Removal of Fouling from Hybrid Ultrafiltration Membranes

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Abstract

Ultrafiltration (UF) membranes see extensive use in water treatment because of their ability to remove natural organic matter (NOM). These membranes are used primarily for pretreating water to make it safe for human consumption. A major issue with this treatment process is that the membranes are quickly fouled which reduces their performance.

At Shanghai Jiao-Tong University, hybrid ultrafiltration membranes have been developed which have an immobilized layer of TiO_2. When placed under UV light, these membranes have demonstrated a self-cleaning ability that removes fouling, represented as humic acid (HA). This is because photocatalysis occurs and the TiO_2 is a source of highly reactive hydroxyl radicals. This process is classified as an advanced oxidative process (AOP). Other AOPs include the photolysis of H_2O_2 and ozone oxidation.

The goal of this project was to evaluate different AOPs for the removal of HA fouling from these hybrid UF membranes. AOPs were tested individually and in combination. Their performance was evaluated based on the membranes flux recovery and the concentration of HA in the permeate.

Overall, the best AOP combination was the photocatalysis of TiO_2 and the photolysis of H_2O_2 under UV light. While UV and ozone were effective cleaners as well, ozone alone damaged the membranes by reducing their flux and selectivity.

Acknowledgment

I would like to gives thanks to my advisors at Worcester Polytechnic Institute, Professors Hong Susan Zhou and David DiBiaso for their input and advice over the course of the project. I would also like to thank all of those in the IGSD department at WPI for the opportunity to preform this project in China. I would also like the thank Professor Jiahui Shao for her guidance and letting me be part of the exiting research in her department. I am also grateful to Hassan Younas who helped teach me how to operate the equipment and make the membranes. Finally, I would like to thank the students Xia Fan, Fei Yuhuan, along with everyone else in the lab that was so helpful and welcoming during my stay.

Nomenclature

Variable	Definition
J	Flux
J_o	Original flux
J_r	Relative flux
R	Removal of HA (%)
A	Area of the membrane
$\dot{v}$	Volumetric flow rate of permeate
m	Mass of permeate collected
ρ	Density of water
t	Time
AOP	Advanced oxidative process
NOM	Natural organic mater
DBP	Disinfection byproduct
HA	Humic acid
UF	Ultrafiltration
MWCO	Molecular weight cut off
M	Molar, Moles per liter

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Section 1 Introduction

Because of China's massive industrialization since the 1970's and urbanization as people moved to the cities for jobs, local water resources have been severely strained (Kahn, Yardley, 2007). Agriculture has demanded more water from already limited resources to grow increasing amounts of food. Large manufacturing industries use massive quantities of water for their processes and are left with contaminated water afterwards. With cities like Shanghai and Beijing becoming the most populous in the world, the infrastructure to support those populations is being strained. All of this is leading to less available freshwater water and pollution of current sources. This is a major problem and there have several approaches to solving this issue. The use of ultrafiltration membranes promises to be part of that solution due their ability to selectively remove certain key pollutants.

A major source of water pollution is natural organic matter (NOM). This can result from both the natural environment and human activity. Removal of NOM is critical to treating water and making safe for drinking (Leenheer, Croue, 2003). While NOM adds dissatisfying color and taste to water, it becomes more dangerous as it undergoes conventional water treatment. For example, when water undergoes chlorination, which has been successfully used to kill pathogens for nearly a century, the NOM can react with disinfection chemicals like chlorine and create disinfection by products (DBPs). Several of these DBPs such as trihalomethanes and haloacetic acids are known carcinogens.

Removal of this NOM is critical for maintaining a safe water supply. One popular way to remove NOM is to use ultrafiltration. NOM is mostly humic in composition and is often represented as humic acid (HA) in experiments. HA is composed of a very complicated organic structure with several aromatics, rings, and other functional groups. UF membranes have what is known as molecular weight cut off (MWCO) that matches with the average molecular weight of HA. Unfortunately, the major issue with using ultrafiltration is the high fouling rate. The NOM builds up on the membrane and decreases the flux, which inhibits their ability to produce clean water. Much of the major research centered on ultrafiltration membrane is removal of fouling. Some promising candidates for the removal of fouling are advanced oxidative processes (AOP).

AOPs have been extensively investigated fore the direct removal of NOM in water, but are usually limited by their high cost (Bekbolet, Uyguner, Selcuk, Rizzo, Nikolaou, Meriç, Belgiorno, 2005). Common AOP's include the photocatalytic effect of activating titanium dioxide with UV light, ozone treatment, or hydrogen peroxide in the presence of a catalyst. All three methods lead to the formation of hydroxyl radicals which are highly reactive and can oxide organic matter. Because the NOM is deposited directly on the surface of the membrane during fouling, AOPs are a strong candidate in removing that fouling.

At Shanghai Jiao Tong University, hybrid ultrafiltration membranes have been developed for removing NOM. Like conventional UF membranes, they are highly effective in removing NOM from water until the fouling drastically decreases their performance. But these membranes have an immobilized layer of TiO_2 that promotes self-cleaning under UV light. Integrating this AOP has already shown to successfully remove fouling and recover the flux of the membrane.

This project looked at exploring other AOPs and testing their effectiveness in removing fouling from the hybrid UF membranes. The AOPs were tested individually and in combination with each other. The overall experiments would focus on recording the performance of the membrane as they were fouled. After fouling, the membranes would be cleaned and then fouled a second time. The performance of the 2nd fouling would be compared to the first fouling. The best AOP combination would be the one with the highest flux recovery and highest rejection rate of contaminates.

Theoretically, this could serve as a model if these membranes and AOPs were to be scaled up to an industrial scale. UF membranes would remove NOM from water, likely as a pretreatment for some other purification method such as reverse osmosis or disinfection. Once fouled, the membranes would stop producing purified water and would under go an AOP cleaning procedure to remove the fouling. Ideally, this AOP would be simple and effective at recovering flux while ensure the proper quality of the permeate. After being cleaned, the membrane would be returned to service to start the process over again.

Section 2 Background

2.1 Water Issues World Wide

All over the world, the issue of water scarcity is becoming more prevalent. The current estimate is that 700 million people are suffering from water scarcity (UN 2014). This is due to a variety of issues such as available water verses demand, climate change, and human activity. With growing population and increased industrialization, this problem is expected to worsen (IWMI, 2014).

For China, with a population of over 1.3 billion people and with the fastest growing economy in the world, this issue is quickly become a major obstacle to the peoples well being. Like many countries in the world, China is facing a water crisis. Current sources of water are primarily derived from rivers and ground water. Northern China derives most its water from ground water, but due to over extraction; the water tables are falling to record lows and quickly being depleted. Southern China, while home to 80% of the available water in the country, derives most of this from surface waters such as rivers and lakes (FAO, 2015). One attempt to address this issue is the South to North Water transfer project, an attempt to bring water from the south to the parched north. But even if this project succeeds, the water will be significantly polluted once arriving and require significant treatment.

Even water rich southern China is having water issues; due to rapid industrialization, pollution is a major threat to water resources. This is due to the run off of wastewater from several large industries and sewage. Pollution from heavy metals, bacteria, and organic contaminates are reaching critical levels and threatening the secure access to freshwater. Access to clean freshwater is one of the most important resource for a nation. This promises to make water treatment a growing field for the foreseeable future and part of the solution to the global water shortage issue.

2.2 Water Pollution

Water pollution is such as a diverse topic because there are so many different kinds of pollution. Pollutants can range from chemical contamination, such heavy metals, pesticides, or fertilizers or biological pathogens that cause illnesses. A major source of pollution is natural organic matter (NOM), big organic complexes with many different and stable functional groups such as aromatics and rings. NOM can come from natural sources such as biomass near water sources or increasingly more common, run off from human activities. It is estimated that 80% of NOM is humic in nature. When run through common disinfection processes, these molecules can be convert to harmful disinfection byproducts that are known carcinogens (Nikolaou, Golfinopoulos, Lekkas, Kostopoulou, 2004).

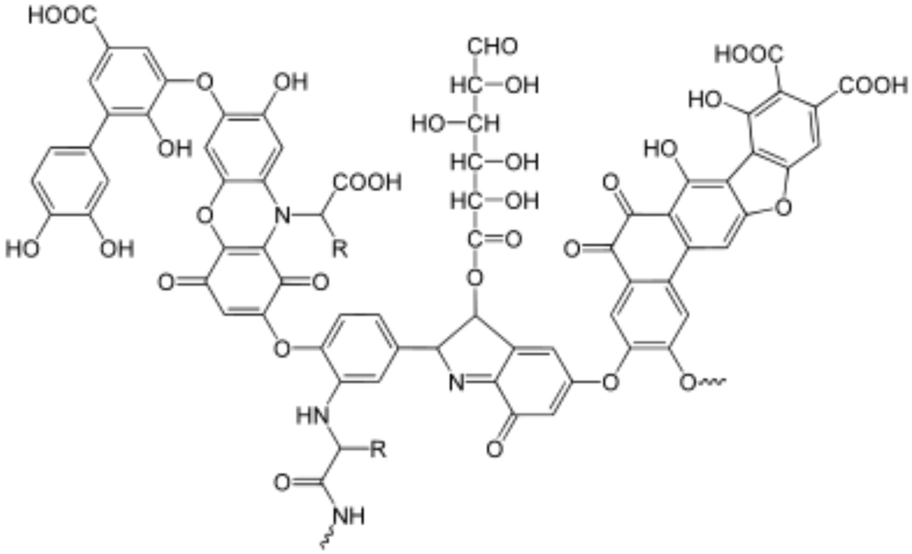

Figure 1 General structure of Humic Acid (Wikipedia)

2.3 Membrane Water Treatment

Ultrafiltration membranes have been used in industry for years. UF membranes separate material based on size with their selective pores which can be controlled for various applications. This sizing of UF membranes is defined as the molecular weight cut off of (MWCO) which can range from 10^3-10^6 Daltons (Pall, 2015). Most UF membranes typically operate around 0.2-0.7 MPa (AIChE, 2015). This technology has been extensively used in pharmaceutical applications for the separation of biological molecule such as antibodies.

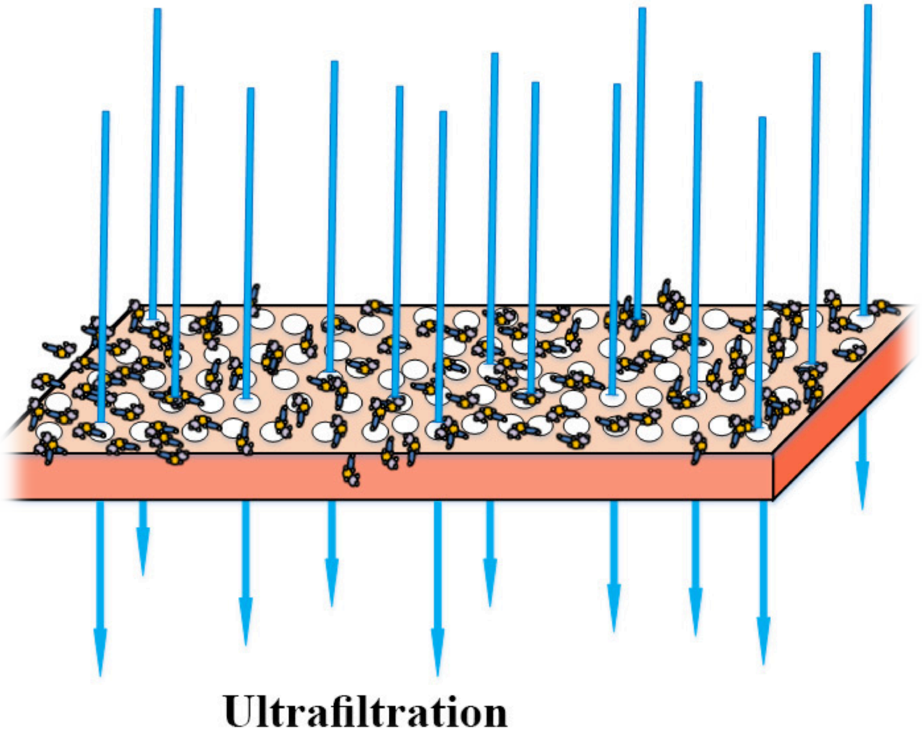

Figure 2 Ultrafiltration schematic

UF membranes are of interest for wastewater treatment because of their ability to filter out NOM. By doing this, the amount of DBPs in treated drinking water can be reduced. NOM pollutants are composed of very large molecules that usually range from 5,000-50,000 Daltons (Zularisam, Ismail, Salim, 2006), which is ideal for UF. The major issue facing UF membranes is how quickly they foul. NOM rapidly accumulates on the surface of the membrane, clogging pores and reducing membrane performance.

2.4 Advanced Oxidative Processes

There are several different types of advanced oxidative processes (AOP). These chemical reactions focus on the generation of hydroxyl radicals which are one of the most highly oxidative species known. The hydroxyl radical can be generated many different ways. One method is to use $TiO_{2,}$ which is a photocatalyst. When activated by UV light, and sometimes even visible light, an exited electron leaves the surface and results in an electron hole. When water absorbs onto the surface of the hydrophilic TiO_2, the high reactivity of the electron hole will split the water molecule and release a hydroxyl radical. (Hashimoto, Irie, Fujishima, 2005). Another source of hydroxyl radicals is H_2O_2, breaking the bond between the two oxygen releases two-hydroxyl radicals. There are several catalysts that can split this bond, a common one is any source of Fe^{2+} ions, and this is called the Fenton reaction. Another common catalysis is UV light, which causes H_2O_2 to under go photolysis (Chang, 2000). The other most common AOP is ozone, which can be produced several ways but the two most common are electric arc discharge and UV light. Then the ozone is dissolved into water where it undergoes a reaction that generates hydroxyl radicals.

After theses hydroxyl radicals are generated, they rapidly attack organic compounds in the aqueous phase and are capable of destroying stable compounds such as aromatic rings (Chin, Bérubé, 2005). Destroying these complex molecules and removing them from solution helps to minimize the DBP concentration in water as it undergoes further treatment. AOPs are still being extensively researched for their ability to remove NOM from water. Ultimately, whether the NOM is in solution or built up on the surface of a membrane, it can be destroyed by AOPs. This has lead to recent research of using AOPs to remove NOM fouling on membranes. Therefore, AOPs are a very promising answer to the removal of NOM fouling on ultrafiltration membranes.

Section 3 Methodology

3.1 Research Goals

Upon arriving at Shanghai Jiao Tong University, the main goal for this project was to investigate and compare different methods of cleaning hybrid ultrafiltration membranes. Backwashing and turbulent flow would be the two physical means and they would be compared to AOPs. The AOPs used would be the photocatalysis of TiO_2 under UV light, the photolysis of hydrogen peroxide, and oxidation by ozone.

3.2 Results From Previous Research

Cross flow filtration is a well know separation process where applied pressure drives mass transfer across a medium of some type. This medium is generally a membrane that is selective for one material over another. As this happens, the flow of feed liquid is tangential to the surface of the membrane which helps to dislodges molecules too big to pass through. Ultrafiltration, defined by its molecular weight cut-off of (MWCO) of 1,000-1,000,000 Daltons has been extensively used in industry (Shi, Tal, Hankins, Gitis, 2014). They are used in food processing for dairy and cheese production. They have also seen used in desalination for pretreating salt water for reverse osmosis. This separation ability is because of the small pores which block the passage of larger molecules (DOW, 2015). As long as one can control the size of the pores, then they can control the selectivity of the membrane.

A major issue when using ultrafiltration membranes is how rapidly they foul. Generally, when fouled by the small molecules of NOM found in water supplies, a permanent layer immediately bounds to the surface of the membranes. This initial fouling is due to surface interaction of the small molecules and the surface of the membrane. This is generally referred to as irreversible fouling because it can only be removed through chemical means (Song, Elimelech, 1993). Then the selective pores within the membrane are blocked with contaminates. This reduces the number of paths for permeate to travel. As the membrane fouls, more contaminates build up on the surface. This is concentration polarization. As the layer of fouling builds up on the membrane surface, the performance worsens. With this layer of surface fouling, the permeate must not only travel through the membrane with clogged pores, but also must move through the thickening layer of surface fouling.

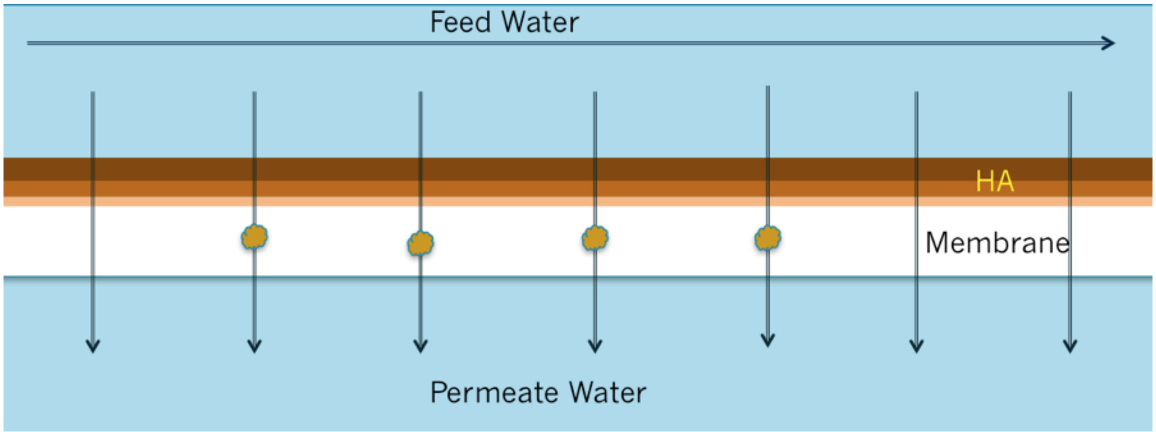

Figure 3 Clogging of pores and the build up of HA on the membrane surface

Previous experiments with these hybrid membranes demonstrated that the addition of TiO_2 to the structure of the membrane increases hydrophilicity. This increase in hydrophilicity improved the flux of water though the membrane. After the membrane became too fouled by NOM, represented as humic acid in the lab, the TiO_2 also aids in cleaning the membrane. When exposed to UV light, the TiO_2 was photocatalytically activated and produced hydroxyl radicles. These radicles are highly oxidative and could break down the humic acid on the membranes and unclog the pores. This allows the membranes to be quickly and noninvasively cleaned. After cleaning, the membranes could be used for further filtration to remove NOM.

Another study examined the effects further modifying these membranes with a surface layer of TiO_2. This layer of TiO_2 was found to further increase the hydrophilicity of the membrane. In addition to increasing the hydrophilicity, the increased area of TiO_2 on the surface greatly increased the self-cleaning ability.

Turbulent Flow:

One way of cleaning membranes is to run pure water at a reduced pressure and higher flow rate. This turbulent flow helps dislodge fouling from the membranes. This also helped to set a benchmark because all of the other cleaning methods would be carried out under similar operating conditions. Unfortunately with the experimental setup, the flow rate of water could not be increased from the ordinary run conditions.

Backwash:

This was the only experiment that operated at a different pressure then all of the others. Periodic backwashing is a common method in industry to remove fouling. The change in pressure direction causes the membranes to flex, which can disturb the cake layer of fouling on the surface of the membrane (Ye, Chen, Le-Clech, 2011). This flexing causes the cake layer to dislodge and come off of the surface. The pores of the membranes, which may be clogged by large molecules, can also be unclogged.

UV and TiO_2:

Activating TiO_2 with UV light and is a well-known AOP and has been used in other studies to destroy NOM. The two most common methods are to use TiO_2 suspended in solution or to fix it upon a substrate. TiO_2 suspended in solution is shown to have a better ability to break down NOM due to the increased surface area, but adds additional complications because it must be removed from the treated water (Kent, Montreuil, Brookman, Sanderson, Dahn, Gagnon, 2011). TiO_2 fixed to a substrate is adequate for removing NOM and does not need to be removed down the line.

The key features of the hybrid ultrafiltration membranes in these experiments is the fixed layer of TiO_2 for self-cleaning. It has been demonstrated that when exposed to UV light, the TiO_2 breaks down the built-up HA on the surface and within the pores of the membranes. As shown in Figure 4, this is due to the hydroxyl radicals generated by the activation of TiO_2 by UV light.

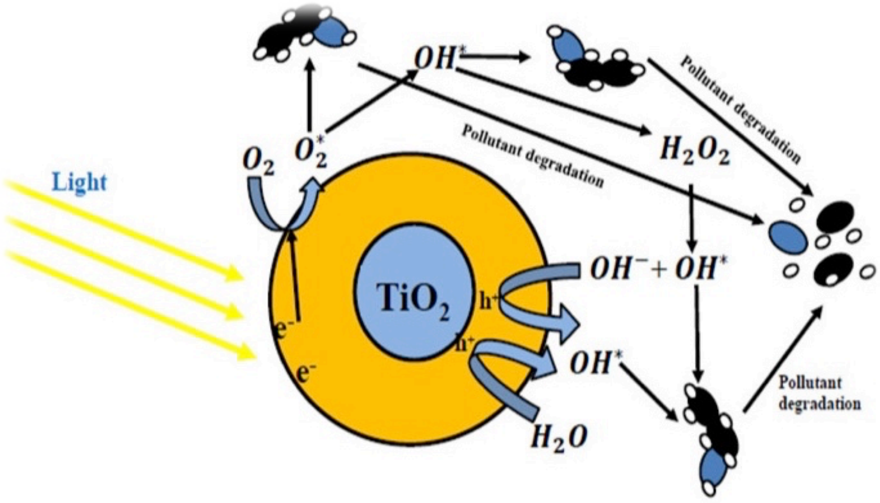

Figure 4 UV light activating TiO_2 and generating hydroxyl radicals

H_2O_2:

Hydrogen peroxide is a very powerful oxidizer and is a source of hydroxyl radicals. When the bond between the two oxygen atoms in the molecules is cleaved, hydroxyl radicals are produced. One way of producing these radicals is to use UV light. With the experimental setup in the lab, the only way to expose the hydrogen peroxide to UV light also involved exposing the TiO_2. The only way to generate these hydroxyl radicals without the activation of the TiO_2 would be to use a source of Fe^{2+} ions in what is known as the Fenton reaction (Kitis, Kaplan, 2007). But, the main feature of the membranes was the photocatalytic effect of the TiO_2, and the focus of this research was on comparing the combinations of AOPs. Due to these factors, the hydrogen peroxide was run by itself with no additional catalyst.

Ozone:

Ozone is a very strong and unstable oxidizer that generates hydroxyl radicals in water. In addition, any double bonds in the HA could be directly oxidized by ozone (Gunten, 2003). Because of its instability, ozone had to be generated onsite in the laboratory. The ozone gas was bubbled into the water used for cleaning the membrane. Due to the lack of equipment for testing ozone concentration in water, this was run as a qualitative test to just to see ozone's cleaning potential for these membranes.

An LCD manufacturer in Taiwan experimented with using ozone to remove fouling from ultrafiltration membranes used for cleaning discharged wastewater (You, Tsai, 2010). On a bench scale test, they used PVDF membranes for their ozone resistance and successfully removed fouling. For their test, they set their ozone generator to 100% with a pure oxygen input and an output of 4.74 grams of ozone per hour.

UV H_2O_2:

With this combination of AOPs, hydroxyl radical radicals were being generated through two separate phenomenons. This first was the photocatalytic reaction with the UV light activating the TiO_2; the second was the UV light splitting the O-O bond in the hydrogen peroxide molecule. The process has been investigated for killing microbes and removing NOM from water directly. Experimentally, it has been found that the optimal concentration of H_2O_2 is between 0.0032-0.0163M (Matilainen, Sillanpää, 2010). At too low of a concentration, there is little effect from the H_2O_2 AOP, but when at too high of a concentration, H_2O_2 acts as a hydroxyl scavenger.

UV Ozone:

In this experiment, the ozone was dissolved into the cleaning water just like before. The UV light was run to activate the TiO_2 layer. In theory, hydroxyl radicals would be generated by the photocatalytic effect of the TiO_2 and the ozone in the water. One study found that ozonizing wastewater beforehand improved the efficiency of UV treatment (Puspita, Roddick, Porter, 2015). This was attributed to the ozone oxidizing UV absorbing compounds. However, it is known that ozone can absorb shorter wavelengths of UV light (EPA, 2010), potentially blocking it from reaching the TiO_2. So there could be some potential inference with the two AOPs.

H_2O_2 Ozone:

The Hydrogen Peroxide was added to water at the desired concentration. This water was then ozonated and used to clean the membrane. In this reaction the H_2O_2 speeds up the rate that ozone generates hydroxyl radicals (Katsoyiannis, Canonica, Gunten, 2011). By doing this, the extra radicals would be able to more readily oxidize HA. In addition, any compounds that were originally resistant to direct oxidation by ozone and would be vulnerable to increased concentration of hydroxyl radicals.

UV H_2O_2 Ozone:

The procedure for H_2O_2 and Ozone was replicated but with the addition of the UV light. This allowed for the three AOPs to work together. A study that looked at the potential treatment of wastewater from a winery found that a combination of UV light, ozone, and hydrogen peroxide were very effective in removing contaminates (Lucas, Peres, Puma, 2010). Though this worked for them, a major difference is that the UV light used in their experiment was not used for activating TiO_2, but only for the photolysis of H_2O_2. For removing the fouling from the membranes, the UV light would activate the TiO_2 and photolysis the H_2O_2. The H_2O_2 would also increase hydroxyl radical production from the ozone.

3.3 Equipment For Testing

The membranes were run in a custom built cross flow membrane filtration unit. The unit featured a quartz crystal glass that would allow UV light to activate the TiO2 catalyst embedded on the surface. The unit was capable of Pressures from 0.01 to 0.2 MPa. With an adjustable flow that ranged from 0.02 to 0.6 L/m of fluid.

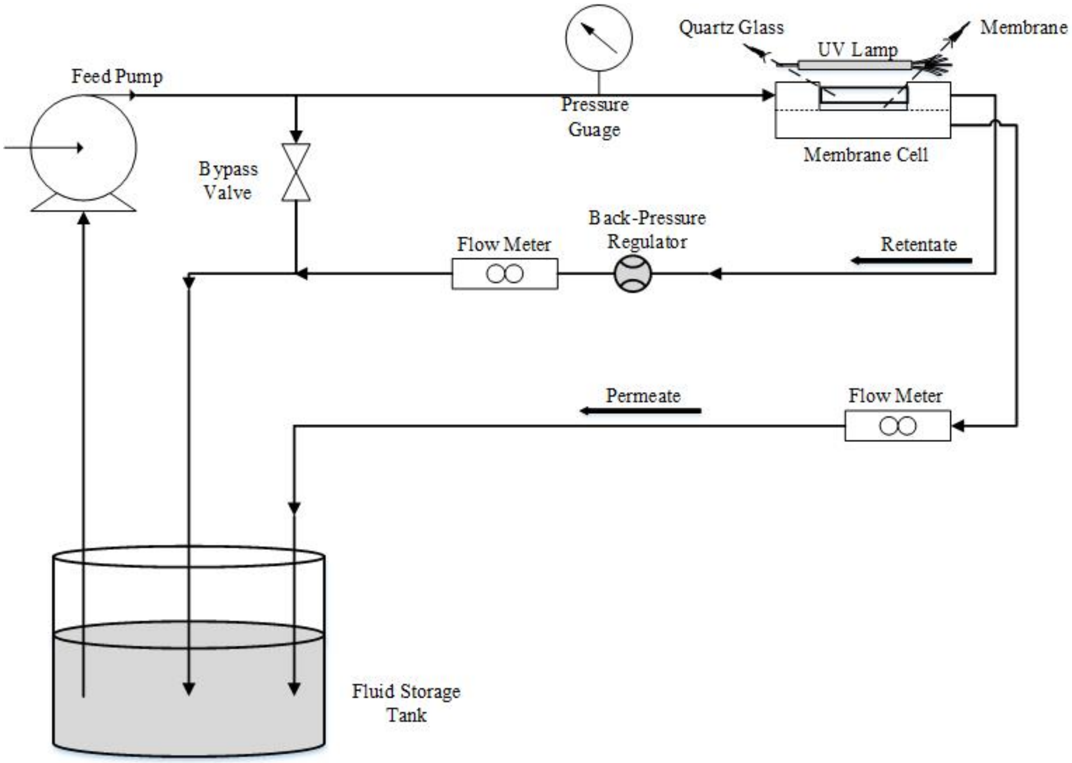

Figure 5 Schematic of the cross flow filtration unit used

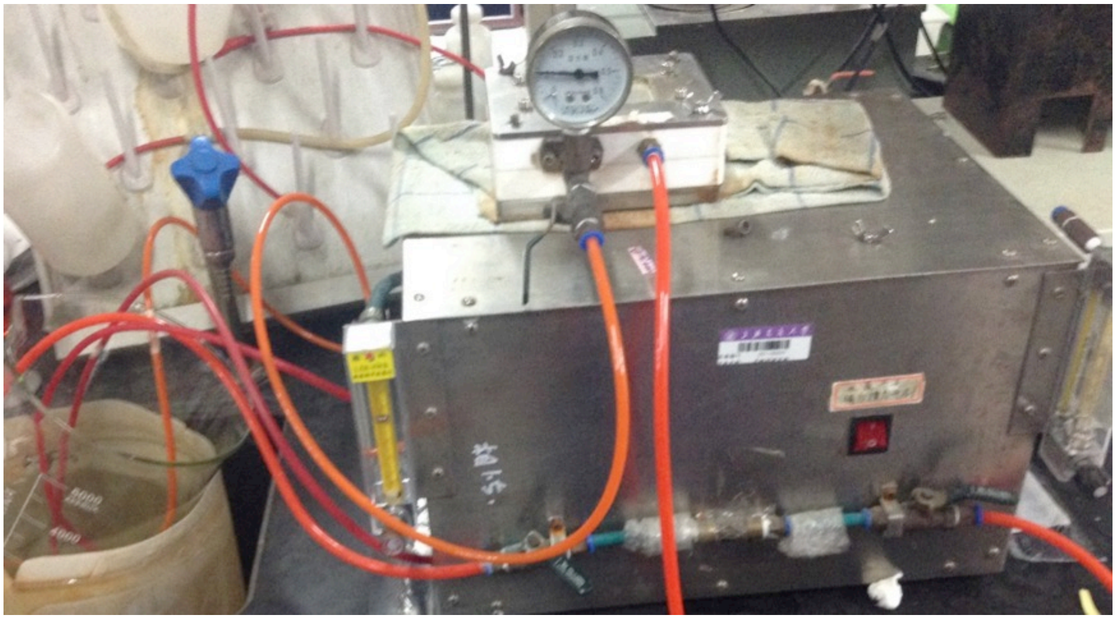

Figure 6 The actual filtration unit used

Humic acid (Sigma-Aldrich) was mixed to an initial concentration of 200 ppm by adding 0.200 grams to 1 liter of pure water (Millipore). This mixture was diluted to 2ppm during experiments to best mimic polluted water.

Figure 7 Concentrated Humic Acid 200 ppm

Concentrations of Humic Acid were measured with a UV spectrometer set to 254 nm. At this wavelength, the aromatic bonds in the HA absorbed the most UV light. Absorption of the UV light was linear with increasing concentration.

Figure 8 The spectrometer used for detecting HA concentration

The permeate and reservoir samples were placed in crystal vials 1 cm in width. The vials were cleaned prior to experimenting to reduce the HA buildup on their sides. One vial would be used for sampling while another held pure water. This way, while HA built up on the side of the vial, the vial with clean water could be used to track the error of the sampling vial.

Figure 9 The crystal vials used for holding permeate and feed samples

For activating the TiO_2 layer on the surface of the Ultrafiltration membrane, a UV lamp with a peak output of 365 nm light was used (Bilon Corporation, China)

Figure 10 The UV light used on the membranes

Hydrogen Peroxide was initially at 30% concentration. It was pipetted to the pure water reservoir used for membrane cleaning to achieve the desired concentration.

Figure 11 Concentrated 30% hydrogen peroxide

Ozone had to be generated onsite with an electric arc ozone generator. Atmospheric air would be pumped through the machine were the ozone would be made and passed though an air stone. The amount of ozone dissolved into the water would be dependent on temperature, contact time, and the half-life of the ozone. Because there was no equipment to measure the ozone concentration, this was turned into a qualitative test to see what the effects of ozone on PVDF ultrafiltration membranes and its ability to remove fouling. The ozone generating level was turned to its highest level of 10 grams per hour and an airflow rate of 0.192 cubic meters per hour.

Figure 12 Ozone being bubbled into the water with an air stone

3.4 Membranes

The ultrafiltration membranes were composed of polyvinylidene fluoride (PVDF) and TiO_2 nanoparticles. A thin layer of TiO_2 nanoparticles were immobilized on the topside of the membrane in the casting procedure. The membrane solution was casted on glass plates and coagulated in pure water. After being cut to size, the membranes were compacted by running them in the membrane machine with pure water for 30 minutes at 0.1MPa and 0.5 l/m. This was done because the flux of the membrane decreases as it is compacted until stabilizing after approximately 30 minutes. As seen in figure 13, this leave defined imprints from the support screen in the membrane. After this, the flux for pure water through the membrane was recorded. Theoretically, the flux of the membrane during any experiment should not exceed this value. Initial experiments utilized membranes made by Hassan Younas. Membranes were made for subsequent experiments. A detailed description is in the appendix.

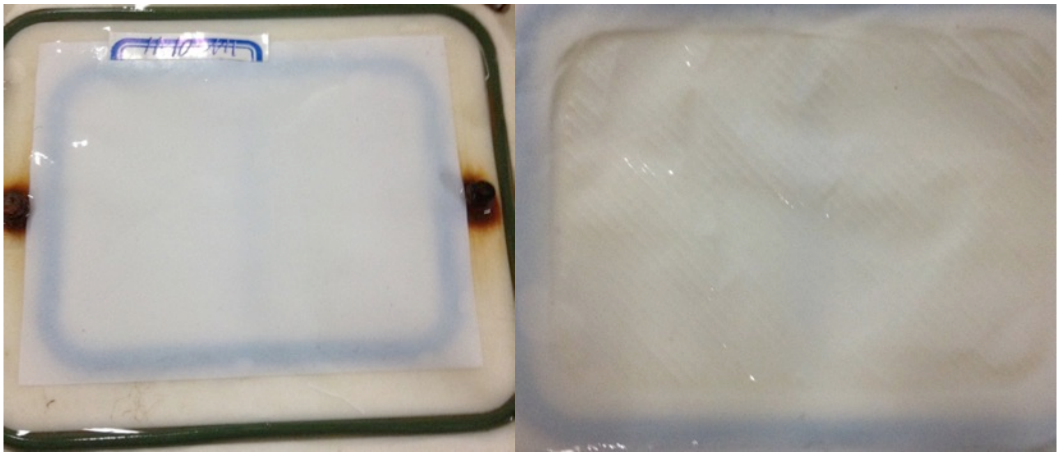

Figure 13 Before and after compaction of membrane

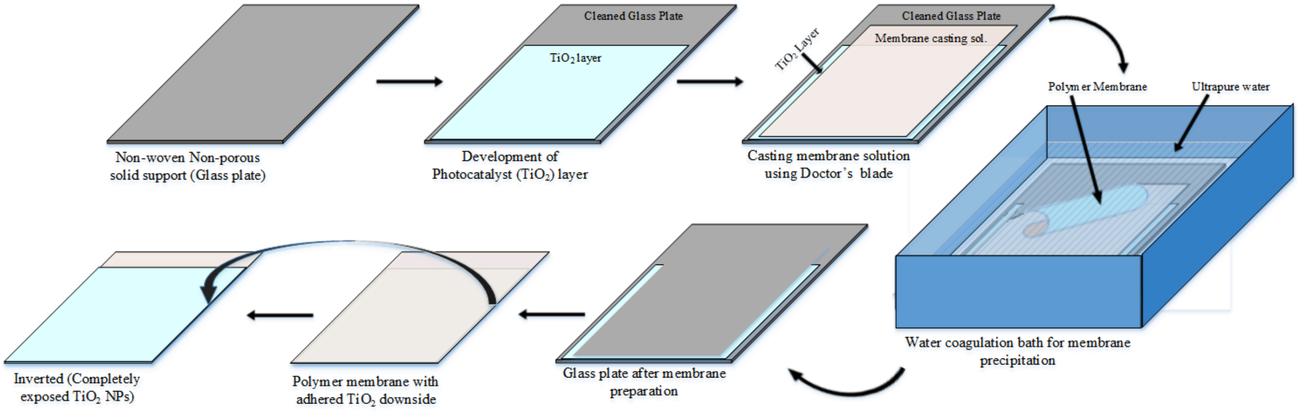

Figure 14 Process flow for making the hybrid ultrafiltration membranes.

3.5 Procedures

The general layout of the experiments was to initially foul the all of the membranes equally. After the membranes were fouled, they were cleaned with a variety of cleaning methods. After being cleaned, they were fouled again with the same procedures as their first fouling. Measuring their flux and selectivity while filtering HA solution allowed the membranes to be compared. The flux of pure water was also measured for the membranes before both 1st and 2nd fouling.

3.5.1 First Fouling

After the membrane was compacted and the initial flux of pure water was recorded, it was ready to be fouled. A 2 liter solution of 2ppm HA was made in a 5 liter beaker. The beaker was immersed in a room temperature water bathe with a continuous supply of tap water to help regulate the temperature. The starting concentration of the HA was measured with the UV spectrometer. The pump was switched on, after the air had evacuated the system, the pressure was set to 0.1 MPa, and the volumetric flow rate of the feed was set to 0.5 l/m. At this point, a timer was started, and the initial permeate was collected. This permeate was massed and the HA concentration was also measured in the spectrometer. The permeate flow rate, along with the concentration of HA in the permeate and reservoir was recorded every 10 minutes for the next 90 minutes. After all data points were taken, the pump was shut off, and the membrane was removed before the change in pressure would cause deformation by stretching.

3.5.2 Cleaning the membranes

Cleaning with pure water

The fouled membrane was placed in the membrane carrier. 2 liters of pure water were placed in the 5-liter beaker. The beaker was placed into the temperature regulating water bath. The pump was turned on and the flow rate of water was brought to 0.5 l/m, and the pressure was 0.05 MPa. For one hour, the membrane was washed. After 1 hour had passed, the water was replaced with 2 more liters of pure water. This time, the pressure was returned to 0.1 MPa and run for 30 minutes. The flux of pure water was then recorded for the membrane. Afterwards, the pump was shut off and the membrane was removed, ready for a second fouling.

Cleaning by backwash

The fouled membrane was placed upside down in the membrane carrier. 2 liters of pure water were placed in the 5-liter beaker. The beaker was placed into the temperature regulating water bath. The pump was turned on and the flow rate of water was brought to 0.5 l/m, and the pressure was 0.1 MPa. After 1 hour had passed, the water was replaced with 2 more liters of pure water and the membrane was returned to its proper position. The membrane ran at 0.1 MPa and 0.5 l/m for 30 minutes. The flux of pure water was then recorded for the membrane. Afterwards, the pump was shut off and the membrane was removed, ready for a second fouling.

Cleaning with UV

The procedure for cleaning with pure water was repeated with this experiment. The only difference was that during the cleaning, the membrane was exposed to UV light for the 1-hour duration. Also, every 10 minutes during the clean, a permeate sample was taken at the reduced pressure to observe the performance of the cleaning.

Cleaning with H_2O_2

The same procedure was used as the pure water cleaning procedure. Like the UV experiment, permeate measurements were taken every 10 minutes to observe the change in flux during the course of the cleaning. Because of a previous study that determined the optimal H_2O_2 concentration to be between 0.0032-0.0163M, the average 0.0098 M was used. So for the 2-liter cleaning water solution, 2.1 ml of the 30% H_2O_2 solution was added.

Cleaning with ozone

Being the first time ozone was used to clean these ultrafiltration membranes in this laboratory setting, the initial procedures for this experiment were modified for further experiments utilizing ozone. Trying to be consistent with previous experiments, 2 liters of pure water were placed into the 5-liter beaker. The ozone machine was turned on to the maximum output and flow rate setting. As soon as the air stone was placed into the water with the lines for the membrane machine, the pump was turned on. Initially, the procedure called for 1 hour of cleaning. But this was increased to 2 hours during the experiment to observe the continued effects of ozone exposure on the membrane. Permeate measurements were taken every 10 minute to record the progress of the cleaning. After cleaning, the water was changed with 2 liters of pure water and the membrane was run for 30 minutes a 0.1 MPa to get a new flux for pure water.

Cleaning with UV and H_2O_2

The procedure for cleaning with H_2O_2 was repeated with the addition of UV light. In this cleaning, the concentration of the hydrogen peroxide was increased to 0.0163 M, so 3.5 ml of the 30% solution was added to the cleaning water. After the pump was started and the UV light was turned on, permeate samples were taken every 10 minutes to record the changing flux. The entire cleaning was 1 hour. Permeate readings were taken every 10 minutes.

Cleaning with H_2O_2 and ozone

The amount of pure water was increased to 3 liters to allow for better head and reduce the amount of bubbles entering the pump system. Because of the increased amount of water, 5.3 ml of the 30% hydrogen peroxide was added to keep the concentration at 0.0163 M. This kept the hydrogen peroxide at the same concentration as the UV H_2O_2 cleaning. The water was ozonized for 30 minutes before running the pump to ensure fully ozonated water. The pressure and flow rate were identical to the previous ozone experiment. Permeate samples were collected every 10 minutes. The procedure for collecting a pure water flux was repeated afterwards

Cleaning with ozone and UV

Starting with 3 liters of cleaning water like the H_2O_2 ozone cleaning experiment, the water was ozonized for 30 minutes before running the pump. After starting the pump, the UV light was switched on for the 1 hour cleaning period. The pressure and flow rate were identical to the previous ozone experiment. Permeate samples were collected every 10 minutes. The procedure for collecting a pure water flux was repeated afterwards

Cleaning with UV, ozone, and H_2O_2

The procedure from cleaning with H_2O_2 and ozone was repeated. After starting the pump, the UV light was activated and the cleaning process lasted for 1 hour. Permeate measurements were taken every 10 minutes during the cleaning. The procedure for collecting a pure water flux was repeated afterwards

3.5.3 Second Fouling Performance

The same procedure for the first fouling was carried out for the second fouling. A 2-liter 2ppm HA solution was made up and the membrane was fouled. Flux and concentrations of HA in the permeate were measured every 10 minutes.

3.6 Analysis of the Data

For measuring the flux of the membranes, both the physical flux, in terms of liters per square meter per hour (LMH), and relative flux are used. Measuring the flux in LMH offers real world performance data critical to the design of process system. While relative flux allows for the change in flux of a single membrane to be easily analyzed throughout its fouling and cleaning.

Permeate reading were measured in grams collected per a set amount of time, usually 30 or 60 seconds. It was assumed that the humic acid and had no effect on the density of the water. Therefore, the volumetric flow rate of the permeate could be calculated with the following equation

$$\dot{v} = \frac{m}{\rho t}$$

Where m is the mass of the permeate in grams, ρ is the density of the permeate g/l, t is the collection time for the permeate in hours, and $\dot{v}$ is the volumetric flow rate of the permeate l/h

The flux can then be calculated by dividing the volumetric flow rate of the permeate by the area of the membrane.

$$J_v = \frac{\dot{v}}{A}$$

Where J_v is the flux in l/m^{2}h (LMH) and A is the area of the membrane.

Relative flux allows for the performance of the membrane to be easily tracked and compared to other membranes over the course of the experiment. For relative flux, the first permeate reading from the first fouling is set as a benchmark. All subsequent measurements are reported with respect to this value. There is also a value for the flux of pure water, which is recorded before the first fouling.

$$J_R = \frac{J}{Jo}$$

Where J_R is the relative flux, Jo is original flux, and J is the flux a measured throughout the course of the experiment.

The removal of HA by the membranes was evaluated by looking at the removal rate.

$$R(\%) = 100\left(1 - \frac{A_p}{A_f}\right)$$

Where A_p is the absorbance of HA in the permeate and A_f is the original absorbance of HA in the feed. A high rejection rate means that the majority of the HA contaminates are being removed.

Section 4 Results and Discussion

4.1 Physical Cleaning of Membrane

Washing with Water

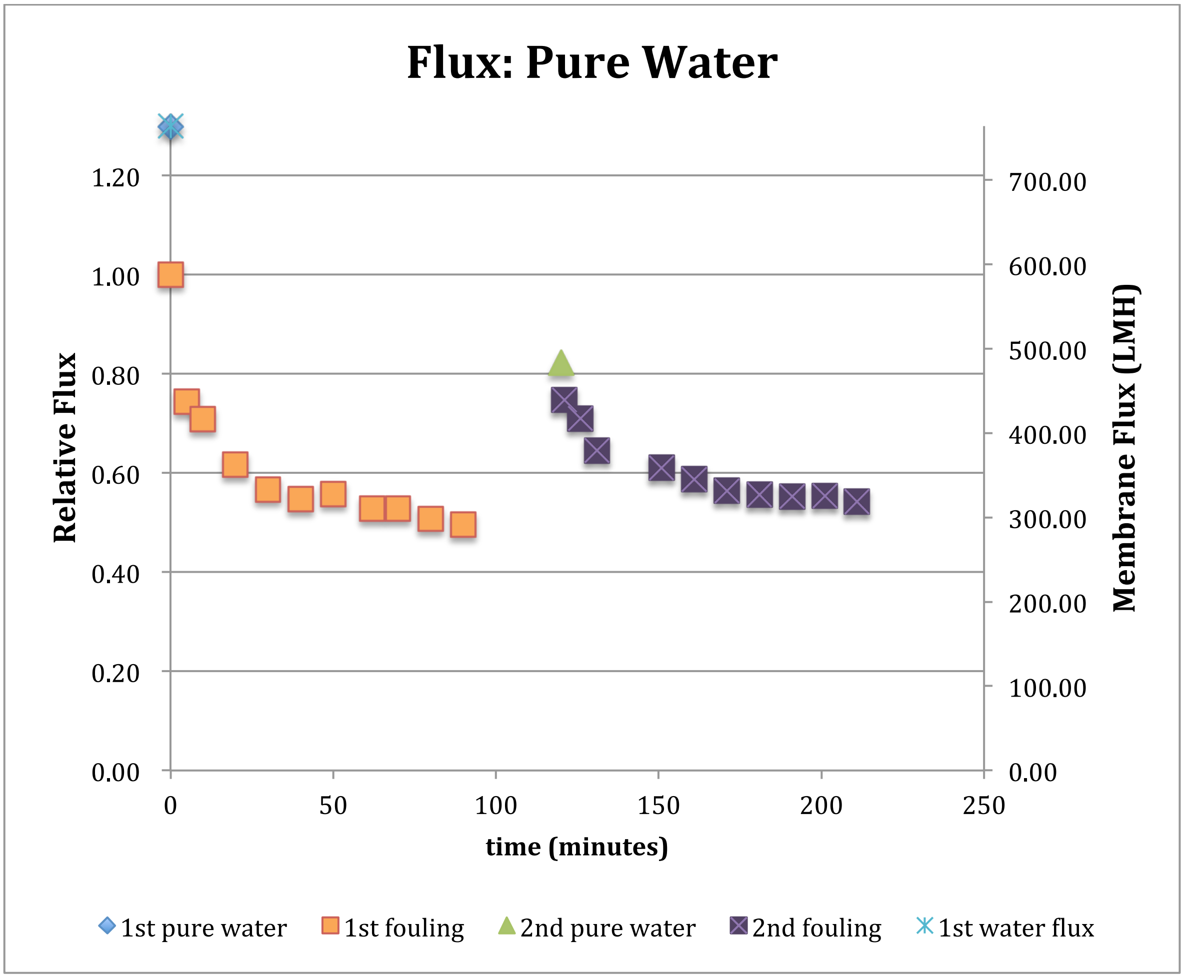

Figure 15 Cleaning with pure water, flux recovery

The overall process shows how the flux of the membrane decreases as it was fouled. After cleaning, the there is flux recovery present during the second fouling. Washing with water saw about 77% of the flux recovered. Towards the end of the 1st fouling, the relative flux had reduced to about 50% while during the 2nd fouling; the relative flux had reduced to about 55%.

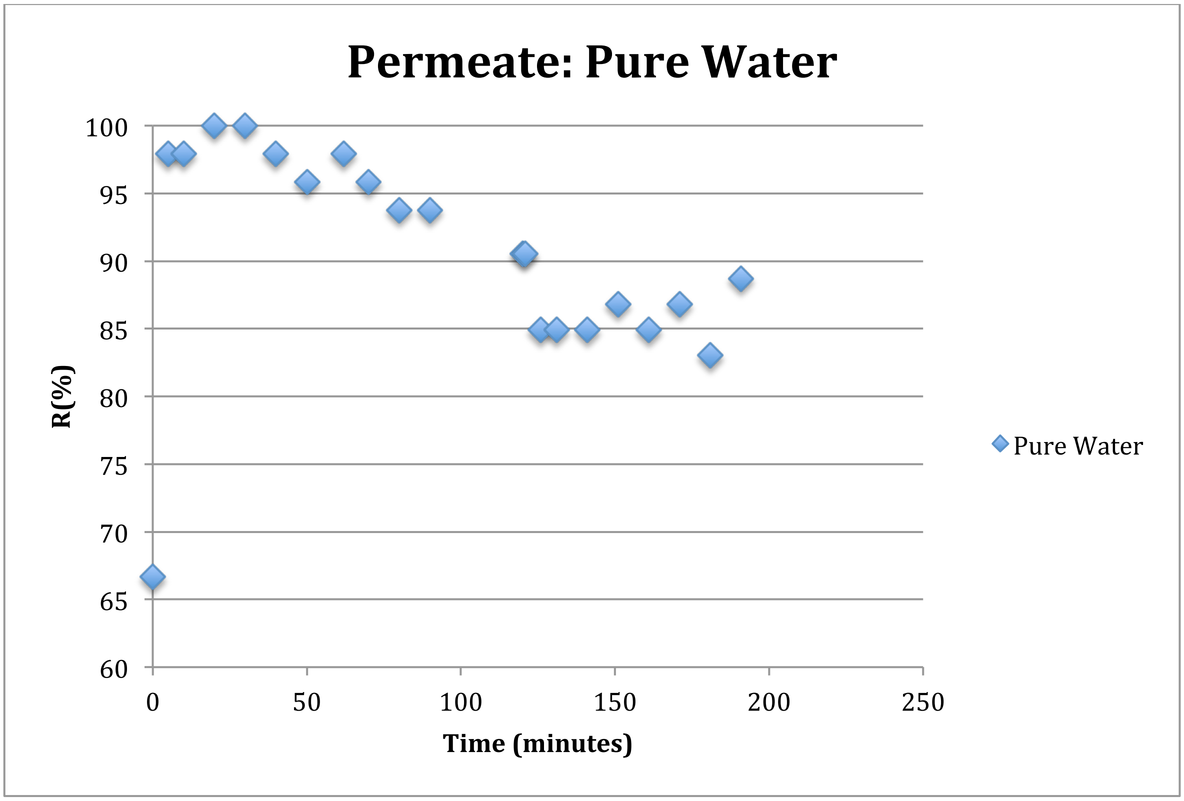

Figure 16 HA in the permeate of the membrane cleaned with pure water

The removal rate R(%) of the membranes steadily declined over the course of the experiment, it was initially around 97% but gradually decreased to 85% during the second fouling.

Figure 17 HA on the membrane, before and after cleaning with pure water

Backwashing

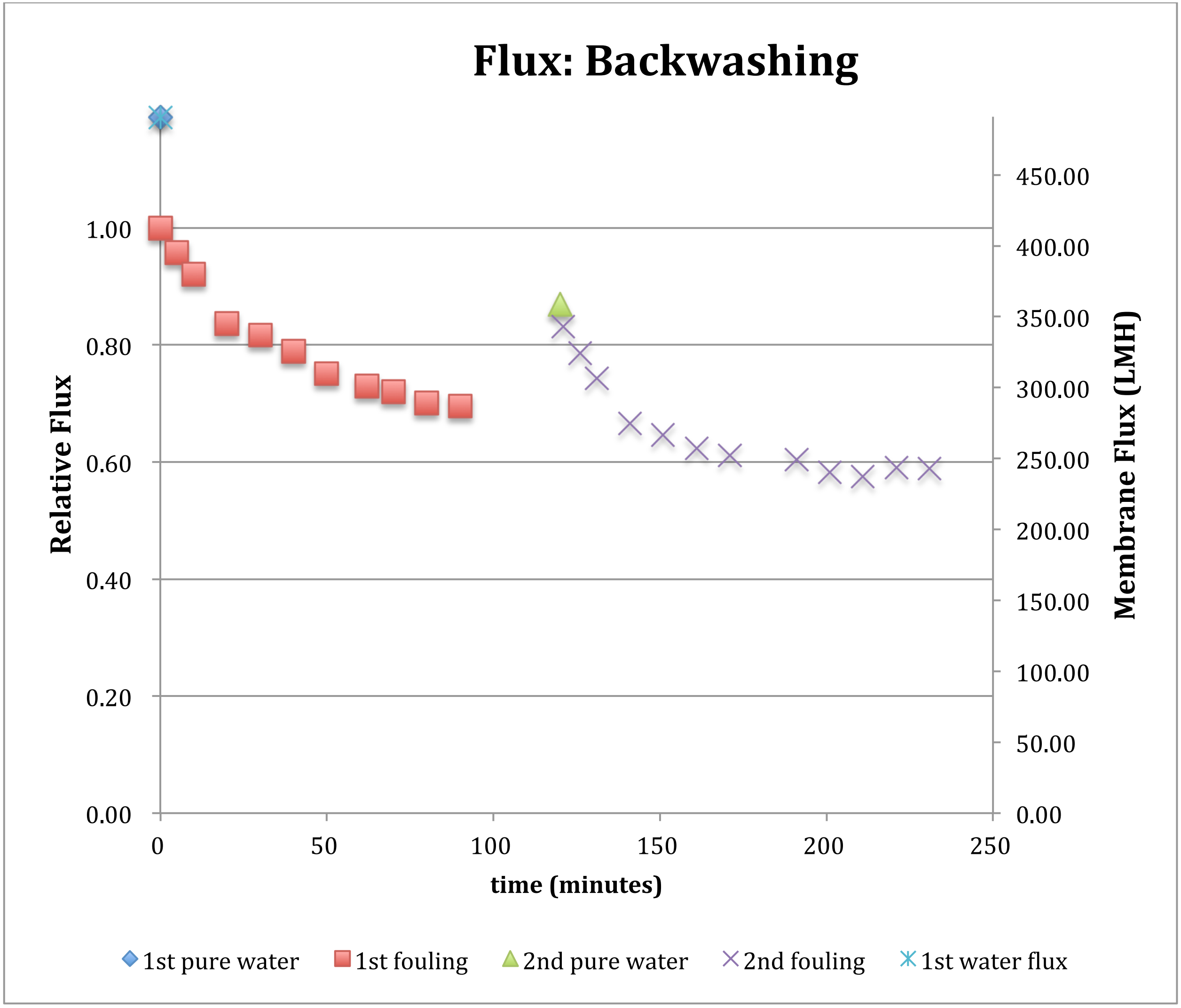

Figure 18 Flux of membrane cleaned with backwash

Backwash also had over 80% of the flux being recovered. During the first fouling, the flux decreased to about 70% but on the second fouling it decreased to below 60%

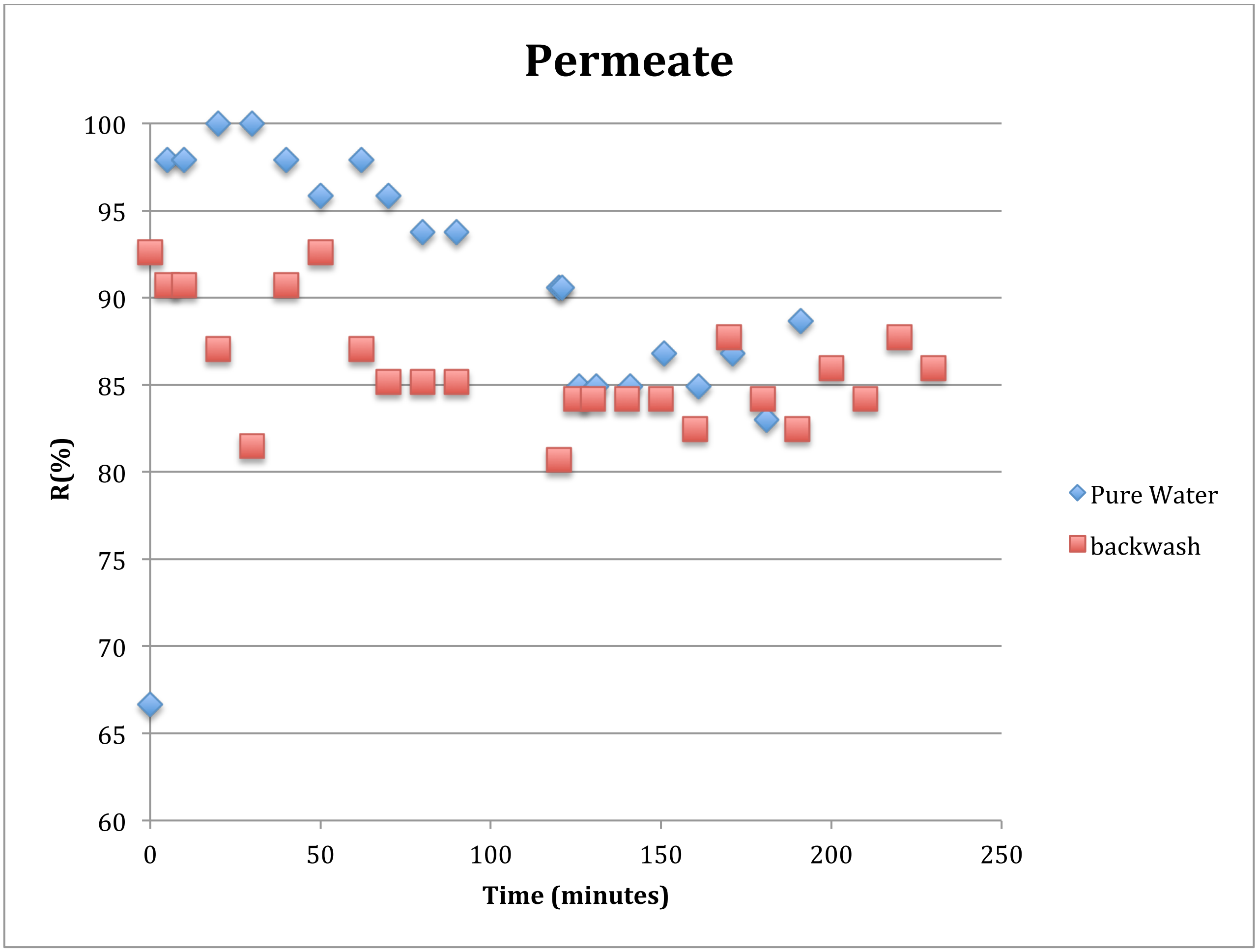

Figure 19 Comparing the permeate of membrane cleaned with pure water vs. backwash

The permeate of the membrane cleaned with backwash had a consistent rejection rate of 81-93%. Though this was lower over all then the pure water it stayed more consistent and did not have the decreasing trend the membrane cleaned with pure water.

4.2 AOP Cleaning of Membrane

UV light

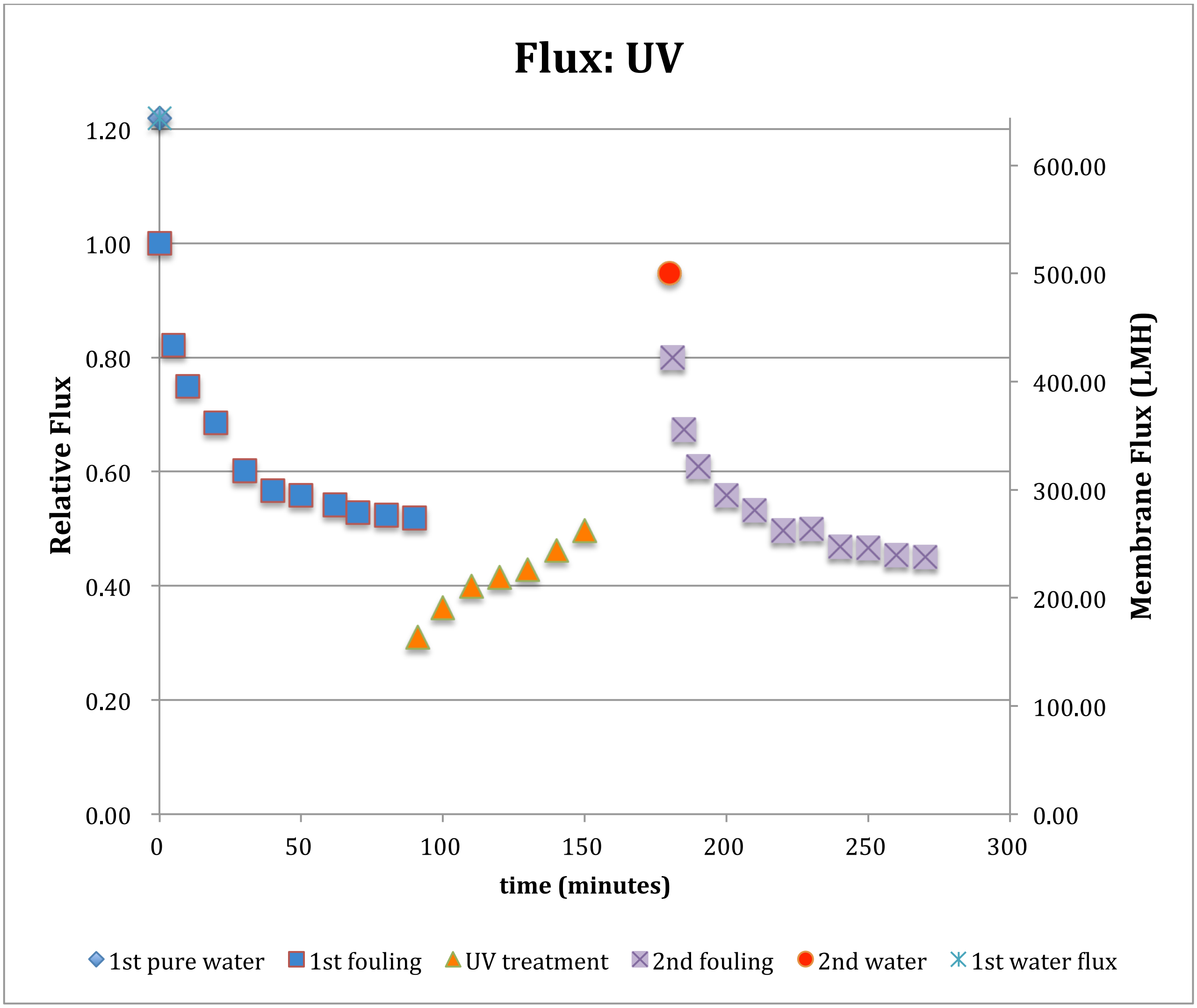

Figure 20 Flux recovery of membrane cleaned with UV/TiO_2 AOP

UV light cleaning brought the membrane to 80% of its original flux. Towards the end of the fouling, the relative flux for the 1st and 2nd fouling were 50% and 45% respectively.

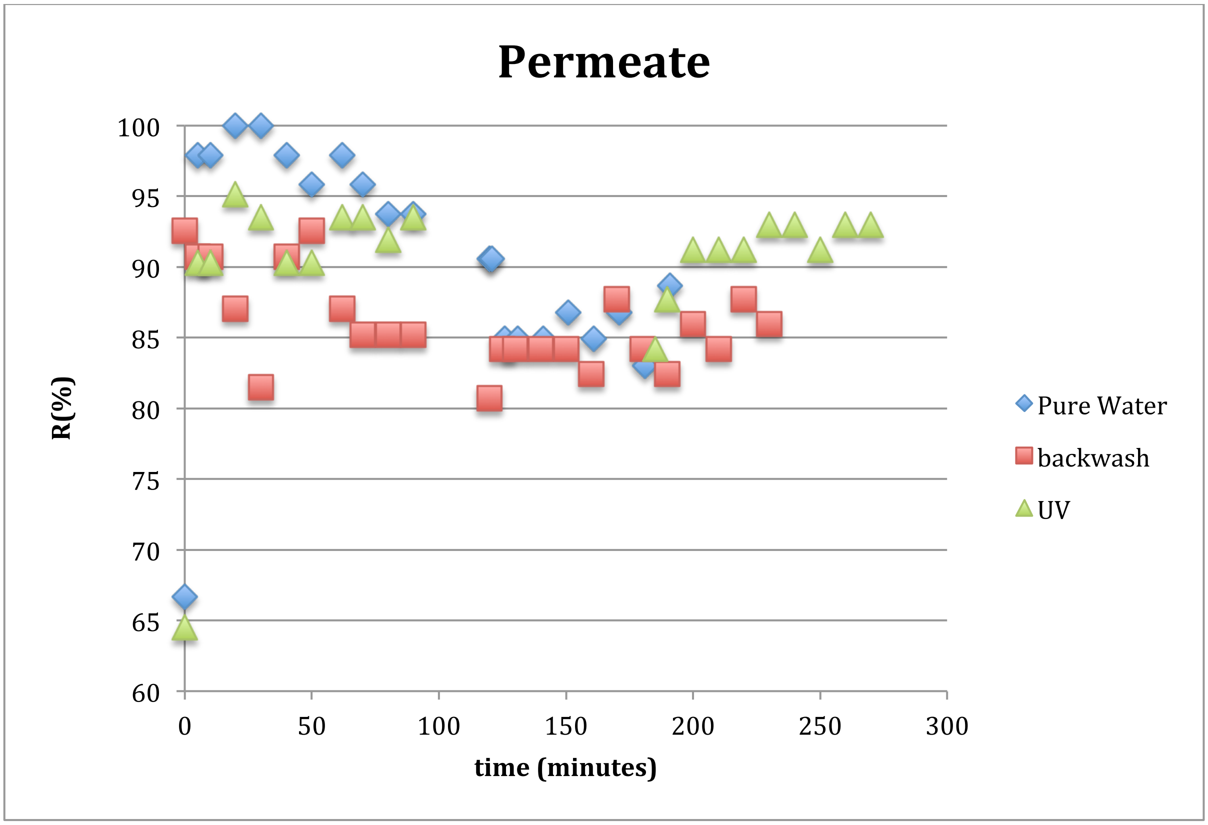

Figure 21 comparing permeates, UV, backwash, and pure water.

The removal rate of the membrane cleaned with UV was also constantly around 90-95 percent for both fouling runs. The removal rate did not decrease as much as the membrane cleaned with pure water. Though the membrane cleaned with UV overall had a higher removal rate then the membrane cleaned with backwashing, both stayed relatively consistent. It is unclear if this is the result of the cleaning process or the properties of the respective membranes.

Figure 22 Change in appearance of membrane while being cleaned.

In figure 22, the photo of the membrane on the left is immediately after fouling. The middle photo is right after being cleaned with UV light. The AOP of UV light activating the TiO_2 oxidized some the HA and added the dark color. After being cleaned with UV light, a new flux of pure water was recorded. As seen in the photo on the right, the pure water during that process washed off some of the oxidized humic acid.

Hydrogen Peroxide

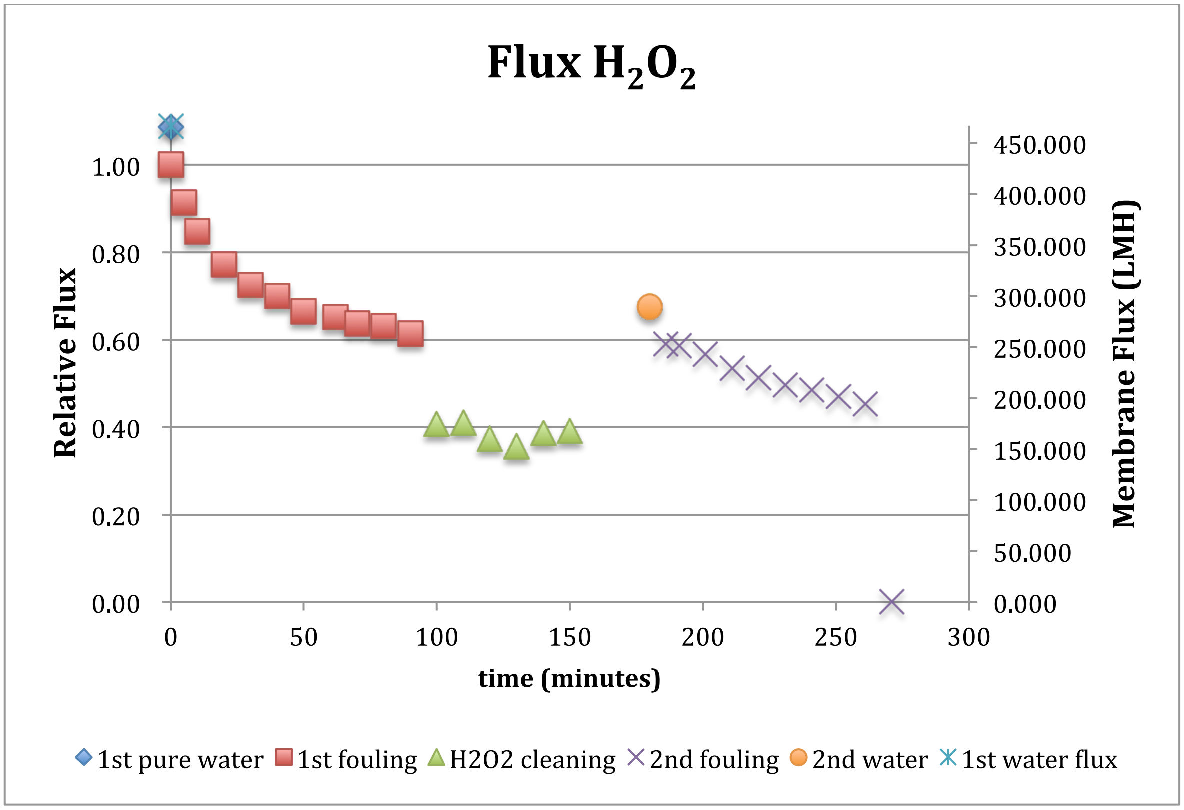

Figure 23 Flux of the membrane cleaned with H_2O_2

Hydrogen peroxide had virtually no flux recovery. Without the UV light to cleave the oxygen-oxygen bond, no hydroxyl radicals were made. Interestingly, despite being under the same turbulent condition as the pure water cleaning method, there was still no flux recovery.

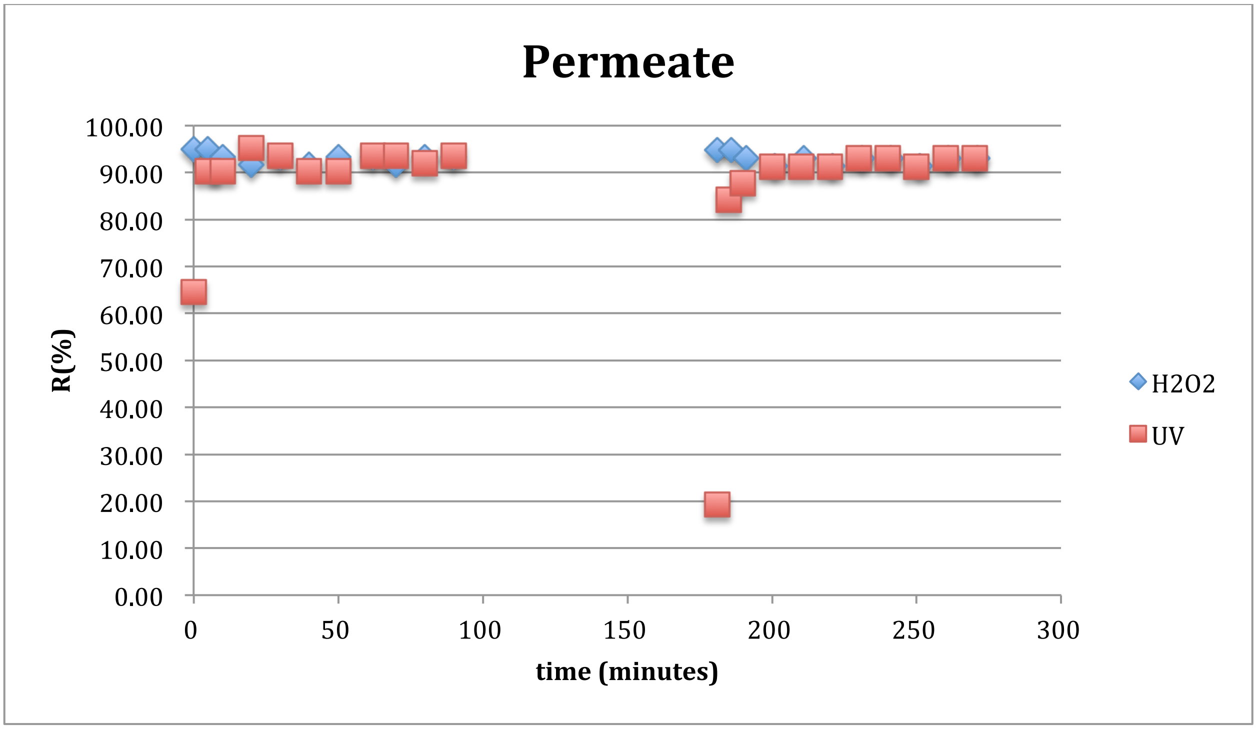

Figure 24 Comparing the permeate of the membranes cleaned with UV and H_2O_2

Comparing the removal rate for the membrane cleaned with UV and the membrane cleaned with H_2O_2 reveals little difference. The initial removal of HA is low for the membrane cleaned with UV for both foulings. But then the removal rate returns to the normal level very quickly. This is because there are larger pores that initially let small amounts of HA pass through but then are quickly clogged by larger HA particles. In figure 25, the image on the left is the membrane after fouling. On the right is after being cleaned with H_2O_2, very little if any HA was removed from the surface.

Figure 25 Before and after appearance of membrane cleaned with H_2O_2

Ozone

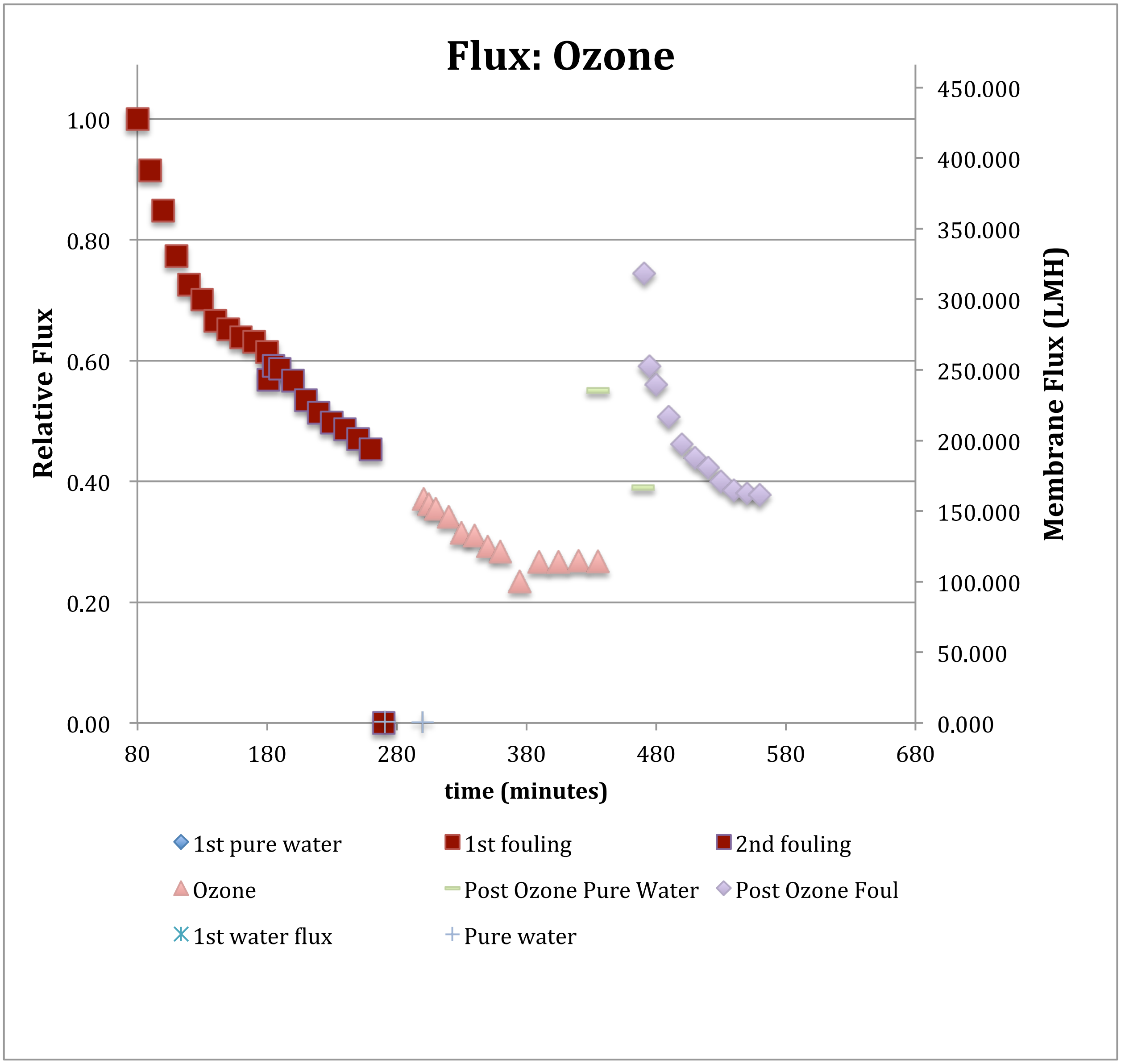

Figure 26 The flux recovery of the membrane as it was cleaned with ozone

To save time, the membrane that was used in hydrogen peroxide cleaning was reused in the ozone experiment. This was because there was virtually no flux recovery from the hydrogen peroxide cleaning. Coupled with fact that the ozone was a qualitative test, reusing the membrane was a simple way to observe the effects of cleaning with ozone. The 1st fouling on the graph is the 1st and 2nd fouling of the membrane cleaned with H_2O_2.

Not only was the ozone ineffective at recovering the flux, but also the flux decreased during the cleaning. Because the flux kept decreasing, the cleaning process was allowed to run for another hour to see what would happen. Eventually the decreasing flux leveled off.

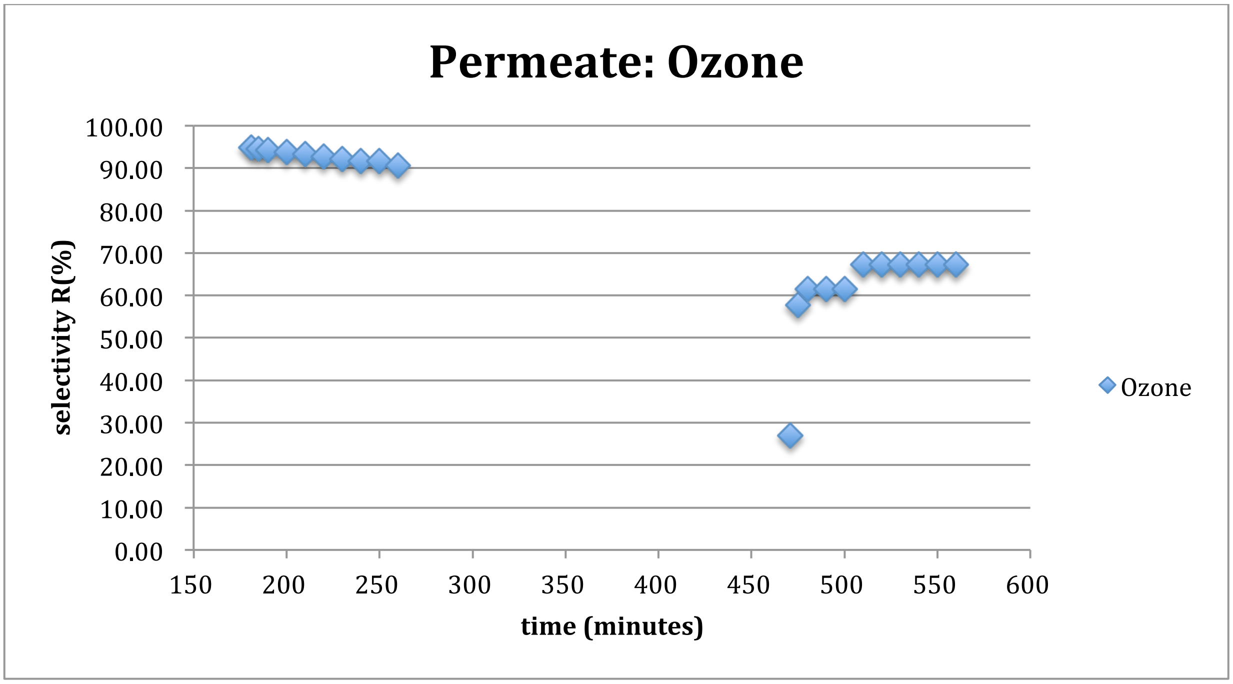

Figure 27 The rejection rate of the membrane cleaned with ozone.

In addition to very little flux recovery, ozone also decreased the selectivity of the membrane. After being washed with H_2O_2 solution, the removal rate was over 90%. But after being cleaned with ozone, the removal rate fell to about 70%. Despite this, the humic acid was still oxidized and removed from membrane making it look very clean

Figure 28 Changing appearance of membrane cleaned with ozone.

In figure 28, on the left is the membrane immediately after fouling, with the brown color coming form the HA. In the middle is the membrane while still in the cross flow unit; it is 90 minutes into the 120-minute clean. The photo on the right is the cleaned membrane, much of the HA has been oxidized and removed from the membrane.

4.3 AOP Combinations

UV and H_2O_2

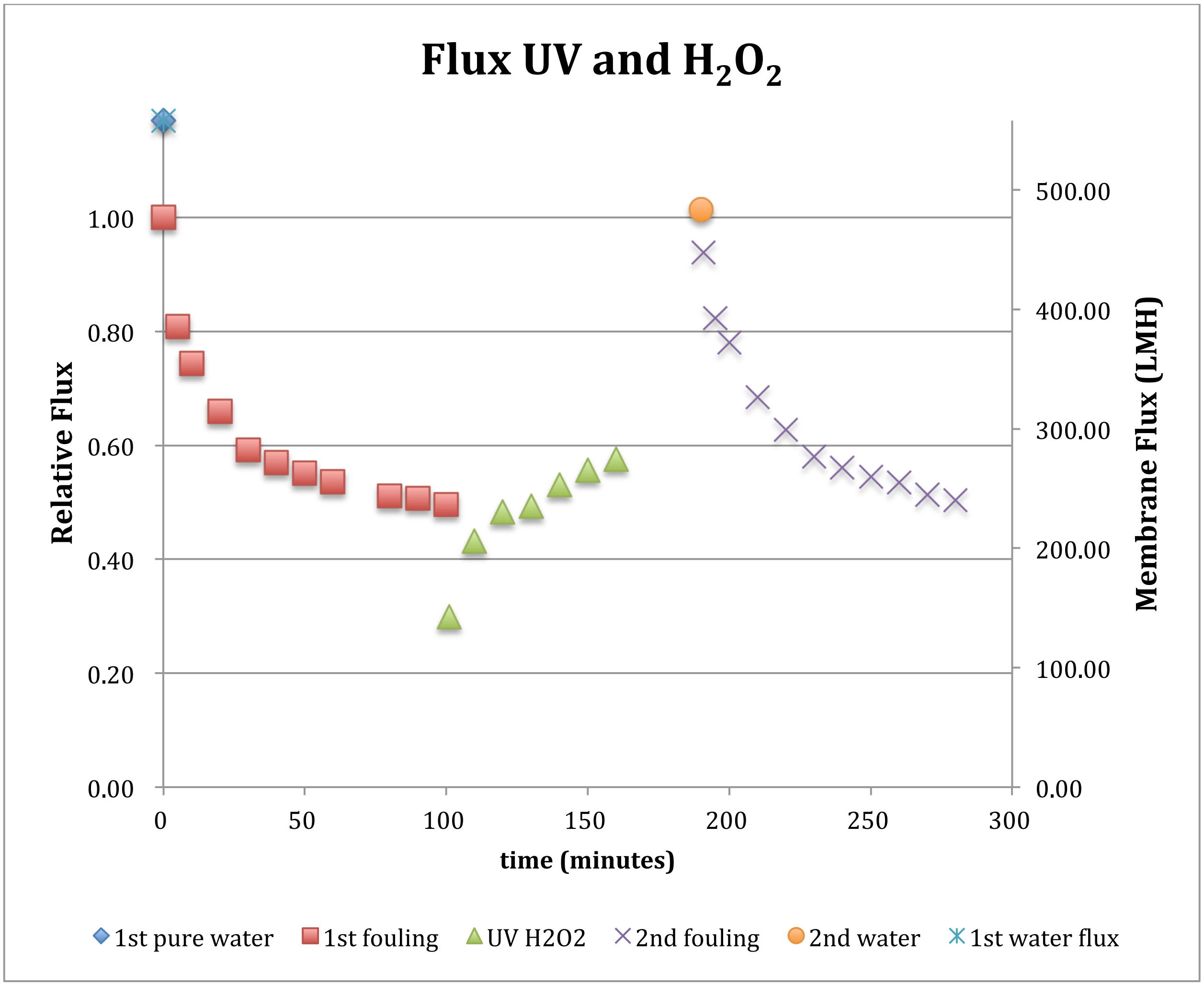

Figure 29 The flux of the membrane cleaned with UV/TiO_2 and H_2O_2 AOP

With UV light photo catalyzing TiO_2 and cleaving the O-O bond in hydrogen peroxide, the cleaned membrane recovered nearly 94% of its flux. In addition, the fouling profile of the 2nd run almost completely matches the first. Both fouling runs end with the membrane at nearly 50% of their original flux.

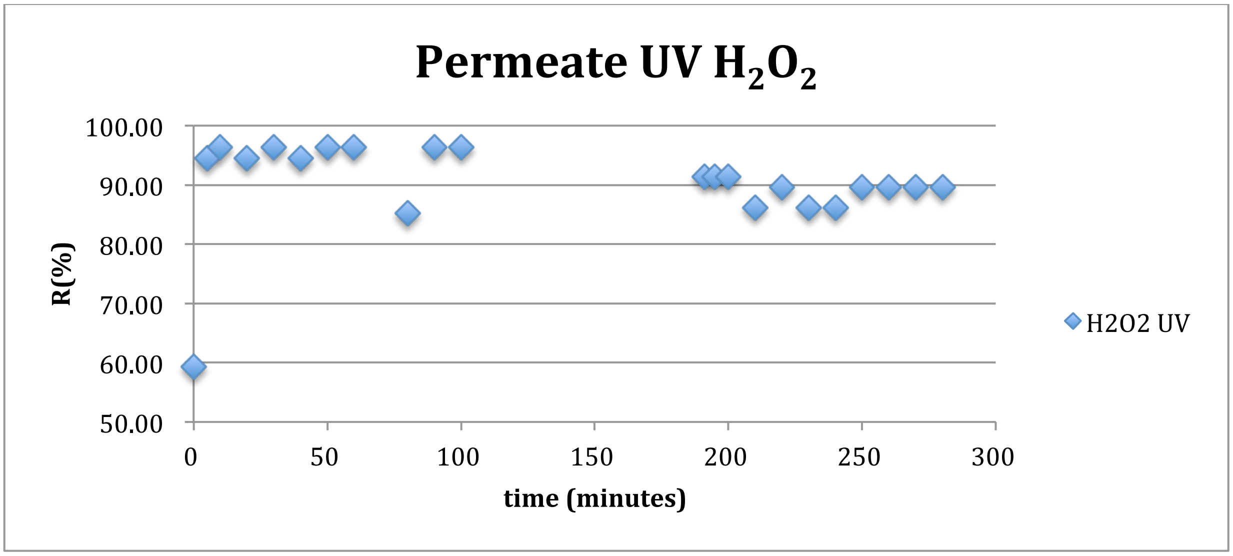

Figure 30 The permeate of membrane cleaned with UV and H_2O_2

The selectivity of the membranes was not negatively impacted either. The original removal rate was around 95%while the 2nd run had a removal rate of 90% still. As seen in figure 31, much of the HA was oxidized and removed from the membrane.

Figure 31 Before and after appearance of the membrane cleaning with UV/H_2O_2

Ozone and H_2O_2

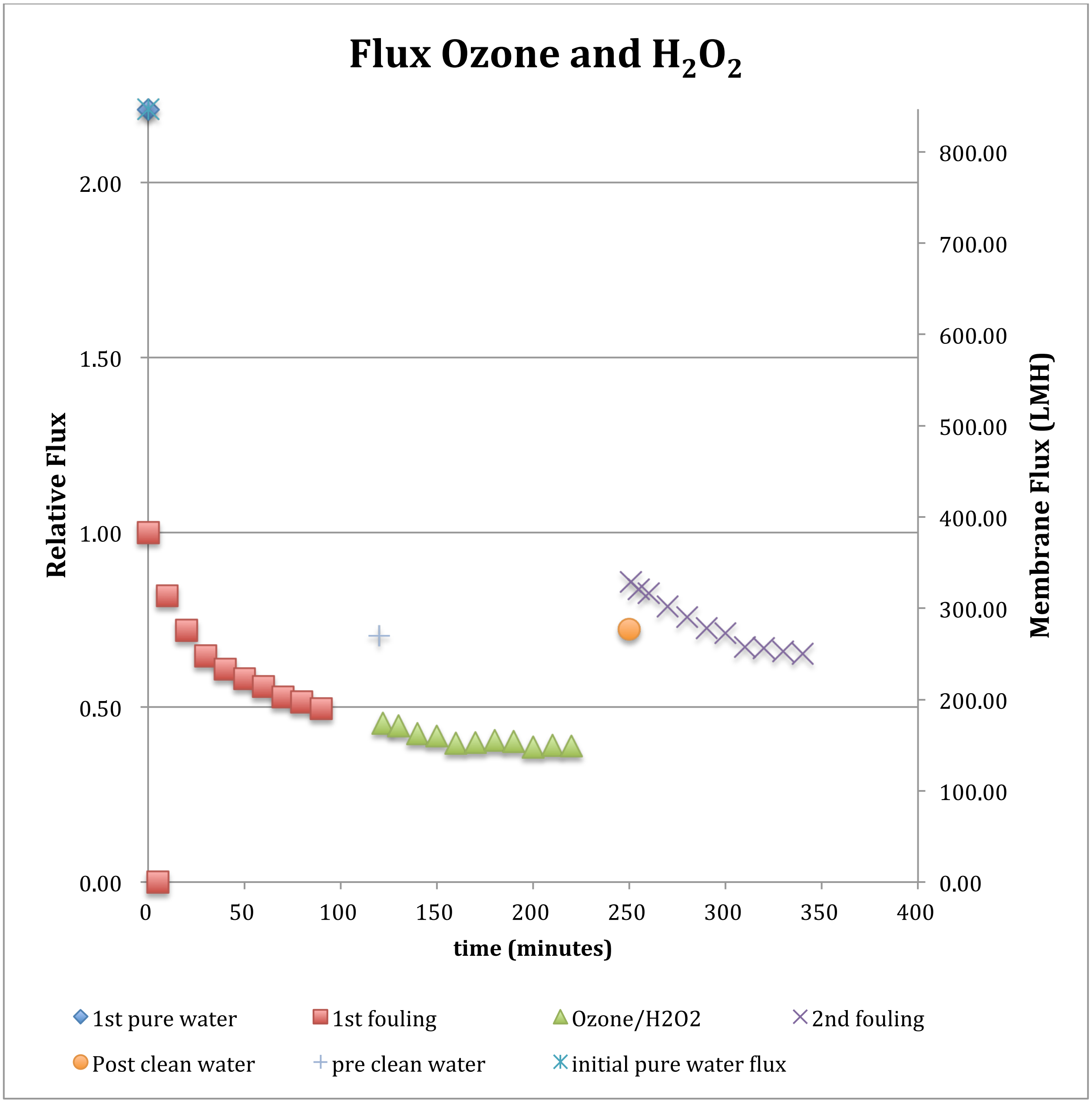

Figure 32 Flux of the membrane cleaned with ozone and H_2O_2

Like the ozone graph, during the cleaning process there was no flux recovery measured like there was in the UV experiment. Additionally, only 85% of the flux was recovered. Oddly, after the first fouling the membranes ends with a relative flux of about 50%. But after the 2^{nd} run, the flux ends at 65%.

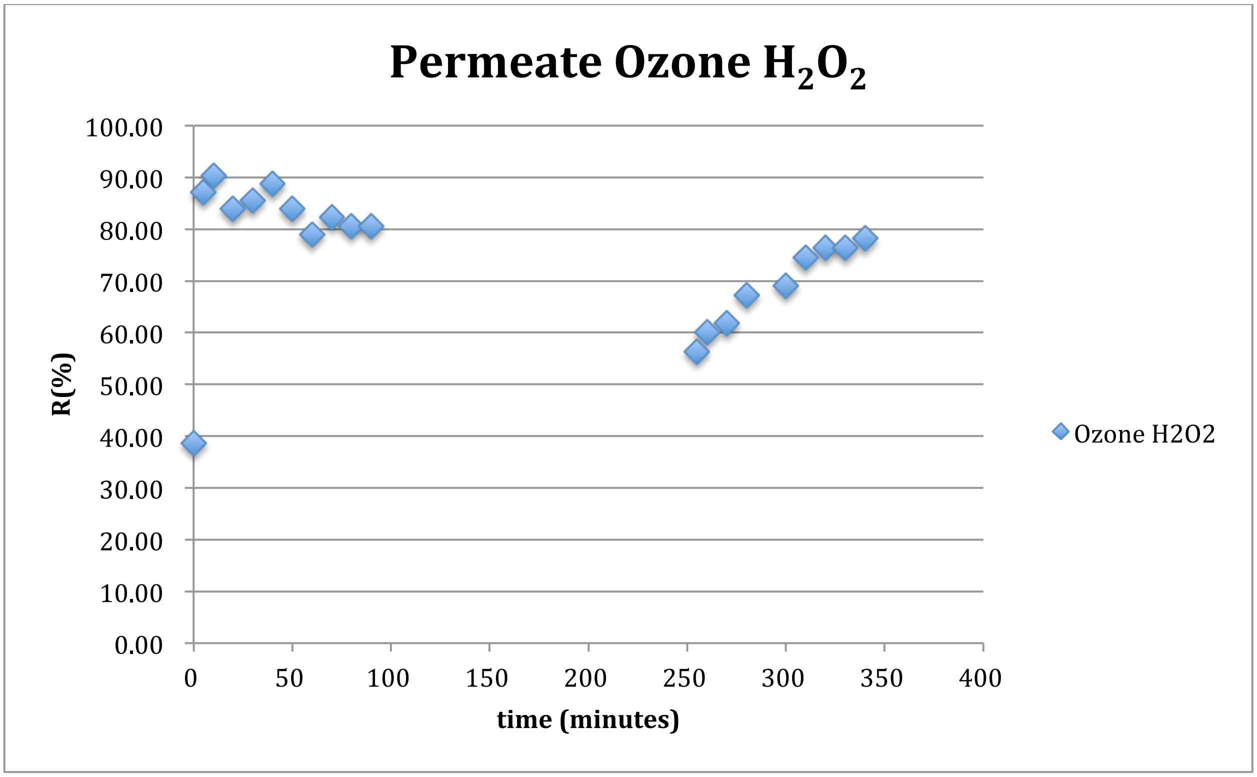

Figure 33 Permeate of the membrane during the 1st fouling and the 2nd fouling.

Like the prevous cleaning that involved ozone, the selctivity of the membranes decreased after using ozone. Initially at around 80-90%, af the cleaning the selectivtiy fell to 55%. As seen in figure 34, there was some color chang to the HA on the membrena surface, but it wasn't significatly removed like the membrane cleaned with only ozone.

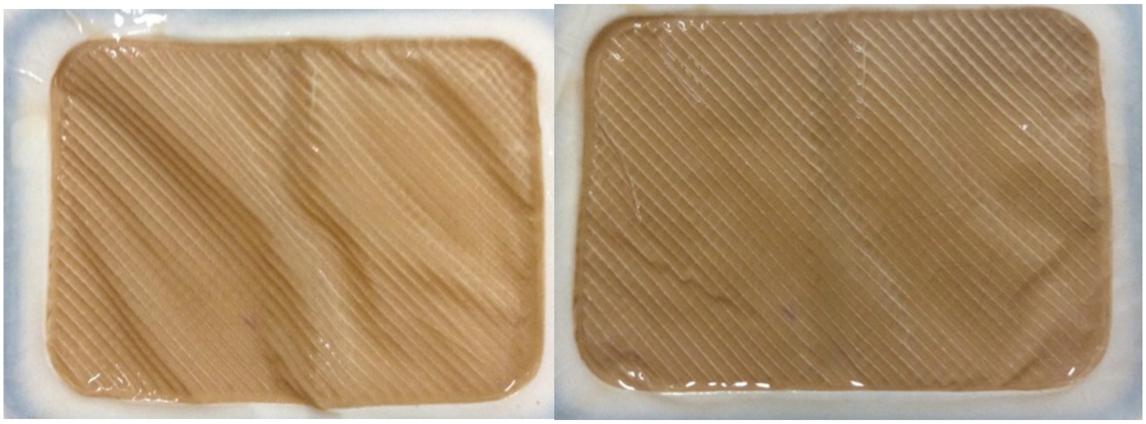

Figure 34 Before and after appearance of membrane cleaned with ozone/H_2O_2

UV and Ozone

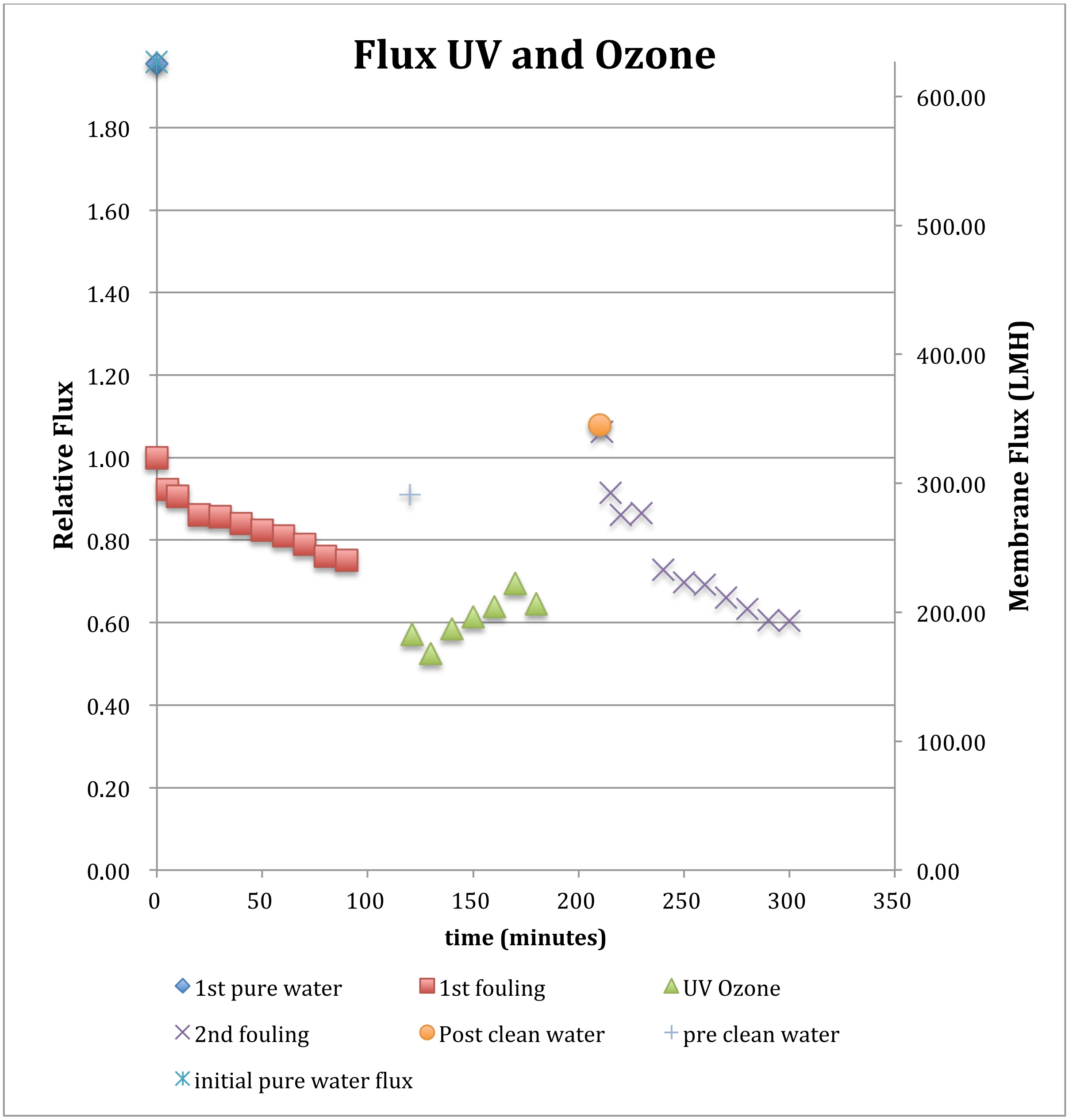

Figure 35 The flux of the membrane cleaned with UV and ozone

The cleaning with Ozone and UV saw the relative flux climb to over 107% of its initial value. This means that the initial flux after cleaning was higher then the flux when it started out clean. Unfortunately, there was not enough time to run multiple trials of this experiment determine if the extra flux was an error in measuring or a side effect of the cleaning. However, the 2nd fouling saw the flux decrease to 60% while it only decreased to 75% on the first.

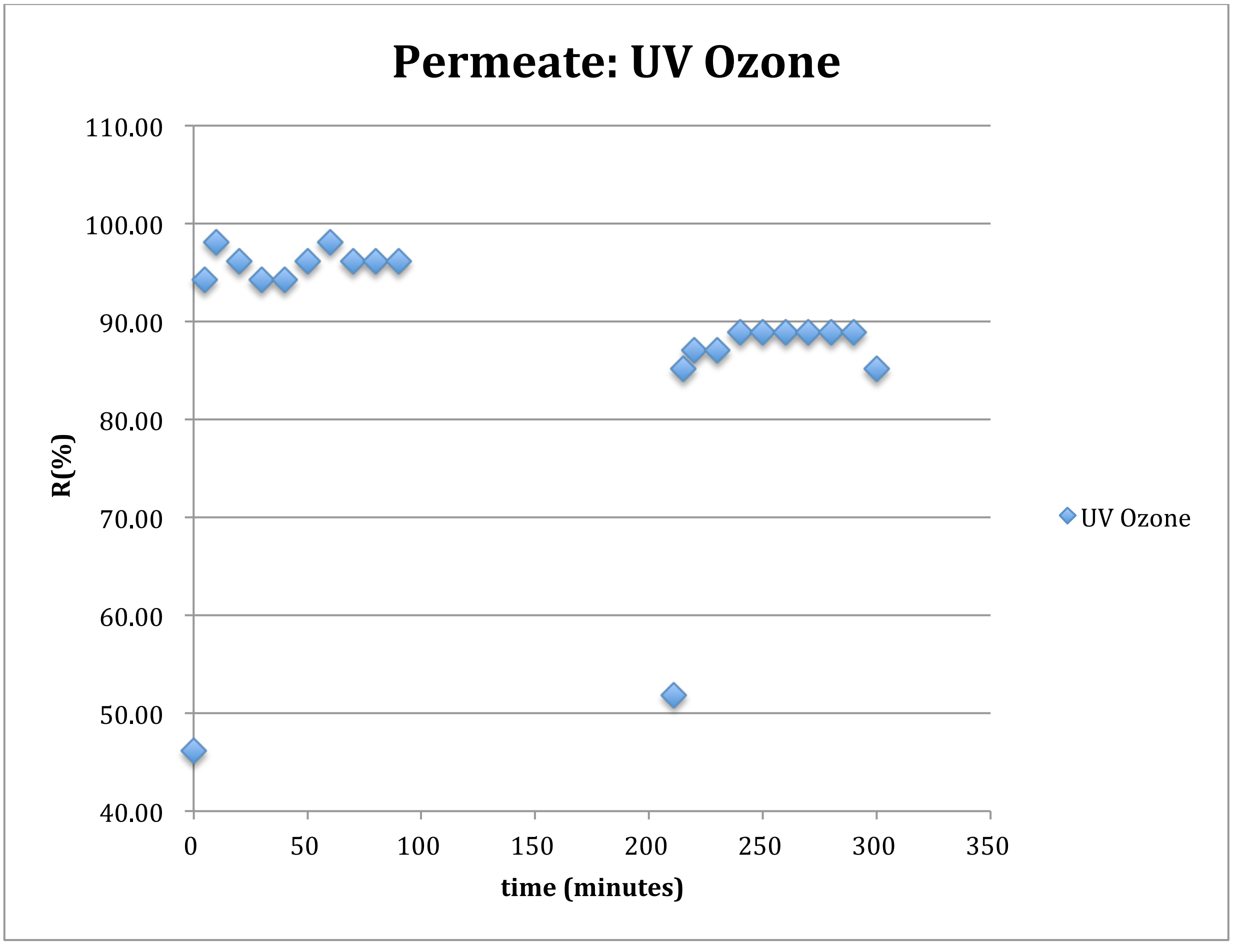

Figure 36 Permeate of the membrane during 1st and 2nd fouling

Unlike the last two experiments that involved ozone, the selectivity was not drastically reduced from the cleaning. The original selectivity was 96% and it only fell to about 89% during the second fouling. As seen in figure 37, the left shows HA built up on the surface, and the right side shows that the ozone and UV oxidized the some of the HA forming the black discoloration.

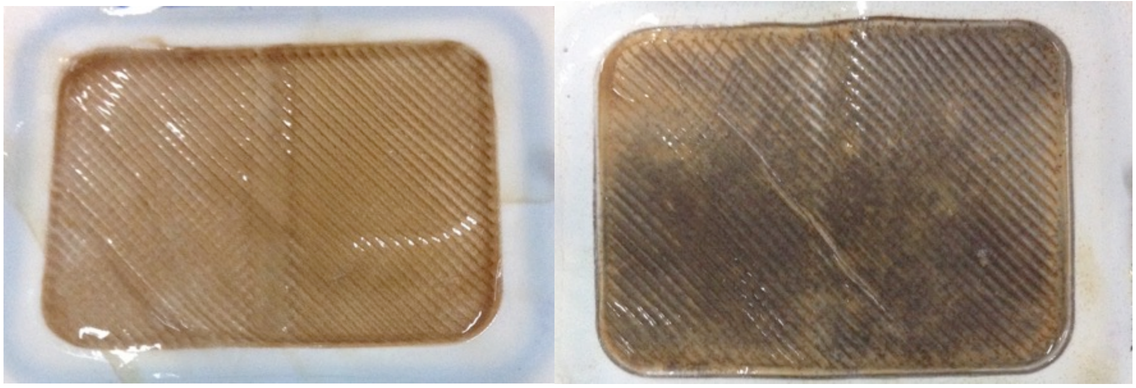

Figure 37 Before and after appearance of membrane cleaned with UV and ozone

UV H_2O_2 and Ozone

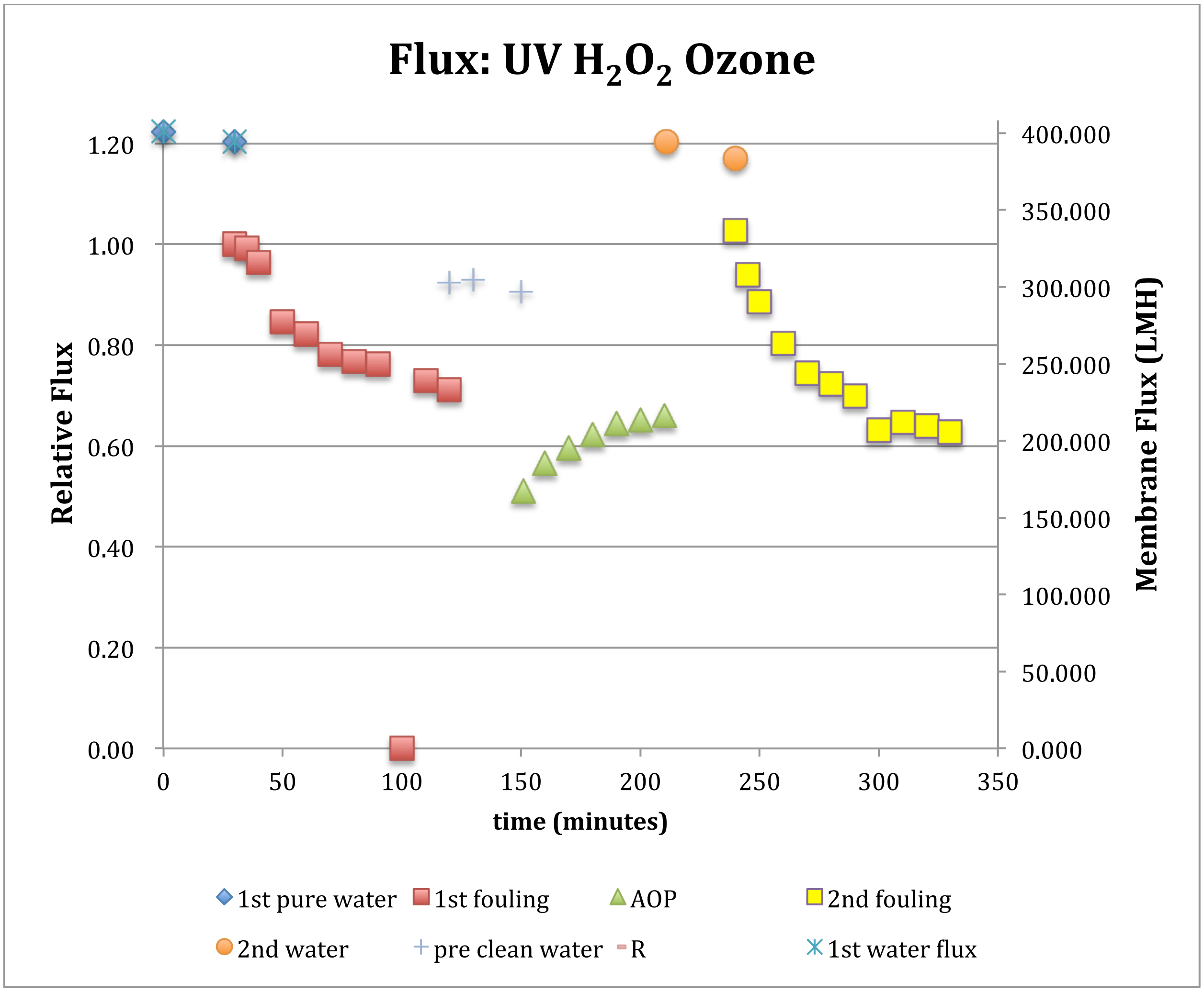

Figure 38 Flux of the membrane cleaned with all three AOPs

The flux recovery was very similar to the cleaning that was just UV and ozone. The 2nd fouling saw an initial flux that was slightly higher then the original flux during the 1st foul. Additionally, the flux for pure water after cleaning was nearly the same as the membranes initial pure water flux.

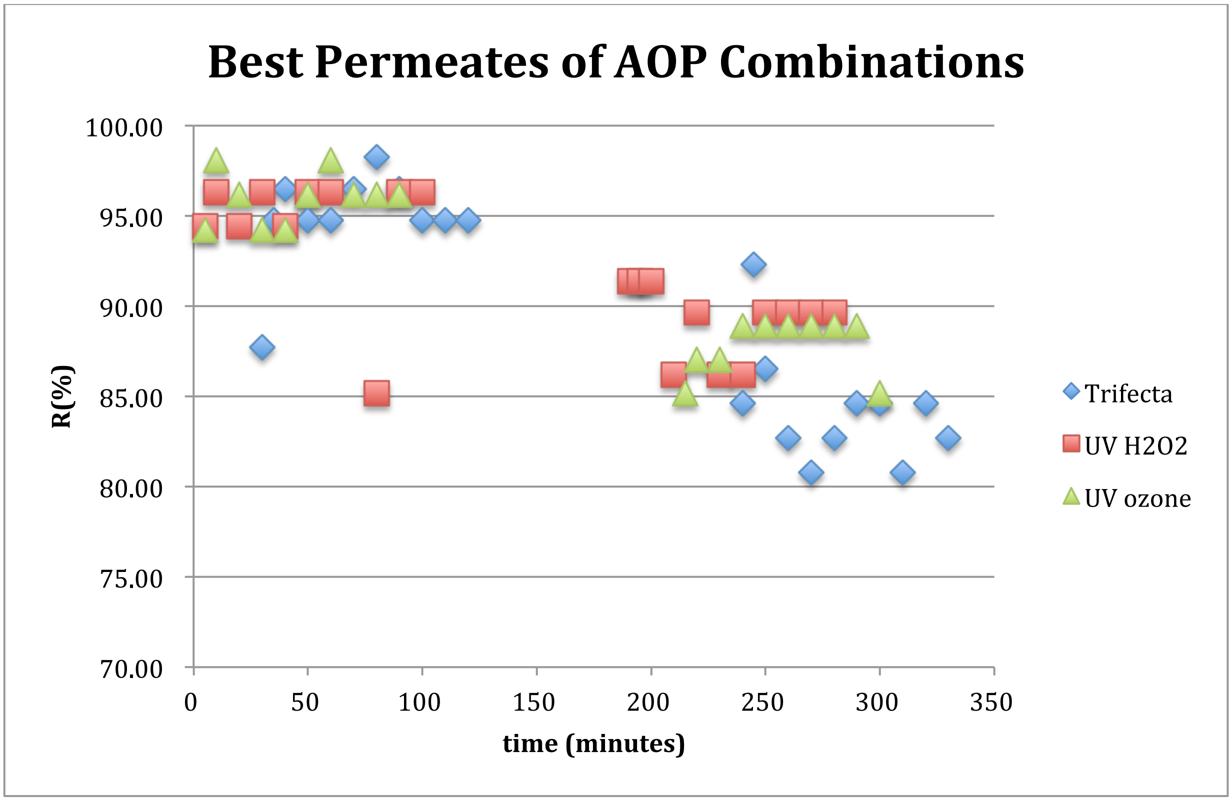

Figure 39 Comparing the permeates of all 3 AOPs, UV with H_2O_2 and UV with ozone

Like the UV and ozone cleaning, the selectivity of the membrane decreased after the cleaning. Initially at 95%, it decreased to about 82% during the 2nd cleaning. As seen in figure 40, much of the HA on the membrane surface was removed by all three AOPs.

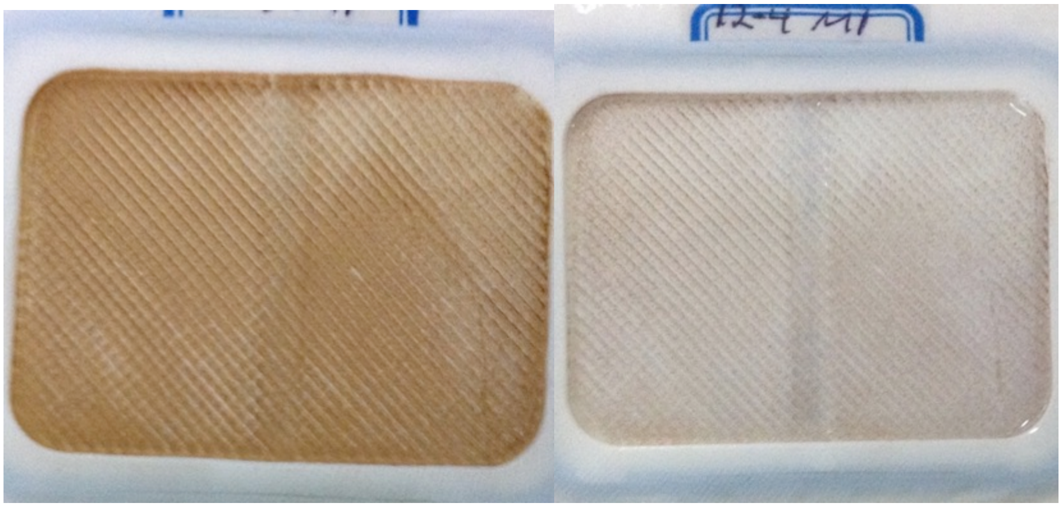

Figure 40 Before and after appearance of membrane cleaned with all AOPs

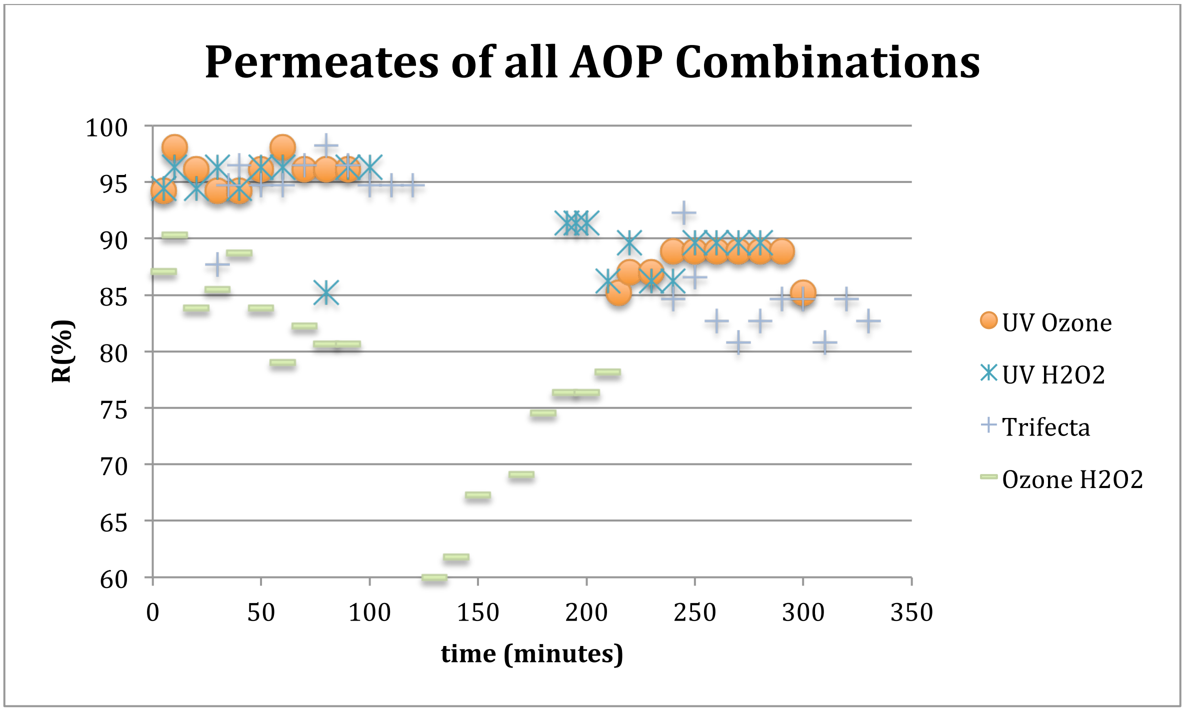

Figure 41 All of the AOP combination permeates compared

The membrane cleaned with ozone and H_2O_2 had the lowest selectivity in the 2nd fouling, much like the membrane cleaned with only ozone. The membrane cleaned with UV, H_2O_2 and ozone initially had very high selectivity that hovered around 95%, but then decreased to about 83% during the second fouling. The best selectivity's were with UV-ozone cleaning and UV H_2O_2 cleaning.

Section 5 Conclusion and Recommendations

5.1 Ozone Can Damage the Membranes

The membranes are primarily composed of polyvinylidene fluoride (PVDF), a thermoplastic that is highly used in industry for its chemical resistance to reactive agents like ozone (Arkema, 2009). Some studies have reported successful flux recovery of PVDF membranes using ozone (You, Tseng, Hsu, 2007). That was not the case though in this study. During the cleaning process, the flux actually decreased and recovered flux during the 2nd fouling was much lower then the other AOP processes. Additionally, the rejection rate of the membrane was significantly reduced. But, from figure 28, the brown HA deposits on the surface of the membrane after cleaning appear to be removed.

Interestingly, the membrane cleaned with H_2O_2 and Ozone did not have as much of the brown HA build up oxidized and removed, see figure 34. But this cleaning process had higher flux recovery. Also the rejection rate was similar, but slightly superior compared to the membrane cleaned with only ozone.

5.2 A Catalyst is Required for H_2O_2

Without a catalyst to generate hydroxyl radicals from H_2O_2, this cleaning method had virtually no ability to recover flux as seen in figure 23. Interestingly, the membrane cleaned with pure water was under the same pressure and flow rate and had significant flux recovery. Despite the small concentration of 0.0098 M in the experiment, it did not have the same cleaning ability as the pure water.

5.3 H_2O_2 and UV are the Best AOP Combination

For practical purposes, the most promising combination of AOPs for cleaning these membranes it to photocatalytically activate the TiO_2 with UV light while simultaneously generating hydroxyl radicals from H_2O_2 through photolysis. This method saw excellent flux recovery while retaining a high rejection rate. Adding H_2O_2 to a cleaning solution is a simple process and easy to integrate with UV light. By avoiding ozone, there is no need to integrate more ozone resistant materials for tubing and seals or to run a separate generating system.

5.4 Recommendations

Determine the maximum amount of HA that can be absorbed on the membrane

A major part of the cleaning process is the activation of TiO_2 on the surface of the membrane by UV light. But HA also deposits on the surface and makes a thicker and more opaque layer as the cleaning continues. Theoretically, if enough HA built up on the surface of the membrane, the TiO_2 would be completely obscured and the UV light would not reach it. At this point, cleaning the membrane would become much more intensive. Knowing how much HA can be absorbed on the surface of these membranes before reaching this point would be valuable information. For any industry that would potentially employ these membranes in the their process, this would be essential knowledge.

Determine long-term performance of the membranes with multiple cycles of fouling and cleaning

Each of these experiments was simply two cycles of fouling. The membrane was made, fouled, cleaned, and then fouled again. Because this project was focused on the immediate aftermath of the cleaning, there was less focus on the long-term performance. Long-term performance is vital information to any industry that would potentially use these membranes.

Find the optimal concentrations of H_2O_2 and UV light Duration

Only one concentration of H_2O_2 was used for the membrane cleaned with UV and H_2O_2. Also the UV light was always used for one hour. It would be useful to see how different exposure times under UV with different concentrations of H_2O_2 would effect the cleaning of the membranes.

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Appendix

Making membranes

In a round bottom flask, using 29.575 g of N,N-dimethylacetamide as a solvent, 4.2g of PVDF powder, 0.7 g of polyethylene glycol, and 0.525 g of TiO_2 nanoparticles were mixed together. The nanoparticles were p25 meaning the average diameter was 25 nanometers. The mixture was placed into a heated water bathe stirrer for 24 hours. The stirred covered the top of the flask and made sure no foreign matter could enter. After mixing, the stirrer was removed and the flask was covered, then it stayed in the water bath for 24 hours for bubbles to come out of solution.

Figure 42 Stirred membrane solution

A glass plate was cleaned with ethanol and made level on a table. A border was made with clear tape that was 18 cm by 19 cm. A glass beaker was cleaned and dried in an oven at 50° C. 10 ml of ethanol and 0.2 g of the TiO_2 nanoparticles were mixed into a suspension with the aid of an ultrasonic water bathe. The beaker was covered to ensure no water got into it. After all the TiO_2 was in suspension, the mixture was poured into the center of the taped square on the glass plate.

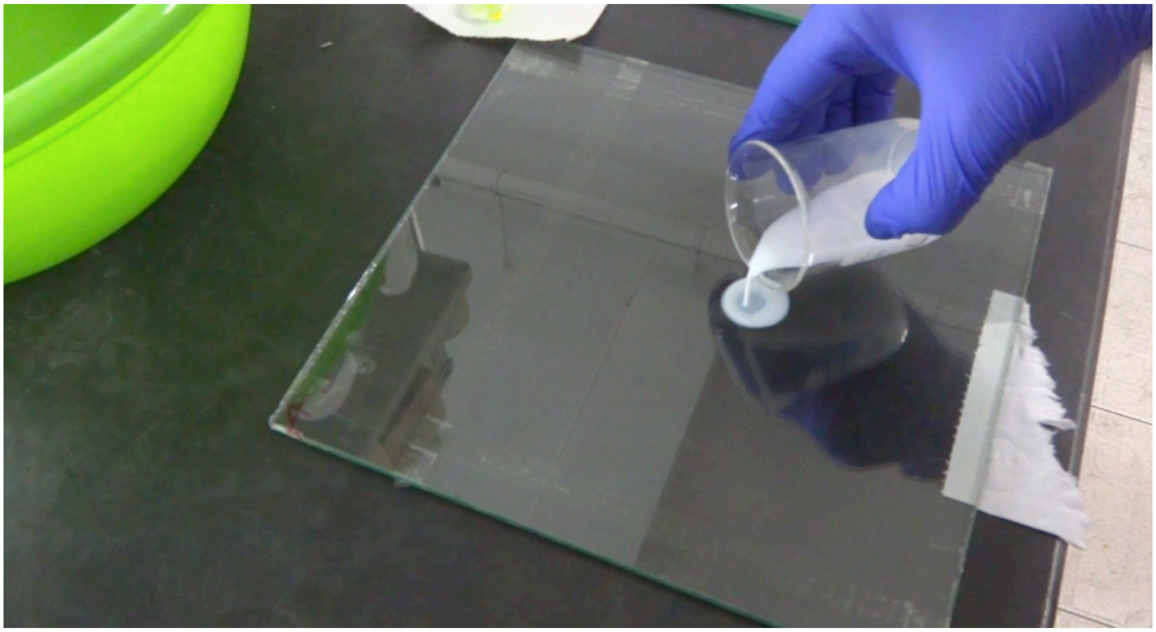

Figure 43 TiO_2 suspended in ethanol being poured

The glass plate with the TiO_2 suspension was allowed to sit for several minutes while the ethanol evaporated. After the ethanol was visibly evaporated, the plate with the attached TiO_2 nanoparticles was placed into an oven at 50° C for 5 minutes to remove any excess ethanol.

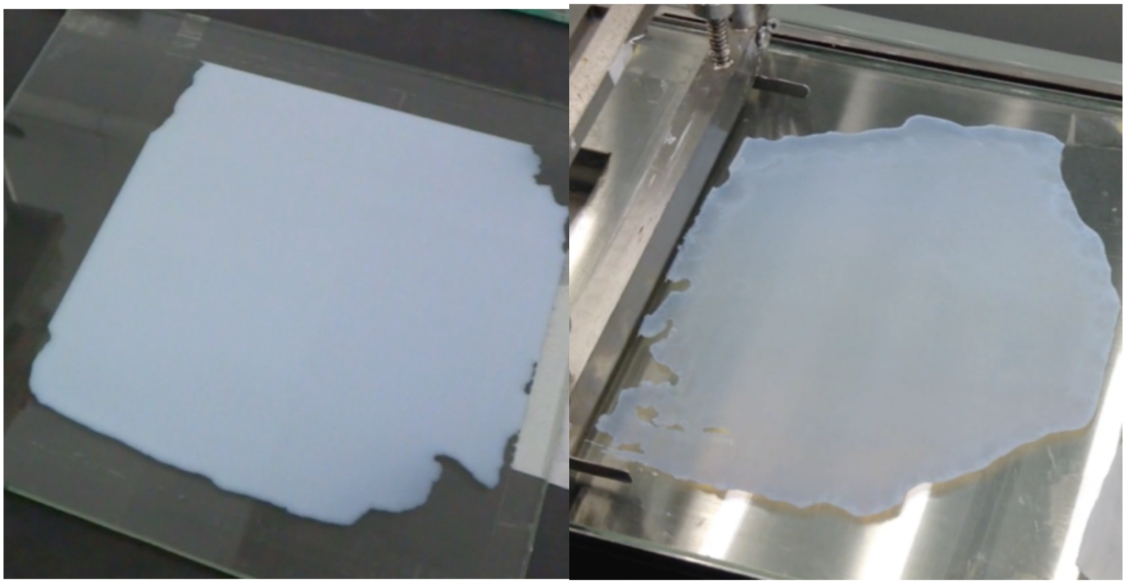

Figure 44 Ethanol evaporating, leaving TiO_2

The glass plate was placed onto a membrane-casting machine. The blade of the casting machine, which is what physically casts the membranes, was cleaned with ethanol soaked cotton. After cleaning the casting blade, a casting knife was used to make sure that the space between the blade and the plate was 0.20 mm. Approximately half of the membrane mixture from the flask was poured in an even line across the glass plate.

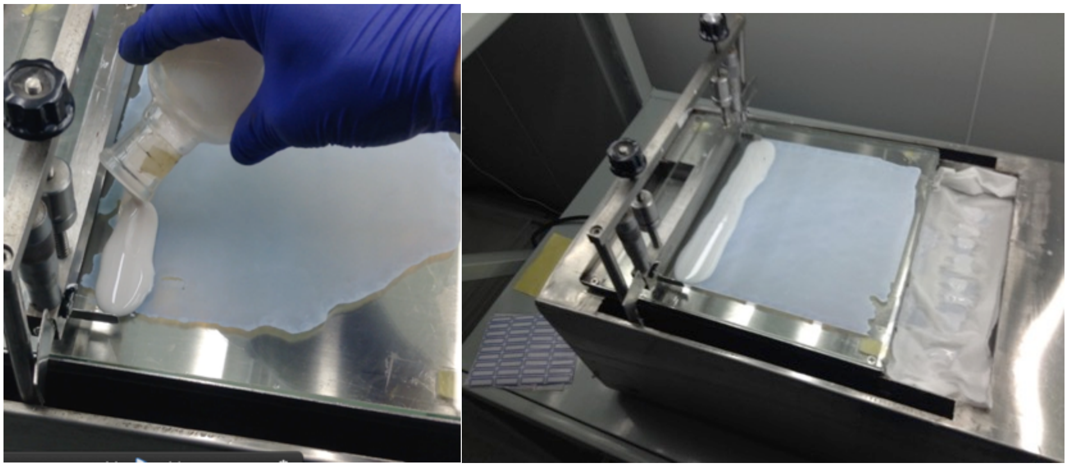

Figure 45 PVDF mixture being poured on casting glass

The blade on the membrane-casting machine was activated, the membrane was cast over the TiO_2 layer on the glass plate. Excess PVDF was collected on tissue paper to be disposed of.

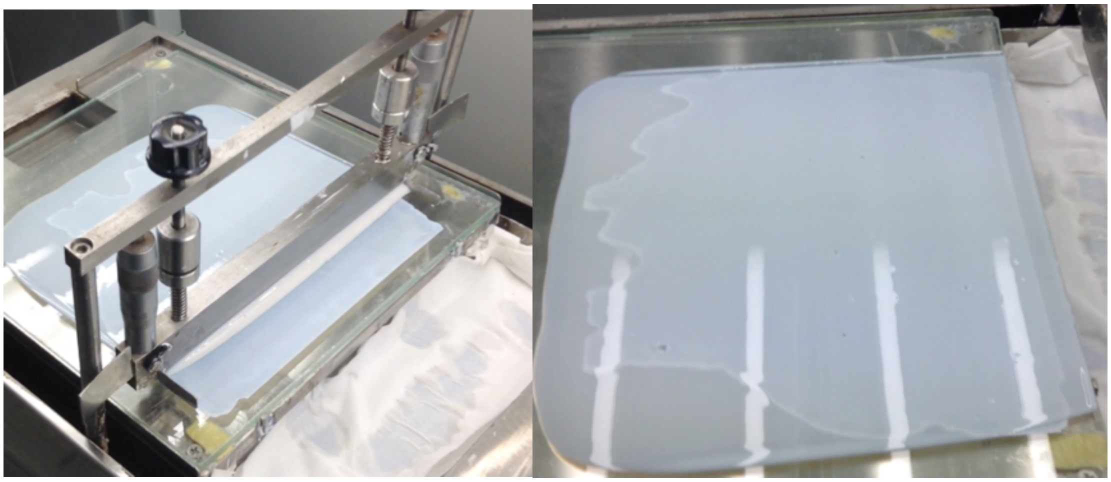

Figure 46 Casting of PVDF on TiO_2

The glass plate with the casted membrane was placed into the pure water coagulation bathe which was at 25° C. After a few minutes, the membrane would detach from the surface with the TiO_2 layer bound to the side. The topside of the membrane was designated as the side with the attached TiO_2 layer. The membrane was labeled on the topside with the date it was made and its batch number. The membranes were placed in plastic bags with pure water for storage.

Figure 47 Membranes in the coagulation bathe

When being cut to size, the topside of the membrane was placed against the same glass plates used for casting. The glass plate with the attached membrane was held to a light, and any potential holes in the membrane were identified as bright points where more light shined through.

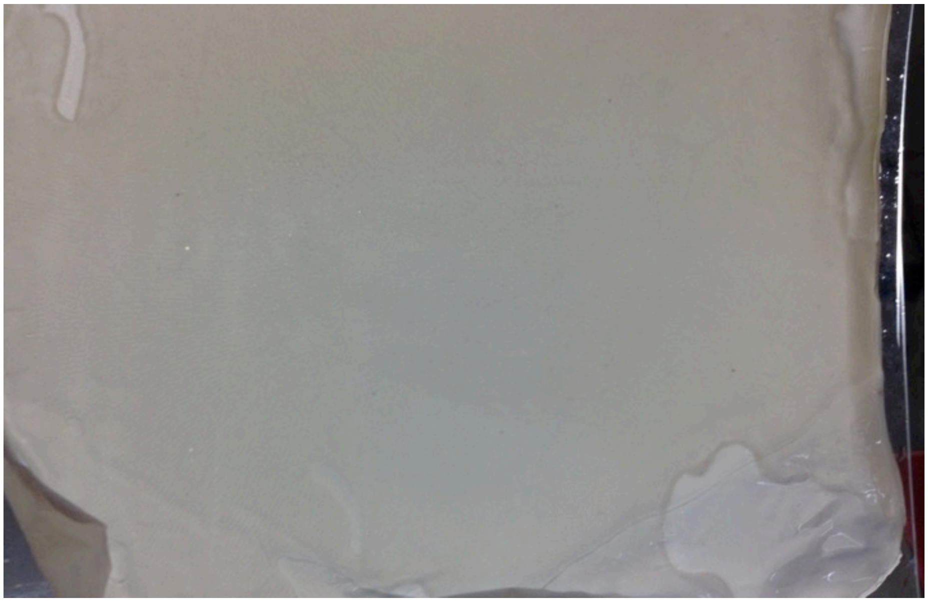

Figure 48 Checking for holes in the membrane

A plastic template cut to the size of the membranes used in the experiments was used to select an area with the minimal number of holes. This template was placed on the backside of the membrane so the selected area was pressed between the glass plate and the template. Then, the template was traced with a razorblade which cut the membrane to size. The membrane was inverted and the tope side with the TiO_2 layer was labeled with the membrane information. Multiple readings were taken with a caliper across various points of the membrane to compile an average thickness of the membrane. The membrane was then placed in a plastic bag filled with pure water for storage.

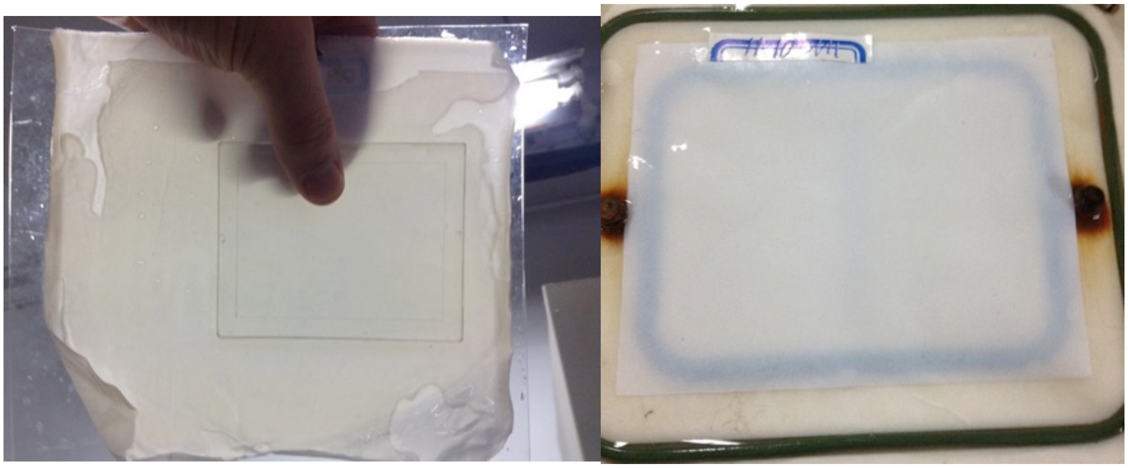

Figure 49 Finished membrane cut to size

Super Fouling

Background

The super fouling experiment was started just to examine the long-term performance of the membranes. The goal was to run the membranes with a large volume of HA contained in water for several hours vs. the normal 90 minutes per membrane run. If these membranes were used in an industrial setting, this long-term performance data would be critical to the overall design.

As ultrafiltration membranes remove NOM from water, the contaminants build up on the membrane surface as fouling progresses. While running the experiments, the concentration of HA in the reservoir (A_f) can be tracked and compared to the original HA concentration in solution (A_{fo}). With this information, the approximate percentage of HA (removed HA_r) can be calculated. The original concentration was known to be 2 ppm, or 0.002 grams of HA per liter of water. So the amount of HA deposited onto the surface of the membrane (HA_m) can be calculated with the following equations.

$$HA_r(\%) = 100 * \frac{A_f}{A_{fo}}$$

$$HA_m = \frac{HA_r * v * 0.002}{100}$$

First Super Fouling

For the first super fouling, the membrane was run for 31 hours. The initial reservoir was increased to 4 liters of 2ppm HA solution. UV absorbance could be used to track the HA concentration in the reservoir because a reading of approximately 0.050 corresponded to a 2ppm HA concentration. Over the 31 hours of running, 90 ml of 200 ppm HA was added incrementally to the solution to replace the HA that absorbed on to the membrane. Even with this addition, the amount of HA absorbed onto the membrane surface could be determined with starting and ending absorbance of the reservoir. This is because every 10 ml of 200 ppm Ha solution contained 2 mg of HA.

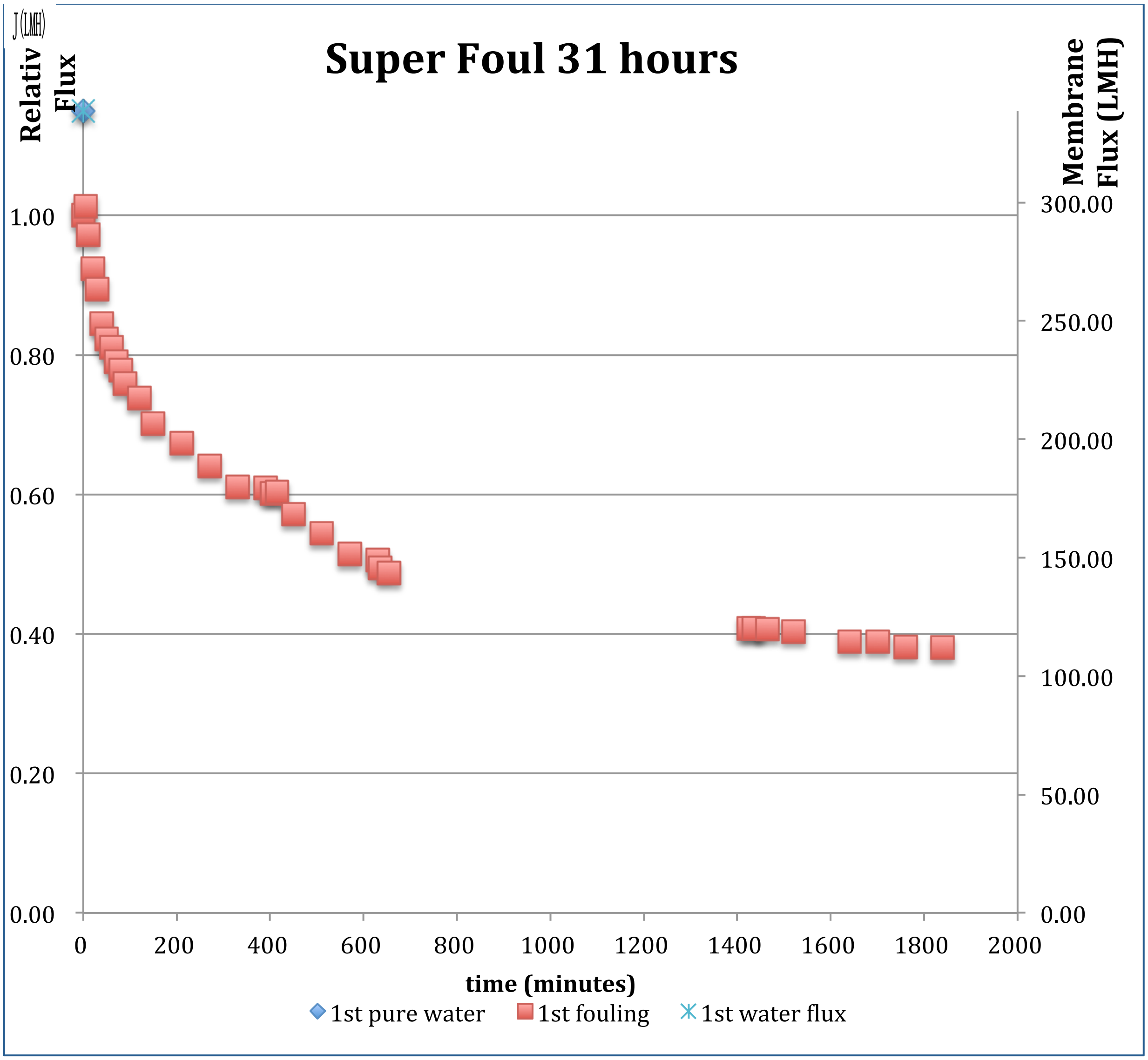

Figure 50 Flux of the membrane during the 31 hours of super fouling

The flux of the membrane kept decreasing as the experiment was run. Presumably it would have continued to decrease as more fouling built up.

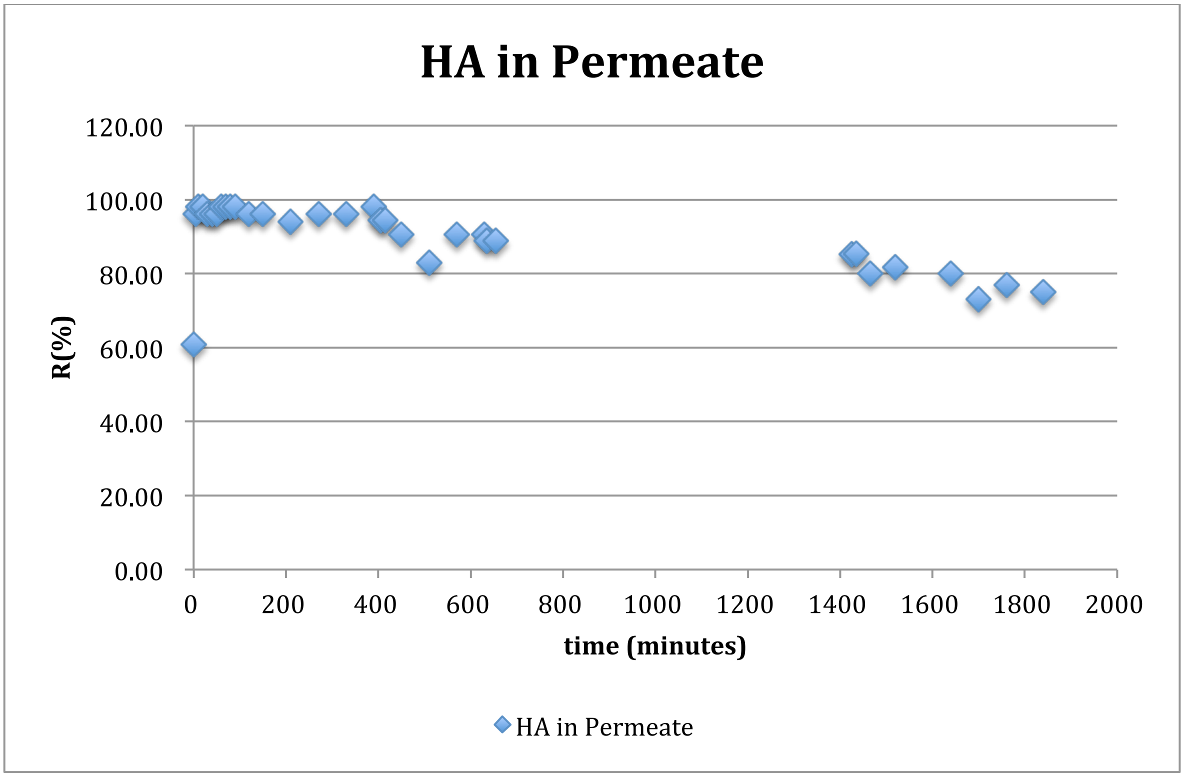

Figure 51 Permeate of the membrane during 31 hours of super fouling

The permeate quality also decreased as the super fouling proceeded. The membrane had become so fouled that it was loosing selectivity.

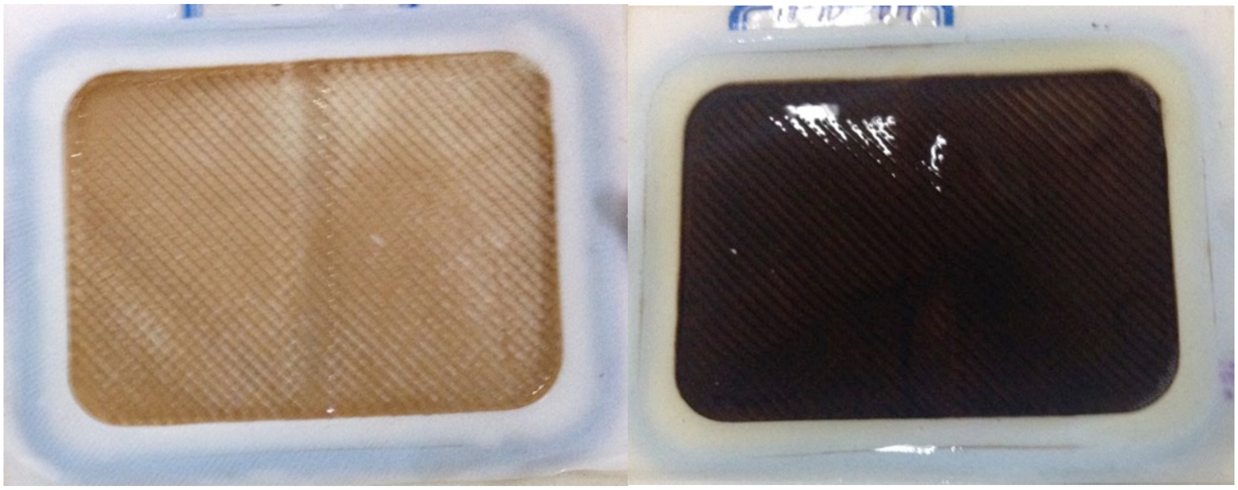

Figure 52 Appearance of 2.4 mg of HA vs. 20 mg on membrane surface

In Figure 52, on the left is the membrane from the UV H_2O_2 ozone experiment after its first fouling; there is about 2.4 mg of HA of the surface. This layer of HA is thin enough to allow

UV light to activate the TiO_2 layer. On the right is the membrane after this first super fouling; there is about 20 mg of HA. This layer of HA was too thick to allow UV light to reach the TiO_2. Because of this, the membrane was mechanically cleaned. Mechanical cleaning involves scrubbing the membrane with an abrasive material to remove fouling but not damage the membrane.

Figure 53 Post mechanical cleaning, then UV/H_2O_2 AOP cleaning

In this experiment, the HA was rubbed off the membrane by hand while wearing nitrile gloves. This removed a considerable amount of the HA and allowed for the UV light to reach the TiO_2. From figure 55, this cleaning procedure was able to recover the flux. This flux recovered was seen both with the new pure water flux through the membrane and with the flux of 2ppm HA solution during the second fouling.

Second Super Fouling

The goal for this second fouling was to absorb less HA on the surface of the membrane to see if it could be cleaned only with the UV/H_2O_2 AOP instead of mechanical means. So for this experiment, the membrane was fouled for 10 hours. Again, 4 liters of 2 ppm HA was in the initial reservoir, then over the course of the experiment, 40 ml of 200 ppm HA was incrementally added to the solution. The 2nd super fouling only absorbed about 9.2 mg of HA onto the surface of the membrane. From the appearance, of the membrane, it looked like UV light would not be able to reach TiO_2. But the membrane was cleaned with the same procedure using H_2O_2 and UV so see if the additional production of hydroxyl radicals from H_2O_2 would break down the HA.

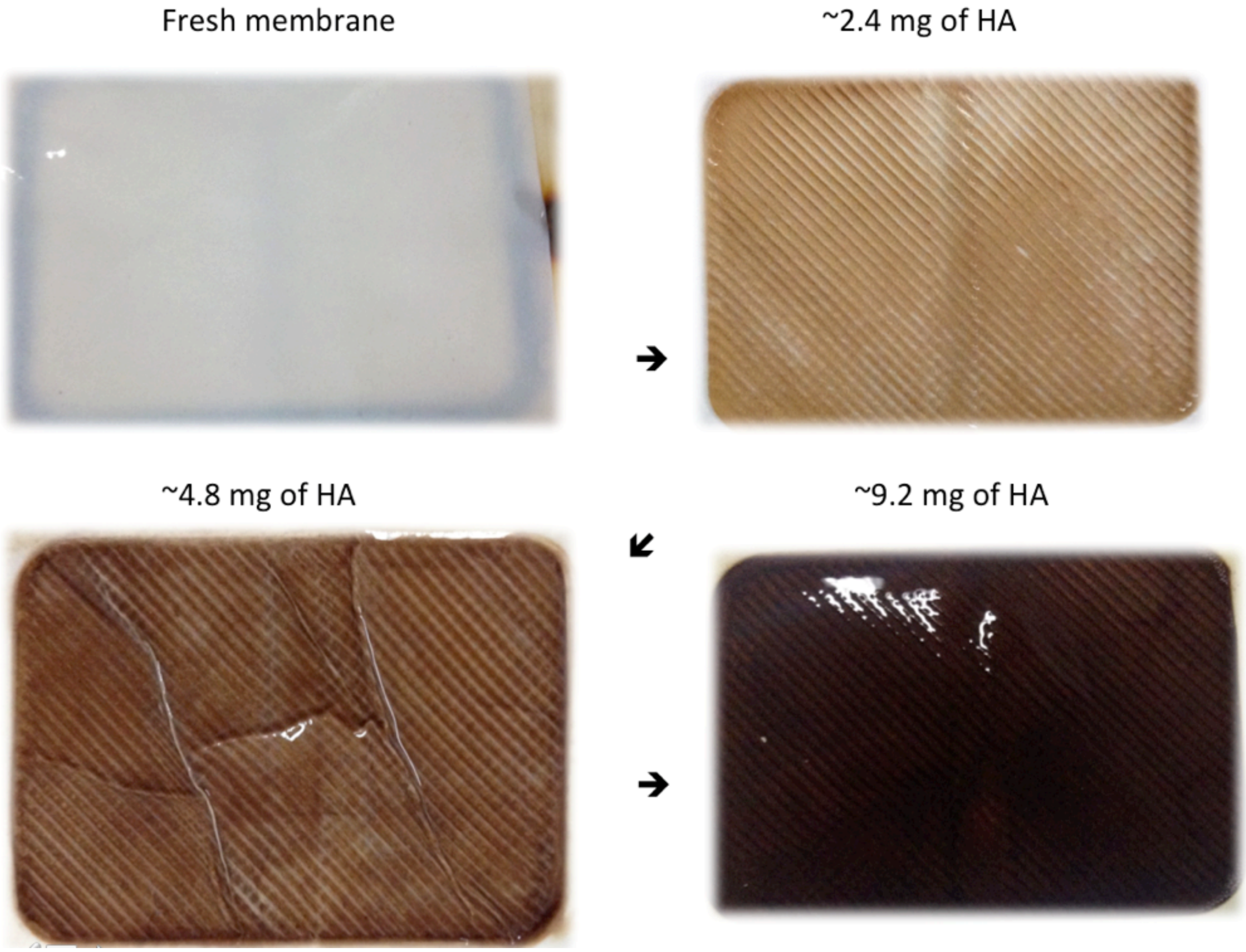

Figure 54 Stages of fouling with different amounts of HA

In Figure 54, these images of the membrane taken at different stages of the fouling shows how the addition of HA to the surface creates an opaque layer. This layer blocks UV light from reaching the TiO_2 and prevents the AOP.

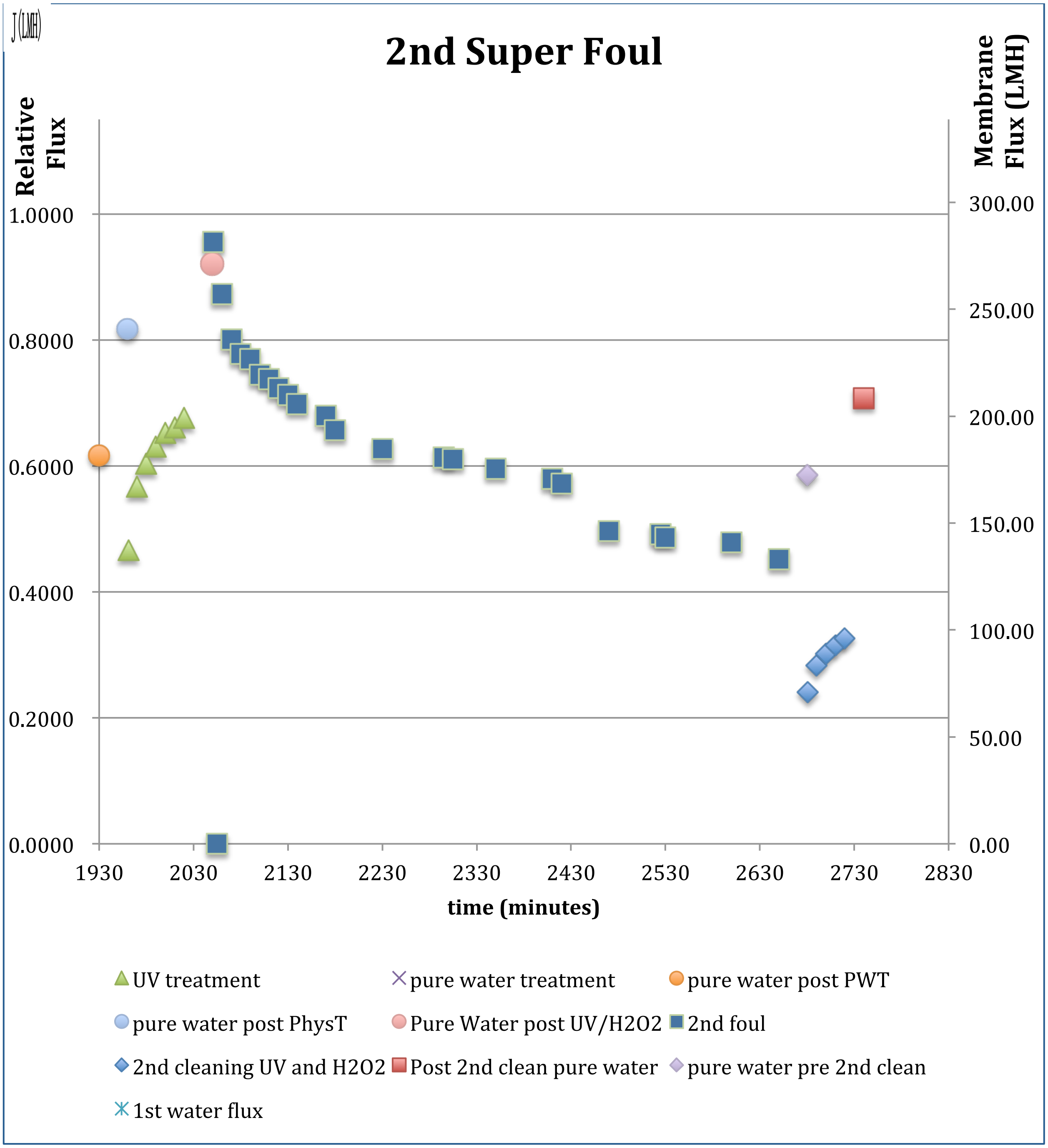

Figure 55 Flux of the membrane during 2^{nd} super foul

In figure 55, after being mechanically cleaned, the flux is almost completely recovered following the first UV/H_2O_2 AOP cleaning. Then during the 2^{nd} super fouling, the flux decreases again as large amounts of HA are built up on the surface.

After being fouled the second time, the flux of pure water through the membrane was measured to be 172 L/m^2h. Then, the membrane was cleaned with the same cleaning procedure used in the in the UV/H_2O_2 AOP cleaning. The flux of pure water following that cleaning was 209 L/m^2h. Or, in terms of relative flux, that cleaning brought the membrane from 58% of its flux to only 70% of its flux. From section 4.3, during the AOP cleaning with UV and H_2O_2, the flux was recovered from 50% to 94%.

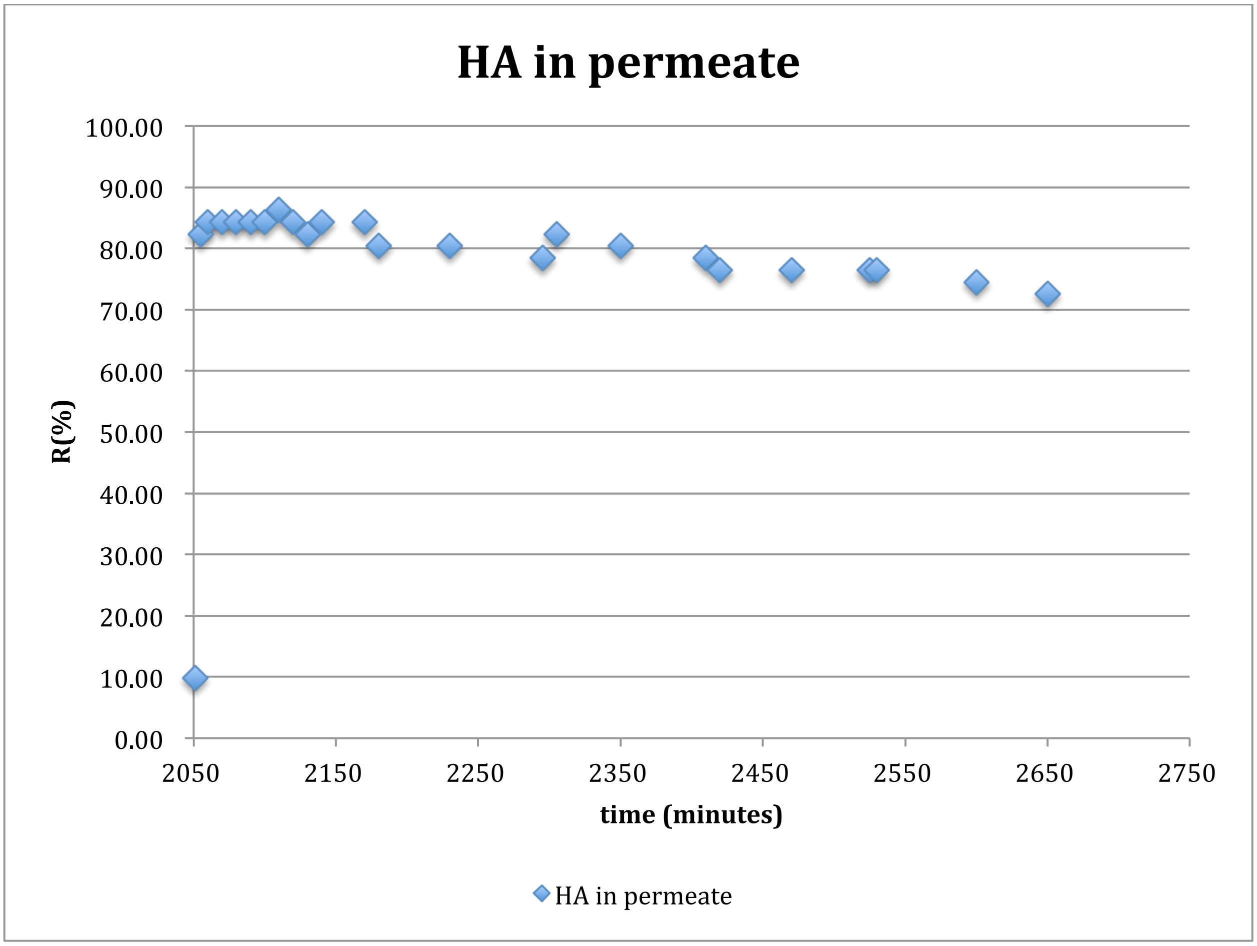

Figure 56 permeate of the membrane during the 10 hour super fouling

During the second fouling, the permeate showed a decreasing trend in selectivity like in the first fouling. Though first fouling ended with a selectivity of 75%, the second fouling had a selectivity of 82% after stabilizing. But as fouling progressed, the selectivity dropped to 72%.

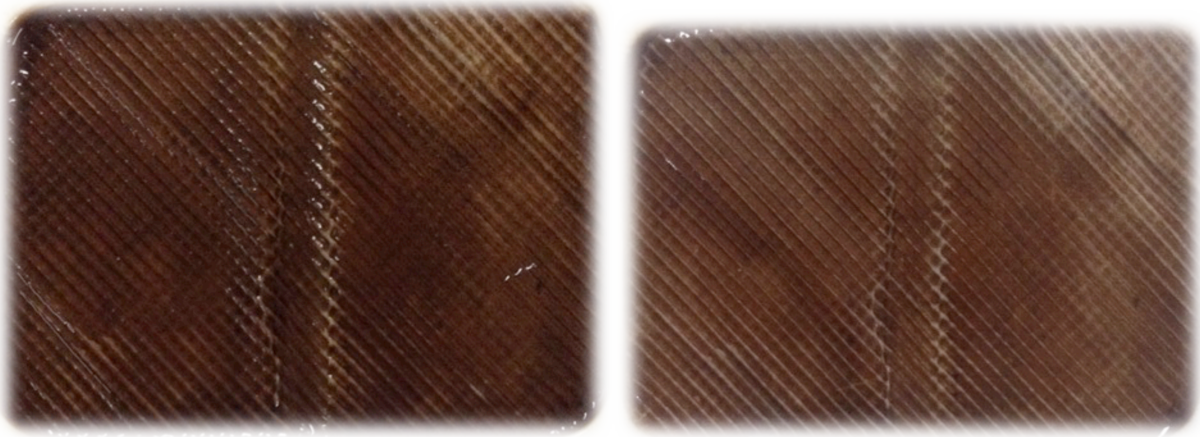

Figure 57 Before and after of membrane cleaned with UV/H_2O_2 AOP

After being cleaning with UV and H_2O_2 after the second fouling, while there was some flux recovery, there was still a lot of HA absorbed onto the surface of the membrane that needed to be removed. In addition to being a greater volume of HA to remove, it was also obscuring the TiO_2 from the UV light.

Conclusions from super fouling

The goal of the super fouling experiment was to find out how much HA could be removed by the membrane before the UV light and H_2O_2 AOPs were ineffective at removing fouling. Because this experiment was implemented during the last week of research at SJTU, that goal was not met. However, it is known from all of the other AOP cleaning experiments that 2.4 mg absorbed onto the surface of the membranes is easily removal with the UV/ H_2O_2 AOP. But 9.2 mg of HA is too much. From this data, an optimization problem could be developed that could determine the optimal amount of HA that the membranes could remove before needing to be cleaned with AOPs.

Experimental Data

Pure water

t(min)	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)	**Pure Water Flux**
30	21.8	500.0	20.12	20	60.36	754.50	
30	21.8	500.0	20.61	20	61.83	772.88	

PP-1			23.53						**Membrane Thickness**	
(P_0=0.1MPa, HA=2mg/L)									165	
0	21.8	500.0	23.01	30	46.02	575.25	1.32			
		(mL/min)			(mL/min)			Abs		
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	R(%)
0	21.8	500.0	20.00	30	40.00	500.00	1.0000	0.048	0.016	66.67
5	21.8	500.0	17.49	30	34.98	437.25	0.8745	0.043	0.001	97.92
10	21.8	500.0	16.67	30	33.34	416.75	0.8335	0.040	0.001	97.92
20	21.8	500.0	14.52	30	29.04	363.00	0.7260	0.033	0	100.00
30	21.8	500.0	13.35	30	26.70	333.75	0.6675	0.029	0	100.00
40	21.8	500.0	12.89	30	25.78	322.25	0.6445	0.028	0.001	97.92
50	21.8	500.0	13.13	30	26.26	328.25	0.6565	0.023	0.002	95.83
62	22.0	500.0	12.44	30	24.88	311.00	0.6220	0.020	0.001	97.92
70	22.0	500.0	12.43	30	24.86	310.75	0.6215	0.019	0.002	95.83
80	22.0	500.0	11.95	30	23.90	298.75	0.5975	0.018	0.003	93.75
90	22.0	500.0	11.66	30	23.32	291.50	0.5830	0.016	0.003	93.75
120			19.35	30	38.70	483.75	1.1063			
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	R(%)
121	21.8	500.0	17.58	30	35.16	439.50	0.8790	0.053	0.009	83.02
126	21.8	500.0	16.72	30	33.44	418.00	0.8360	0.048	0.005	90.57
131	21.8	500.0	15.19	30	30.38	379.75	0.7595	0.045	0.005	90.57
141	21.8	500.0	13.48	30	26.96	337.00	0.6740	0.042	0.008	84.91
151	21.8	500.0	14.38	30	28.76	359.50	0.7190	0.036	0.008	84.91
161	21.8	500.0	13.84	30	27.68	346.00	0.6920	0.033	0.008	84.91
171	21.8	500.0	13.28	30	26.56	332.00	0.6640	0.029	0.007	86.79
181	22.0	500.0	13.11	30	26.22	327.75	0.6555	0.027	0.008	84.91
191	22.0	500.0	13.00	30	26.00	325.00	0.6500	0.024	0.007	86.79
201	22.0	500.0	13.03	30	26.06	325.75	0.6515	0.024	0.009	83.02
211	22.0	500.0	12.76	30	25.52	319.00	0.6380	0.021	0.006	88.68

Backwash

		(mL/min)			(mL/min)					
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	**Pure Water Flux**			
30	21.8	500.0	13.00	10	78.00	975.00	PP-1			
30	21.8	500.0	12.95	10	77.70	971.25			**Membrane Thickness**	
									145	
0	21.8	500.0	12.98	10	77.88	973.50	1.20			

(P_0=0.1MPa, HA=2mg		(mL/min)			(mL/min)			Abs		
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	R(%)
0		500.0	21.59	20	64.77	809.63	1.0000	0.054	0.004	92.59
5		500.0	17.06	20	51.18	639.75	0.7902	0.047	0.005	90.74
10		500.0	15.60	20	46.80	585.00	0.7226	0.042	0.005	90.74
20		500.0	14.22	20	42.66	533.25	0.6586	0.035	0.007	87.04
30		500.0	12.74	20	38.22	477.75	0.5901	0.031	0.01	81.48
40		500.0	12.59	20	37.77	472.13	0.5831	0.029	0.005	90.74
50		500.0	12.50	20	37.50	468.75	0.5790	0.020	0.004	92.59
62		500.0	11.89	20	35.67	445.88	0.5507	0.017	0.007	87.04
70		500.0	11.62	20	34.86	435.75	0.5382	0.014	0.008	85.19
80		500.0	11.43	20	34.29	428.63	0.5294	0.013	0.008	85.19
90		500.0	11.01	20	33.03	412.88	0.5100	0.012	0.008	85.19
120		500.0	19.82	30	39.64	495.50	0.6120			

	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	
120		500.0	19.42	30	38.84	485.50	0.5997	0.057	0.011	80.70
125		500.0	16.60	30	33.20	415.00	0.5126	0.049	0.009	84.21
130		500.0	15.69	30	31.38	392.25	0.4845	0.047	0.009	84.21
140		500.0	14.27	30	28.54	356.75	0.4406	0.043	0.009	84.21
150		500.0	12.98	30	25.96	324.50	0.4008	0.041	0.009	84.21
160		500.0	12.58	30	25.16	314.50	0.3885	0.036	0.01	82.46
170		500.0	12.40	30	24.80	310.00	0.3829	0.030	0.007	87.72
180		500.0	12.07	30	24.14	301.75	0.3727	0.030	0.009	84.21
190		500.0	11.79	30	23.58	294.75	0.3641	0.025	0.01	82.46
200		500.0	11.67	30	23.34	291.75	0.3604	0.023	0.008	85.96
210		500.0	11.61	30	23.22	290.25	0.3585	0.023	0.009	84.21
220		500.0	11.59	30	23.18	289.75	0.3579	0.022	0.007	87.72
230		500.0	11.47	30	22.94	286.75	0.3542	0.022	0.008	85.96

UV

Pure Water Flux

t(min)	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)	PP-1
30	21.8	500.0	25.67	30	51.34	641.75	
30	21.8	500.0	25.82	30	51.64	645.50	
(P_0=0.1MPa, HA=2mg/L)							
0	21.8	500.0	25.74	30	51.48	643.50	1.22

Membrane Thickness

83

t(min)	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)	J/J_0	Abs **Reservoir**	**Permeate**	R(%)
0	17.0	500.0	21.12	30	42.24	528.00	1.0000	0.062	0.022	64.52
5		500.0	17.35	30	34.70	433.75	0.8215	0.051	0.006	90.32
10		500.0	15.83	30	31.66	395.75	0.7495	0.045	0.006	90.32
20		500.0	14.48	30	28.96	362.00	0.6856	0.038	0.003	95.16
30	21.0	500.0	12.70	30	25.40	317.50	0.6013	0.034	0.004	93.55
40		500.0	11.98	30	23.96	299.50	0.5672	0.031	0.006	90.32
50		500.0	11.79	30	23.58	294.75	0.5582	0.028	0.006	90.32
62		500.0	11.44	30	22.88	286.00	0.5417	0.026	0.004	93.55
70		500.0	11.15	30	22.30	278.75	0.5279	0.025	0.004	93.55
80	22.0	500.0	11.06	30	22.12	276.50	0.5237	0.021	0.005	91.94
90	22.0	500.0	10.96	30	21.92	274.00	0.5189	0.020	0.004	93.55

	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0
91	14.0	500.0	6.54	30	13.08	163.50	0.3097
100	14.0	500.0	7.63	30	15.26	190.75	0.3613
110	15.0	500.0	8.43	30	16.86	210.75	0.3991
120	16.0	500.0	8.76	30	17.52	219.00	0.4148
130	16.0	500.0	9.06	30	18.12	226.50	0.4290
140	16.0	500.0	9.77	30	19.54	244.25	0.4626
150	16.0	500.0	10.50	30	21.00	262.50	0.4972
180	21.8	500.0	20.02	30	40.04	500.50	0.9479

	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)	J/J_0	Abs **Reservoir**	**Permeate**	
181	13.0	500.0	16.88	30	33.76	422.00	0.7992	0.057	0.046	19.30
185	14.0	500.0	14.23	30	28.46	355.75	0.6738	0.050	0.009	84.21
190	15.0	500.0	12.85	30	25.70	321.25	0.6084	0.047	0.007	87.72
200	15.0	500.0	11.79	30	23.58	294.75	0.5582	0.044	0.005	91.23
210	15.0	500.0	11.24	30	22.48	281.00	0.5322	0.038	0.005	91.23
220	15.0	500.0	10.49	30	20.98	262.25	0.4967	0.035	0.005	91.23
230	15.0	500.0	10.55	30	21.10	263.75	0.4995	0.032	0.004	92.98
240	16.0	500.0	9.89	30	19.78	247.25	0.4683	0.030	0.004	92.98
250	16.0	500.0	9.84	30	19.68	246.00	0.4659	0.029	0.005	91.23
260	16.0	500.0	9.59	30	19.18	239.75	0.4541	0.026	0.004	92.98
270	16.0	500.0	9.51	30	19.02	237.75	0.4503	0.024	0.004	92.98

H_2O_2

		(mL/min)			(mL/min)		**Pure Water Flux**
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	PP-1
30	21.8	500.0	13.28	10	79.68	996.00	(P_0=0.1MPa, HA=2mg/L)
30	21.8	500.0	13.10	10	78.60	982.50	

PP-1										
(P_0=0.1MPa, HA=2mg/L)									**Membrane Thickness**	
									79	
flow rate 0.5 l/m			18.65	30.00	37.300	466.250	1.09			
		(mL/min)			(mL/min)			Abs		
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	R(%)
0	18.4	500.0	17.16	30	34.32	429.00	1.0000	0.060	0.003	95.00
5		500.0	15.69	30	31.38	392.25	0.9143	0.048	0.003	95.00
10		500.0	14.56	30	29.12	364.00	0.8485	0.045	0.004	93.33
20	21.0	500.0	13.26	30	26.52	331.50	0.7727	0.042	0.005	91.67
30		500.0	12.45	30	24.90	311.25	0.7255	0.037	0.004	93.33
40	22.0	500.0	12.02	30	24.04	300.50	0.7005	0.033	0.005	91.67
50	22.0	500.0	11.42	30	22.84	285.50	0.6655	0.030	0.004	93.33
62		500.0	11.19	30	22.38	279.75	0.6521	0.028	0.004	93.33
70	23.0	500.0	10.95	30	21.90	273.75	0.6381	0.026	0.005	91.67
80		500.0	10.83	30	21.66	270.75	0.6311	0.024	0.004	93.33
90	23.0	500.0	10.54	30	21.08	263.50	0.6142	0.023	0.004	93.33

t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0		
100	15.0	500.0	7.00	30	14.00	175.00	0.4079	0	0
110	16.0	500.0	7.05	30	14.10	176.25	0.4108	0	0
120	16.0	500.0	6.42	30	12.84	160.50	0.3741	0	0
130	16.0	500.0	6.12	30	12.24	153.00	0.3566	0	0
140	17.0	500.0	6.65	30	13.30	166.25	0.3875	0	0
150	17.0	500.0	6.72	30	13.44	168.00	0.3916	0	0
180	15.0		11.59	30	23.18	289.75	0.6754		

		(mL/min)			(mL/min)			Abs		
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	R(%)
181	14.0	500.0	9.76	30	19.52	244.00	0.5688	0.058	0.017	94.83
186	15.0	500.0	10.14	30	20.28	253.50	0.5909	0.055	0.005	94.83
191	15.0	500.0	10.06	30	20.12	251.50	0.5862	0.052	0.007	93.10
201	16.0	500.0	9.73	30	19.46	243.25	0.5670	0.049	0.008	91.38
211	16.0	500.0	9.17	30	18.34	229.25	0.5344	0.045	0.009	93.10
221	16.0	500.0	8.81	30	17.62	220.25	0.5134	0.041	0.008	91.38
231	16.0	500.0	8.53	30	17.06	213.25	0.4971	0.038	0.008	93.10
241	16.0	500.0	8.34	30	16.68	208.50	0.4860	0.036	0.009	93.10
251	17.0	500.0	8.07	30	16.14	201.75	0.4703	0.036	0.009	91.38
261	17.0	500.0	7.78	30	15.56	194.50	0.4534	0.032	0.009	93.10
271		500.0		30	0.00	0.00	0.0000			93.10

Ozone

		(mL/min)			(mL/min)					
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	**Pure Water Flux**			
30	21.8	500.0	13.28	10	79.68	996.00				
30	21.8	500.0	13.10	10	78.60	982.50			**Membrane Thickness**	
									79	
0			18.65	30.00	37.300	466.250	1.09			
		(mL/min)			(mL/min)			Abs		
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	R(%)
80	18.4	500.0	17.16	30	34.32	429.00	1.0000	0.060	0.003	95.00
90		500.0	15.69	30	31.38	392.25	0.9143	0.048	0.003	93.75
100		500.0	14.56	30	29.12	364.00	0.8485	0.045	0.004	93.33
110	21.0	500.0	13.26	30	26.52	331.50	0.7727	0.042	0.005	92.86
120		500.0	12.45	30	24.90	311.25	0.7255	0.037	0.004	91.89
130	22.0	500.0	12.02	30	24.04	300.50	0.7005	0.033	0.005	90.91
140	22.0	500.0	11.42	30	22.84	285.50	0.6655	0.030	0.004	90.00
150		500.0	11.19	30	22.38	279.75	0.6521	0.028	0.004	89.29
160	23.0	500.0	10.95	30	21.90	273.75	0.6381	0.026	0.005	88.46
170		500.0	10.83	30	21.66	270.75	0.6311	0.024	0.004	87.50
180	23.0	500.0	10.54	30	21.08	263.50	0.6142	0.023	0.004	86.96

	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)			
100		500.0	7.00	30	14.00	175.00	0.4079	0	0
110		500.0	7.05	30	14.10	176.25	0.4108	0	0
120		500.0	6.42	30	12.84	160.50	0.3741	0	0
130		500.0	6.12	30	12.24	153.00	0.3566	0	0
140		500.0	6.65	30	13.30	166.25	0.3875	0	0
150		500.0	6.72	30	13.44	168.00	0.3916	0	0

180			11.59	30	23.18	289.75	0.6754			
		(mL/min)			(mL/min)			Abs		
	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)		**Reservoir**	**Permeate**	
181	15.0	500.0	9.76	30	19.52	244.00	0.5688	0.058	0.017	94.83
185	15.0	500.0	10.14	30	20.28	253.50	0.5909	0.055	0.005	94.55
190	15.0	500.0	10.06	30	20.12	251.50	0.5862	0.052	0.007	94.23
200	16.0	500.0	9.73	30	19.46	243.25	0.5670	0.049	0.008	93.88
210	16.0	500.0	9.17	30	18.34	229.25	0.5344	0.045	0.009	93.33
220	16.0	500.0	8.81	30	17.62	220.25	0.5134	0.041	0.008	92.68
230	16.0	500.0	8.53	30	17.06	213.25	0.4971	0.038	0.008	92.11
240	16.0	500.0	8.34	30	16.68	208.50	0.4860	0.036	0.009	91.67
250	16.0	500.0	8.07	30	16.14	201.75	0.4703	0.036	0.009	91.67
260	16.0	500.0	7.78	30	15.56	194.50	0.4534	0.032	0.009	90.63
270	16.0	500.0		30	0.00	0.00	0.0000			

271	14.0	500.0	10.91	30	21.82	272.75	0.6358			
300	15.0	500.0	10.51	30	21.02	262.75	0.6125			
301	15.0	500.0	6.36	30	12.72	159.00	0.3706			
305	15.0	500.0	6.21	30	12.42	155.25	0.3619			
310	15.0	500.0	6.09	30	12.18	152.25	0.3549			
320	15.0	500.0	5.86	30	11.72	146.50	0.3415			
330	15.0	500.0	5.4	30	10.80	135.00	0.3147			
340	15.0	500.0	5.33	30	10.66	133.25	0.3106			
350	15.0	500.0	5.02	30	10.04	125.50	0.2925			
360	15.0	500.0	4.87	30	9.74	121.75	0.2838			
375	15.0	500.0	4.03	30	8.06	100.75	0.2348			
390	15.0	500.0	4.57	30	9.14	114.25	0.2663			
405	15.0	500.0	4.58	30	9.16	114.50	0.2669			
420	15.0	500.0	4.61	30	9.22	115.25	0.2686			
435	15.0	500.0	4.6	30	9.20	115.00	0.2681			
435	16.0	500.0	9.45	30	18.90	236.25	0.5507			
470	16.0	500.0	6.69	30	13.38	167.25	0.3899			
471	16.0	500.0	12.77	30	25.54	319.25	0.7442	0.052	0.038	26.92
475	14.0	500.0	10.13	30	20.26	253.25	0.5903	0.054	0.022	57.69
480	14.0	500.0	9.61	30	19.22	240.25	0.5600	0.054	0.02	61.54
490	14.0	500.0	8.7	30	17.40	217.50	0.5070	0.054	0.02	61.54
500	14.0	500.0	7.92	30	15.84	198.00	0.4615	0.053	0.02	61.54
510	14.0	500.0	7.53	30	15.06	188.25	0.4388	0.049	0.017	67.31
520	14.0	500.0	7.26	30	14.52	181.50	0.4231	0.045	0.017	67.31
530	13.0	500.0	6.86	30	13.72	171.50	0.3998	0.044	0.017	67.31
540	13.0	500.0	6.61	30	13.22	165.25	0.3852	0.046	0.017	67.31
550	14.0	500.0	6.53	30	13.06	163.25	0.3805	0.046	0.017	67.31
560	14.0	500.0	6.48	30	12.96	162.00	0.3776	0.043	0.017	67.31

UV H_2O_2

		(mL/min)			(mL/min)					
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	**Pure Water Flux**			
30	21.8	500.0	25.67	30	51.34	641.75			**Membrane Thickness**	
30	21.8	500.0	25.82	30	51.64	645.50			93	
0		500.0	22.31	30	44.62	557.75	1.17			

		(mL/min)			(mL/min)			Abs		
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	R(%)
0	17.7	500.0	19.07	30	38.14	476.75	1.0000	0.054	0.022	59.26
5	18.1	500.0	15.42	30	30.84	385.50	0.8086	0.051	0.003	94.44
10	18.1	500.0	14.19	30	28.38	354.75	0.7441	0.046	0.002	96.30
20	18.6	500.0	12.58	30	25.16	314.50	0.6597	0.042	0.003	94.44
30	18.8	500.0	11.28	30	22.56	282.00	0.5915	0.037	0.002	96.30
40	18.9	500.0	10.86	30	21.72	271.50	0.5695	0.035	0.003	94.44
50	18.8	500.0	10.51	30	21.02	262.75	0.5511	0.032	0.002	96.30
60	18.9	500.0	10.23	30	20.46	255.75	0.5364	0.030	0.002	96.30
80	18.7	500.0	9.74	30	19.48	243.50	0.5107	0.029	0.008	85.19
90	18.8	500.0	9.67	30	19.34	241.75	0.5071	0.024	0.002	96.30
100	18.8	500.0	9.47	30	18.94	236.75	0.4966	0.022	0.002	96.30

	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0
101	19.3	500.0	5.70	30	11.40	142.50	0.2989
110	20.4	500.0	8.23	30	16.46	205.75	0.4316
120	21.1	500.0	9.21	30	18.42	230.25	0.4830
130	21.8	500.0	9.39	30	18.78	234.75	0.4924
140	22.1	500.0	10.11	30	20.22	252.75	0.5302
150	22.6	500.0	10.62	30	21.24	265.50	0.5569
160	22.8	500.0	10.99	30	21.98	274.75	0.5763
190		500.0	19.33	30	38.66	483.25	1.0136

		(mL/min)			(mL/min)			Abs		
	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	
191	19.3	500.0	17.90	30	35.80	447.50	0.9386	0.058	0.005	91.38
195	19.6	500.0	15.70	30	31.40	392.50	0.8233	0.050	0.005	91.38
200	19.9	500.0	14.88	30	29.76	372.00	0.7803	0.045	0.005	91.38
210	19.9	500.0	13.05	30	26.10	326.25	0.6843	0.040	0.008	86.21
220	20.1	500.0	11.96	30	23.92	299.00	0.6272	0.037	0.006	89.66
230	20.1	500.0	11.06	30	22.12	276.50	0.5800	0.034	0.008	86.21
240	10.1	500.0	10.69	30	21.38	267.25	0.5606	0.032	0.008	86.21
250	20.2	500.0	10.39	30	20.78	259.75	0.5448	0.031	0.006	89.66
260	20.3	500.0	10.21	30	20.42	255.25	0.5354	0.028	0.006	89.66
270	20.2	500.0	9.80	30	19.60	245.00	0.5139	0.024	0.006	89.66
280	22.2	500.0	9.60	30	19.20	240.00	0.5034	0.022	0.006	89.66

Ozone H_2O_2

Pure Water Flux

Membrane Thickness
57

	t(min)	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)
	30	21.8	500.0	25.67	30	51.34	641.75
	30	21.8	500.0	25.82	30	51.64	645.50
0	14.0	500.0	22.58	20	67.74	846.75	2.21

t(min)	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)	J/J_0	Abs **0.065**	**Permeate**	R(%)
0	14.0	500.0	15.34	30	30.68	383.50	1.0000	0.062	0.038	38.71
5	15.0	500.0		30	0.00	0.00	0.0000	0.061	0.008	87.10
10	15.0	500.0	12.55	30	25.10	313.75	0.8181	0.055	0.006	90.32
20	15.0	500.0	11.04	30	22.08	276.00	0.7197	0.050	0.01	83.87
30	16.0	500.0	9.93	30	19.86	248.25	0.6473	0.047	0.009	85.48
40	16.0	500.0	9.33	30	18.66	233.25	0.6082	0.043	0.007	88.71
50	17.0	500.0	8.92	30	17.84	223.00	0.5815	0.040	0.01	83.87
60	17.0	500.0	8.57	30	17.14	214.25	0.5587	0.040	0.013	79.03
70	17.0	500.0	8.12	30	16.24	203.00	0.5293	0.040	0.011	82.26
80	16.0	500.0	7.89	30	15.78	197.25	0.5143	0.039	0.012	80.65
90	16.0	500.0	7.61	30	15.22	190.25	0.4961	0.038	0.012	80.65
120			10.80	30	21.60	270.00	0.7040			

	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0
122	18.0	500.0	6.96	30	13.92	174.00	0.4537
130	17.0	500.0	6.85	30	13.70	171.25	0.4465
140	16.0	500.0	6.50	30	13.00	162.50	0.4237
150	15.0	500.0	6.41	30	12.82	160.25	0.4179
160	15.0	500.0	6.10	30	12.20	152.50	0.3977
170	15.0	500.0	6.11	30	12.22	152.75	0.3983
180	15.0	500.0	6.21	30	12.42	155.25	0.4048
190	15.0	500.0	6.18	30	12.36	154.50	0.4029
200	15.0	500.0	5.92	30	11.84	148.00	0.3859
210	15.0	500.0	6.00	30	12.00	150.00	0.3911
220	15.0	500.0	5.97	30	11.94	149.25	0.3892
250	15.0	500.0	11.09	30	22.18	277.25	0.7229

	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)	J/J_0	Abs **Reservoir**	**Permeate**	
251	17.0	500.0	13.16	30	26.32	329.00	0.8579	0.055	0.06	-9.09
255	17.0	500.0	12.84	30	25.68	321.00	0.8370	0.051	0.024	56.36
260	18.0	500.0	12.67	30	25.34	316.75	0.8259	0.050	0.022	60.00
270	18.0	500.0	12.09	30	24.18	302.25	0.7881	0.047	0.021	61.82
280	18.0	500.0	11.63	30	23.26	290.75	0.7581	0.044	0.018	67.27
290	18.0	500.0	11.14	30	22.28	278.50	0.7262			
300	18.0	500.0	10.92	30	21.84	273.00	0.7119	0.038	0.017	69.09
310	18.0	500.0	10.32	30	20.64	258.00	0.6728	0.038	0.014	74.55
320	18.0	500.0	10.25	30	20.50	256.25	0.6682	0.034	0.013	76.36
330	18.0	500.0	10.11	30	20.22	252.75	0.6591	0.034	0.013	76.36
340	18.0	500.0	10.02	30	20.04	250.50	0.6532	0.033	0.012	78.18

UV Ozone

		(mL/min)			(mL/min)					
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	**Pure Water Flux**			
30	21.8	500.0	25.67	30	51.34	641.75				
30	21.8	500.0	25.82	30	51.64	645.50				
	PP-1								**Membrane Thickness**	
	(P_0=0.1MPa, HA=2mg/L)								140	
0	14.0	500.0	25.08	30	50.15	626.88	1.95			
		(mL/min)			(mL/min)				Abs	
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**resivor**	**Permeate**	R(%)
0	14.0	500.0	12.83	30	25.66	320.75	1.0000	0.052	0.028	46.15
5	14.0	500.0	11.84	30	23.68	296.00	0.9228	0.049	0.003	94.23
10	15.0	500.0	11.62	30	23.24	290.50	0.9057	0.047	0.001	98.08
20	16.0	500.0	11.04	30	22.08	276.00	0.8605	0.043	0.002	96.15
30	17.0	500.0	10.99	30	21.98	274.75	0.8566	0.041	0.003	94.23
40	18.0	500.0	10.79	30	21.58	269.75	0.8410	0.037	0.003	94.23
50	18.0	500.0	10.58	30	21.16	264.50	0.8246	0.031	0.002	96.15
60	18.0	500.0	10.39	30	20.78	259.75	0.8098	0.030	0.001	98.08
70	19.0	500.0	10.13	30	20.26	253.25	0.7896	0.025	0.002	96.15
80	19.0	500.0	9.76	30	19.52	244.00	0.7607	0.024	0.002	96.15
90	19.0	500.0	9.63	30	19.26	240.75	0.7506	0.022	0.002	96.15
120			11.68	30	23.36	292.00	0.9104			
	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0			
121	14.0	500.0	7.34	30	14.68	183.50	0.5721			
130	14.0	500.0	6.73	30	13.46	168.25	0.5246			
140	15.0	500.0	7.50	30	15.00	187.50	0.5846			
150	15.0	500.0	7.88	30	15.76	197.00	0.6142			
160	15.0	500.0	8.19	30	16.38	204.75	0.6383			
170	15.0	500.0	8.92	30	17.84	223.00	0.6952			
180	14.0	500.0	8.28	30	16.56	207.00	0.6454			
210		500.0	13.84	30	27.68	346.00	1.0787			
		(mL/min)			(mL/min)			Abs		
	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	
211	13.0	500.0	13.64	30	27.28	341.00	1.0631	0.054	0.026	51.85
215	14.0	500.0	11.74	30	23.48	293.50	0.9150	0.053	0.008	85.19
220	15.0	500.0	11.04	30	22.08	276.00	0.8605	0.050	0.007	87.04
230	15.0	500.0	11.10	30	22.20	277.50	0.8652	0.050	0.007	87.04
240	16.0	500.0	9.34	30	18.68	233.50	0.7280	0.046	0.006	88.89
250	15.0	500.0	8.96	30	17.92	224.00	0.6984	0.040	0.006	88.89
260	15.0	500.0	8.88	30	17.76	222.00	0.6921	0.038	0.006	88.89
270	15.0	500.0	8.48	30	16.96	212.00	0.6610	0.036	0.006	88.89
280	15.0	500.0	8.12	30	16.24	203.00	0.6329	0.035	0.006	88.89
290	15.0	500.0	7.77	30	15.54	194.25	0.6056	0.034	0.006	88.89
300	15.0	500.0	7.76	30	15.52	194.00	0.6048	0.033	0.008	85.19

UV ozone H_2O_2

		(mL/min)			(mL/min)		**Pure Water Flux**			
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	membrane			
30	21.8	500.0	13.28	10	79.68	996.00	12-4-M2			
30	21.8	500.0	13.10	10	78.60	982.50	(P_0=0.1MPa, HA=2mg/L)			
First foul		(mL/min)			(mL/min)			Abs		
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	R(%)
30	16.0	500.0	13.11	30	26.22	327.75	1.0000	0.057	0.007	87.72
35	18.0	500.0	13.01	30	26.02	325.25	0.9924	0.051	0.003	94.74
40	18.0	500.0	12.64	30	25.28	316.00	0.9641	0.046	0.002	96.49
50	17.0		11.47	31	22.20	277.50	0.8467	0.044	0.003	94.74
60	17.0	500.0	10.78	30	21.56	269.50	0.8223	0.038	0.003	94.74
70	17.0	500.0	10.25	30	20.50	256.25	0.7818	0.035	0.002	96.49
80	17.0	500.0	10.06	30	20.12	251.50	0.7674	0.032	0.001	98.25
90	18.0	500.0	10.00	30	20.00	250.00	0.7628	0.030	0.002	96.49
100	18.0	500.0		30	0.00	0.00	0.0000	0.028	0.003	94.74
110	18.0	500.0	9.56	30	19.12	239.00	0.7292	0.025	0.003	94.74
120	18.0	500.0	9.32	30	18.64	233.00	0.7109	0.023	0.003	94.74
Pure water										
120	18.0	500.0	12.12	30	24.24	303.00	0.9245			
130	19.0	500.0	12.19	30	24.38	304.75	0.9298			
150	20.0	500.0	11.87	30	23.74	296.75	0.9054			
cleaning										
	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0			
151	18.0	500.0	6.70	30	13.40	167.50	0.5111			
160	17.0	500.0	7.42	30	14.84	185.50	0.5660			
170	16.0	500.0	7.82	30	15.64	195.50	0.5965			
180	16.0	500.0	8.16	30	16.32	204.00	0.6224			
190	16.0	500.0	8.45	30	16.90	211.25	0.6445			
200	16.0	500.0	8.54	30	17.08	213.50	0.6514			
210	16.0	500.0	8.66	30	17.32	216.50	0.6606			
pure water										
211	16.0	500.0	15.78	30	31.56	394.50	1.2037			
240	16.0	500.0	15.34	30	30.68	383.50	1.1701			
2nd foul		(mL/min)			(mL/min)			Abs		
	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	**Reservoir**	**Permeate**	
240	14.0	500.0	13.46	30	26.92	336.50	1.0267	0.052	0.008	84.62
245	15.0	500.0	12.32	30	24.64	308.00	0.9397	0.048	0.004	92.31
250	16.0	500.0	11.62	30	23.24	290.50	0.8863	0.046	0.007	86.54
260	17.0	500.0	10.53	30	21.06	263.25	0.8032	0.044	0.009	82.69
270	17.0	500.0	9.76	30	19.52	244.00	0.7445	0.040	0.01	80.77
280	17.0	500.0	9.48	30	18.96	237.00	0.7231	0.039	0.009	82.69
290	17.0	500.0	9.16	30	18.32	229.00	0.6987	0.035	0.008	84.62
300	17.0	500.0	8.27	30	16.54	206.75	0.6308	0.033	0.008	84.62
310	17.0	500.0	8.48	30	16.96	212.00	0.6468	0.032	0.01	80.77
320	17.0	500.0	8.39	30	16.78	209.75	0.6400	0.031	0.008	84.62
330	17.0	500.0	8.22	30	16.44	205.50	0.6270	0.031	0.009	82.69

Super Foul

Pure Water Flux

t(min)	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)
30		500.0	13.56	30	27.12	339.00
30		500.0	13.54	30	27.08	338.50

Membrane Thickness

'a, HA=2mg/L)

0		500.0	13.55	30	27.10	338.75	1.15

t(min)	T(℃)	(mL/min) Inlet	Out(mL)	Out(s)	(mL/min) Outlet	J(LMH)	J/J_0	Abs Reservoir	Permeate	R(%)	ml of 200 p HA added
0	16.5	500.0	11.79	30	23.58	294.75	1.0000	0.051	0.02	60.78	
5	16.8	500.0	11.94	30	23.88	298.50	1.0127	0.049	0.002	96.08	
10	16.8	500.0	11.46	30	22.92	286.50	0.9720	0.048	0.001	98.04	
20	17.5	500.0	10.89	30	21.78	272.25	0.9237	0.045	0.001	98.04	
30	17.6	500.0	10.54	30	21.08	263.50	0.8940	0.044	0.002	96.08	
40	17.8	500.0	9.96	30	19.92	249.00	0.8448	0.043	0.002	96.08	
50	17.9	500.0	9.70	30	19.40	242.50	0.8227	0.042	0.002	96.08	
60	18.1	500.0	9.56	30	19.12	239.00	0.8109	0.038	0.001	98.04	
70	18.3	500.0	9.32	30	18.64	233.00	0.7905	0.036	0.001	98.04	
80	18.1	500.0	9.18	30	18.36	229.50	0.7786	0.036	0.001	98.04	
90	18.1	500.0	8.94	30	17.88	223.50	0.7583	0.034	0.001	98.04	
120	18.3	500.0	8.70	30	17.40	217.50	0.7379	0.030	0.002	96.08	
150	18.1	500.0	8.27	30	16.54	206.75	0.7014	0.029	0.002	96.08	
210	18.1	500.0	7.94	30	15.88	198.50	0.6735	0.025	0.003	94.12	
270	18.1	500.0	7.55	30	15.10	188.75	0.6404	0.020	0.002	96.08	
330	18.2	500.0	7.20	30	14.40	180.00	0.6107	0.017	0.002	96.08	
390	18.2	500.0	7.18	30	14.36	179.50	0.6090	0.013	0.001	98.04	
											30
405	18.1	500.0	7.09	30	14.18	177.25	0.6014	0.053	0.003	94.34	
415	18.1	500.0	7.11	30	14.22	177.75	0.6031	0.051	0.003	94.34	
450	18.1	500.0	6.74	30	13.48	168.50	0.5717	0.045	0.005	90.57	
510	18.1	500.0	6.42	30	12.84	160.50	0.5445	0.041	0.009	83.02	
570	17.9	500.0	6.06	30	12.12	151.50	0.5140	0.034	0.005	90.57	
630	18.0	500.0	5.96	30	11.92	149.00	0.5055	0.030	0.005	90.57	
											20
635	18.0	500.0	5.83	30	11.66	145.75	0.4945	0.054	0.006	88.89	
655	18.0	500.0	5.74	30	11.48	143.50	0.4869	0.053	0.006	88.89	
1425	17.9	500.0	9.61	60	9.61	120.13	0.4075	0.015	0.008	85.19	
											30
1435	17.8	500.0	9.61	60	9.61	120.13	0.4075	0.055	0.008	85.45	
1465	17.9	500.0	9.59	60	9.59	119.88	0.4067	0.051	0.011	80.00	
1520	17.0	500.0	9.51	60	9.51	118.88	0.4033	0.047	0.01	81.82	
1640	18.2	500.0	9.17	60	9.17	114.63	0.3889	0.039	0.011	80.00	
											10
	18.2	500.0		60	0.00	0.00	0.0000	0.052	0.012	76.92	
1700	18.1	500.0	9.16	60	9.16	114.50	0.3885	0.048	0.014	73.08	
1760	18.0	500.0	8.98	60	8.98	112.25	0.3808	0.044	0.012	76.92	
1840	18.1	500.0	8.97	60	8.97	112.13	0.3804	0.038	0.013	75.00	

t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	pure water
	19.3	500.0		60	0.00	0.00	0.0000	
1850	20.4	500.0	5.52	60	5.52	69.00	0.2341	
1860	21.1	500.0	5.53	60	5.53	69.13	0.2345	
1870	21.8	500.0	5.64	60	5.64	70.50	0.2392	
1880	22.1	500.0	5.66	60	5.66	70.75	0.2400	
1890	22.6	500.0	5.64	60	5.64	70.50	0.2392	
1900	22.8	500.0	5.69	60	5.69	71.13	0.2413	
1930		500.0	14.55	60	14.55	181.88	0.6170	
1960		500.0	19.28	60	19.28	241.00	0.8176	
t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	#VALUE!	J/J_0	UV/H2O2
1961	19.3	500.0	5.68	31	10.99	137.42	0.4662	
1970	20.4	500.0	6.68	30	13.36	167.00	0.5666	
1980	21.1	500.0	7.11	30	14.22	177.75	0.6031	
1990	21.8	500.0	7.43	30	14.86	185.75	0.6302	
2000	22.1	500.0	7.69	30	15.38	192.25	0.6522	
2010	22.6	500.0	7.79	30	15.58	194.75	0.6607	
2020	22.8	500.0	7.97	30	15.94	199.25	0.6760	
2050		500.0	10.86	30	21.72	271.50	0.9211	pure water

			(mL/min)			(mL/min)			Abs			ml of 200 p
SN	t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	J(LMH)	J/J_0	Reservoir	Permeate	R(%)	HA added
0	2051	17.9	500.0	11.27	30	22.54	281.75	0.9559	0.051	0.046	9.80	
1	2055	17.8	500.0	//8.23	30	#VALUE!	#VALUE!	#VALUE!	0.050	0.009	82.35	
2	2060	18.0	500.0	10.29	30	20.58	257.25	0.8728	0.048	0.008	84.31	
3	2070	18.2	500.0	9.44	30	18.88	236.00	0.8007	0.047	0.008	84.31	
4	2080	18.6	500.0	9.17	30	18.34	229.25	0.7778	0.046	0.008	84.31	
5	2090	18.4	500.0	9.07	30	18.14	226.75	0.7693	0.046	0.008	84.31	
6	2100	19.4	500.0	8.78	30	17.56	219.50	0.7447	0.045	0.008	84.31	
7	2110	19.6	500.0	8.70	30	17.40	217.50	0.7379	0.043	0.007	86.27	
8	2120	19.6	500.0	8.53	30	17.06	213.25	0.7235	0.043	0.008	84.31	
9	2130	19.6	500.0	8.40	30	16.80	210.00	0.7125	0.040	0.009	82.35	
10	2140	19.8	500.0	8.23	30	16.46	205.75	0.6980	0.039	0.008	84.31	
11	2170	20.1	500.0	8.01	30	16.02	200.25	0.6794	0.035	0.008	84.31	
												10
12	2180	20.1	500.0	7.74	30	15.48	193.50	0.6565	0.047	0.01	80.39	
13	2230	10.6	500.0	7.39	30	14.78	184.75	0.6268	0.040	0.01	80.39	
14	2295	20.9	500.0	7.23	30	14.46	180.75	0.6132	0.037	0.011	78.43	
												10
15	2305	20.9	500.0	7.20	30	14.40	180.00	0.6107	0.049	0.009	82.35	
16	2350	21.1	500.0	14.04	60	14.04	175.50	0.5954	0.042	0.01	80.39	
	2410	21.8	500.0	13.66	60	13.66	170.75	0.5793	0.037	0.011	78.43	
												10
	2420	21.8	500.0	13.48	60	13.48	168.50	0.5717	0.049	0.012	76.47	
	2470	17.9	500.0	11.71	60	11.71	146.38	0.4966	0.042	0.012	76.47	
	2525	17.7	500.0	11.58	60	11.58	144.75	0.4911	0.038	0.012	76.47	
												10
	2530	17.7	500.0	11.46	60	11.46	143.25	0.4860	0.051	0.012	76.47	
	2600	17.9	500.0	11.28	60	11.28	141.00	0.4784	0.045	0.013	74.51	
	2650	17.9	500.0	10.64	60	10.64	133.00	0.4512	0.043	0.014	72.55	
	2680			13.80	60	13.80	172.50	0.5852				pure water

SN	t(min)	T(℃)	Inlet	Out(mL)	Out(s)	Outlet	#VALUE!	J/J_0	UV/H2O2
0	2681	15.0	500.0	5.68	60	5.68	71.00	0.2409	
1	2690	16.0	500.0	6.68	60	6.68	83.50	0.2833	
2	2700	17.0	500.0	7.11	60	7.11	88.88	0.3015	
3	2710	17.0	500.0	7.43	60	7.43	92.88	0.3151	
4	2720	17.0	500.0	7.69	60	7.69	96.13	0.3261	
5	2730	17.0	500.0	16.69	60	16.69	208.63	0.7078	pure water
6	2740	17.0	500.0	13.80	60	13.80	172.50	0.5852	