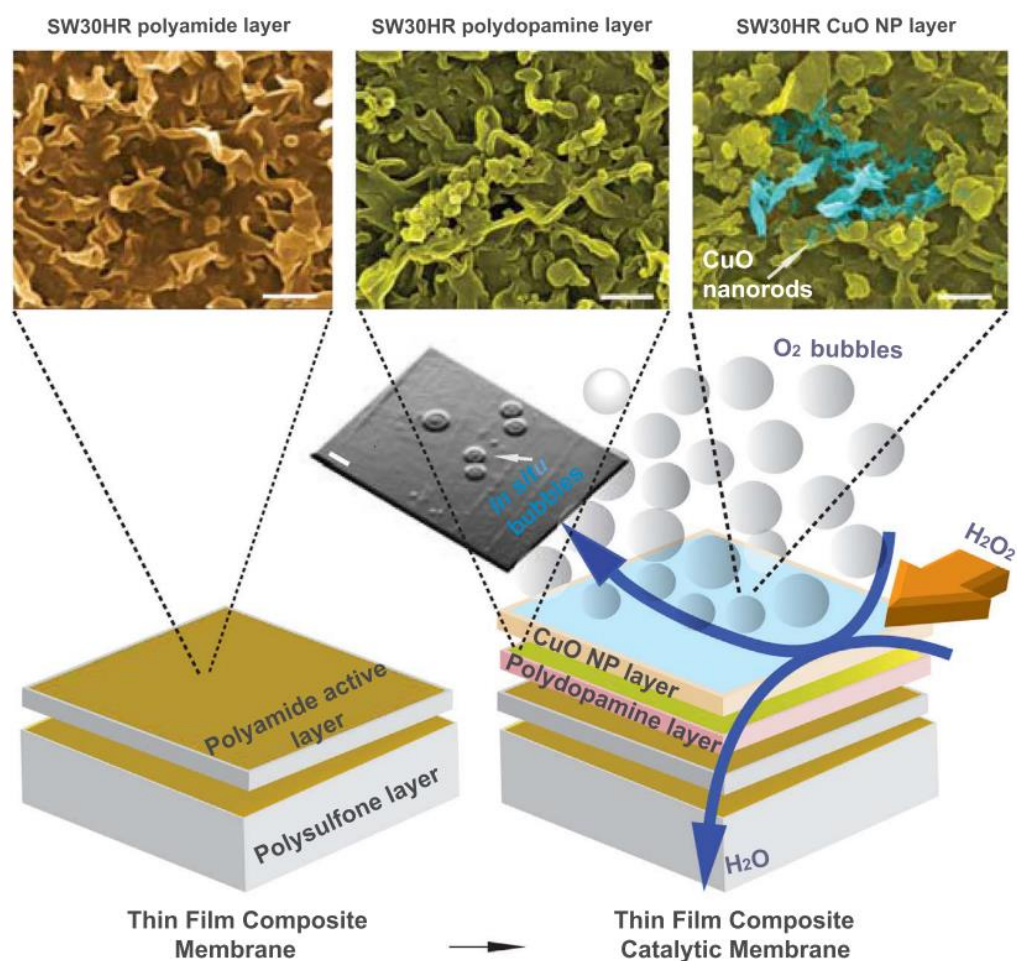


Figure 9. Schematic of the theoretical fouling and CP mitigation via catalytic degradation of hydrogen peroxide proposed by Guha et al.²³

2.2 Methods and Materials

Two different commercially used membranes were used in this study: seawater RO membranes (SW30HR) and NF membranes (NF90). Both of these membranes are made by Dow Water and Process Solutions (now Dow-Dupont) and both were obtained in flat-sheet form, though they are used industrially in spiral-wound membrane module form. The NF90 membrane

was used in biofouling control experiments and the SW30HR membrane was used in colloidal/organic fouling control experiments.

2.2a Membrane Coating

Both membranes were coated with polydopamine in the same manner. Dopamine hydrochloride readily polymerizes into PDA in Tris-HCl buffer solution (10 mM, pH 8.5). The buffer solution was made and solid dopamine hydrochloride was added. This polymerizing solution was then placed on top of the membrane and shaken, allowing PDA to form and adhere to the membrane surface. Copper oxide nanoparticles were grown *in-situ* using drop-by-drop addition of sodium hydroxide to hydrous copper (II) nitrate.

2.2b Nanoparticle and Membrane Characterization

SEM and TEM imaging were performed on the coated membranes in order to get a qualitative gauge of nanoparticle formation and surface anchoring.

2.2c Kinetic Evaluation of Membrane Performance

Catalytic properties were measured in small, batch-style experiments. Once coated, 1 cm x 2 cm rectangles of membrane were randomly cut and placed in vials. 5 mL of a solution of methylene blue (12 mg/L) and 3% hydrogen peroxide were placed in each vial and left to react. Qualitative, visual bubble production measurements were taken. Additionally, the degradation of methylene blue, which can be measured via absorbance in UV-VIS spectrophotometry, was used to characterize the kinetics of the hydrogen peroxide degradation.

2.2e Organic/Colloidal RO Membrane Fouling and CP Mitigation Performance in Cross Flow System

Colloidal silica particles and humic acid were obtained to test for colloidal and organic fouling, respectively. These are commonly used in experiments regarding colloidal and organic

fouling. The SW30HR membranes, now coated with PDA and CuO nanoparticles, were placed in a bench scale cross flow RO system with a filtration area of 138 cm². They were then compacted in DI water for 24 hours and conditioned with 20 mM NaCl for an additional 12 hours. Finally, foulants were charged separately (0.017% silica nanoparticles and 50 ppm humic acid) for separate experiments and the system was allowed to foul for 24 to 48 hours. The feed was then pulse charged with hydrogen peroxide (60 to 240 ppm) and the flux was measured throughout the experiment at constant pressure. Additionally, concentration polarization experiments were performed in this same setup. The beginning stages were identical, but 0-250 mM NaCl solution was fed instead of silica or humic acid and the feed was then pulse-charged with 240 ppm hydrogen peroxide at each tested NaCl solution.

2.2f NF Membrane Biofouling Mitigation Performance in Dead-End Stirred Cell System

Wild type red fluorescent protein (rfp) incorporated E. coli was grown on NF90 membranes for 24 hours using M9-0.4% glucose with chloramphenicol antibiotic in an Advantec MFS UHP-76 stirred cell. The biofilms created were visualized via laser scanning confocal microscope (TCS SP5). After a 24 hour growth period, hydrogen peroxide was added to the feed. The flux was measured throughout the experiment at constant pressure.

2.3 Results and Discussion

2.3a Membrane Coating

Copper oxide nanoparticles were successfully grown and anchored to the PDA coated membrane surfaces of NF90 and SW30HR membranes. This *in-situ* modification was performed on commercial membranes, which leads to believe that it could be an easy, cost-effective

modification to large-scale membrane modules. The SEM and TEM imaging of the membrane surface at two different CuO concentrations (Fig. 10) shows the growth and anchoring of CuO nanoparticles on the membrane surface.

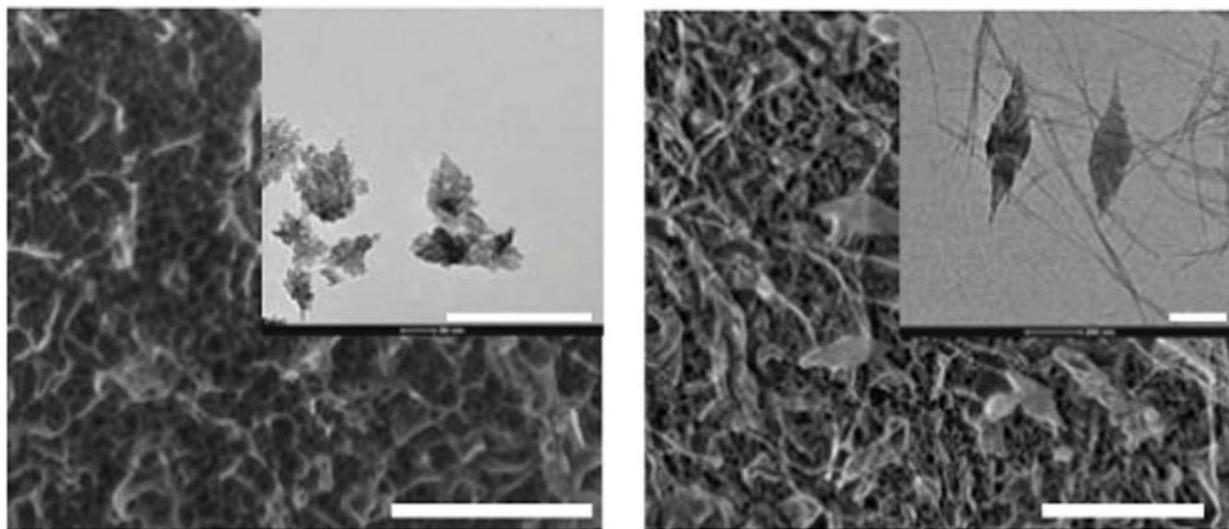


Figure 10. SEM images with inset TEM images of 8 ppm CuO/PDA (left) and 80 ppm CuO/PDA (right). The inset images show the CuO nanoparticles.²³

2.3b Kinetic Evaluation of Membrane Performance

When studied via batch-style experiments with methylene blue as a kinetic indicator, it was shown that the degradation of hydrogen peroxide by membrane-anchored CuO nanoparticles was seemingly first order with respect to hydrogen peroxide concentration. This means that the rate of degradation at CuO concentrations of 8 and 80 ppm was directly dependent on the concentration of hydrogen peroxide and not on the concentration of CuO. This is shown by the fact that the rate constant is nearly the same between methylene blue degradation trials with 8 and 80 ppm CuO concentrations (Fig. 11), a ten-fold difference. Visually, oxygen bubble formation can be seen on the membrane surface at the micro level (Fig. 12).

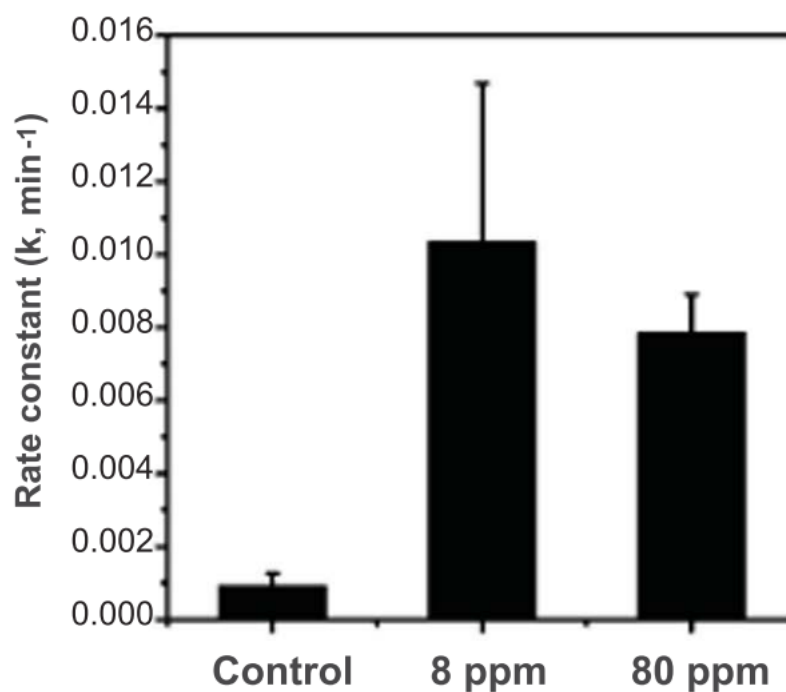


Figure 11. Rate constant of hydrogen peroxide degradation with respect to the concentration of CuO solution used to coat the membranes. This is relatively clear indicator that, at these concentrations of CuO, the reaction kinetics of the degradation of hydrogen peroxide are first order.²³

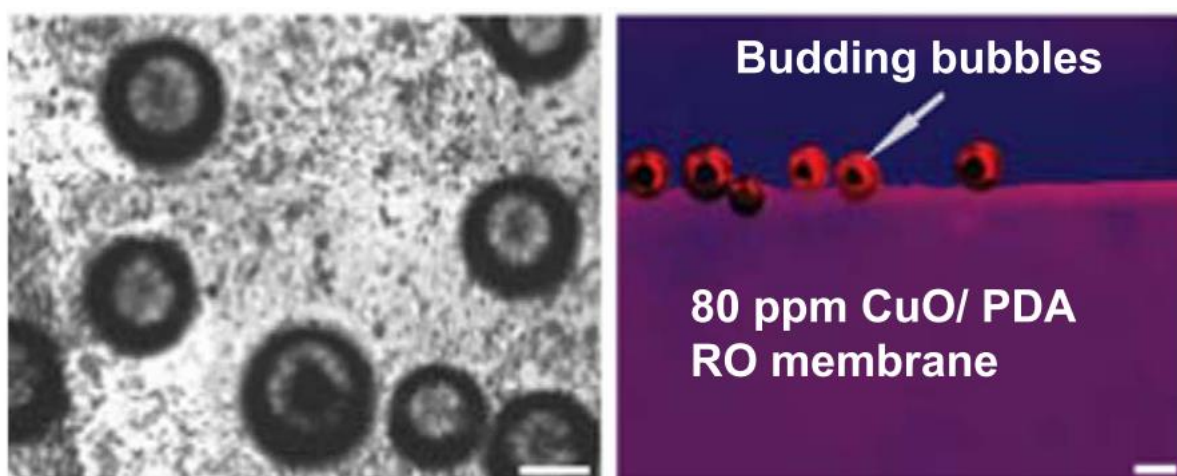


Figure 12. Oxygen bubble formation on the membrane surface. The image on the right has a scale bar of 150 μm .²³

2.3c Organic/Colloidal RO Membrane Fouling and CP Mitigation Performance in Cross Flow

The pulse-charged addition of ppm levels of hydrogen peroxide to the feed stream of an organically (humic acid) or colloiddally (silica) fouled SW30HR membrane coated in PDA and CuO nanoparticles rapidly and effectively reversed fouling and returned flux to pre-fouling levels in a cross flow system. Control experiments in which DI water was added to the system instead of hydrogen peroxide showed a continued decrease in flux. The normalized results of this experiment can be seen in Figure 13 below. Additionally, it can be seen that the flux recovery rate post hydrogen peroxide injection is three times and six times that of flux decline rate before hydrogen peroxide for silica and humic acid fouling, respectively. These results are easily scalable and reproducible. This proves that coating RO membranes with PDA and CuO nanoparticles followed by regular injection of hydrogen peroxide is a viable method for stopping and even reversing the flux-loss due to colloidal and organic fouling.

The pulse-charged addition of ppm levels of hydrogen peroxide to the feed stream of a cross flow RO membrane system plagued by concentration polarization was shown to reduce CP levels and thereby increase flux. When the system contained an SW30HR membrane coated with 80 ppm CuO/PDA was under steady flux of 18.3 liters per meter squared per hour (LMH), it was found to have a CP modulus (f_{CP}) of 1.2 (Eqn. 1). When charged with 240 ppm hydrogen peroxide, the CP modulus was reduced to 1.1. Furthermore, when the same system was charged with 240 ppm hydrogen peroxide and 10 ppm humic acid, the CP modulus was reduced further to 1.03. This was tested as the result of the normalized organic fouling flux returning to a value higher than 1 (Fig. 13c) and can be attributed to humic acid acting as an electron shuttle and further increasing the rate of peroxide degradation. In any case, the addition of hydrogen peroxide to the cross-flow system plagued by CP reduced the CP levels and increased the flux.

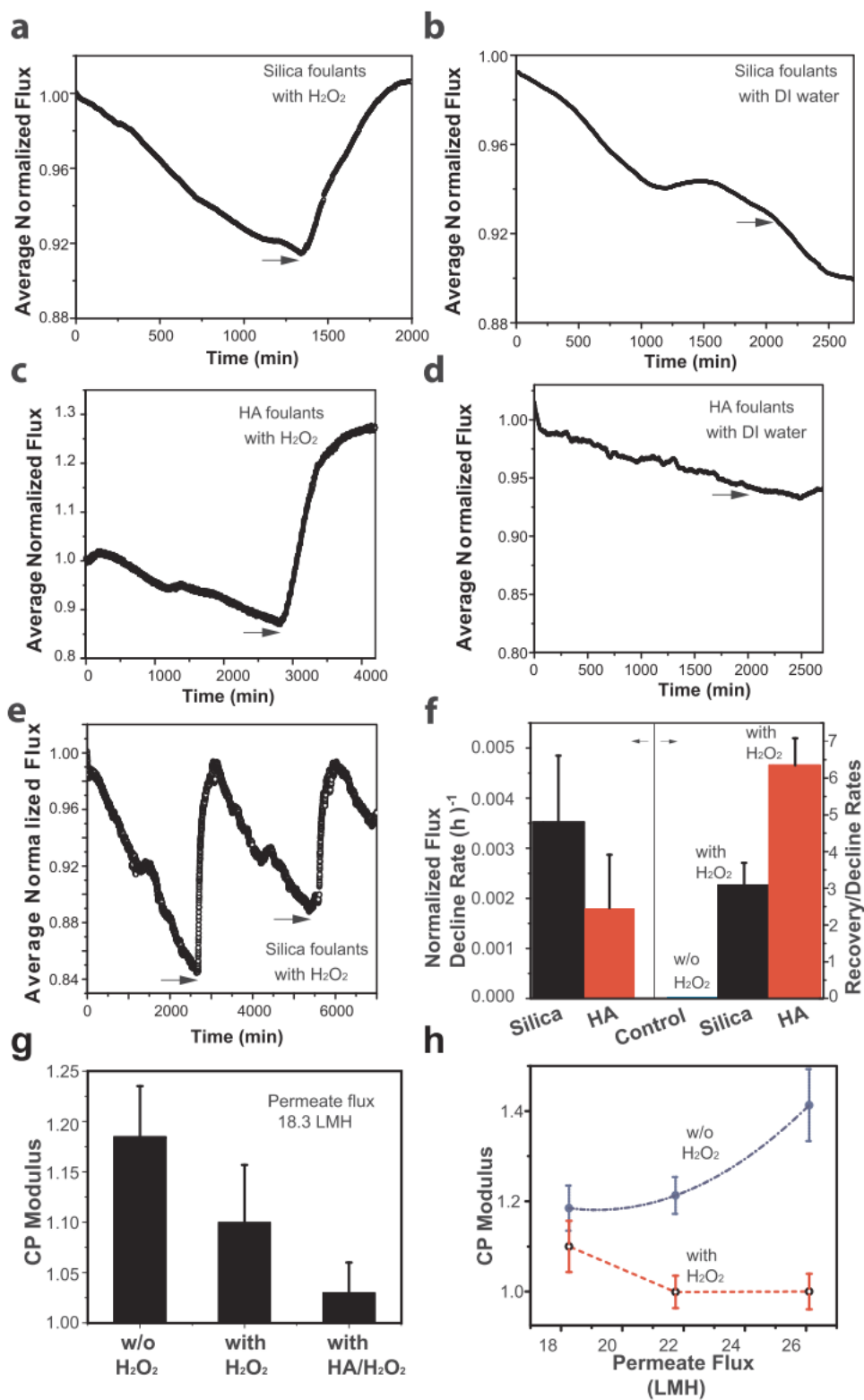


Figure 13. Normalized flux decline and return in a cross flow CuO/PDA coated RO membrane system under colloidal fouling conditions when charged with hydrogen peroxide

(a) and DI water (b). Normalized flux decline and return in a cross flow CuO/PDA coated RO membrane system under organic fouling conditions when charged with hydrogen peroxide (c) and DI water (d). (e) Normalized flux decline and return in a cross flow CuO/PDA coated RO membrane system under colloidal fouling conditions when charged with hydrogen peroxide over several cycles. (f) Normalized flux decline and recovery rates in systems of colloidal and organic fouling with charged with hydrogen peroxide. The control was charged with DI water. (g) The CP modulus values of a system under CP conditions and a flux of 18.1 LMH charged with no hydrogen peroxide, 240 ppm hydrogen peroxide, and 240 ppm hydrogen peroxide / 10 ppm humic acid. (h) The CP modulus of systems at varying flux levels charged with nothing vs. 240 ppm hydrogen peroxide.²³

2.3d NF Membrane Biofouling Mitigation Performance in Dead-End Stirred Cell System

NF90 membranes coated with PDA and CuO nanoparticles proved highly resistive to biofilm accumulation and growth and were therefore found to be a highly effective biofouling mitigation tactic. Interestingly, NF90 membranes coated only with PDA had 3-fold higher levels of biofilm formation on the membrane surface than NF90 membranes with no alteration. This is likely due to an increase in surface roughness on membranes coated with only PDA. Additionally, it was found that higher concentrations of CuO reduced the formation of biofilms even further. With respect to the unmodified NF90 filter, the membranes coated in 8 ppm and 80 ppm CuO/PDA had 88% and 95% reduced biomass, respectively. Finally, while the additional charging of hydrogen peroxide did reduce biomass slightly further, it was not a substantially larger reduction than the coated membranes on their own. Thus, while charging the system with hydrogen peroxide is useful, it probably needs to be completed with less frequency than in the RO systems fouled by colloids and organics as previously described. The graphical results can be seen in Figure 14 below.

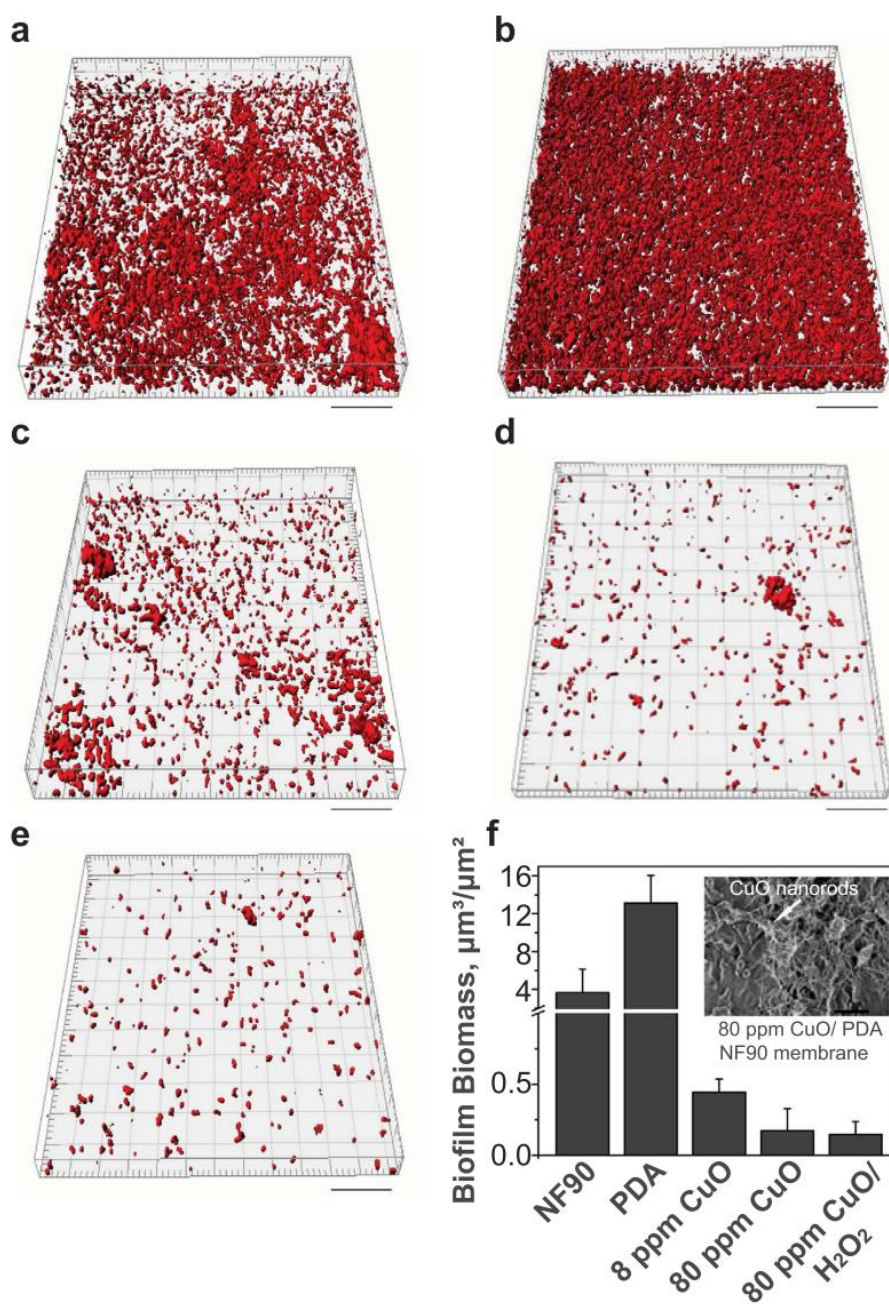


Figure 14. Biofilm formation on the surface of an NF90 membrane that is (a) unmodified, (b) coated with PDA, (c) coated with 8ppm CuO/PDA, (d) coated with 80 ppm CuO/PDA, and (e) coated with 80 ppm CuO/PDA and charged with hydrogen peroxide. (f) A comparison of the biofilm mass per area of the differently coated membranes described by a-e.²³

2.3e Scaling and Implementation for an Industrially Useful Catalytic Membrane

While certainly and reproducibly effective at the bench scale level, it is important to think about ways in which the results from this study can be scaled up to meet industrial and municipal needs. For this reason, commercially available and regularly used NF and RO membranes were used with *in-situ* application of PDA and CuO in this study. In this way, it is much easier for the membranes in spiral wound modules to be modified in the manufacturing process to include these two new layers. Further studies will need to be completed in order to determine the most efficient methods for coating such large membranes.

An important variable is the frequency in which the system is charged with hydrogen peroxide. As can be seen from the results, this study shows an example of on demand flux decline elimination. This means that hydrogen peroxide can be injected into the feed at any time in order to increase flux or, in a large-scale system, decrease pressure drop needs rapidly. So, a possible system is one in which hydrogen peroxide is routinely injected into the feed at normal time intervals. This would routinely remove deposited particles and bacteria and reduce concentration polarization temporarily. The other method would be a continuous feed of hydrogen peroxide into the system. This would prevent the deposition of bacteria and particles altogether and continually mitigate the buildup of concentration polarization. The latter of these options, while likely more effective, would also cost more money in the form of more hydrogen peroxide.

In the Guha et al. study, it was estimated that a CuO/PDA coating and periodic pulsing of hydrogen peroxide would show 19% energy savings in low pressure RO systems and 32%

energy savings in high pressure RO systems. The dramatic difference is due to the fact that CP is a far bigger issue in high-pressure systems than in low.

One more issue that may be seen if implemented on a larger scale for a longer period of time is the degradation of the CuO/PDA coatings when subjected to usage and injection of hydrogen peroxide over the course of several months. Though catalytic performance degradation was not seen in this study, none of the experiments lasted more than seven days. So, A future study that is necessary for the validation of this application on a large-scale is looking at the catalytic performance over the course of several weeks or even months when subjected to different types of fouling and regularly injected with hydrogen peroxide.

2.4 Study Conclusions

Guha et al. proved with this study that there is huge potential for the usage of catalytic coatings in large-scale water treatment systems in order to mitigate the effects of fouling and concentration polarization, the two most costly issues in municipal and industrial water treatment systems. While very quantitative, this study is still at the proof of concept phase and will need far more research in order to be implemented in a large-scale setting. However, based on its validity and reproducibility, it seems that the solution to the inefficiencies of large-scale water treatment resides in catalytic coatings. It is an exciting time to be a water engineer as global demand for clean water pushes the limits of scientific research in the pursuit of incredible solutions. For the remainder of this thesis, a new avenue of catalytic coatings will be conceptually explored for its potential usage in similar applications to copper oxide nanoparticles.

Chapter 3: Catalase; an Enzymatic Approach

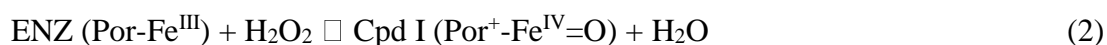
3.1 A Conceptual Background and Proposed Solution

It has been shown that adding catalytic nanoparticles to the surface of RO and NF membranes can greatly decrease the negative effects of fouling and concentration polarization when charged with hydrogen peroxide.²³ However, metallic salt nanoparticles are not the only catalysts for the degradation of hydrogen peroxide. Catalases, a family of enzymes, reside in almost all aerobically respiring organisms and serve to catalyze the hydrogen peroxide degradation reaction within the organism.³¹ It would be a unique and informative exercise to test the validity of using catalase as the catalyst to induce reactive micromixing on water treatment membranes instead of copper oxide.

When determining solutions to issues such as fouling and CP on RO and NF membranes, it is important to develop a variety of possible solutions. Every treatment system is different and so are the common fouling issues found in each. So, having a multitude of coatings and membrane alterations allows for a diversified problem-solving portfolio. Additionally, catalase is found in nature. It is used by a large multitude of organisms in a wide variety of conditions.³¹ Water treatment systems are often run in a variety of conditions, depending on the product needs. It could therefore be possible to select a specific type of catalase to apply to a membrane for a specific treatment facility given the known operating conditions of that facility. Historically, there are countless instances when synthetic replications cannot match what nature has evolved for millions of years. Therefore, finding a 'natural' catalytic coating for treatment membranes is a desirable goal. Once the specific catalase protein is determined, the genes that code for said

catalase could be put into bacteria for the purpose of ‘farming’ the enzyme on a large scale. Determining catalase to be an appropriate catalyst for fouling and CP mitigation would be a productive step in the direction of lowering energy costs in water treatment processes.

In organisms that practice aerobic respiration, a common metabolic byproduct is hydrogen peroxide. Hydrogen peroxide is a powerful oxidant that can damage cells if in sufficient concentration. Catalases (Fig. 15) are ubiquitous enzymes that have developed naturally and exist in the organism to catalyze the decomposition of hydrogen peroxide to water and oxygen.³¹ They play an important role in mutagenesis, inflammation, tumor stimulation, and apoptosis prevention by regulating peroxide concentrations.³¹ The mechanism by which catalase catalyzed peroxide degradation occurs has long been a topic of study. The consensus is that catalase reacts with a single peroxide molecule to form a higher energy intermediate known as Compound 1 (CPD I) and then is further oxidized by a second peroxide molecule to return to its low energy state (Eqn. 3 & 4).³¹



It should be noted that unlike the metallic salt nanoparticle catalyzed peroxide degradation, the catalase mechanism produces no hydroxyl free radical intermediate. So, while hydroxyl radicals could no longer be used for the degradation of persistent organic molecules in water treatment, less emphasis would need to be placed on protecting the polyamide membrane surface from unintentional oxidative damage.

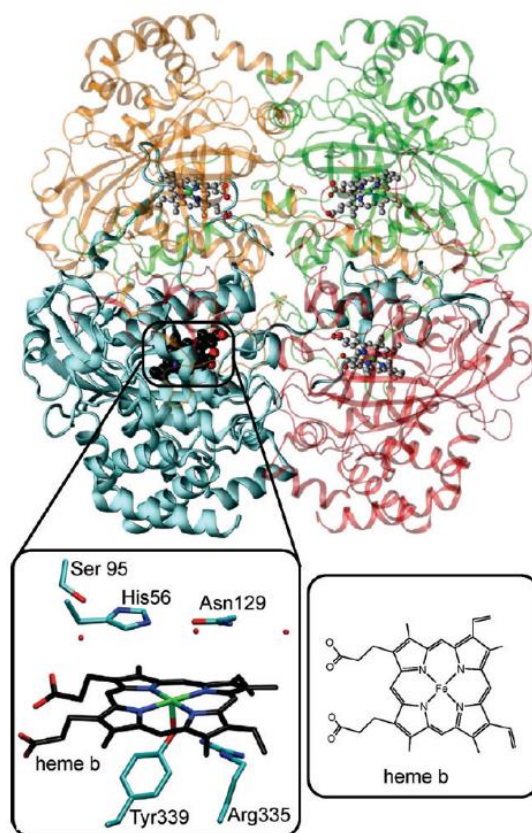


Figure 15. Molecular structure of catalase found in *H. Pylori*. The zoomed in portion depicts the heme b binding pocket.¹⁵

3.2 Notes for Potential Coating Procedures

Theoretically, catalase could simply replace the CuO nanoparticles in the coating procedures described in the reactive micromixing study by Guha et al. However, as previously stated, hydroxyl free radical is not produced in the catalase mechanism. Therefore pre-coating the membrane with PDA becomes unnecessary, as the membrane surface no longer needs protection. That said, given that PDA does not negatively effect pre-fouled membrane flux²⁹, the addition of PDA is useful as it still aids in making the surface more hydrophilic.

In order to maintain enzymatic activity during treatment, specific immobilization measures must be taken in order to ensure that the catalase is properly anchored to the membrane surface yet can still be accessed by hydrogen peroxide substrate under normal mass transfer conditions. A method that was briefly tested in Kumar research group is the creation of PDA microcapsules that encapsulate catalase enzyme. The PDA capsule, which as previously stated, consists of a polymer network 'net', would allow for the transport of hydrogen peroxide to catalase and electrostatic interactions would allow the microcapsules to 'stick' to the polyamide membrane surface. More extensive research will need to be conducted to validate this method for catalase immobilization.

Catalase is currently available to buy commercially from wholesale chemical distributors. However, given that its usage currently resides mostly in research, bulk catalase could be an expensive undertaking. Thus, it would likely be more cost effective to develop large-scale genetically modified bacteria farming practices for the purpose of large polyamide membrane coatings. This would likely be the cheapest and most efficient method for producing catalase as synthesis of such a complex protein is an extremely difficult undertaking.

There are some important considerations to take into account if catalase were to be used in membrane water treatment. The first and foremost potential issue is protein deactivation. This can occur via temperature denaturing and will occur via direct chemical substrate deactivation.³² Essentially, catalase can become deactivated if temperatures are too high and they will deactivate over time simply by doing their job of hydrogen peroxide degradation. This, although potentially problematic, can also be solved by proper organism selection. In order to mitigate the possibility of temperature denaturing, the specific catalase used to coat membranes can be sourced from a thermophilic organism (one that exists in and can withstand high temperature environments). A

study conducted by Vasudevan and Weiland showed that, although catalase is deactivated by the direct action of substrate hydrogen peroxide, it does so at a rate that is an order of magnitude slower in *Aspergillus niger* vs. bovine catalase even at comparable levels of activity (Table 1).³² Again, this shows that careful research and subsequent selection of the organism supplying the DNA for catalase production can slow the rate of deactivation to a minimum and therefore lengthen the period of time in between membrane module replacement. This showcases the beauty of using a naturally made enzyme instead of metallic nanoparticles: nature has done all of the work of engineering a variety of catalases for a variety of environments. It is now up to us to determine the desired qualities and choose the right one for water treatment membrane coating.

Table 1: Activity and deactivation constant of several types of catalase. At similar activities, the catalase from *Aspergillus niger* has a significantly slower rate of deactivation.³²

Catalase	Activity	Deactivation Constant k_d ($\times 10^4 \text{ s}^{-1}$)
Bovine C10	20.9	6.3 ± 0.14
Bovine C40	34.9	6.8 ± 0.25
<i>Aspergillus</i>	30.6	0.46 ± 0.022

3.3 Catalase-Coated Oil Emulsion Experiment

Several small experiments were conducted in the Kumar Lab Group by Abigail White, Siddharth Sharma, and myself to preliminarily test the proof of concept of using catalase as a catalytic coating in membrane systems. One of the more notable experiments was that which tested the usage of catalase-coated RO membranes against fouling cause by canola oil. Oil is a common organic foulant which is found in surface water because of both natural occurrences and

human pollution. It has the tendency to form a hydrophobic layer on the membrane surface that slows the transfer rate and, like any other foulant, increases the pressure needs of the system. It was hypothesized that when charged with hydrogen peroxide, a catalase coated reverse osmosis membrane system would foul less than one not charged with hydrogen peroxide.

3.3a Methods and Materials

DOW FilmTec BW30 brackish water RO membranes were coated first with a layer of polyethylenimine (PEI). PEI is a cationic polymer that will alter the surface charge of the membrane in order to create an electrostatic attraction to catalase, which is negatively charged. The membranes were then coated with a solution of catalase (1ml/100ml) made by *Corynebacterium glutamicum* for 20 minutes each. These coated membranes were then run in a dead-end stirred cell filtration unit (Fig. 16) under 200 psig pressure while the permeate was collected and massed every minute for a period of time. Trials involving three different feed solutions were completed. The solutions were pure DI water, an emulsion of canola oil without hydrogen peroxide, and an emulsion of canola oil with 250 ppm of hydrogen peroxide. The emulsions were made by blending 300 ml of DI water, 4.5 g of canola oil, and 0.45 g of triton x-100, a commonly available surfactant.

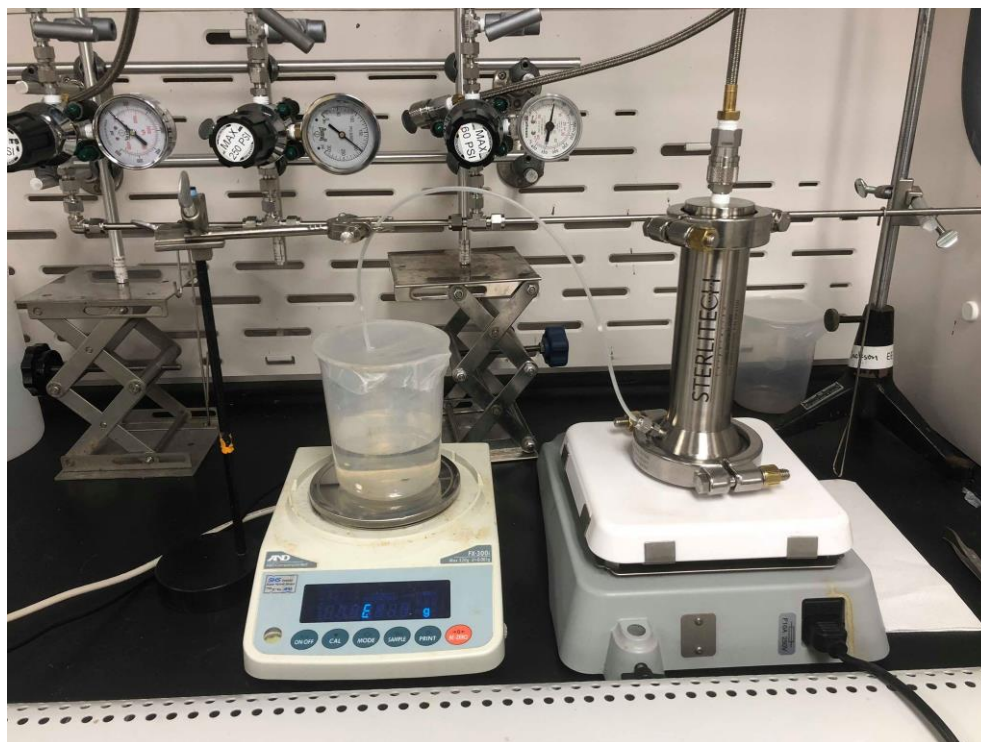


Figure 16. Dead-end stirred cell unit for testing catalase-coated BW30 RO membranes

3.3b Results and Discussion

The emulsion solution containing hydrogen peroxide performed significantly better in promoting unhindered mass transport of clean water through catalase-coated membranes than that which contained no hydrogen peroxide. These results can be seen in Figure 17, which shows that after 550 minutes of operation, the hydrogen peroxide-charged system produced 14% more clean permeate than that which was not charged with hydrogen peroxide.

These results, though preliminary, prove the concept that catalase can potentially be used as a catalytic coating in order to produce reactive micromixing in water treatment systems. It will be important to replicate these studies in future experimentation in order to verify and quantify in detail the capabilities of catalase as a surface coating.

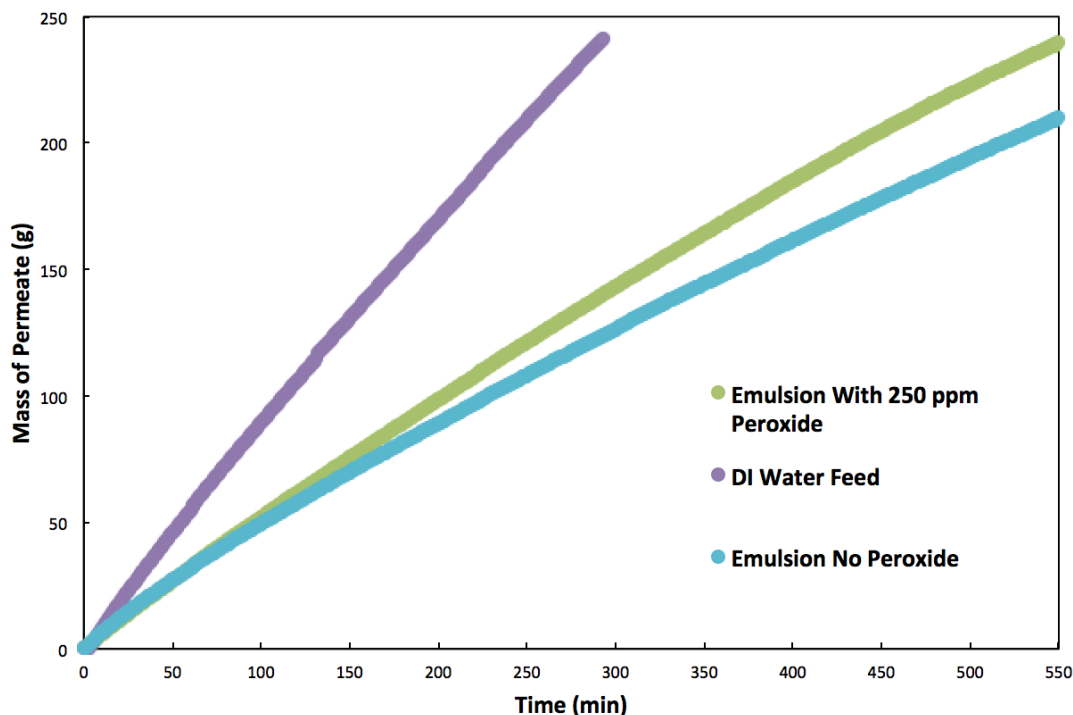


Figure 17. Total mass of permeate vs. time for catalase-coated BW30 membranes charged with various feeds in a dead-end stirred cell unit

3.4 Catalase Reactive Micromixing Conclusions

There is a great deal of potential for the usage of catalase coated on water treatment membranes to establish reactive micromixing at the membrane surface when charged with hydrogen peroxide. Catalase is valued in this usage for its variability and ability to withstand various environments. Deriving solutions to modern problems from natural sources is often times a desirable goal as nature has already done the tedious task of engineering the catalase protein. It is hypothesized here that catalase coatings would yield similar results as those found in the study conducted by Guha et al. because catalase catalyzes the degradation of hydrogen peroxide similarly to CuO nanoparticles. This hypothesis was tested in a small, proof of concept

experiment which showed catalase-coated membranes to withstand the effects of organic fouling when charged with hydrogen peroxide. Production of the selected catalase would simply consist of genetically modifying some common bacteria to rapidly ‘farm’ the desired protein. Further research will need to be conducted in order to determine the best method for catalase immobilization onto the membranes surface. Optimal immobilization would involve a measure of protection for the enzyme without hindering substrate transport to the active site. It has been proven that catalytic membrane coatings are a promising solution for large-scale water treatment systems. It is now time to expand this research to discover the best catalyst for each application.

Chapter 4: Conclusion

Global population increases and climate change are increasing the demand for efficient treatment of drinking and sanitation water. It is projected that by 2050, 3.1 billion people will reside in areas considered to be water scarce.³ This need, both domestically and globally, has driven innovation in water treatment systems to be more efficient and cost effective.

The current standard for water treatment membranes on the industrial or municipal scales is the thin film composite polyamide nanofiltration or reverse osmosis membrane in a spiral-wound modular configuration. Though this membrane system allows for large fluxes in cleaned water, it is commonly subjected to fouling and concentration polarization, which serve to clog the membranes and increase pressure requirements. As a result, extensive research has been conducted around altering membrane structures and/or changing operational practices in order to clean the membrane and mitigate fouling while in use.

A study conducted by Guha et al. at the University of Penn State set out to test the usage of metal oxide nanoparticle membrane coatings for the mitigation of fouling and concentration polarization. In this study it was found that, when the feed water is routinely charged with hydrogen peroxide, the negative effects of colloidal fouling, organic fouling, biofouling, and concentration polarization were greatly reduced via a membrane surface reactive micromixing mechanism. While this study did not test the long-term validity of this solution, it provides confirmation that catalytic coatings used to promote reactive micromixing at the membrane surface are a robustly viable solution to the industrial issues of membrane fouling and concentration polarization.

In an attempt to find a different, naturally derived catalyst for RO and NF membrane coating, catalase, an enzyme found in nearly all aerobically respiring organisms, has been hypothesized to work in similar fashion to CuO nanoparticles. There are several important considerations to take into account when designing a reactive micromixing membrane experiment with catalase including immobilization practices, enzyme deactivation rates and conditions, and thermal denaturing issues. If the correct type of catalase is found and used for membrane coating, it would provide a natural alternative solution to fouling and concentration polarization in large-scale water treatment systems.

Global water needs are presenting an issue that is forcing solutions that allow for greater water treatment capacity on a large scale. The industry of water treatment, driven by the demand for clean water, is expanding its capabilities and there is no end in sight to the current rate of innovation. Whatever the possibilities are, however, the usage and proliferation of new treatment applications firmly rests on the need for profit and the economic viability of the process. Thus, extensive research is being conducted on a daily basis in order to determine the cost-effective solutions to the ubiquitous treatment operation issues of fouling and concentration polarization. The future is not set in stone. The water scarcity predictions are just that, predictions. There is still time to change the future of water treatment for the global good, one membrane at a time.

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