Optimization of O$_3$ as Pre-Treatment and Chemical Enhanced Backwashing in UF and MF Ceramic Membranes for the Treatment of Secondary Wastewater Effluent and Red Sea Water

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ABSTRACT

Optimization of $O_3$ as pre-treatment and Chemical Enhanced Backwashing in UF and MF Ceramic Membranes for the treatment of Secondary Wastewater Effluent and Red Sea Water

Catalina Ivovich Herrera

Ceramic membranes have proven to have many advantages over polymeric membranes. Some of these advantages are: resistance against extreme pH, higher permeate flux, less frequent chemical cleaning, excellent backwash efficiency and longer lifetime. Other main advantage is the use of strong chemical agent such as Ozone ($O_3$), to perform membrane cleaning.

Ozone has proven to be a good disinfection agent, deactivating bacteria and viruses. Ozone has high oxidation potential and high reactivity with natural organic matter (NOM). Several studies have shown that combining ozone to MF/UF systems could minimize membrane fouling and getting higher operational fluxes.

This work focused on ozone – ceramic membrane filtration for treating wastewater effluent and seawater. Effects of ozone as a pre – treatment or chemical cleaning with ceramic membrane filtration were identified in terms of permeate flux and organic fouling.
Ozonation tests were done by adjusting O$_3$ dose with source water, monitoring flux decline and membrane fouling. Backwashing availability and membrane recovery rate were also analyzed. Two types of MF/UF ceramics membranes (AAO and TAMI) were used for this study.

When ozone dosage was higher in the source water, membrane filtration improved in performance, resulting in a reduced flux decline. In secondary wastewater effluent, raw source water declined up to 77% of normalized flux, while with O$_3$ as pre – treatment, source water at its higher O$_3$ dose, flux decreased only 33% of normalized flux. For seawater, membrane performance increase from declining to 37% of its final normalized flux to 21%, when O$_3$ as a pre – treatment was used. Membrane recovery rate also improved even with low O$_3$ dose, as an example, with 8 mg/L irreversible fouling decreases from 58% with no ozone addition to 29% for secondary wastewater effluent treatment. For seawater treatment, irreversible fouling decreased from 37% with no ozone addition to 21% at 8 mg/L, proving ozone is a useful chemical to be used as pre – treatment for both source waters.

Finally, transparent exopolymer particles (TEP) showed a decrease in concentration on the active layer of the membrane surface after chemical enhanced backwashing (CEB) using ozone (O$_3$).
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LIST OF ABBREVIATIONS

3-D FEEM: 3-Dimensional Fluorescence Excitation Emission Matrix
AAO: Anodic Oxide Aluminum membrane
Al₂O₃: Alumina
ATP: Adenosine 5’Triphosphate
BW: Backwashing
CEB: Chemical Enhanced Backwashing
DBP: Disinfection by-product
DOC: Dissolved Organic Carbon
DI: Deionized
DOC: Dissolved Organic Carbon
KDa: Kilo Daltons
KI: Potassium Iodide
LC – OCD: Liquid Chromatography coupled with Organic Carbon Detector
LMH: Lh/m²
LMW: Low Molecular Weight
MF: Microfiltration
MWCO: Molecular weight cut-off
NF: Nanofiltration
NOM: Natural Organic Matter
PWP: Pure Water Permeability
O₃: Ozone
OM: Organic Matter
RLU: Relative Lights Units
RO: Reverse Osmosis

RSW: Red Sea Water

SiO₂: Silica

SEM: Scanning Electron Microscopy

SUVA: Specific Ultraviolet Absorbance

TEP: Transparent Exopolymer Particles

TMP: Transmembrane Pressure

TiO₂: Titanium

TOC: Total Organic Carbon

UF: Ultrafiltration

µm: nanometers

UVA: Absorbance (optical density) of UV Irradiation

WQA: Water Quality Analysis

WW: Secondary Wastewater Effluent

ZP: Zeta Potential

ZrO₂: Zirconium
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1. **Introduction**

1.1. **Background**

With an increasing demand for fresh water in most of the cities of the world, water treatment plants worldwide needs to become more efficiency, or by the near future there will be water shortage and many developing cities will present water stress conditions, especially in Middle East and North Africa.

New technologies have become available for drinking water/wastewater treatments plants in the past years. Membrane filtration is one of the advanced treatment technique that is gaining an important role in water treatment plants. (Zhu, Wen et al. 2008)

Worldwide there has been an increasingly stringed discharge standard for wastewater, as well an increased water reclamation demand. The use of microfiltration and ultrafiltration membranes to treat secondary effluent provides a smaller footprint than conventional water treatments technologies as well as reaching enhanced water quality objectives. (Kim, Davies et al. 2008; Lehman and Liu 2009) The main disadvantage membrane filtration has is loss of productivity over time due to membrane fouling. (Mallevialle 1993; Adham, Jacangelo et al. 1996)

Ceramic Membranes have shown unique advantages over polymeric membranes, such us better resistance to aggressive chemical cleaning, pH variations, higher operational fluxes and less frequent chemical cleaning. (Lehman and Liu 2009) Due to this, several studies
has been conducted on ceramic membranes. (Burggraaf and Cot 1996; Picard, Larbot et al. 2001; Larbot, Gazagnes et al. 2004; Lee and Cho 2004; Karnik, Davies et al. 2005; Lehman and Liu 2009; Xu, Chang et al. 2010) Another advantage of ceramic membranes is it’s resistant to ozone. This chemical, is a good known cleaning and disinfection agent. Ozone can oxidize most organic and inorganic matter, removing color, suspended solids and microorganisms. (You, Tseng et al. 2007)

This study will focus on ozone – ceramic membrane filtration for treating wastewater and seawater. Effects of ozone as a pretreatment or chemical cleaning with ceramic membrane filtration will be identified in terms of permeate flux and organic fouling.

1.2 Hypothesis

- With addition of ozone ($O_3$) as a pretreatment, membrane fouling is expected to reduced, resulting in improving membrane flux in impaired quality source application, such as secondary wastewater effluent (WW) and seawater (RSW).

- Higher flux recovery by chemically enhanced backwashing (CEB) with ozone, would be possible, resulting in a degradation of micro – organisms and natural organic matter (NOM).

- Transparent exopolymer particles (TEP), that are problematical as foulants, may be destroyed with ozone ($O_3$) as both a pre – treatment and chemical enhanced backwashing.
1.3 Goals and Objectives

1.3.1 Main Goal

The main goal of this research is to study the effects of ozone as pre-treatment mechanism to reduce membrane fouling and improve water flux filtration in microfiltration (MF) and ultrafiltration (UF) membranes. Ozone will be applied to two source waters before filtration; also ozone will be use to backwash fouled membranes as a chemical enhanced backwashing (CEB). For this purpose, the water quality analysis and membrane surface layer analysis were done before and after ozonation and before and after filtration.

1.3.2 Specific Objectives

The specific objectives are the following:

- Analysis of O$_3$ dose, by measuring the ozone concentration in the Milli-Q water (PWP) and in the source waters (WW and RSW) at different contact times in the O$_3$ generator set up.

- Optimization of the O$_3$ dose necessary to reduce membrane fouling, reducing the flux decline set at a same pressure.

- Analysis of recovery rate due to backwashing mechanisms at different backwashed pressures in the system.
• Analysis of recovery rate due to backwashing mechanism with pre – ozonated water.

• Analysis of the filtration productivity in the flux decline due to the destruction of TEP.

• To degrade transparent exopolymer particles (TEP) accumulated on the membrane by chemical cleaning with ozone to the membranes.
2. Literature Review

2.1 Pressure Driven Membranes Technologies

Pressure-driven membrane processes use the pressure difference between the feed and permeate side as the driving force to transport the solvent (usually water) through the membrane. Particles and dissolved components are (partially) retained based on properties such as size, shape, and charge. (Jacangelo, Rhodes Trussell et al. 1997; Van der Bruggen, Vandecasteele et al. 2003)

Pressure-driven membrane processes can be classified by several criteria: the characteristics of the membrane (pore size), size and charge of the retained particles or molecules, and pressure exerted on the membrane. These classifications distinguish Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO). (Van der Bruggen, Vandecasteele et al. 2003)

Traditional materials used in pressure-driven membrane processes are organic polymers, such as: Polysulfone, Polyethersulfone, Polyphenylsulfone, Polyvinylidene Fluoride (PVDF), Polypropylene (PP), Polyethylene (PE), Cellulose and Cellulose acetates (CA and CTA), Polyamide (PA), Polyacrylonitrile (PAN), Polytetrafluoroethylene (PTFE), Polycarbonate (PC), Polymethylmethacrylate (PMMA) but lately, new ceramic membranes made of Alumina (Al$_2$O$_3$), Titanium (TiO$_2$), Silica (SiO$_2$), and Zirconium (ZrO$_2$). (Adham, Jacangelo et al. 1996)
2.1.1 Membrane Properties

Some of the membranes properties are:

2.1.1.1 Pure water permeability (PWP)

It can be defined as the flux obtained with pure water per unit of transmembrane pressure (L/m$^2$ h bar) (Zhao, Zhou et al. 2000; Environment 2009)

This property indicates the pressure/energy required apply to the membrane to generate permeate. (Zhao, Zhou et al. 2000; Environment 2009)

2.1.1.2 Pore size

Pore size in a membrane refers to the average size of pores inside the membrane. Its value commonly in nanometers (µm), this function determines whether a molecule can diffuse into or not into the membrane. (Zhao, Zhou et al. 2000; Cromotography 2011)

2.1.1.3 Molecular Weight Cut-Off (MWCO)

Molecular weight cut – off refers to the smallest molecular weight solute that is 90% retained by the membrane to become permeate (filtrate solution); the larger particles (are thus "cut off" from the permeate. Values usually are given in kilo Dalton (KDa). (Novasep 2010; Dow 2011)

2.1.1.4 Hydrophobicity / Hydrophilicity

Refers to whatever the membrane has attraction or not to the water.

A hydrophilic membrane will have an affinity to water and are usually charged or have polar side groups to their structure that will attract water on the other hand, a hydrophobic membrane will be made out of compounds that repelled water and are usually neutral (no charge.) (Hughes 2011)
2.1.1.5 Surface Roughness

Surface roughness of a membrane is important in evaluating the performance of it, as it may affect the transmembrane transport and the fouling potential of it. (Khulbe and Matsuura 2008)

Figure 1 shows a comparison between AAO rough surface membrane and TAMI rough surface membrane. TAMI membrane on the left will have more fouling than AAO membrane on the right, due to its rough surface.

Figure 1: Roughness of surface membrane on TAMI and AAO membrane

2.1.1.6 Chemical stability / chlorine tolerance

Chemical stability and chlorine tolerance are very important membrane properties as it will define the resistance of the membranes for backwashing tests as also for the different pH source water may have. (Cromotography 2011)
2.1.2 Membrane Operation

There are two main mechanisms for membranes filtration; it can be either Dead End Operation or Cross Flow Operation.

2.1.2.1 Dead End Operation

Figure 2: Dead End Operation

![Dead End Operation Diagram]

Figure 2 shows the schematics for dead end operation in membrane filtration. In here, the feed flow is perpendicular to membrane surface and the retained particles form a cake layer on the surface and there is no concentrate stream formation. This operation is preferable for dilute solutions due to lower energy requirements (pumping pressure).

2.1.2.2 Cross Flow Operation

Figure 3: Cross Flow Operation

![Cross Flow Operation Diagram]

Figure 3 shows the schematics for cross flow operation in membrane filtration. In here, the feed flow is parallel to the membrane surface and the retained particles are scoured inside the membrane, leaving a concentrate stream in parallel and the permeate solution is
perpendicular to the membrane. The main advantage of this mechanism is that the filter cake layer is substantially washed away during the filtration process, increasing the length of time that a filter unit can be operational. This mechanism of membrane filtration is preferred when concentrated solutions will be filtered as a way to control thickness of membrane fouling. (Association 2005)

2.1.3 Membrane Classification

The four main categories for pressure driven membranes are Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO). In this literature review, only two of them will be explained, Microfiltration and Ultrafiltration, since research will focus on both of them.

2.1.3.1 Microfiltration (MF) Membranes

Microfiltration is the oldest of the four pressure driven membrane technologies. MF membranes are the biggest pore size membranes out of the four, their pore size ranges between 0.05 to 0.5 µm. It is used primarily for particle removal (clarification), microbial removal, (protozoa and bacteria) but only if further actions are taken to avoid bacterial regrowth. (Van der Bruggen, Vandecasteele et al. 2003; Association 2005) Because of its pores size, MF membranes can operates at ultra low pressure values, and for most MF systems, transmembrane flux ranges between 80 to 200 L h/m². (Jacangelo, Rhodes Trussell et al. 1997; Association 2005)
The main applications of MF membranes are:

- Filtrations for non-potable reuse; by adding MF after secondary wastewater treatment and producing good quality water for irrigation process.
- Pre treatment for Reverse Osmosis; inserting MF before RO, will produce a better water quality for RO process, which will allows RO membranes have a better performance. (Van der Bruggen, Vandecasteele et al. 2003)

2.1.3.2 Ultrafiltration (UF) Membranes

Ultrafiltration (UF) is considered as a clarification and disinfection operation. The main difference between MF and UF membranes is their pore size, ranging between 2 to 100 µm. (Van der Bruggen, Vandecasteele et al. 2003) rejects most macromolecules, microorganisms, bacteria and viruses. Their typical operating pressure ranges between 0.5-5 bars. UF membranes are typically characterized using their MWCO and their main application, apart as pre – treatment for RO operations, is to remove large dissolved molecules, constituting natural organic matter. (Van der Bruggen, Vandecasteele et al. 2003)

2.2 Ceramic Membranes

Ceramic membranes, which can be used in Microfiltration and Ultrafiltration, have superior chemical, thermal, and mechanical stability compared to polymeric membranes. (Burggraaf and Cot 1996), also their pore size can be more easily controlled.
Sintering and the sol/gel process are the most common techniques to prepare ceramic MF membranes. Practically all UF membranes are prepared with the sol-gel technique. (Burggraaf and Cot 1996)

The main advantages ceramic membranes have over polymeric membranes are:

- Resistance against extreme pH
- Resistance to higher temperature ranges.
- Enabling rigorous cleaning with acid, base, and hot water
- Narrow and well defined Pore Size Distribution
- Higher Porosity
- Excellent Solvent Resistance
- Good Product Recovery Ratios (99%)
- Rejection Rates ranges between 95–100%
- Ozone Resistance
- Higher Permeate Flux
- Less frequent Chemical Cleaning
- Excellent Backwash Efficiency
- Longer lifetime (~ 20 Years)
- Higher durability against Oxidants, Strong Acids and Bases.

Despite the fact that ceramic membranes offer a large number of advantages, no important expansion has been accomplished yet. This can be attributed to the disadvantage of the high price of production. Even though ceramic MF and UF
membranes were developed long time ago, they have always been considered as being a niche product. Their high cost can get to more than $1,000/m² compared to polymeric membranes which price can attend $100/m². (Karnik, Davies et al. 2005).

The base materials for the preparation of ceramic membranes are alumina (A12O3), titanium (TiO2), silica (SiO2), and zirconium (ZrO2). (Burggraaf and Cot 1996)

2.2.1 AAO Membranes

AAO membranes refers to Anodic Aluminium Oxide membrane, an Anapore™ inorganic membrane (Anodisc™), which are fabricated by Whatman (C) Company, a division of GE Health Care Company (USA). Their main material fabrication is Aluminium (Al2O3).

AAO membranes are characterized for having a uniform, two dimensional pore sizes, higher porosity and a cylindrical/conical-shaped pore. Commercially they are not available.
Figure 4: Top View and Cross Section of AAO membrane

Figure 4 shows top view and cross section view of AAO membrane using a Scanning Electron Microscopy (SEM). The principal difference in the cross section view between MF and UF membranes can be seen in the third part of Figure 4, where above image refers to MF membrane and below picture refers to UF membrane. Images were obtained by Ph.D. student, Changwon Ha.

2.2.2 TAMI Membranes

TAMI membranes are fabricated by TAMI Industries (FRANCE). Their main fabrication materials are Zirconia Dioxide (ZrO$_2$) & Titania Dioxide (TiO$_2$).

TAMI membranes are characterized for having a rough, three dimensional pore sizes and an asymmetric structure. They also present uneven thickness through the membranes surface. Commercially they are available on the market.
Figure 5 shows top view and cross section view of TAMI membrane, the principal difference between MF and UF membrane is that MF membranes have a single active layer in the surface, while UF membranes have a double active layer.

Images were taken using a Scanning Electron Microscopy (SEM). Images were obtained by Ph.D. student, Changwon Ha.

2.2.3 Membrane Fouling and Backwashing

2.2.4 Membrane Fouling

Microfiltration (UF) and Ultrafiltration (UF) membranes can be fouled by natural organic matter (NOM). Membrane fouling is a major problem shared by all membranes. (Amy 2008; Lee, Pellegrino et al. 2008)
In general, fouling occurs either on the surface of a membrane or within its pores, and it causes a decrease in flux. There are four major types of fouling: biofouling, scaling, organic, and colloidal. (Mulder 1996; Lee, Pellegrino et al. 2008)

Biofouling results from microbial contamination of feed water and produces a biofilm on the surface of the membrane, which increases the resistance to water permeation through the membrane. Scaling are precipitation and deposition of salts on the membrane surface. Organic fouling comes from substances such as hydrocarbons which coat the surface and plug pores in the support layer. Colloidal fouling mainly stems from particles, such as clay or silica, accumulating on the surface of the membrane. (Mulder 1996; Lim and Bai 2003; Vrouwenvelder, van Paassen et al. 2006)

Fouling can be controlled to some extent by adding disinfectants, anti – scaling agents, and other pre-treatment options. (Vrouwenvelder, van Paassen et al. 2006) However, this does not solve the entire problem, and fouling still remains as an important issue needing an improvement in MF / UF membranes.

2.2.4.1 Natural Organic Matter (NOM)

NOM is a complex heterogeneous mixture of organic material, such as humic substances (HS), polysaccharides, aminosugars, proteins, peptides and lipids among others. (Frimmel, Abbt-Braun et al. 2002) NOM can be divided in two main categories:
Autochthonous NOM, derived from extracellular macromolecules of microorganisms, and, Allochthonous NOM, also referred as humic substances, derived from the decay of plant and animal residues. (Frimmel, Abbt-Braun et al. 2002)

2.2.4.2 Transparent Exopolymer Particles (TEP)
Transparent Exopolymers Particles were first reported in 1993 by (Alldredge, Passow et al. 1993) as microscopic transparent particles in seawater that could be visualized by staining them with Alcian Blue. Further investigations, (Passow 2000; Berman and Holenberg 2005; Berman and Passow 2007) make clear that TEP are presence in freshwater and especially in marine environments.

TEP can range between from ~0.4 μm up to ~100–200 μm. (Berman and Holenberg 2005) TEP are deformable, gel-like particles suspended in the water mass and can appear in many forms; such as clouds, sheets, filaments or clumps. (Bar-Zeev, Berman-Frank et al. 2009)

TEP, as a very sticky substance, may act like a “natural glue” that can entrap or bind organic and inorganic colloids from the feed stream onto the membrane surface. In this way, TEP may not only cause biological or organic fouling but may also enhance colloidal/particulate fouling as well. (Villacorte, Kennedy et al. 2009)
2.2.5 Backwashing

When Backwashing, three kinds of membrane cleaning can occurs:

Figure 6: BW Type 1

Figure 6 shows the first type of backwashing, where backwashed water breaks pore blocking and cake layer formation, leaving an open space for water to pass.

Figure 7: BW Type 2

Figure 7 shows the second type of backwashing, where backwashed water is able to remove particles blocking the membrane but not the cake layer formation on the surface membrane.

Figure 8: BW Type 3

Figure 8 shows the third type of backwashing, where backwashed water is unable to remove particles blocking the membrane pores.
2.3 Ozone

Ozone is a pale blue gas, slightly soluble in water and much more soluble in inert non-polar solvents, it is a colorless gas with a pungent odor readily detectable at concentrations as low as 0.02 to 0.05 ppm (by volume). Ozone gas is highly corrosive and toxic. ((EPA) 1999)

Ozone concentrations used in water treatment are typically below 14 %, limiting mass transfer driving force of gaseous ozone into the water. (Von Gunten 2003) Typical concentrations of ozone found during water treatment ranges between 0.1 to 1 mg/L, although higher concentrations can be attained under optimum conditions. ((EPA) 1999; Von Gunten 2003)

2.3.1 Ozone as a Pre Treatment

Ozone has proven to be a good disinfection agent, deactivating bacteria, protozoa and viruses. Ozone has a high oxidation potential and high reactivity with natural organic matter (NOM). Several studies have shown that combining ozone to MF/UF systems will minimize membrane fouling as well getting higher operational fluxes. (Bader 1982; Karnik, Davies et al. 2005; Wang, Wang et al. 2007)

2.3.2 Ozone Decay (Half – life)

Ozone produce in water will decay rapidly, since it is unstable in water. (Von Gunten 2003; BV 2011; Ozone 2011) Ozone decay in water is known by having a fast initial
decrease phase and second phase is ruled by first – order kinetics. (Von Gunten 2003)

Depending on water quality parameters, ozone half – life is in the range between seconds to hours. (Gottschalk, Libra et al. 2000; Von Gunten 2003; BV 2011) Temperature is also an important factor on ozone half – life, solubility of ozone decreases at higher temperatures and is less stable, as it can be seen in Table 1. (BV 2011)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Half life</th>
<th>T (°C)</th>
<th>Half life</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>3 months</td>
<td>15</td>
<td>30 min</td>
</tr>
<tr>
<td>-35</td>
<td>18 days</td>
<td>20</td>
<td>20 min</td>
</tr>
<tr>
<td>-25</td>
<td>8 days</td>
<td>25</td>
<td>15 min</td>
</tr>
<tr>
<td>20</td>
<td>3 days</td>
<td>30</td>
<td>12 min</td>
</tr>
<tr>
<td>120</td>
<td>1,5 hours</td>
<td>35</td>
<td>8 min</td>
</tr>
<tr>
<td>250</td>
<td>1,5 seconds</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Other factor affecting ozone half – life are pH, water matrix, type and content of natural organic matter (NOM) and its alkalinity. (Von Gunten 2003)
3. **Materials and Methodology**

3.1 **Research Outline**

All experiments that were done are listed in Table 2. The experiments were run with 2 different source waters, Red seawater (RSW) and secondary wastewater effluent (WW) form Jeddah; Milli-Q water (Ultra Pure Deionized Water) was used to identify pure water permeability (PWP) of membranes used for this study.

The first sets of experiments were about ozone optimization, controlling the necessary ozone dose by changing the different contact times, and finally how ozone decays in the sample. The determination of O₃ dose in the water was done by 2 different analysis tools, the indigo method and UV absorbance.

The second set of experiments were about flux decay; after the O₃ concentration in the water is known, different runs were done, in the bench scale test set up, using the appropriate membrane to see if there was an improvement in the flux as a function of time (flux decay) and as a flux volume (volume of water in the permeate).

Backwashing also was tested. After membrane filtration, Milli-Q water was used to backwash at different known pressures for recovery rate of the different membranes. Chemical enhanced backwashing also was done with a known O₃ concentration in Milli-Q water to observe its performance.
Table 2: List of Experiments

<table>
<thead>
<tr>
<th>Number</th>
<th>Experiment</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ozone Dose</td>
<td>Milli-Q</td>
</tr>
<tr>
<td>2</td>
<td>Ozone Decay</td>
<td>Milli-Q</td>
</tr>
<tr>
<td>3</td>
<td>Flux Decline</td>
<td>WW &amp; RSW</td>
</tr>
<tr>
<td>4</td>
<td>Flux Decline w/ O₃ CT</td>
<td>WW &amp; RSW</td>
</tr>
<tr>
<td>5</td>
<td>Backwashing Recovery</td>
<td>Milli-Q, WW &amp; RSW</td>
</tr>
</tbody>
</table>

3.2 Materials

3.2.1 Membranes

Two types of ceramic membranes were used, Microfiltration and Ultrafiltration, TAMI 47 mm and TAMI 90 mm (TAMI Industries, France), and AAO 25mm and AAO 47mm (Whatman Ltd, GE Company, USA). All of them are listed and described in Table 3.

Table 3: MF and UF membrane Characteristics

<table>
<thead>
<tr>
<th>Membrane</th>
<th>TAMI MF</th>
<th>TAMI UF</th>
<th>AAO MF</th>
<th>AAO UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCO [Da] / Average pore diameter [µm]</td>
<td>0.14 µm</td>
<td>150 kD</td>
<td>0.1 µm</td>
<td>0.02 µm</td>
</tr>
<tr>
<td>Material</td>
<td>Zirconia Dioxide (ZrO₂) &amp; Titania Dioxide (TiO₂)</td>
<td>Zirconia Dioxide (ZrO₂) &amp; Titania Dioxide (TiO₂)</td>
<td>Alumina (Al₂O₃)</td>
<td>Alumina (Al₂O₃)</td>
</tr>
<tr>
<td>Process</td>
<td>Sintering</td>
<td>Sintering</td>
<td>Anodic Alumina Oxide</td>
<td>Anodic Alumina Oxide</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>TAMI Industries</td>
<td>TAMI Industries</td>
<td>GE Health Care Company</td>
<td>GE Health Care Company</td>
</tr>
</tbody>
</table>

The molecular weight cut-off (MWCO) is different for every membrane. The TAMI MF, TAMI UF, AAO UF and AAO MF were use for membrane filtration and backwashing recovery. Only AAO MF and AAO UF were used for membrane characterization.
TAMI membranes, after being treated by chemical cleaning per manufacturer instructions, were preserved in Milli-Q water until they were used in the tests. The effective membrane area for the 90 mm disc is 56.3 cm$^2$ and for the 47 mm disc is 13.1 cm$^2$. The material of the cell was stainless steel and a plastic spacer was used to provide the same conditions of the membrane modules.

The TAMI MF membrane has higher MWCO (0.14 µm) than the TAMI UF membrane (150 KDa), this is why TAMI MF membrane has higher permeability so they necessitates lower pressure to obtain the same permeate flow than UF membranes.

The effective area of the AAO membrane 47 mm discs is 13.1 cm$^2$.

3.2.2 Sample Water

Ultra Pure Deionized Water (Milli-Q water) was used to determine the pure water permeability (PWP) of the membranes, also was used for the preparation of ozonated water to provide a targeted ozone dose and its desired contact time.

Secondary wastewater effluent (WW) was collected every two weeks from Al-Ruwais Wastewater Treatment Plant in Jeddah City. Here, after primary treatment, the wastewater is treated in activated sludge aeration tanks. Wastewater was kept in the cold storage room until 24 hours before experiments were run. Prior to experiments, wastewater was pre-filtered with a 0.45 µm pore size filter.
The TOC of the wastewater was 4.60 mg/L, with a pH of 7.3; conductivity of 2850 µS/cm and a turbidity of 0.387 NTU. Calcium ions (Ca$_2^+$) were found in a concentration of 107 mg/L. Finally, Specific Ultraviolet Absorbance (SUVA) was 2.54 L/mg m. These values are from an effluent sample taken on March 2011. Because samples were brought every two weeks to the lab, these values may change from sample to sample, giving different conditions for each experiment run.

Red sea water (RSW) sample was taken from the pipe that feeds the desalination plant in KAUST, located by the Red Sea coast. Sea water also was collected every two weeks and kept in the cold storage room of the lab until 24 hours before experiments were run.

The TOC of the sea water was 1.12 mg/L, with a pH of 7.8 and a conductivity of 57500 µS/cm. Calcium ions (Ca$_2^+$) were found in a concentration of 573.4 mg/L. Finally, SUVA was 1.07 L/mg m. These values are from a water sample taken on March 2011. As explained before, because sample was change every two weeks to the lab, these values may change from sample to sample, giving different conditions for each experiment run.

3.2.3 Ozone Generator

An ozone generator was used to provide a targeted O$_3$ dose and contact time. The ozone system use for the experiments was the LAB2B Ozone Generator from Degremont Technologies. (Triogen Ltd, Scotland, UK)
The LAB2B ozone generator is a small air-cooled unit specifically designed for bench use incorporating function indicators, feed gas flow meter and variable output control. Output variation is manually adjustable using a control knob mounted on the front panel. (Technologies 2011)

3.3 Experimental Set Up

The overall layout of the equipment setup is shown in Figure 11; depending of what type of membrane was used (TAMI or AAO), the specific configuration of the layout varied. Figures are for TAMI membranes (top) and for AAO membrane (bottom).

Dead End filtration system was used in the experiment. The Milli-Q and Sample vessels are made of stainless steel, while the pipes are made of Polyurethane (PUR). The stainless steel vessels have a capacity of 5L. The feed pressure was controlled by a digital pressure device checking the analogue pressure gauge. To monitor permeate flow decline; an electrical balance was connected to a computer.

3.3.1 Ozone Dose and Contact Time

Figure 9: Ozone Dose Generator Set Up
3.3.2 Pure Water Permeability Test

Figure 10: Experimental Set Up for PWP Test. Tami Membrane (Top), AAO Membrane (Bottom)
3.3.3 Flux Decay Test

Figure 11: Flux Decay Set Up. Tami Membrane (Top), AAO Membrane (Bottom)
3.3.4 Backwashing Test

Figure 12: Backwashing Set Up. Tami Membrane (Top), AAO Membrane (Bottom)

For Anapore Backwashing the membrane was flipped in the same module, (AMICON STIRR CELL SYSTEM; USA) so, the set up, does not change.
3.4 Experimental Methods

3.4.1 Standards Conditions

At the beginning of the tests, pure water permeability test with Milli-Q water was filtrated to stabilize water flux. Filtration system of the source water was done by setting a fixed pressure and provided the flux for 30 minutes for the desire time.

3.4.2 Ozone Dose (O₃ dose)

To obtain the targeted ozone concentration, 2 liters of Milli-Q water are put in the ozone contractor and then the oxygen line, coming from the ozone generator, is put in contact with it. A gas line goes from the ozone contractor to a 2L vessel containing KI Solution (16.6 g/L) to destroy the excess of ozone that does not dissolve in water.

The operational conditions of the ozone generator where the following:
Oxygen Pressure: 0.2 bar
Flow meter: 2 L/min Magnet Ring: 350 rpm

As soon as the ozone generator was turned on, the time was measured with a chronometer, and samples of ozonated water were taken at 0.5, 1, 2, 3, 4, 5, 7, 10 and 15 minutes. Immediately, samples were measured by the Indigo Method or by UV Absorbance.
This experiment was done in Milli-Q water because it is Ultra Pure Deionized Water, O₃ will react with any chemical or specie in the water and the concentration of O₃ will be the highest reachable concentration.

When the source water is ozonated, it is expected that O₃ dose in water will decrease because of the reactions of ozone with the different species present in the two sample waters, when all this chemical reaction are finished, eventually will reach the same O₃ concentration in the sample water as in Milli-Q water.

3.4.2.1 Indigo Method Measurement

The indigo method for the determination of ozone was developed by the Swiss Federal Institute for Water Resources and Water Pollution Control (Bader 1982). It is based on determining the ozone concentration according to the gradually change of color in a concentration and also by UV Absorbance at 600 nm.

3.4.2.2 UV Absorbance Measurement

Another method to determine the concentration of ozone in the water is through UV Absorbance. When water is measured at 254 nm, the concentration of ozone in water is known in mg/L.

3.4.3 Ozone Decay

When ozone concentration in the water reaches its maximum, after 15 minutes running, the ozone generator was switched off, and a sample of ozonated Milli-Q was measured by UV absorbance at every minute for 1 hour.
3.4.4 Pure Water Permeability Test

Pure water permeability test was done to determine the stable flux of the membranes at different fixed pressures. To be able to compare all the membranes 1 bar pressure was used as an initial pressure.

Because each membrane has a different permeability, a different pressure point was used for each membrane.

3.4.5 Preliminary Tests

3.4.5.1 Ozone Optimization

Flux was set at an exact pressure (0.1 bars for MF and 0.7 bars for UF) with Milli-Q to stabilize it until there were no significant changes in the flux. Source water was ozonated at the required O₃ dose, with the ozone generator system and then the pre – treated source water passed through the membrane for 30 minutes. Filtered volume was measured with an electrical balance and recorded in the computer every 30 seconds.

To know the exact O₃ dose in the water, the O₃ contact time graph will be integrated to have the exact O₃ concentration that was used as the time of the measurement.
This was done until it was determined the minimum amount of ozone necessary to provide a significantly decrease on the flux decline of the membrane. Each experiment was done with a new water sample.

3.4.6 Flux Decline

3.4.6.1 Flux Decline in Secondary Wastewater Effluent and in Red Sea Water

Flux was set at an exact flow (400 LHM) with Milli-Q to stabilize it until there were no significant changes in the flux. Source water was passed through the membrane for 30 minutes. Filtered Volume was measured with an electrical balance and recorded in the computer every 30 seconds. Each experiment was done with a new water sample.

3.4.6.2 Flux Decline in Secondary Wastewater Effluent and in Red Sea Water with O₃ dose

Flux was set at an exact flow (400 LHM) with Milli-Q to stabilize it until there were no significant changes in the flux. Source water was ozonated at the required O₃ dose, with the ozone generator system and then pre – treated source water was passed through the membrane for 30 minutes. Filtered volume was measure with an electrical balance and recorded in the computer every 30 seconds. Each experiment was done with a new water sample.
3.4.7 Backwashing and Recovery Rate

3.4.7.1 Backwashing with Milli-Q water at Different Pressures

For this set of experiments, flux was set at an exact flow (400 LMH) with Milli-Q to stabilize it until there were no significant changes in the flux. Source water was passed through the membrane for 30 minutes. Filtered volume was measured with an electrical balance and recorded in the computer every 30 seconds. Then pressure was increased from its original value and membrane was backwashed for 2 minutes with Milli-Q water. Backwash pressures used were 2, 5, 10 and 20 times original pressure value. After that, pressure was decrease back down to its original value and source water was filtered for 10 minutes to determine membrane recovery rate. Each experiment was done with a new water sample.

3.4.7.2 Backwashing with Milli-Q water at a Specific O₃ dose

Flux was set at an exact flow (400 LMH) with Milli-Q to stabilize it until there were no significant changes in the flux. Source water was passed through the membrane for 30 minutes. Filtered volume was measured with an electrical balance and recorded in the computer every 30 seconds. Milli-Q water was ozonated for 8 mg/L, in the generator system and then pressure was double from its original value and the membrane was backwashed for 2 minutes. After that, pressure was decrease back down to its original value and source water was filtered for 10 minutes to determine membrane recovery rate.
3.4.7.3 Backwashing with Ozonated Source Water

Flux was set at an exact flow (400 LMH) with Milli-Q to stabilize it until there were no significant changes in the flux. Source water was ozonated at the required O$_3$ dose, with the ozone generator system and then pre – treated source water was passed through the membrane for 30 minutes. Pressure was doubled from its original value and the membrane was backwashed for 2 minutes. After that, pressure was decrease back down to its original value and the source water was filtered for 10 minutes to determine membrane recovery rate. Each experiment was done with a new water sample.

3.5 Analytical Methods

3.5.1 Treatment of Samples

Permeate was collected in a 2L glass vessel. For the water quality analysis samples, permeate was put in a 125mL sample bottle and preserved in a cold room (4 °C) for a maximum of 2 days until they were analyzed.

Fouled membranes were conserved in a Petri dish with Milli-Q water in the cold room for a maximum of 1 day until they were analyzed.

3.5.2 General Analysis Outline

Analytical parameters mainly consist of two parts; water quality analysis during the tests, and membrane surface visualization.
3.5.3 Water Quality Analysis

Water quality analysis was done before and after ozonation tests, and before and after filtration test. Water that was used to backwashed the membrane was also analyzed.

3.5.3.1 ATP

An ACelsis Advance Luminometer (Belgium) was used to calculate the amount of adenine 5’ triphosphate (ATP) in the samples ozonated water as well as for water samples.

Active biomass was determined in duplicate by measuring the ATP concentration from 50 µL samples. The luminometer added 100 µL of CelsisLuminEX-B reagent to a sample to release ATP from the bacterial cells. Subsequently, 100 µL of CelsisLumATE-PM was added for light production. Finally the amount of light produced in the reaction was measured in relative light units (RLU).

3.5.3.2 Zeta Potential

A Zetasizer Nano Series instrument from Malvern Company (Worcestershire, UK) was used to obtain zeta potential for different water samples and also particle size was measured after ozonation of sample water. No dilution or pH adjustment was performed.

Laser Doppler Micro-electrophoresis is the technique used to measure zeta potential. An electric field is applied to a solution of molecules or a dispersion of particles, which will
then move with a velocity related to their zeta potential. This velocity is measured using a patented laser interferometric technique called M3-PALS (Phase analysis Light Scattering).

3.5.3.3 3-D FEEM

Several 3-Dimensional Fluorescence Excitation Emission Matrixes (3-D FEEM) were obtained with a Fluoromax-4 Spectrofluorometer (Horiba, USA) for different water sample. The preparation of the samples is simple, consisting only in the filtration of the water with a 0.45μm filter. No dilution was performed, nor pH adjustment.

3.5.3.4 LC – OCD

A Liquid Chromatography coupled with Organic Carbon Detector analyzer (LC-OCD) Model 8, DOC LABOR DR. HUBER (Germany) was used to analyze the organic carbon content in the water samples. The process consists of three size exclusion chromatography (SEC) columns that divide the organic carbon into several fractions based on size and hydrophobic and inorganic characteristics. Around 1000μL of sample are injected into the instrument and filtered in-line with a 0.45μm filter when using diluted wastewater effluent (2000μL for seawater). The deposit on the filter is backwashed after 5 min and directly analyzed with the TOC analyzer to determine the particulate organic carbon (POC) content. This process will take 130 minutes per sample. The organic carbon detector used is based on a thin film reactor principle (“Gräntzel” type). Inorganic carbon is removed with air stripping. The organic carbon is oxidized to CO₂ by UV radiation at 185 nm. The CO₂ is analyzed using non dispersive infrared
detection. The detection limits are in the parts per billion concentrations. UV absorbance was also determined in parallel. CDOC is the chromatographable fraction of DOC, which refers to the hydrophilic fraction of DOC. Results were calculated using peak area. HOC is the hydrophobic fraction (Huber 1998).

3.5.4 Membrane Analysis

Membrane surface visualization and membrane characterization were performed only for AAO membranes (UF & MF) since it was not possible to do it in TAMI membranes, due to their thickness and materials constitution.

3.5.4.1 Zeta Potential

Zeta Potential was done on AAO UF and MF membranes to determine the electrical charge of the active layer. The instrument used was an Anton Paar Zeta Potential Analyser (Austria). It uses a clamping cell where two pieces of membrane are used to create a channel of 25mm of length and 5mm width, with the active layers facing each other, and then the charge of the membrane in mVolts is measured when an electrolyte flows through it. In this case, two electrolytes (NaCl and KCl) were used to determine the electrical surface charge of the membrane. The ZP is measured over the pH range in which the membrane can operate (3 to 11), so the proper injection of acid (0.1M HCl) or base (0.1M NaOH) is added in the titration process.
3.5.4.2 Transparent Exopolymer Particles (TEP) Visualization

To visualize TEP in WW and RSW membranes are stained with Alcian Blue solution 0.025% of Alcian blue 8GX powder (SIGMA-ALDRICH®).

The membrane was at room temperature was rinsed with ultra pure water for 1 min, then it was submerged in Alcian Blue Solution for 10 minutes and finally rinsed again in ultra pure water for 1 minute.

An Olympus BX61 Motorized Transmitted and Reflected Light Research Microscope (Japan) was used with different objectives (60x and 100x) to take images of a fouled membrane. Images were taken with the 100x lens.

3.6 Calculations

3.6.1 Ozone Calculations

To known the concentration of ozone in water, is necessary to know the amount of ozone mass (mg/L) that was injected into the system as well as the concentration of O₃ (mg/L) that reacted during the ozonation experiment.
The following equation was used to obtain the mass of O₃ reacted.

\[
O₃\text{Reacted}(n) = \sum_{i=0}^{n} (y - f(t_i)) \ast \Delta t_i
\]

Where:

\( y \) = maximum concentration of O₃ achieved in the system (mg/L)

\( f(t_i) \) = concentration of O₃ at measure \( t_i \)

\( \Delta t_i = t_i - t_{(i-1)} \)

\( t_i \) = measured time in the experiment

After data was obtained from the computer, several calculations have to be made in order to compare the performance of the membranes.

3.6.2 Flux at (20°C)

Filtration Flux (J) was obtained through the Flow Rate (Q) data, obtained from the computer, divided by the surface area of the membrane (S). Flux data were corrected to a standard temperature of 20 °C using the following formula to account for the variation of water viscosity with temperature.

\[
J (20°C) = Q \ast \frac{1,024^{20-T}}{S}
\]
Where:

\( J \) = filtrate flux (L/hm²)
\( Q \) = measured flow rate (L/h)
\( T \) = measured temperature (°C)
\( S \) = membrane surface area (m²)

3.6.3 Normalized Flux

Specific flux \( (J_s) \) refers to the filtrate flux \( (J) \) that has been normalized by the transmembrane pressure (TMP). Normalized Specific flux \( (J_s/J_s, 0) \) is calculated as the ratio of Specific flux \( (J_s) \) to the initial Specific flux at the beginning of the filtration \( (J_s, 0) \). (Lehman and Liu 2009)

3.6.4 Filtered Volume

Filtered Volume was calculated with the following equation:

\[
FV = Q \times \frac{ITBM}{S}
\]

Where:

\( FV \) = Filtrated Volume (L/m²)
\( Q \) = measured flow rate (L/h)
\( ITBM \) = Interval time between measurements (sec)
\( S \) = membrane surface area (m²)
4. Results and Discussion

4.1 Ozone Concentration and Ozone Decay

4.1.1 Ozone Dose vs. Contact Time

This experiment was done several times under different conditions in the beginning to find the optimal contact time versus O₃ concentration. Finally it was decided that conditions described in the methodology were the one that would be used for all the experiments. With these conditions the experiment was done several times to have a consistency in the results.

4.1.1.1 Milli-Q Water

The conditions of the Milli-Q water were the following:

pH = 7.2

Temperature = 21°C

Figure 13: Ozone Concentration versus Time Milli-Q Water
As it can be seen in Figure 13, the maximum $O_3$ concentration reached in Milli-Q was around 13 mg/L.

Since Milli-Q water is ultra pure water, there is no possible interaction of Ozone with ions or minerals in the water, but because in wastewater as well as in seawater there is natural organic matter and different ions concentration in them, in the beginning, while ozone is reacting with them, there will be less concentration of $O_3$ at the different measured times, eventually, when ozone stop reacting, the concentration of ozone achieved in the sample water will be the same.

Table 4: Ozone Concentration and Ozone Reacted during the experiment for Milli-Q

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$O_3$ Concentration (mg/L)</th>
<th>$O_3$ Reacting (mg/L)</th>
<th>$O_3$ Reacted Accumulated (mg/L)</th>
<th>Mass of $O_3$ Injected (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.8</td>
<td>5.8</td>
<td>5.8</td>
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<td>10.7</td>
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<td>1.2</td>
<td>22.9</td>
<td>67.0</td>
</tr>
<tr>
<td>7</td>
<td>13.0</td>
<td>0.8</td>
<td>23.8</td>
<td>93.9</td>
</tr>
<tr>
<td>10</td>
<td>13.2</td>
<td>0.5</td>
<td>24.3</td>
<td>134.1</td>
</tr>
<tr>
<td>15</td>
<td>13.4</td>
<td>0.0</td>
<td>24.3</td>
<td>201.1</td>
</tr>
</tbody>
</table>

Table 4 shows in the first column ozone concentration measured at the exact indicated time while column two represent the concentration of $O_3$ that was reacting for the specific time that a measurement was done and $O_3$ reacted accumulated refers to the total concentration of ozone that was consumed during the entire experiment.
4.1.1.2 Secondary Wastewater Effluent (WW)

For secondary wastewater effluent, ozonation conditions were the following:

\[ \text{pH} = 7.3 \]

\[ \text{Temperature} = 19.2^\circ\text{C} \]

Figure 14: Ozone Concentration versus Time for WW

As it can be seen in Figure 14, ozone concentration in secondary wastewater effluent is different from ozonation in Milli-Q water, comparing both of them, in the first minutes; ozone concentration is lower in WW than in Milli-Q water, but after minute 7, ozone concentration in the secondary wastewater effluent reached similar concentration than Milli-QW water and after 10 minutes ozone concentration in WW is higher than in Milli-Q water reaching a stable concentration of 15 mg/L as it can be seen in Table 5.

The total amount of ozone mass injected into the system was higher than in Milli-Q water, as there are many chemicals reactions, between natural organic matter and other ions consuming ozone in the wastewater.
Table 5: Ozone Concentration and Ozone Reacted during the experiment for WW

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>O₃ Concentration (mg/L)</th>
<th>O₃ Reacting (mg/L)</th>
<th>O₃ Reacted Accumulated (mg/L)</th>
<th>Mass of O₃ Injected (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>0.26</td>
<td>7.48</td>
<td>7.48</td>
<td>7.61</td>
</tr>
<tr>
<td>1</td>
<td>1.95</td>
<td>6.64</td>
<td>14.12</td>
<td>15.22</td>
</tr>
<tr>
<td>2</td>
<td>5.76</td>
<td>9.46</td>
<td>23.58</td>
<td>30.45</td>
</tr>
<tr>
<td>3</td>
<td>9.05</td>
<td>6.18</td>
<td>29.76</td>
<td>45.67</td>
</tr>
<tr>
<td>4</td>
<td>10.11</td>
<td>5.11</td>
<td>34.87</td>
<td>60.90</td>
</tr>
<tr>
<td>5</td>
<td>11.80</td>
<td>3.42</td>
<td>38.29</td>
<td>76.12</td>
</tr>
<tr>
<td>7</td>
<td>12.07</td>
<td>6.30</td>
<td>44.60</td>
<td>106.57</td>
</tr>
<tr>
<td>10</td>
<td>15.21</td>
<td>0.05</td>
<td>44.64</td>
<td>152.24</td>
</tr>
<tr>
<td>15</td>
<td>15.22</td>
<td>0.00</td>
<td>44.64</td>
<td>228.36</td>
</tr>
</tbody>
</table>

4.1.1.3 Red Sea Water

For seawater, ozonation conditions were the following:

pH = 7.8

Temperature = 19.2°C

Figure 15: Ozone Concentration versus Time for RSW

As Figure 15 shows, in seawater, ozone concentration is similar to Milli-Q water, reaching a maximum concentration of 13.71 mg/L, but it takes longer to reach.
affected by the reactions of ozone and ions presents in the seawater. The total amount O3 mass injected in the system is higher than Milli-Q water, but lower than in secondary wastewater effluent. In seawater, ozone concentration reached it stability after 10 minutes of the start of the ozonation test as in can be seen in Table 6.

Table 6: Ozone Concentration and Ozone Reacted during the experiment for RSW

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>O₃ Concentration (mg/L)</th>
<th>O₃ Reacting (mg/L)</th>
<th>O₃ Reacted Accumulated (mg/L)</th>
<th>Mass of O₃ injected (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>2.35</td>
<td>5.68</td>
<td>5.68</td>
<td>6.86</td>
</tr>
<tr>
<td>1</td>
<td>4.36</td>
<td>4.68</td>
<td>10.36</td>
<td>13.71</td>
</tr>
<tr>
<td>2</td>
<td>6.19</td>
<td>7.52</td>
<td>17.88</td>
<td>27.42</td>
</tr>
<tr>
<td>3</td>
<td>8.73</td>
<td>4.98</td>
<td>22.86</td>
<td>41.14</td>
</tr>
<tr>
<td>4</td>
<td>9.50</td>
<td>4.22</td>
<td>27.08</td>
<td>54.85</td>
</tr>
<tr>
<td>5</td>
<td>10.69</td>
<td>3.02</td>
<td>30.10</td>
<td>68.56</td>
</tr>
<tr>
<td>7</td>
<td>12.39</td>
<td>2.64</td>
<td>32.74</td>
<td>95.98</td>
</tr>
<tr>
<td>10</td>
<td>13.60</td>
<td>0.33</td>
<td>33.08</td>
<td>137.12</td>
</tr>
<tr>
<td>15</td>
<td>13.71</td>
<td>0.00</td>
<td>33.08</td>
<td>205.68</td>
</tr>
</tbody>
</table>

4.1.2 Ozone Decay

After the ozone generator is switch off, ozone concentration in the water starts decaying really fast, several experiments were done to know the exact concentration of ozone in the sample water at the exact moment that the experiments were initiated.

4.1.2.1 Milli-Q Water

Ozone decay was done twice for Milli-Q water; results shown in Table 7 are the average concentration for both experiments.
Table 7: Ozone Concentration Decay versus Time for Milli-Q Water

<table>
<thead>
<tr>
<th>T (min)</th>
<th>O₃ (mg/L)</th>
<th>T (min)</th>
<th>O₃ (mg/L)</th>
<th>T (min)</th>
<th>O₃ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,5</td>
<td>13,30</td>
<td>11</td>
<td>4,82</td>
<td>21</td>
<td>2,62</td>
</tr>
<tr>
<td>1</td>
<td>12,42</td>
<td>12</td>
<td>4,46</td>
<td>22</td>
<td>2,53</td>
</tr>
<tr>
<td>2</td>
<td>10,22</td>
<td>13</td>
<td>4,22</td>
<td>23</td>
<td>2,40</td>
</tr>
<tr>
<td>3</td>
<td>9,62</td>
<td>14</td>
<td>3,90</td>
<td>24</td>
<td>2,38</td>
</tr>
<tr>
<td>4</td>
<td>8,98</td>
<td>15</td>
<td>3,55</td>
<td>25</td>
<td>2,27</td>
</tr>
<tr>
<td>5</td>
<td>7,38</td>
<td>16</td>
<td>3,36</td>
<td>26</td>
<td>2,13</td>
</tr>
<tr>
<td>6</td>
<td>7,06</td>
<td>17</td>
<td>3,18</td>
<td>27</td>
<td>2,08</td>
</tr>
<tr>
<td>7</td>
<td>6,48</td>
<td>18</td>
<td>2,96</td>
<td>28</td>
<td>1,94</td>
</tr>
<tr>
<td>8</td>
<td>5,87</td>
<td>19</td>
<td>2,86</td>
<td>29</td>
<td>1,90</td>
</tr>
<tr>
<td>9</td>
<td>5,50</td>
<td>20</td>
<td>2,75</td>
<td>30</td>
<td>1,84</td>
</tr>
<tr>
<td>10</td>
<td>5,20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to literature, (BV 2011; Solutions 2011), the half life of ozone at 20°C generally occurs at 20 minutes of ozone decay, not taking into consideration wall effects, humidity, organic loading or other catalytic effects.

In this case, ozone half life was seven minutes after the ozone generator is switched off, and after 30 minutes, a minimum amount of ozone concentration remains in the water.

Figure 16: Ozone Concentration Decay versus Time for Milli-Q Water
In Figure 16, it can be seen how fast ozone starts decreasing, before reaching its half-life, after seven minutes, ozone concentration continues to decrease in a constant way.

4.1.2.2 Secondary Wastewater Effluent (WW)

Table 8: Ozone Concentration Decay versus Time for WW

<table>
<thead>
<tr>
<th>T (min)</th>
<th>(O_3) (mg/L)</th>
<th>T (min)</th>
<th>(O_3) (mg/L)</th>
<th>T (min)</th>
<th>(O_3) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>14.73</td>
<td>11</td>
<td>7.30</td>
<td>22</td>
<td>4.01</td>
</tr>
<tr>
<td>1</td>
<td>14.62</td>
<td>12</td>
<td>6.62</td>
<td>23</td>
<td>3.72</td>
</tr>
<tr>
<td>2</td>
<td>13.36</td>
<td>13</td>
<td>6.5</td>
<td>24</td>
<td>3.59</td>
</tr>
<tr>
<td>3</td>
<td>12.27</td>
<td>14</td>
<td>6.15</td>
<td>25</td>
<td>3.32</td>
</tr>
<tr>
<td>4</td>
<td>11.53</td>
<td>15</td>
<td>5.68</td>
<td>26</td>
<td>2.90</td>
</tr>
<tr>
<td>5</td>
<td>10.99</td>
<td>16</td>
<td>5.37</td>
<td>27</td>
<td>2.73</td>
</tr>
<tr>
<td>6</td>
<td>10.01</td>
<td>17</td>
<td>5.10</td>
<td>28</td>
<td>2.59</td>
</tr>
<tr>
<td>7</td>
<td>9.41</td>
<td>18</td>
<td>4.90</td>
<td>29</td>
<td>2.48</td>
</tr>
<tr>
<td>8</td>
<td>8.92</td>
<td>19</td>
<td>4.43</td>
<td>30</td>
<td>2.30</td>
</tr>
<tr>
<td>9</td>
<td>8.12</td>
<td>20</td>
<td>4.31</td>
<td>35</td>
<td>1.77</td>
</tr>
<tr>
<td>10</td>
<td>7.74</td>
<td>21</td>
<td>4.16</td>
<td>45</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 8 shows that for secondary wastewater effluent ozone half life is at 11 minutes after the ozone generator is switched off, which gives 4 minutes more than Milli-Q water, this may be due to ozone interaction with natural organic matter and ions present in the source water.
In Figure 17 it can be seen that for the first 10 minutes ozone declines really fast, but after it gets to its half life, ozone concentration in the wastewater continues to decrease in a constant way. After 30 minutes, the concentration of ozone in the water is still above 2 mg/L and after 45 minutes, a minimum amount of ozone concentration remains in the water.

4.1.2.3 Red Sea Water (RSW)

Table 9: Ozone Concentration Decay versus Time for RSW

<table>
<thead>
<tr>
<th>T (min)</th>
<th>O₃ (mg/L)</th>
<th>T (min)</th>
<th>O₃ (mg/L)</th>
<th>T (min)</th>
<th>O₃ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>13.13</td>
<td>11</td>
<td>6.01</td>
<td>21</td>
<td>4.02</td>
</tr>
<tr>
<td>1</td>
<td>12.07</td>
<td>12</td>
<td>5.87</td>
<td>22</td>
<td>3.73</td>
</tr>
<tr>
<td>2</td>
<td>11.56</td>
<td>13</td>
<td>5.53</td>
<td>23</td>
<td>3.59</td>
</tr>
<tr>
<td>3</td>
<td>10.24</td>
<td>14</td>
<td>5.32</td>
<td>24</td>
<td>3.32</td>
</tr>
<tr>
<td>4</td>
<td>9.82</td>
<td>15</td>
<td>5.01</td>
<td>25</td>
<td>2.98</td>
</tr>
<tr>
<td>5</td>
<td>9.01</td>
<td>16</td>
<td>4.88</td>
<td>26</td>
<td>2.75</td>
</tr>
<tr>
<td>6</td>
<td>8.75</td>
<td>17</td>
<td>4.67</td>
<td>27</td>
<td>2.59</td>
</tr>
</tbody>
</table>
As Table 9 shows, for seawater, ozone decays similar to Milli-Q water, its ozone half life is at nine minutes, two minutes higher than Milli-Q, this is because of the interactions of ozone and ions present in the water, because seawater does not have a high concentration of natural organic matter as secondary wastewater effluent, ozone half life in seawater is two minutes lower than in wastewater.

Figure 18 shows how fast ozone declines for the first nine minutes, but after it reached its half life, ozone concentration in seawater continues to decrease in a constant way. After 30 minutes, the concentration of ozone in the water is below 2 mg/L.

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>7.98</td>
<td>18</td>
<td>4.39</td>
<td>28</td>
<td>2.48</td>
</tr>
<tr>
<td>8</td>
<td>7.14</td>
<td>19</td>
<td>4.25</td>
<td>29</td>
<td>2.35</td>
</tr>
<tr>
<td>9</td>
<td>6.56</td>
<td>20</td>
<td>4.12</td>
<td>30</td>
<td>2.13</td>
</tr>
<tr>
<td>10</td>
<td>6.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2 PWP Test

Pure Water Permeability was done previously in all flux decline experiments to check membrane performance and after chemical cleaning. Typical values for PWP at 1 bar pressure can be seen in Figure 19.

Figure 19: Pure Water Permeability Test in all membranes

UF membranes have a lower permeability than MF membranes; also there is a bigger permeability range between UF and MF among TAMI membranes. The TAMI MF membrane has a permeability eight times higher than the TAMI UF membrane. In AAO the difference between UF and MF is less than two times, as it can be seen in Table 10.

Table 10: PWP Test in all membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Flux (L/m²·h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAMI MF</td>
<td>2228.45</td>
</tr>
<tr>
<td>TAMI UF</td>
<td>407.97</td>
</tr>
<tr>
<td>AAO MF</td>
<td>1903.56</td>
</tr>
<tr>
<td>AAO UF</td>
<td>1152.03</td>
</tr>
</tbody>
</table>
4.3 Preliminary Tests

4.3.1 Ozone Optimization

4.3.1.1 Ozone Concentration

This set of experiments was done to get an idea of how flux decline change with different ozone concentrations.

As it was explained before, because ozone concentration in water starts declining at the minute the ozone generator is switch off, a calculated ozone concentration will be used for the exact moment that experiments starts. Around 90 seconds pass between the ozone generator is switch off, sample water is taken from the ozone generator system and put in the vessel and the experiment start. Results for the ozone concentration that is measured again, after the 90 seconds have passed are shown below in Table 11.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>( \text{O}_3 ) Concentration Milli-Q (mg/L)</th>
<th>( \text{O}_3 ) Concentration WW (mg/L)</th>
<th>( \text{O}_3 ) Concentration RSW (mg/L)</th>
<th>Average Concentration (mg/L)</th>
<th>( \text{O}_3 ) Concentration expressed (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>1.3</td>
<td>0.87</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.9</td>
<td>2.7</td>
<td>2.23</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.7</td>
<td>4.7</td>
<td>5.30</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>7.5</td>
<td>8.17</td>
<td>8</td>
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</tr>
<tr>
<td>4</td>
<td>10.8</td>
<td>9</td>
<td>9.60</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>11.3</td>
<td>10.2</td>
<td>10.67</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>12.1</td>
<td>11.6</td>
<td>11.57</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>12.3</td>
<td>12.4</td>
<td>12.63</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>12.3</td>
<td>12.4</td>
<td>12.63</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>
An average of the three ozone concentrations was done to use as ozone optimization, for this, the less concentration of ozone was assumed, the expressed ozone concentration will be used to compare the two different sample waters.

4.3.1.2 Experiments

In Figure 20 and Figure 21 it can be seen that there is no difference in the flux between 1 mg/L, 2 mg/L and 5 mg/L. After 8 mg/L flux improve considerably, flux decline does not show a significant difference between 8 mg/L and 10 mg/L, and finally at 12 mg/L flux is the most stable of all, having been the maximum ozone concentration reached in the ozone generator.
It was determined that the minimum concentration of ozone necessary to reduce flux decline was a concentration of 8 mg/L. Based on these results, 8 mg/L was used to do chemical enhanced backwashing (CEB).

Also, several experiments were done to compare the difference between ozone residual in the water and no ozone residual, sample water was put in contact with nitrogen gas for two minutes to eliminate all ozone residual in the water. After comparing experiments with residual and non residual for ozone concentration of 2mg/L, 5 mg/L, and 10 mg/L in the water for all the membranes, no changes between them were found and the rest of the experiments were done without eliminating ozone residual from the sample water.
4.4 Flux Decline

Normalized flux versus time graphics will be presented for each experiment, since all experiments have a different flux starting point (around 400 LMH, but depending on the membrane it could vary from 390 LMH to 410LMH) it is not possible to compare flux decline, unless results are showed as normalized flux decline, in which case, experiments can be compared.

By comparing normalized flux to time, it can be determined how long it will take to foul the membrane, and by comparing normalized flux to filtered volume it can be determined after how much filtration volume, the membrane starts decreasing its performance.

4.4.1 Flux Decline with Secondary Wastewater Effluent and with Red Sea Water

4.4.1.1 Secondary Wastewater Effluent

Figure 22 shows results obtained from filtering untreated secondary wastewater effluent, comparing flux decline for both membranes in microfiltration and ultrafiltration.

TAMI membranes for the first 5 minutes show a steeper flux decline, which can be associated to a pore blocking mechanism, after the first 5 minutes, flux decline is much
smoother, corresponding to cake layer formation, related to the second step of fouling formation. There is no significant difference between MF and UF membrane.

AAO membranes show a much smoother flux decline. Although there is a difference between MF and UF membrane for the first 5 minutes, MF has a little steep in its flux decline, which UF membrane does not shows.

Figure 22: Normalized Flux Decline for Wastewater

One of the reasons why AAO shows higher permeability might be associated with the smoother roughness than that TAMI membrane.
4.4.1.2 Red Sea Water

Figure 23 shows the results for seawater flux decline. Compared to wastewater, flux does not decline as much and for TAMI membranes and the steep phase is much smoother. For AAO no steep decrease can be seen, just a smooth decline in the flux.

![Figure 23: Normalized Flux Decline for Seawater](image)

4.4.2 Flux Decline with Secondary Wastewater Effluent and with Red Seawater with O₃ dose/CT

Because of the large numbers of runs made, one run for each different ozone contact time, the results presented are divided according to AAO and TAMI membranes, as well as MF and UF membranes, there are 8 different graphics to represent:

- WW AAO MF Runs
- WW AAO UF Runs
- WW TAMI MF Runs
• WW TAMI UF Runs
• RSW AAO MF Runs
• RSW AAO UF Runs
• RSW TAMI MF Runs
• RSW TAMI UF Runs

4.4.2.1 Secondary Wastewater Effluent (WW)

4.4.2.1.1 WW AAO MF Runs

Figure 24: WW AAO MF Ozone Flux Decline

As it can be seen in Figure 24, flux improves according to different O₃ contact time, from 10 mg/L, membrane permeability increases significantly and for 11 mg/L and 12 mg/L, membrane filtration reaches its maximum permeability according to time.
For the case of flux decline compared to filtered volume, the amount of volume filtered by the membrane increases from 120 L/m² to 160 L/m².

4.4.2.1.2 WW AAO UF Runs

Figure 25: WW AAO UF Ozone Flux Decline

Figure 25 shows that for the UF membrane, the difference between pre treating source water with ozone and normal membrane filtration is not much, although there is a difference, especially after 8 mg/L, where the flux decline is smoother. Filtered volume also increases after 8 mg/L, it increases from 100 l/m² up to 120 L/m². With 12 mg/L membrane filtration improved from 67%, flux decline with no ozone pre – treatment to 50% of its normalized flux.
The main comparison between MF and UF membrane is the improvement reached with ozone as pre-treatment for MF membranes, where the flux at 12 mg/L improve up to 35% of its normalized flux, while in UF membranes, did not improve above 50% of its normalized final flux.

4.4.2.1.3 WW TAMI MF Runs

Figure 26: WW TAMI MF Ozone Flux Decline

In TAMI membranes there is a big difference between adding O₃ as pre-treatment or not. With O₃ membrane permeability increases, flux declines becomes smoother and the steep phase that can be seen in the first 2 runs of Figure 26, (0 mg/L and 1 mg/L), is gone after 9 mg/L of O₃ and 10 mg/L of O₃ concentration.

Filtered Volume is almost doubled, for 0 mg/L, the filtered volume is 85 L/m² and for 12 mg/L, it increases up to 150 L/m².
4.4.2.1.4 WW TAMI UF Runs

Figure 27: WW TAMI UF Ozone Flux Decline

Figure 27 shows the results for secondary wastewater effluents runs with different O$_3$ concentration, as a pre – treatment for TAMI UF membranes. It can be seen that, as in previously results, flux improves as well as O$_3$ concentration is increased.

There is no difference between non pre treatment and 1 mg/L of O$_3$, since O$_3$ concentration is too low, from 2 mg/L of O$_3$ and above, membrane permeability increases. The best flux improvements can be seen in 11 mg/L and 12 mg/L O$_3$ when O$_3$ concentration is at the highest concentration. Filtered Volume also improves from 90 L/m$^2$ to 140 L/m$^2$. 
In all membrane filtration test done with secondary wastewater effluent in the first 5 minutes, there was a big decline in the flux (steep phase), attributed to membrane pore blocking and later in the test, flux continues declining but with a smoother decline, related to cake layer formation in the membrane surface.

4.4.2.2 Red Sea Water (RSW)

RSW membrane filtration tests show that there is not a large decline in the first 5 minutes, as it was observed in the WW membrane filtration tests. MF membrane test shows that more pore blocking occurs with no pre treated water than in UF membranes, where membrane particle size is not big enough for the particles to create pore blocking, making cake layer formation on the membrane surface.

4.4.2.2.1 RSW AAO MF Runs

Figure 28: RSW AAO MF Ozone Flux Decline
In Figure 28 and Figure 29, it can be seen that there is an improvement in the flux as O$_3$ concentration increases, especially for the AAO UF membrane where there is a big difference between no pretreatment of source water and pre – treated water.

For the AAO MF membrane after 5 mg/L of O$_3$, flux improves significantly and between 10 mg/L and 12 mg/L, there is almost no difference in flux decline. In filtered volume, there is a big improvement between concentration of 5mg/L and 12 mg/L from 107 L/m$^2$ up to 183 L/m$^2$. For the AAO UF membrane, between 10 mg/L of O$_3$ and 12 mg/L of O$_3$, there is no difference in the flux and flux does not decline beyond 10% of normalized flux.

4.4.2.2.2 RSW AAO UF Runs

Figure 29: RSW AAO UF Ozone Flux Decline
Because membrane flux in seawater does not decline as much as in secondary wastewater effluent, in both figures (Figure 28 and Figure 29), the scale is different from all other graphics in order to appreciate more the difference of the flux declines. The rest of the graphics have the same scale in order to compare them to secondary wastewater effluent.

4.4.2.2.3  RSW TAMI MF Runs

Figure 30: RSW TAMI MF Ozone Contact Time

Figure 30 shows that there is an improvement of flux filtration due to adding O$_3$ to water as a pre – treatment. In normal source water, with no pre treatment, flux decline is lower than 60% of normalized flux, producing cake layer formation in the membrane surface, while using O$_3$ flux provides an improvement, with decline not any lower than 15% of it normalized flux.
4.4.2.2.4 RSW TAMI UF Runs

Figure 31: RSW TAMI UF Ozone Flux Decline

Figure 31 shows the results for the membrane filtration test with the TAMI UF membranes for seawater, flux does not decline significantly reaching 60% of its normalized flux. Using O₃ as a pre-treatment, flux improves and, for 11 mg/L of O₃ and 12 mg/L of O₃, flux does not decrease lower than 10% of its normalized flux.

As a result of this first set of experiments it can be said that the AAO membranes in general have a better performance in membrane filtration after ozone is used as pre-treatment than TAMI membranes. Seawater (RSW) also shows better performance in its flux decline than secondary wastewater effluent (WW). With no pre-treatment RSW did not decline further than 50% of its normalized flux while WW declined beyond 70% of its initial normalized flux. When adding O₃ as pre-treatment, RSW shows better improvement in membrane filtration than WW.
4.5 Backwashing and Recovery Rate

As was explained above, because of the large numbers of runs made, results are provided for each different membrane. Graphics are shown as:

- WW AAO MF Recovery Rate
- WW AAO UF Recovery Rate
- WW TAMI MF Recovery Rate
- WW TAMI UF Recovery Rate
- RSW AAO MF Recovery Rate
- RSW AAO UF Recovery Rate
- RSW TAMI MF Recovery Rate
- RSW TAMI UF Recovery Rate

4.5.1 Backwashing with Milli-Q at Different Pressures and Specific Ozone Dose

The previous results indicated how flux decline changes with different O₃ concentrations as a pre – treatment. These sets of experiments were focused on backwashing (BW) of the membranes and their recovery rate.

As an easier way to understand the results, they are presented in bar diagrams where, with the exception of bar 1 and 2, each bar represents an experiment. Bar 1 represent normalized initial flux, which was set at 400 LMH and bar 2 represent normalized final flux after 30 minutes run.
The difference between final flux and recovery rate for each experiment represents hydraulically reversible fouling (as flux that can be retrieved after backwashing), and the difference between initial flux and recovery rate for each experiment represents irreversible fouling (flux that cannot be recovered after backwashing).

For MF membranes it was possible to do a backwashing test at all desired different pressures, but for UF membranes because of their higher pressure, it was only possible to do backwashing tests with 2 times the original pressure (2x).

Chemical enhanced backwashing (CEB) with low O₃ dosage (8 mg/L of O₃) was done and compared with highest backwashing pressure (20x) for MF membranes and to normal backwashing pressure (2x) for UF membranes.

Showing results in this way makes it easier to compare which backwashing system (ultra high pressure, or chemical enhanced backwashing) is more effective in removing foulants from the membrane.

4.5.1.1 Secondary Wastewater Effluent (WW)
4.5.1.1.1 WW AAO MF Recovery Rate

Figure 32: WW AAO MF Backwashing Different Pressures

Figure 32 shows that as BW pressure increased, recovery rate also increased. There is not much difference between BW 2x and BW 5x; for BW 10x there is an improvement of the recovery rate and for BW 20x, recovery rate is even higher. Finally with chemical enhanced backwashing (CEB), recovery rate is higher than 90% of initial flux.

4.5.1.1.2 WW AAO UF Recovery Rate

Figure 33: WW AAO UF Backwashing Different Pressures
In Figure 33 it can be seen that for UF membranes, normal BW does not provide a good recovery rate, but when CEB is applied, recovery rate is higher than 90% of initial flux.

4.5.1.1.3 WW TAMI MF Recovery Rate

In Figure 34 it can be seen that because secondary wastewater effluent causes pore blocking in the TAMI MF easily, recovery rate is not very good. Only when CEB and high BW pressure is applied (20x), recovery rate increases, leaving a small amount of irreversible fouling on the membrane.
4.5.1.1.4  WW TAMI UF Recovery Rate

Figure 35: WW TAMI UF Backwashing Different Pressures

Figure 35 indicates that UF membranes do not have a good recovery rate after normal BW. Even after CEB, recovery rate is not as good as for MF membranes.

For secondary wastewater effluent it can be seen that in general, there is a good recovery rate for almost all membranes, with the exception of WW TAMI UF, all of them reached around 90% of recovery rate, leaving only around 10% of irreversible fouling on the membrane.

In all experiments, no significant difference was found between BW at the highest pressure (20x) and chemical enhanced backwashing, the only significant difference was seen for the WW AAO UF membrane, where irreversible fouling decrease from 36% to 9% of its normalized flux.
4.5.1.2 Red Sea Water (RSW)

4.5.1.3 RSW AAO MF Recovery Rate

As it can be seen in Figure 36, generally, there is not a good recovery rate for most of the different BW pressures; only for CEB and BW 20x due, recovery rate reaches to normalized initial flux levels.

4.5.1.3.1 RSW AAO UF Recovery Rate
Figure 37 indicates that there is not a good recovery rate after normal BW. Even after CEB, recovery rate is not as good as for MF membranes.

4.5.1.3.2 RSW TAMI MF Recovery Rate

Figure 38 shows that TAMI membranes with seawater have an excellent recovery rate; comparing BW 5x to BW 2x, there is an improvement in foulants that can be removed by higher pressure backwashing.

After BW 10x, more than 90% of initial flux can be recovered, as there is not much difference between pressure BW 10x, 20x and chemical enhanced backwashing (CEB) with O₃.
Figure 39: RSW TAMI UF Backwashing Different Pressures

Figure 39 shows an improvement from normal pressure backwashing to chemical enhanced backwashing, with a decrease in irreversible fouling from 22% to less than 10%, respectively; when the last one is applied, almost all foulants are removed from the membrane.

Red seawater experiments show good recovery rate for almost all experiments; all experiment reached recovery rate over 88% with O₃ as chemical enhanced backwashing (CEB).

Overall TAMI membranes showed a better performance than AAO membranes for both sources waters (WW) and (RSW) in these set of experiments.
4.5.2 Backwashing with Ozonated Source Water

Backwashing is done almost all the time with permeate, reversing the flux for a short period of time (e.g., a couple of minutes). These set of experiments were done to compare the difference between backwashing with Milli-Q water (previous experiments done) and backwashing for 2 minutes with normal pressure pre-treated source water.

4.5.2.1 Secondary Wastewater Effluent (WW)

4.5.2.1.1 WW AAO MF CEB

Figure 40: WW AAO MF Chemical Enhanced Backwashing

Figure 40 shows how recovery rate improves as O$_3$ concentration is increased. With 12 mg/L of O$_3$, recovery rate flux is double compared to the original final flux, but as O$_3$ concentration increases, there is not a significant improvement on the recovery rate.
Comparing this to Milli-Q BW of the previous experiment, there is a decrease in the reversible fouling while with Milli-Q, the highest pressure recovery rate was above 90%; here only 81% was reached with maximum O$_3$ dose.

4.5.2.1.2 WW AAO UF CEB

A similar trend for MF membrane occurs with UF membranes, as it can be seen below in Figure 41. Recovery rate is not enough if it is compared to Milli-Q highest pressure backwashing, or Milli-Q chemical enhanced backwashing, as it reached only 80% of reversible fouling with the maximum O$_3$ dose.

Figure 41: WW AAO UF Chemical Enhanced Backwashing
4.5.2.1.3 WW TAMI MF CEB Backwashing

Figure 42: WW TAMI MF Chemical Enhanced Backwashing

Pore blocking in wastewater experiments with TAMI membranes is a big issue as was shown before. Figure 42 shows that, after 12 mg/L of O₃, flux recovery are only 86% of its original normalized flux.

4.5.2.1.4 WW TAMI UF CEB Backwashing

Figure 43: WW TAMI UF Chemical Enhanced Backwashing
In TAMI UF membranes with wastewater experiments, chemical enhanced backwashing does not show a high recovery rate. Figure 43 shows that less than 70% can be recovered after maximum O\textsubscript{3} concentration is applied.

These results show a similar tendency in both backwashing experiments done for the WW TAMI UF membrane; in both cases, irreversible fouling could not be decreased below 32% from its original normalized flux.

In general, results show that although there is an improvement from normal pressure Milli-Q backwashing to ozonated source water chemical enhanced backwashing (CEB), this is not enough to have provide recovery rate compared to those achieved with Milli-Q highest pressure backwashing (20x) or Milli-Q chemical enhanced backwashing (CEB).
4.5.2.2 Red Sea Water

4.5.2.2.1 RSW AAO MF CEB Backwashing

As it can be seen in Figure 44 recovery rate for AAO MF membrane in seawater is a little bit lower than Milli-Q chemical enhanced backwashing in the previous experiment, compared to backwashing at the highest pressure, there is an improvement in the recovery rate, decreasing irreversible fouling from 37% to 15% when backwashing with ozonated source water.

4.5.2.2.2 RSW AAO UF CEB Backwashing

![Figure 45: RSW AAO UF Chemical Enhanced Backwashing](image-url)
Seawater has a better recovery rate than wastewater, due to the low amount of natural organic matter. Since for UF membranes applied pressure is higher, backwashing is better than with MF membranes as it can be seen in Figure 45; in here, recovery rate is almost 100%.

### 4.5.2.2.3 RSW TAMI MF CEB Backwashing

For TAMI membranes after 5 mg/L of O₃, recovery rate is above 80% and higher, providing almost 100% of recovery of flux in both cases for maximum O₃ concentration, as it can be seen in Figure 46 for MF membranes and in Figure 47 for UF membranes.

Results shows equals recovery rates for ozonated source water at its maximum O₃ concentration and for Milli-Q chemical enhanced backwashing (CEB).
Overall, for seawater there is no difference between applying ozonated source water or ozonated Milli-Q for chemical enhanced backwashing (CEB), as both set of experiments shows similar recovery rates. TAMI membranes, on average, have better recovery rates than AAO membranes since for both membranes (MF/UF), irreversible fouling is less than a 10%, while for the AAO MF membrane, irreversible fouling is 16% of its normalized original flux.
4.6 Water Quality Analysis

4.6.1 ATP

Table 12 shows the conversion rate between relative light units (RLU) and ATP concentration present in the sample.

Table 12: Conversion Rate from RLU to ATP concentration

<table>
<thead>
<tr>
<th>ATP (mg/L)</th>
<th>RLU</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>16611590</td>
</tr>
<tr>
<td>10</td>
<td>1741320</td>
</tr>
<tr>
<td>1</td>
<td>159805</td>
</tr>
<tr>
<td>0.1</td>
<td>11758</td>
</tr>
</tbody>
</table>

The results for both source waters show as a calibration graph are as follows:

Table 13: ATP results for Secondary Wastewater Effluent

<table>
<thead>
<tr>
<th>Sample</th>
<th>ATP (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WW 0 mg/L of O₃</td>
<td>1.762</td>
</tr>
<tr>
<td>WW 1 mg/L of O₃</td>
<td>1.116</td>
</tr>
<tr>
<td>WW 2 mg/L of O₃</td>
<td>0.770</td>
</tr>
<tr>
<td>WW 5 mg/L of O₃</td>
<td>0.032</td>
</tr>
<tr>
<td>WW 8 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>WW 9 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>WW 10 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>WW 11 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>WW 12 mg/L of O₃</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Table 14: Red Sea Water ATP results

<table>
<thead>
<tr>
<th>Sample</th>
<th>ATP (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSW 0 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>RSW 1 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>RSW 2 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>RSW 5 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>RSW 8 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>RSW 9 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>RSW 10 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>RSW 11 mg/L of O₃</td>
<td>0.000</td>
</tr>
<tr>
<td>RSW 12 mg/L of O₃</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Low levels of ATP can be found in the samples, with a concentration below 2mg/L for Secondary wastewater effluent. This concentration can be related to Natural Organic
Matter. After the 1 mg/L of ozone concentration, ATP concentration decrease under 1 mg/L and after 5 mg/L of O₃, ATP concentration is undetectable.

Low level of relative light units was found in RSW, meaning that no ATP concentration could be found in the water.

4.6.2 Zeta Potential

4.6.2.1 Tables:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WW 0 mg/L of O₃</td>
<td>-13.30</td>
</tr>
<tr>
<td>WW 1 mg/L of O₃</td>
<td>-13.13</td>
</tr>
<tr>
<td>WW 2 mg/L of O₃</td>
<td>-11.52</td>
</tr>
<tr>
<td>WW 5 mg/L of O₃</td>
<td>-13.13</td>
</tr>
<tr>
<td>WW 8 mg/L of O₃</td>
<td>-15.93</td>
</tr>
<tr>
<td>WW 9 mg/L of O₃</td>
<td>-15.57</td>
</tr>
<tr>
<td>WW 10 mg/L of O₃</td>
<td>-16.60</td>
</tr>
<tr>
<td>WW 11 mg/L of O₃</td>
<td>-17.13</td>
</tr>
<tr>
<td>WW 12 mg/L of O₃</td>
<td>-18.07</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSW 0 mg/L of O₃</td>
<td>-15.70</td>
</tr>
<tr>
<td>RSW 1 mg/L of O₃</td>
<td>-13.93</td>
</tr>
<tr>
<td>RSW 2 mg/L of O₃</td>
<td>-13.13</td>
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<tr>
<td>RSW 5 mg/L of O₃</td>
<td>-11.73</td>
</tr>
<tr>
<td>RSW 8 mg/L of O₃</td>
<td>-11.01</td>
</tr>
<tr>
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<td>-10.97</td>
</tr>
<tr>
<td>RSW 10 mg/L of O₃</td>
<td>-10.13</td>
</tr>
<tr>
<td>RSW 11 mg/L of O₃</td>
<td>-10.01</td>
</tr>
<tr>
<td>RSW 12 mg/L of O₃</td>
<td>-9.97</td>
</tr>
</tbody>
</table>
4.6.2.1.1 Figures:

Figure 48: Effect of O₃ on Zeta Potential in WW particles

As it can be seen in Figure 48, zeta potential of particles becomes more negative in WW as O₃ concentration increases, due to the low amount of calcium in source water. There is no visible interaction between O₃ particles and calcium present in sample.

Figure 49: Effect of O₃ on Zeta Potential in RSW particles

For RSW, as can be seen in Figure 49, zeta potential of particles becomes less negative as O₃ concentration increases; because of an increase in calcium/magnesium association
with induced ozone, flux performance in membrane filtration increases when O$_3$ dose/CT is increased.

4.6.3 FEEM

3-Dimensional Fluorescence Excitation Emission Matrix was used for natural organic matter characterization in both sample waters.

Figure 50 explains the principles for FEEM analysis, where 3 types of distinctive fluorescence peaks from Raw WW effluent can be seen.

Figure 50: Principles of FEEM analysis
**Peak A:** represents humic-like organic matter where, $\lambda_{ex/em}$ ranges between 237 ~ 260/380 ~ 460, respectively.

**Peak C:** represents humic-like organic matter where $\lambda_{ex/em}$ ranges between 300 ~ 370/380 ~ 480, respectively.

**Peak T:** represents protein-like organic matter, where $\lambda_{ex/em}$ ranges between 275/310 ~ 340, respectively.

4.6.3.1 Secondary Wastewater Effluent

4.6.3.1.1 Ozone Contact Time

Due to the high amount of organic matter in secondary wastewater, it was analyzed by FEEM after several different $O_3$ concentrations. (Raw WW, 1 mg/L, 2 mg/L, 8 mg/L, 10 mg/L and finally, 12 mg/L).

Results are shown in Figure 51 trough Figure 56.
Figure 51: WW 0 mg/L of O₃

Figure 52: WW 1 mg/L of O₃

Figure 53: WW 2 mg/L of O₃

Figure 54: WW 8 mg/L of O₃

Figure 56: WW 10 mg/L of O₃

Figure 55: WW 12 mg/L of O₃
As shown above, organic matter decreases as O$_3$ concentration is increased. After 8 mg/L of O$_3$ concentration, peak A has decreased and for 12 mg/L, most of humic like matter has have been removed.

Peak C, corresponding to small humic like matter has decreased its level after 10 mg/L of O$_3$ concentration; a similar trend occurs for peak T, representing protein like matter.
4.6.3.1.2 Membrane Filtration and Backwashing

Analyses on FEEM were done after membrane filtration, backwashing and after chemical enhanced backwashing for MF and UF membranes in AAO membranes.

4.6.3.1.2.1 MF membranes

Figure 57 WW AAO MF permeate  
Figure 58: Milli-Q BW AAO MF permeate

Figure 59 Milli-Q O$_3$ BW AAO MF permeate  
Figure 60: Mili Q
As it can be seen in Figure 57 after membrane filtration peak A has decreased indicating partial removal of humic like matter and peak T also has decreased, indicating partial remove of protein like matter.

Figure 58 and Figure 59 are both Milli-Q water used to BW the membrane, comparing them to Figure 60, blank Milli-Q water, there are little amount of humic like and protein like particles retain in the used backwashing water.

After membrane filtration and backwashing natural organic matter (NOM) also decrease.

4.6.3.1.2.2 UF Membranes

Figure 61: WW AAO UF permeate
There is good removal of humic like matter for peak C, as shown in Figure 61, and also peak T shows removal of protein like matter. Concerning peak C, there is not much difference between source wastewater and UF permeate.

Milli-Q water used for BW test in Figure 62 and Figure 63 shows there is not much organic matter in O₃ Milli-Q water after chemical enhanced backwashing (CEB).
4.6.3.2 Red Sea Water

4.6.3.2.1 MF membranes

Figure 65: Raw Red Seawater

Figure 64: RSW AAO MF permeate

Figure 66: Milli-Q BW RSW AAO MF membrane

Figure 67: Milli-Q O₃ BW RSW AAO MF membrane
Red sea water shows less humic like matter but more protein like matter as Figure 64 shows; after MF membrane filtration, some protein like matter has been removed as can be seen in Figure 65, and also humic like matter in peak C shows a decreased.

Using chemical enhanced backwashing, many proteins like matter retained in Milli-Q water, as shown in Figure 67. Normal BW does not retain humic like or protein like matter in the BW Milli-Q as is seen in Figure 66.

4.6.3.2.2 UF membranes

Figure 68: RSW AAO UF permeate
Figure 68 shows RSW permeate for the UF membrane. Much protein like matter and humic like matter for both peaks, have been removed.

In this case, Milli-Q water used to backwash the membrane, shows significant humic like matter was removed from the membrane surface, as a small peak C can be seen in Figure 69.

O₃ Milli-Q water used for CEB in Figure 70 shows a good removal of protein like matter from the membrane surface as a small peak T appears in the FEEM analysis.
4.6.4 LC – OCD

Liquid Chromatography coupled with Organic Carbon Detector analyzer (LC-OCD) was also used for natural organic matter characterization in both sample waters. Analyzed samples were obtained from TAMI membranes.

In Figure 71 it can be seen the principal analysis mechanism for a LC –OCD chromatogram, where main five peak areas can be identified.

Figure 71: LC-OCD Principal Analysis

Area A: Biopolymers; higher molecular weight (MW), polysaccharides bigger than 10 KDa.

Area B: Humic Substances (HS); humic and fulvic acids ranging bigger than 1 KDa.

Area C: Building Blocks; breakdown of products HS or HS- like.
**Area D**: Low molecular weight (LMW) and co-eluted with LMW – HS.

**Area E**: LMW Neutrals.

4.6.4.1 Secondary Wastewater Effluent

4.6.4.1.1 MF permeate

Figure 72: WW LC - OCD MF analysis

As Figure 72 shows, there is a decrease of all areas as secondary wastewater effluent (WW) is treated. Chemical enhanced backwashing with O₃ as pre-treatment shows a major retention of biopolymers and building blocks products. Also, Milli-Q BW effluent shows a good retention of LMW neutrals.
4.6.4.1.2 UF permeate

Figure 73: WW LC - OCD TAMI UF analysis

WW UF LC - OCD analysis shows similar results of MF analysis, as it can be seen in Figure 73, as the membrane is chemical enhanced backwashed with O₃; biopolymers and humic substances (HS) are almost 100% removed. Like before, Milli-Q BW effluent shows a good retention of LMW neutrals.
4.6.4.2 Red Sea Water

4.6.4.2.1 MF permeate

Figure 74: RSW LC - OCD TAMI MF analysis

Red sea water has a large amount of biopolymers (areas A), LMW – HS like substances and LMW neutrals. There is a removal of humic substances and building blocks particles after membrane filtration, LC - OCD analysis shows that Milli-Q used to BW retains from the MF membrane a large amount of biopolymers and HS as it can be seen in Figure 74. In O3 Milli-Q effluent retention of HS and building block particles is even larger.
4.6.4.2.2 UF permeate

Figure 75: RSW LC - OCD TAMI UF analysis

As Figure 75 shows, for the UF membrane the removal of biopolymers and HS is quite low with normal Milli-Q backwashing; when O₃ Milli-Q is used for chemical enhanced backwashing (CEB), biopolymers, HS and building blocks are retained in the O₃ Milli-Q effluent.

4.7 Membrane Analysis

4.7.1 Zeta Potential

As explain in the methodology, two electrolytes (NaCl and KCl), were used to measure the electrical surface charge of the membrane. KCl as electrolyte showed better results than NaCl as electrolyte, and for this reason, only KCl results are shown in this thesis.
Two different KCl concentrations were used while running zeta potential, 5 mM and 10 mM; best results were obtained from 10 mM, since the 5 mM concentration was too low.

4.7.1.1 MF membrane

Figure 76: ZP AAO MF membrane KCl Electrolyte

Figures 76 and 77 show that, as pH is increased on the membrane surface, zeta potential becomes more negative. Its isoelectric point ranges between pH 8 and 9 which it is consistent with many publications. (Huisman, Trägårdh et al. 1998; Fievet, Szymczyk et al. 2001)

Zeta Potential was analyzed to compare AAO and TAMI membranes in terms of surface charge to characterize adsorption of natural organic matter (NOM) to the surface membrane; because it was not possible to run zeta potential on TAMI membranes, because of the membrane thickness, this comparison could not be done.
4.7.2 Transparent Exopolymer Particles (TEP) Visualization

4.7.2.1 Secondary Wastewater Effluent (WW)

4.7.2.1.1 MF Membranes

In Figure 78, TEP cannot be seen as clusters, but particulate TEP is easily seen on the entire membrane with some small clusters between them.
Normal pressure backwashing for the MF membrane does not remove much of the TEP; still there is a lot of particulate TEP visible on the membrane as Figure 79 shows.

In Figure 80 it can be seen that with chemical enhanced backwashing most of TEP particles are gone, leaving only small amount of disaggregated clusters of colloidal TEP visible in the membrane.

For secondary wastewater effluent with MF membrane transparent exopolymer particles (TEP) visualization shows an excellent removal of them with chemical enhanced backwashing (CEB). TEP was seen all over the fouled membrane and while normal backwashing removed some of them, CEB leaves only small amount of disaggregated clusters of colloidal TEP visible on the membrane surface.
Figure 81 shows that for AAO UF membranes, TEP clusters can easily be seen throughout the membrane. These clusters can be related to colloidal TEP that is retained by UF Membranes.

Normal backwashing of the membrane can remove some TEP, but still there are many visible clusters remaining, as Figure 82 shows.

With chemical enhanced backwashing most of the TEP clusters are gone; it appears that ozone is able to disaggregate colloidal TEP into small TEP particles, still, same TEP clusters visible on the membrane surface, as can be seen in Figure 83.
Transparent exopolymer particles (TEP) can be seen as clusters on the UF membrane surface; while normal backwashing does not remove much TEP from the membrane surface as backwashing of MF membranes did, chemically enhanced backwashing appears to remove almost all clusters of TEP of the active layer, leaving only small colloidal TEP particles visible.

4.7.2.2 Red Sea Water (RSW)

4.7.2.2.1 MF Membranes

Figure 84: RSW AAO MF TEP Foulants

Figure 84 shows how TEP sticks to a membrane surface, creating clusters. Because RSW has high concentration of calcium ions (573.4 mg/L), there are large colloidal TEP particles on the membrane surface.

Figure 85: RSW AAO MF TEP Foulants BW

Normal pressure backwashing does not remove TEP from the membrane surface, as many TEP clusters and colloidal TEP can be seen in Figure 85.
Figure 86 shows that chemically enhanced backwashing seems to destroy colloidal TEP into small TEP particles, leaving only small colloidal TEP on the membrane surface.

Although much more colloidal transparent exopolymer particles (TEP) clusters are formed on the MF membrane surface, and little is removed with normal backwashing; when chemical enhanced backwashing of the membrane is performed, almost all TEP clusters are gone leaving only small colloidal TEP on the membrane surface, suggesting a better performance for seawater than for secondary wastewater.

4.7.2.2.2 UF Membranes

In UF membranes after seawater filtration, colloidal TEP can easily be seen on the membrane surface as Figure 87 shows, several clusters, are found in the membrane.
For UF membranes, normal backwashing shows better performance than MF membranes, as can be seen in Figure 88, where clusters of colloidal TEP are highly disaggregated.

Chemically enhanced backwashing of UF membranes seems to work very well, as no colloidal TEP can been seen on the membrane surface as Figure 89 shows. Also, disaggregated TEP particles are not found on the membrane surface.

For UF membrane filtration of seawater, the best removal of all of transparent exopolymer particles is observed, as no detectable TEP can be found when performing chemical enhanced backwashing. Although big clusters of colloidal TEP can easily be seen after membrane filtration, most of them are disaggregated with normal backwashing.

These results are consistent with chemical enhanced backwashing results where 100% of recovery rate was obtained for RSW AAO UF chemical enhanced backwashing (CEB).
5. Conclusions and Future Recommendations

5.1 Conclusions

As O$_3$ concentration increased, ozone dose in Milli-Q water increased as well. After 11 mg/L of O$_3$ concentration, there was no appreciable ozone concentration increase in Milli-Q water, reaching a maximum dose of 13mg/L. Ozone half time was 7 minutes after the ozone generator was switched off. For backwashing and minimizing flux decline, results show that the minimum desired O$_3$ concentration was 8 mg/L.

Results showed that as ozone dosage increased in the source water, membrane filtration improved with decreasing flux decline. As an example, for AAO MF membranes, with secondary wastewater effluent, the raw source water declines to 77% of its normalized flux, while with ozonated source water at a higher O$_3$ dose, flux decreased only 33% of its normalized flux; for seawater, membrane performance increased from declining to 37% of its final normalized flux to 21%, when ozone as a pre – treatment was used. Water quality analysis also shows there was a decrease in natural organic matter when using ozone as a pre – treatment. In FEEM analysis, protein like and big humic like matter were completely remove. Small humic like matter was very much destroyed at 10 min O$_3$ dose.
Membrane filtration results are consistent in showing that AAO membranes have a better performance than TAMI membranes when the source water is pretreated with ozone (O₃).

Backwashing at different pressures also shows an improvement in membrane recovery rate, especially for MF membranes. For both source waters, when applying 20 times the original pressure (20x), membrane recovery is above 90%, and in some cases almost to its original value. For UF membranes, there was an exception with WW TAMI UF where recovery rate was lower than 69%. In general, TAMI membranes showed a better performance than AAO membrane, giving higher recovery rates for all the cases (MF/UF membranes for secondary wastewater effluent (WW) and seawater (RSW); this can be related to the higher fluxes TAMI membranes need when performing backwashing.

Backwashing and membrane recovery rate also improves even using low O₃ concentration; as an example, for AAO MF membranes, with 8 mg/L of O₃ concentration irreversible fouling decreases from being 58% of its normalized final flux with normal pressure backwashing (2x) to 29% with chemical enhanced backwashing (CEB), for secondary wastewater effluent. In seawater, irreversible fouling decreases from being 37% of its normalized final flux, with normal pressure backwashing (2x) to 21% 8 mg/L of O₃ concentration, as chemical enhanced backwashing (CEB). When using high O₃ dose (12 mg/L) with secondary wastewater effluent (WW), membrane recovery was higher
than 80% and for seawater (RSW) membrane recovery was higher than 90% (reversible fouling).

FEEM analysis shows there is retention of humic like matter for O$_3$ Milli-Q while performing chemical enhanced backwashing (CEB). LC - OCD analysis shows that when chemical enhanced backwashing is done, biopolymers, HS and building blocks are retained in the O$_3$ Milli-Q effluent.

However, when backwashing was done using ozonated source water, secondary wastewater effluent (WW) had worst results than for ozonated Milli-Q with chemical enhanced backwashing (CEB). Seawater (RSW), on the other hand, shows no differences on recovery rates performance with both backwashing systems.

Finally, transparent exopolymer particles (TEP) showed a decrease in concentration on the active layer of the membrane surface after chemical enhanced backwashing (CEB) was done, especially for RSW AAO UF membrane, where all visible TEP was removed from the membrane surface.

All of these results prove that ozone (O$_3$) is a useful powerful chemical that can be used as pre – treatment and chemical enhanced backwashing (CEB) for both source waters.
5.2 Future Work and Recommendations

The next step in this research would be the implementation of the pilot plant. A TAMI MF/UF membrane pilot plant was brought to the lab from TAMI Industries. Experiments should be run three months for seawater, and six months for secondary wastewater effluent, considering seasonal changes in the source water, three months during winter season and three months for summer season. An in – line pre ozonation system is considered in order to have continues pre – treated water supply into the system. Also, additional experiments on ozonation/coagulation pre – treatment systems should be further studied at the bench scale level and incorporated in the pilot plant.
REFERENCES


