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PRETREATMENT OPTIMIZATION FOR CERAMIC MICROFILTRATION WITH
OZONATION AND COAGULATION FOR THE REUSE OF WASTEWATER EFFLUENT

By

NICOLA ELARDO

Bachelor of Science, Environmental Engineering, University of New Hampshire, 2020

THESIS

Submitted to the University of New Hampshire

In Partial Fulfillment of

the Requirements for the Degree of

Master of Science

In

Civil and Environmental Engineering

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List of Abbreviations

AOP	Advanced Oxidation Processes
BOD	Biochemical Oxygen Demand
CEB	Chemically Enhanced Backwash
CIP	Cleaning in Place
CMF	Ceramic Microfiltration
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
EPA	Environmental Protection Agency
EU	European Union
FTU	Formazin Turbidity Units
HHNK	Hoogheemraadschap Hollands Noorderkwartier (Water Board Hollands Northern Quarter)
HRT	Hydraulic Retention Time
ILCA	Inline Coagulation
M.S.	Master of Science
MSc	Master of Science
NOM	Natural Organic Matter
PWN	Provinciaal Waterleidingbedrijf Noord-Holland (Provincial Waterworks North Holland)
PWNT	PWN Technologies
RPM	Rotations per Minute
RWZI	Rioolwaterzuiveringsinstallatie (Sewage Treatment Plant)
STOWA	Stichting Toegepast Onderzoek Waterbeheer (Foundation for Applied Water Research)
TMP	Transmembrane Pressure
TOC	Total Organic Carbon
UNH	University of New Hampshire
US	United States
UVT	Ultraviolet Transmittance
WTP	Water Treatment Plant
WWTP	Wastewater Treatment Plant

Abstract

PRETREATMENT OPTIMIZATION FOR CERAMIC MICROFILTRATION WITH OZONATION AND COAGULATION FOR THE REUSE OF WASTEWATER EFFLUENT

By

Nicola Elardo

University of New Hampshire, May 2022

Ceramic microfiltration (CMF) is a promising alternative to traditional polymeric microfiltration and its chemical resistance makes it particularly attractive for sustainable water reuse applications. This research investigated the ability of ozonation and coagulation as pretreatments to improve the performance of ceramic microfiltration using HHNK's WWTP in Wervershoof, The Netherlands. With a CMF pilot plant design flow of 200 L/h, critical flux tests were completed using ozonation individually and with coagulation sequentially to evaluate the ceramic membrane filtration performance. Results showed that with an ozone residual before the ceramic membrane, the performance increased significantly compared to no pretreatment and without an ozone residual. 11 target pharmaceuticals were also sampled to monitor the removal using different ozone doses testing the requirements from Dutch Water Authority regulations. One limitation to using ozone is the formation of a suspect human carcinogen, bromate. Using a bench scale ozone testing device, different ratios of hydrogen peroxide to ozone dose were tested to observe the formation of bromate and how hydrogen peroxide mitigates it. Results showed that the ozone residual during the experiments was a helpful indication of the resulting bromate formation. The triple bottom line also needs to be taken into consideration when optimizing the pretreatment processes. Specifically, the financial aspect when applying the pretreatment methods at a full-scale facility with more energy and chemical costs.

Acknowledgements

This research was made possible by the support and funding from the University of New Hampshire and PWN Technologies. I am so thankful for the relationship between Dr. James Malley and PWNT that have continued to offer M.S. graduate students a great opportunity to do research abroad. The use of international research facilities is an experience like none other.

Without the supervision and support from Dr. James Malley, Mr. Martin Spruijt, MSc, Dr. Joop Kruithof, Dr.ir. Bram Martijn, and Dr. Paula Mouser, this research and paper would not have been possible. Dr. Malley, I am so grateful that you have been my advisor for the past six years. You have helped me grow as a person and a future engineer, thank you for everything! Martin, it was a pleasure working with you for six months. Thank you for your daily support helping me navigate a new country and a complex research project, it was a blast!

I'd also like to thank Sabine Gabriel and Lourenco Gouveia for their help with the pilot plant and helping me solve all the issues so that it can run smoothly. Linda Greydanus was also essential in helping me with the Dutch immigration, moving between three different accommodations and resolving all my bike difficulties. A special thanks to Maria and Jaap Pennekamp for allowing me to stay in their beautiful home in Andijk for five months and to Marleen Ophorst for being a great roommate and Dutch translator.

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Chapter 1

1. Introduction

PWN Technologies BV is an international company which provides the water supply market with advanced solutions for drinking water challenges which are implemented and optimized into PWN's WTP in Andijk. PWN is responsible for treating and distributing water to the households, companies, and institutions in the North Holland province. Their main intake water source for the WTP in Andijk is the IJsselmeer (White, 2019).

The overall goal of reusing wastewater for industrial use is to create a zero-waste system – closing the water cycle. The Dutch Ministry of Infrastructure and Water Management is working to develop a set of rules to pharmaceutical control by further treating secondary wastewater treatment effluent. As seen in Figure 1, the discharge point for the WWTP of HHNK Wervershoof is very close to the intake point for PWN's WTP, making the IJsselmeer a priority site for the contaminants released. Many pharmaceuticals are released into the IJsselmeer which is both bad for the lake and for the PWN treatment facility (Spruijt et al., 2021). The source protection would be very beneficial for both the overall water quality of the IJsselmeer and future treatment of the water at PWN's surface water treatment plant Andijk.

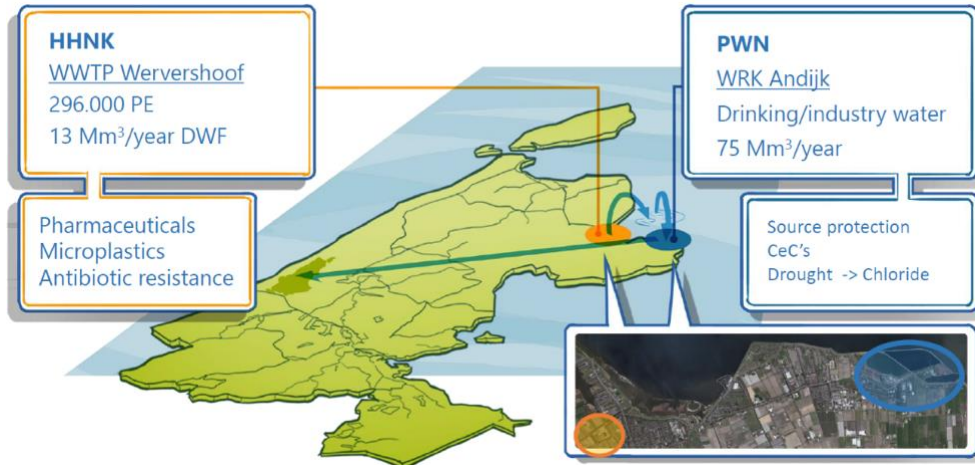


Figure 1: A map showing the HHNK and PWN treatment facilities (Spruijt et al., 2021).

This research is a continuation of past PWNT interns Dan Farley (2017), Bram Delfos (2019), Meghan White (2019), and Marvin Ouma (2021). Dan Farley and Bram Delfos studied the application of ozonation for pharmaceutical degradation and the unwanted formation of bromate. Meghan White and Marvin Ouma studied the feasibility and impacts of ozonation and coagulation on CMF as individual and sequential processes over a 24-hour period. Conclusions from their research showed promising results for implementing the technology in future pilot plants. In this study, the optimization of ozonation individually and with coagulation sequentially as pretreatment for CMF is investigated.

Chapter 2

2. Research Description

This chapter provides an overview of the problem statements and research objectives for this MSc thesis. Additionally, the boundary conditions that apply to the project are described.

2.1 Problem Statements

This research is a collaborative project between PWNT and HHNK on the re-use of secondary wastewater effluent using a pilot plant, coagulation jar tests and ozonation bench scale equipment. In previous PWNT internship research, it was shown that individually and together, ozonation and coagulation have a positive effect on CMF. This was accomplished at pilot scale via 24-hour tests. It was determined that using a coagulation dose of 10 mg/L Fe³⁺ at a pH of 6.8 and an O₃/DOC ratio of 1.9 g/g both improved the membrane performance in comparison to no pretreatment (Ouma, 2021). However, the effect of different ozone residuals before the ceramic membrane at a bench and pilot scale have not yet been studied.

The main challenge of this research is to determine how the ozone dose and residual and the coagulant dose affect the membrane performance and filtrate water quality. This can be broken up into five different sub challenges:

1. Understand how the ozone residual before the membrane affects membrane performance measured via flux.
2. Understand how the coagulation conditions affect the membrane performance measured by the flux.
3. Understand how sequential application of ozonation and coagulation affects CMF performance.

4. Learn how the ozone dose affects the removal of the pharmaceuticals in the wastewater.
5. Determine the optimal $\text{H}_2\text{O}_2/\text{O}_3$ ratio to add to the HHNK Wervershoof wastewater to mitigate the formation of bromate.

2.2 Research Objectives

The main objective of this research is to evaluate the ceramic membrane's performance based off pretreatment optimized process conditions of ozonation and coagulation. This evaluation will be completed via water quality analysis under optimal ceramic membrane performance conditions. The specific goals of this research project are,

- To examine to what extent and in which way the individual and combined techniques of ozonation and coagulation contribute to an optimal operational performance of the re-use treatment train: ozonation – coagulation – CMF.
- To examine how ozonation and bromate formation relate, and how hydrogen peroxide can be used to mitigate bromate formation.
- To evaluate the water quality according to the Dutch Ministry of Infrastructure and Water Management and STOWA regulations for pharmaceutical removal.

2.3 Boundary Conditions

The following boundary conditions apply to this research project:

- The influent water to the pilot is from the HHNK WWTP in Wervershoof, Netherlands
- FeCl_3 is the coagulant chemical
- H_2O_2 is the chemical added to mitigate the formation of bromate
- The research was conducted using the available technology available at PWNT
 - HWL lab analysis
 - ILCA

- Phipps and Bird jar tester
- Bubble column ozonation
- 0.4 m² METAWATER ceramic membrane

Chapter 3

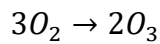
3. Literature Review

This chapter provides an overview of the background information necessary to proceed with the experiments. Each section discusses a different topic within the theme and reasoning behind using ozonation, coagulation, and CMF for secondary wastewater effluent reuse.

3.1 Ozonation

3.1.1 Introduction

Ozone (O₃) can be described as an unstable molecule with a short period of time between generation and decomposition into elemental oxygen. It is produced on-site directly before the point of application, whether it be in wastewater or drinking water facilities (USEPA, 1999). Ozone is formed by combining an oxygen molecule with an oxygen atom (Equation 1). The oxygen atom is formed by dissociating it from oxygen molecules using an energy source. Figure 2 below shows a basic ozone generator (USEPA, 1999).



Equation 1

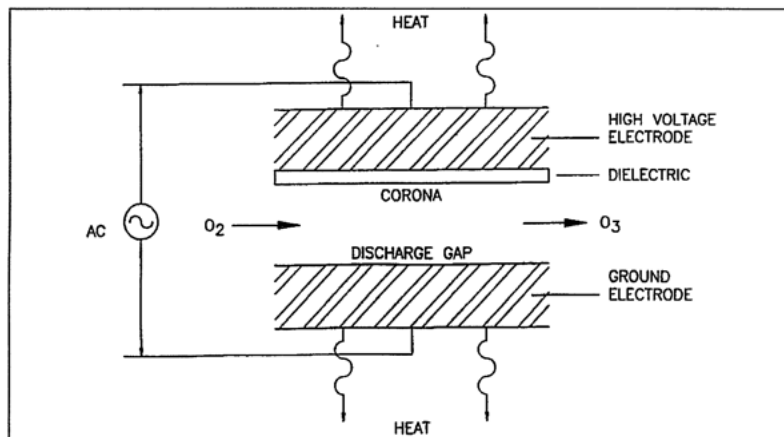


Figure 2: A Basic Ozone Generator (USEPA, 1999).

The reaction to create ozone is endothermic and requires a high amount of input energy. The corona discharge gap in Figure 2 is one example of a silent electrical discharge which allows oxygen-containing gas to flow through the gap two different electrodes separated by a dielectric (electrical insulator). When high voltage is applied to the electrodes, an electron flows across the discharge gap with the oxygen-containing gas to disassociate the oxygen molecules to oxygen atoms which then pair with oxygen molecules to form ozone gas (USEPA, 1999).

To transfer the ozone gas into the water matrix, three common ozone contactors are used – bubble column, injector, and turbine mixer. A bubble column uses a crosscurrent flow configuration to diffuse ozone gas into the water matrix (USEPA, 1999). The advantages to this contact method are no moving parts, effective ozone transfer, low hydraulic head loss, and simplicity with operation. The disadvantages are the requirement for deep contact basins, vertical channeling of bubbles, and consistent maintenance of gaskets and piping (USEPA, 1999). In this study, the pilot used for experiments has bubble column ozonation as the contact method.

Two other ozone to water matrix contact methods are the side stream injector and turbine mixer. The side stream injector adds ozone to the water stream under a negative pressure caused by a venturi section. The negative pressure allows the ozone to be pulled into the side stream which is then combined with the plant flow using high turbulence to disperse the ozone into the water matrix (USEPA, 1999). The third contact method, turbine mixer, uses a high amount of energy to efficiently feed and mix the ozone gas into the water matrix. While this method allows for a smaller contactor depth, the maintenance is more involved with the turbine and motor in use (USEPA, 1999).

Ozone can be applied in both the drinking water and wastewater field. In drinking water, it is primarily used for disinfection by inactivation of bacteria, viruses, cysts, and organic contaminant control. In wastewater, it can be utilized for the,

1. Improvement of the quality of the effluent from biological WWTP
2. Treatment of sludge
3. Treatment of exhaust air
4. Treatment of highly contaminated part streams (Ried et al., 2009)

While the ozone rapidly dissolves in water to react with NOM and pharmaceuticals, reaction by-products will be formed which are biodegradable and some compounds can be harmful to human health. When treating wastewater with ozone, many different ozone doses can be used which impact the by-products formed and the degradation of NOM and pharmaceuticals. The reaction between ozone and NOM changes the composition of NOM, which is an important step for membrane pretreatment, as it is one of the main causes in membrane fouling. NOM in water is characterized/quantified by the TOC and DOC measured (Ried et al., 2009).

During ozonation, the NOM can be oxidized in two ways (see Figure 3).

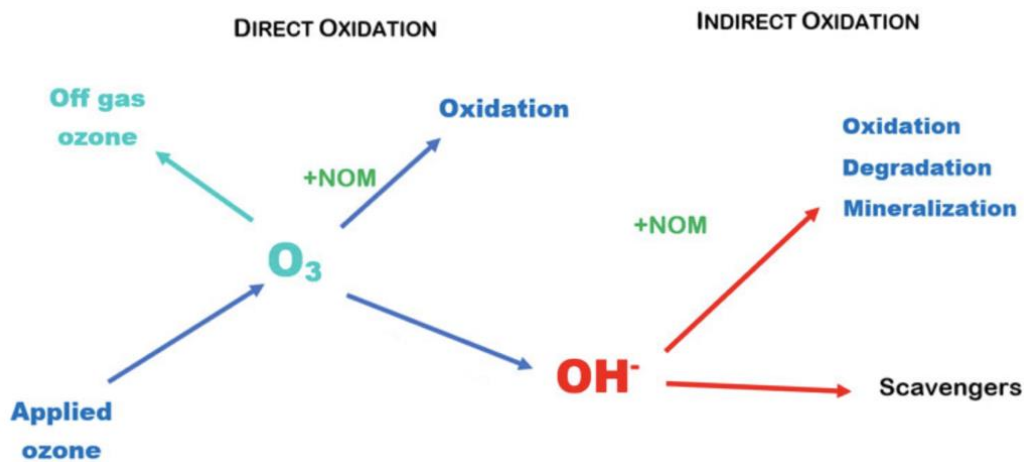


Figure 3: The direct and indirect ozone oxidation process in a water matrix (Flanagan, 2021).

The first way is a direct reaction by molecular ozone with the dissolved chemicals in the water at different rates. This is a highly selective oxidation process. The second oxidation process occurs when ozone is converted into OH radicals via subsequent chain reactions. These OH radicals oxidize the pollutants in the wastewater more unselectively quickly reacting with the water matrix. The formation of OH radicals from ozone is dependent on the presence of NOM, pH, temperature, and ionic strength (Rosenfeldt et al., 2006).

3.1.2 Effect of Ozonation on the Ceramic Membrane

3.1.2.1 Membrane Fouling

Using ozonation as a pretreatment before CMF can allow the membrane to run at a higher flux for longer periods of time, and effectively reduces membrane fouling. In 2018, Im et al. completed pilot scale experiments in Japan using secondary wastewater effluent to evaluate virus removal performance with ozonation. They reported that with increasing ozone doses, the operational period of the ceramic membrane also increased. Using a flux of 4 m/d and an ozone dose of 0 mg/L O₃, the continuous operation period was 108 hours (4.5 days). However, with a dose of 6 mg/L O₃, the run time was 908 hours (37.8 days). During these experiments, they did the necessary CEBs to clean the membrane periodically to remove the reversible fouling (Im et al., 2018).

3.1.2.2 Pharmaceuticals and NOM

Ozonation also can degrade pharmaceuticals and NOM. In 2005, Huber et al. completed a pilot study looking at the oxidation of pharmaceuticals via ozonation of municipal wastewater effluent. Their ozonation pilot plant used bubble column ozonation with an ozone generator and feed water from a WWTP in Switzerland. Their results showed that with a low ozone dose,

certain classes of pharmaceuticals (macrolide and sulfonamide antibiotics, and synthetic and natural estrogens) can be oxidized. Additionally, the suspended solids in the water have minimal effect on the degradation of the pharmaceuticals, and it is the DOC content in the water that has a high influence on the ozone efficiency (Huber et al., 2005). This is because the OH radicals formed are nonselective and will react with most contaminants. For that reason, when there is a higher DOC content in the water, a higher ozone dose is necessary (Papageorgiou et al., 2017).

3.1.2.3 Presence of Ozone Residual

When high doses of ozone are applied to a water matrix, there is also the potential for a residual ozone concentration in the water matrix, which then is filtered through the ceramic membrane. In 2004, Schlichter et al. researched how a residual ozone concentration in the water matrix affects the ceramic membrane's permeability. This was completed using surface water from the Saar River in Germany, and channel tubular CMF membranes. Results showed that an ozone residual ranging between 0.1 – 1.0 mg/L O₃, is required in the water matrix (after ozonation) to for the ceramic membrane to maintain high permeate fluxes and reduce membrane fouling. Schlichter et al. recommends a minimum of 0.1 mg/L O₃ to be permanently present in the membrane and water matrix to reduce membrane fouling (Schlichter et al., 2004). A similar recommendation of 0.9 mg/L O₃ residual before the METAWATER ceramic membrane (used at PWNT) was also recommended by Spencer et al., 2019 to provide long-term sustainable operations with ceramic membranes (Spencer et al., 2019).

3.1.2.4 Interaction between Ozone and Ceramic Membrane

Another important aspect of using ozonation is the interaction between ozone and ceramic membranes. In 2019, Hamid et al. conducted a study to understand the interaction between ozone and a METAWATER ceramic membrane. Using tap water, Hamid et al.'s results observed a

formation of OH radicals between the interaction of ozone and the ceramic membrane. This was caused by a catalytic decay of ozone that occurred when it interacted with the ceramic membrane through an OH radical reaction (Hamid et al., 2019). This research gives insight to one potential reason why an ozone residual before the ceramic membrane enhances the performance.

Another potential reason why an ozone residual on the membrane improve performance is because of the reaction of ozone with NOM to prevent fouling. Van Geluwe et al. conducted a literature review in 2011 about the fouling potential caused by NOM and how ozone can alleviate the potential fouling. First, the size of the NOM is an central parameter for membrane fouling in relation to the ceramic membrane's pore size. It has been observed that ozonation has the ability to change and degrade the size of NOM molecules into smaller sizes (Van Geluwe et al. 2011). Second, the interaction between the negatively charged membrane surface (with neutral water matrix pH) and NOM can also predict the fouling impact. The different types of chemical and physical interactions, such as electrostatic interactions, hydrogen bonds, and hydrophobic interactions can decrease the fouling potential. Finally, the reaction between NOM and ozone changes the structure of NOM in the water matrix. The structural changes, such as removal of aromatic rings (decreases adsorption of NOM to membrane surface), increase number of carboxylic functions (repelled by a negative membrane surface), and decomposition of NOM into smaller molecules can decrease the fouling potential (Van Geluwe et al. 2011).

3.1.3 Bromate Formation

3.1.3.1 Introduction

One drawback to using ozonation is the formation of bromate when bromide is present. Bromate is a suspected human carcinogen and is regulated in the US by the USEPA with a maximum allowable contamination level of 10 µg/L in public water systems. Bromate ingestion

in large quantities can lead to nausea, diarrhea, vomiting, abdominal pain, hearing loss, and kidney/nervous system effects (Cotruvo, 2013). Bromate forms when bromide ions are oxidized by ozone (see Figure 4).

In 2014, Moslemi et al. used an inlet ozone mass injection on a recirculating loop semi batch reactor to determine the formation of bromate. Their results showed that with a higher ozone injection rate, the formation of bromate increased as well. However, with NOM present, the bromate formation decreased which is consistent with other researchers as well. The mitigation of bromate formation is due to the higher NOM concentration and the ozone reacting with NOM more than bromide. It was also determined that with a lower pH, less bromate was formed due to the decreased concentration of hypobromite (BrO^-) as it converts to hypobromous acid (HOBr), less reactive with ozone than hypobromite and is a crucial step in converting bromide to bromate (Moslemi et al., 2014).

3.1.3.2 AOP Potential

To prevent the formation of bromate, researchers have been experimenting with AOP, using H_2O_2 to reduce the ozone residual and to convert hypobromite/hypobromous acid back to bromide. When H_2O_2 is added to a water matrix, an acid-base reaction occurs (see Equation 2) with H_2O_2 as the weak acid.



With HO_2^- as a reaction product, the reaction between ozone and HO_2^- results in two OH radicals and the consumption of two ozone molecules, thereby reducing the ozone residual.

The oxidation of bromide by ozone can follow two pathways, direct and indirect, to form hypobromite (see Figure 4). The addition of H_2O_2 reverts hypobromous acid back to bromide, mitigating the formation of bromate (Von Gunten, 1998). The addition of H_2O_2 can also improve

the degradation of some pharmaceuticals based on the selectivity of their degradation (Delfos, 2019).

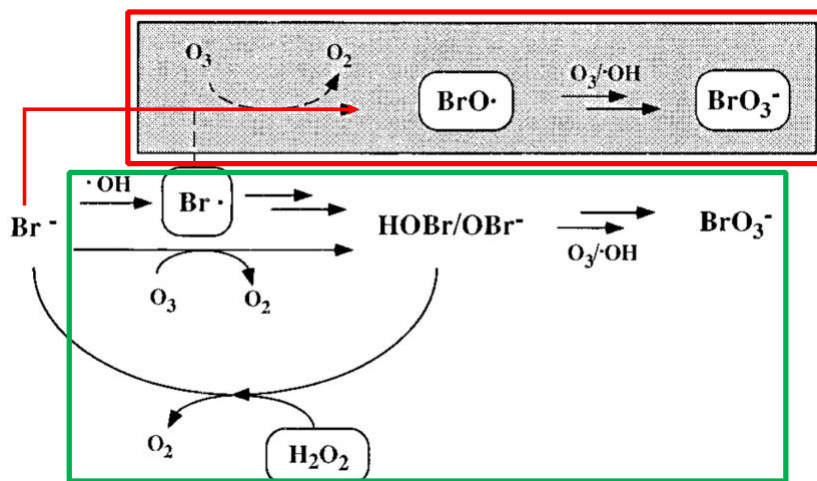


Figure 4: The direct (red) and indirect (pathway) of ozone forming bromate in the presence of bromide (Von Gunten, 1998).

3.2 Coagulation

3.2.1 Introduction

Coagulation is a common process in both drinking water and wastewater treatment facilities. The purpose of coagulation is to clump all the small particles and NOM together into larger flocs. This is achieved using a coagulant such as ferric chloride or aluminum sulfate. Once the water goes through preliminary screening and grit removal, the water is pumped into a tank where the coagulant is added, and rapid and slow mixing is applied. The purpose of the rapid mixing is to mix the coagulant with the influent water, and the slow mixing allows for the growing of the flocs to be removed in later processes by sedimentation or filtration (see Figure 5) (Jiang, 2015).

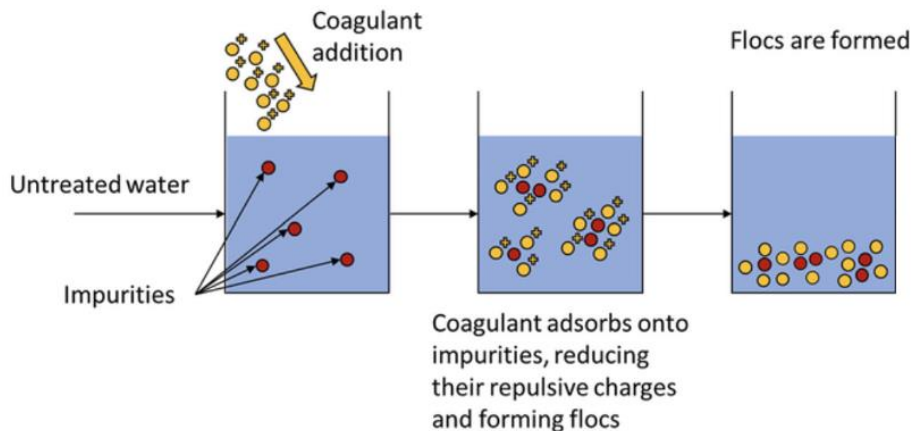


Figure 5: A simple diagram of the coagulation process during wastewater treatment (Turner, Tomi & Oliver, Ian. (2019).

The effect of the coagulation process is different for every treatment plant, and the efficiency of the process is dependent on the influent water characteristics, the speed (RPM) of rapid and slow mixing, pH, temperature, and the coagulant dose (Jiang, 2015). The effectiveness of the process can be measured using multiple water quality measurements in a lab – turbidity, color (UVT₄₂₀), DOC and UVT₂₅₄.

3.2.1.1 Coagulation Mechanisms

There are two major coagulation mechanisms, adsorptive coagulation (charge neutralization), and sweep coagulation (see Figure 6). Adsorptive coagulation occurs at low pH when a coagulant chemical with a high positive charge reacts with negative molecules (humic acids) causing precipitation. Sweep coagulation occurs when a highly concentrated metal salt coagulant, such as aluminum or iron, at a high pH is added to the water matrix. This causes the precipitation of metal hydroxides and the colloids are swept or caught in the transformation to form the resulting precipitate, an insoluble solid that forms flocs to be removed in the next step of the wastewater treatment processes (Suopajärvi, 2015).

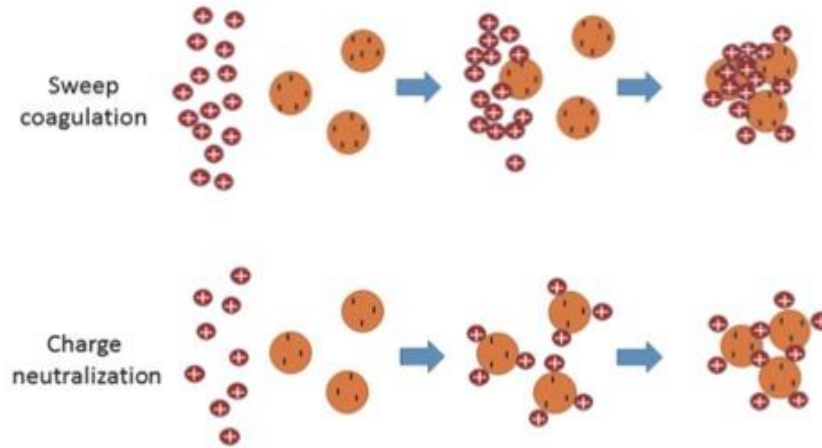


Figure 6: The mechanisms of coagulation (Suopajarvi, 2015).

In this study, the coagulation chemical used is $FeCl_3$. Table 1 shows the two possible mechanisms using adsorptive or sweep coagulation (Suopajarvi, 2015).

Table 1: The two possible coagulation mechanisms, adsorptive and sweep.

Adsorptive	$Fe^{3+} + H_3A \rightarrow FeA + 3H^+$	Equation 3
Sweep	$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$	Equation 4

Prior experiments leading up to this study using the same pilot plant showed that adsorption coagulation had a better impact on the ceramic membrane than sweep coagulation (Ouma, 2021). This was tested at a pH of 6.8 and 8.3 where the maximum flux achieved, 200 LMH, was using a pH of 6.8 compared to 175 LMH at 8.3 pH. The mechanism pursued is adsorptive and not sweep coagulation. Therefore, all experiments with coagulation were completed using a pH of 6.8.

3.2.2 Effect of Coagulation on the Ceramic Membrane

Coagulation can be paired with other treatment technologies to create a hybrid process to yield better results. By adapting the coagulation effluent to fit the subsequent processes, the results could be improved by much more. One pair to coagulation is CMF. Pretreating the water

with coagulants prior to CMF can reduce the membrane fouling and thereby the TMP can increase so that it may run for longer periods of time at a higher flow between CEBs.

Coagulation and CMF can also increase the removal of humic acid, and micropollutants (Jiang, 2015).

3.2.2.1 Turbidity Removal

The underlying relationship of coagulation and the reduction of ceramic membrane fouling can be affected by the influent water quality characteristics, turbidity being one of them according to Park et al., 2019. When the turbidity in the water is high (due to heavy rains), the coagulant dosage needs to be increased to adjust for the change in influent water quality characteristics (turbidity, DOC, color, UVT₂₅₄) (Park et al., 2019). When the turbidity is high in the water, it typically leads to an increase of irreversible fouling due to the lack of coagulant in the treatment process (Park et al., 2019). In this study, the removal of turbidity was not the primary concern because the raw water quality analysis showed low levels of turbidity from the HHNK Wervershoof location. Because of the low turbidity, sweep coagulation where the liquid metal hydroxides and colloids form floc to be removed at a high pH is not pursued and all experiments with coagulation were completed at a pH of 6.8.

3.2.2.2 pH and NOM Removal

The efficiency of the coagulation process also depends on the pH of the water and the NOM present in the influent water. DOC and TOC can also be used to portray the amount of NOM in the water sample. Each different type of coagulant chemical can remove NOM at different levels (Qin et al., 2006). Qin et al. used aluminum sulfate to determine an optimal pH for removal of TOC. Aluminum sulfate was used because it is more commonly used in treatment plants in Singapore. They concluded that at lower pH values, more DOC and TOC were removed from the

raw water collected at Choa Chu Kang Waterworks. The optimum pH in their experiments was 5.2 (Qin et al., 2006). A similar experiment was completed in Croatia by Racar et al. using secondary wastewater effluent from the Agroproteinka WWTP using FeCl_3 as the coagulant. At their optimal pH of 5.58 the removal of DOC was 66.4% (Racar et al., 2017).

One challenge to having several processes in a treatment train is finding a compromise between optimal pH's for each process. The optimum pH for ceramic membranes differs from the lower pH that coagulation only prefers. Black & Veatch completed a demonstration plant that included researching the effect of pH on METAWATER ceramic membranes in 2009. Their experiments used surface water at the Stockholm Lovö WTP, testing between pH 6.1 to 6.9 where the latter is no pH correction. The membrane tested is a 1.5 m long, 25 m² ceramic membrane. To test the effect of pH, coagulation using a dose of 5.5 mg/L Fe^{3+} and a backwash interval of 60 minutes was used (Black & Veatch, 2009).

Their results showed that with a higher operational pH, the TMP also increased accordingly over one hour. At pH 6.1, the TMP increase is 9.7 kPa and at pH 6.9, the TMP increase is 25 kPa. However, after each backwash cycle, the recovery of the membrane (initial TMP) was better using a higher operational pH. This means that the membrane is being cleaned effectively and the flocs created during the higher operational pH can be more easily removed. The daily increase in TMP at pH 6.1 was 1.13 kPa/day whereas at pH 6.9, the TMP increase was ~0 kPa/day meaning that the membrane is recovering during the operational and backwash periods. From this study, it was concluded that the METAWATER ceramic membrane prefers a more neutral pH for best operational performance with less frequent CIPs necessary caused by the isoelectric point of the membrane (Black & Veatch, 2009).

3.3 Ceramic Membrane Filtration

3.3.1 Introduction

Membrane filtration is a common method for filtration of both surface and wastewater. However, the material used to make the membrane can differ between processes and companies. Currently, most membranes are made of a synthetic polymer material due to their inexpensive prices, but ceramic membranes are becoming more popular (Malcolm Pirnie, Inc. et al., 2005).

The material the membrane is made of very important for it to work effectively. Materials with a larger membrane strength can withstand a high TMP which allows for better operational flexibility. The membrane's surface charge is also important and changes with material type. The surface charge attracts different contaminants more than others depending on their opposite surface charge – electrostatic attraction (Malcolm Pirnie, Inc. et al., 2005). The isoelectric point is the point of zero charge at a pH value on the ceramic membrane's surface where the potential becomes zero and the molecule carries no net electrical charge. Knowing the isoelectric point of a membrane gives information on the adsorption of ions (Mullet et al., 1999). It is important to choose the proper material depending on the influent water characteristics for each treatment plant. Finally, the cleaning procedures, duration, and frequency changes depending on the material which can increase operational costs significantly (Malcolm Pirnie, Inc. et al., 2005).

3.3.1.1 Ceramic Membrane Benefits

The ceramic membranes used in this research (METAWATER) offer chemical and thermal durability, good mechanical strength for a wide TMP range, and minimal environmental pollution (Rakruam et al., 2014). Their resistance to acidity allows for operational use during low pH's, and strong fluxes and backwash regimes (Zhu et al., 2012). While called ceramic membranes, the exact materials in the membrane are titania, glass, silicon carbide, zirconia,

alumina, and a mixture of metal oxides. The pore size within each membrane can differ as well depending on the manufacturer (Issaoui et al., 2019). The electrical charge of ceramic membranes comes from the hydroxyl group on the surface. When liquid is flowing over the membrane, the filtration efficiency is heavily impacted by the surface charge and can foul quickly depending on the pH, ionic strength, and influent water characteristics (Zhao et al., 2005).

For CMF, they have the versatility to operate with the water entering from the outside or inside and exiting in the alternate direction. Doing inside-out mode allows for the water to flow in a well-defined pathway but has the potential to become clogged. Running water from the outside-in increases the available membrane surface area but the water flow is less defined (Malcolm Pirnie, Inc. et al., 2005).

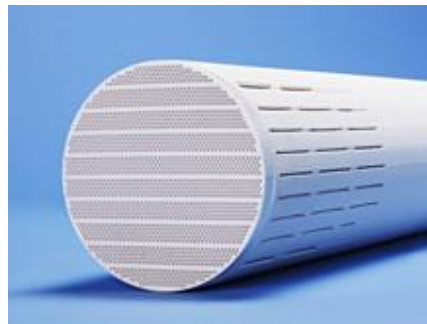


Figure 7: A METAWATER ceramic membrane (METAWATER, 2011).

While wastewater does contain harmful chemicals, toxic compounds and NOM, the treatment technology of integrated membrane systems is becoming more feasible. If used properly, using ceramic membranes to treat secondary wastewater effluent can be economically and environmentally forward (Hakami et al., 2020).

3.3.2 Critical and Sustainable Flux

Flux is used to evaluate the ceramic membrane's performance (Spruijt, 2021). It is calculated by dividing the flow through the membrane by the surface area of the membrane (Equation 5).

The resulting units of flux are liters per square meter hour (LMH) (WEF, 2006).

$$J = \frac{Q_p}{A_{system}} \quad \text{Equation 5}$$

Where: J = Flux (LMH)

Q_p = Permeate flow (L/h)

A_{system} = Ceramic membrane surface area

To assess the membrane performance, two different types of fluxes are determined, critical and sustainable. The critical flux can be defined in two ways (Bacchin, 2006),

- The flux at which the TMP starts to deviate from the pure water line.
- The first permeate flux for which irreversible fouling appears on the membrane surface.

The flux level below the critical flux where no fouling occurs defines the sustainable flux.

Fouling is the accumulation of particles or solutes that remain on the membrane during the operational processes. It can occur in three different forms, adsorption, pore blockage, or deposit (see Figure 8). As foulants build up on the ceramic membrane, the TMP increases, and each ceramic membrane has a maximum TMP. When the maximum TMP is reached, the membrane is considered “fouled out” and it can no longer be used for experiments and needs to be cleaned before use again (Bacchin et al., 2006).

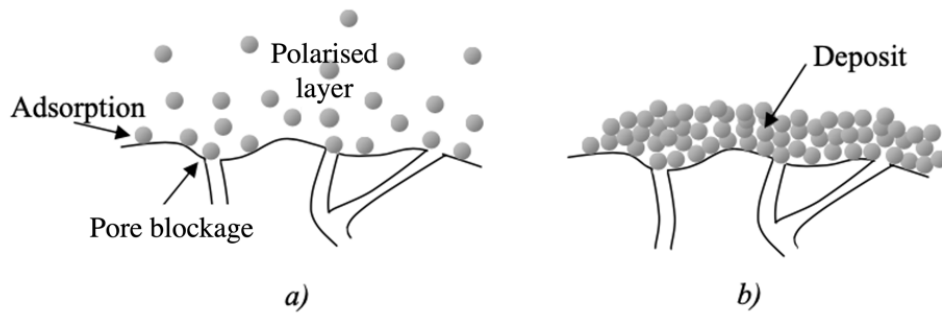


Figure 8: The three fouling mechanisms on a membrane a) below critical flux b) above critical flux (Bacchin et al., 2006).

During experiments, backwashes are completed on the ceramic membrane to lower the TMP. However, there is irreversible fouling that cannot be removed with a CEB. The buildup of irreversible fouling leads to the critical flux. If there are no foulants building up, then the flux is more sustainable (Bacchin et al., 2006).

The simplest method to determine the critical and sustainable flux is to do “flux stepping.” This involves incrementally increasing the flow over the membrane during equally spaced trials (ex. 24-hour period). As the flow over the membrane increases, the TMP can be observed, and if the irreversible fouling is minimal, the flow over the membrane can be increased until the maximum TMP is reached (Bacchin et al., 2006). Because the TMP on the pilot changes with water temperature (affecting viscosity), the TMP is corrected to 10°C for comparison between experiments, see Equation 6 and Equation 7.

$$TMP_{10^{\circ}\text{C}} = TMP_{pilot} * \frac{0.0013077}{\mu} \quad \text{Equation 6}$$

Where: $TMP_{10^{\circ}\text{C}}$ = Corrected TMP to 10°C

TMP_{pilot} = TMP recorded from the pilot

μ = dynamic viscosity (PaS)

$$\mu = \frac{1}{10} * \frac{1}{2.1482 \left\{ (T - 281,585) + \sqrt{[8078.4 + (T - 281.585)^2]} \right\} - 120} \quad \text{Equation 7}$$

Where: T = Water temperature (K)

Evaluation of the membrane performance can be determined by calculating the fouling rate of the membrane. To do so, the initial TMP after each backwash vs time are graphed – a flux pressure profile. From there, a linear trendline can be fit to the graph and the slope of the line is the fouling rate in units of kPa/day. When the slope of the line is flat, it means the flux is sustainable, but when the slope is increasing significantly, the flux is reaching the critical point (Bacchin et al., 2006).

In this study, the critical flux is defined as the flux where the TMP exceeds 200 kPa corrected to 10°C within 24 hours. The sustainable flux is the flux measured (25 LMH) directly below the critical flux with a stable TMP over 24 hours. Critical and sustainable flux definitions will be different for each pilot used. Due to the size and materials that make up the C0.4 pilot, each test was run for a maximum of 24 hours. The maximum TMP the pilot can handle is dependent on the size of METAWATER ceramic membrane used in the pilot. For the experiments conducted, the maximum TMP was set at 200 kPa to compare the effects of the pretreatment on CMF during a period of 24-hours.

Chapter 4

4. Materials and Procedures

This chapter outlines the materials used for each experiment and the procedure followed.

Each material was in a different part of the Netherlands, with procedures created by past PWNT interns.

4.1 Materials

4.1.1 *Phipps and Bird Jar Tester in Andijk*

The student lab in Andijk is where the initial bench scale experiments were completed using the Phipps and Bird jar tester. The lab is located within the pilot facility and supervised by PWNT operators. The CO₂ cover experiment, acid and base titrations, and coagulation and pH jar tests took place in the student lab. The procedures and results for the first two experiments can be found in appendix 1 and 3.

The materials used for all three experiments were,

- Phipps and Bird jar tester
- HI 98127 pH meter
- Stirrer bar and plate
- Hach DR6000 and cuvette
- 40% FeCl₃ coagulant
- Hach 2100Q IS turbidity meter
- RWZI wastewater
- Hach LCK 321 Fe³⁺ measurement kit
- RWZI ozonated wastewater
- 0.45 μL filters and syringes
- Milli-Q water
- Pipettes and pipettor
- 10% HCl as the acid chemical
- Parafilm
- 25% NaOH as the base chemical
- Timer

4.1.2 C0.4 Pilot in Wervershoof

The C0.4 pilot plant is also known as the “small pilot” due to the size of the ceramic membrane which is a METAWATER with a surface area of 0.4 m² and a pore size of 0.1 μm. The membrane itself is hollow and the water flows from the inside to the outside. The maximum TMP is the system can handle is 200 kPa at 10°C. If the pressure exceeds 200 kPa at 10°C the pilot plant will shut down automatically (Gabriel, 2021). pH adjustment is completed via HCl or NaOH and the rapid/slow mixing settings were the same from the jar tests previously completed. Figure 9 below shows a schematic diagram of the C0.4 pilot plant, where the dashed arrows represent alternative water pathways to decrease the HRT. The exact HRT options can be found in Table 2.

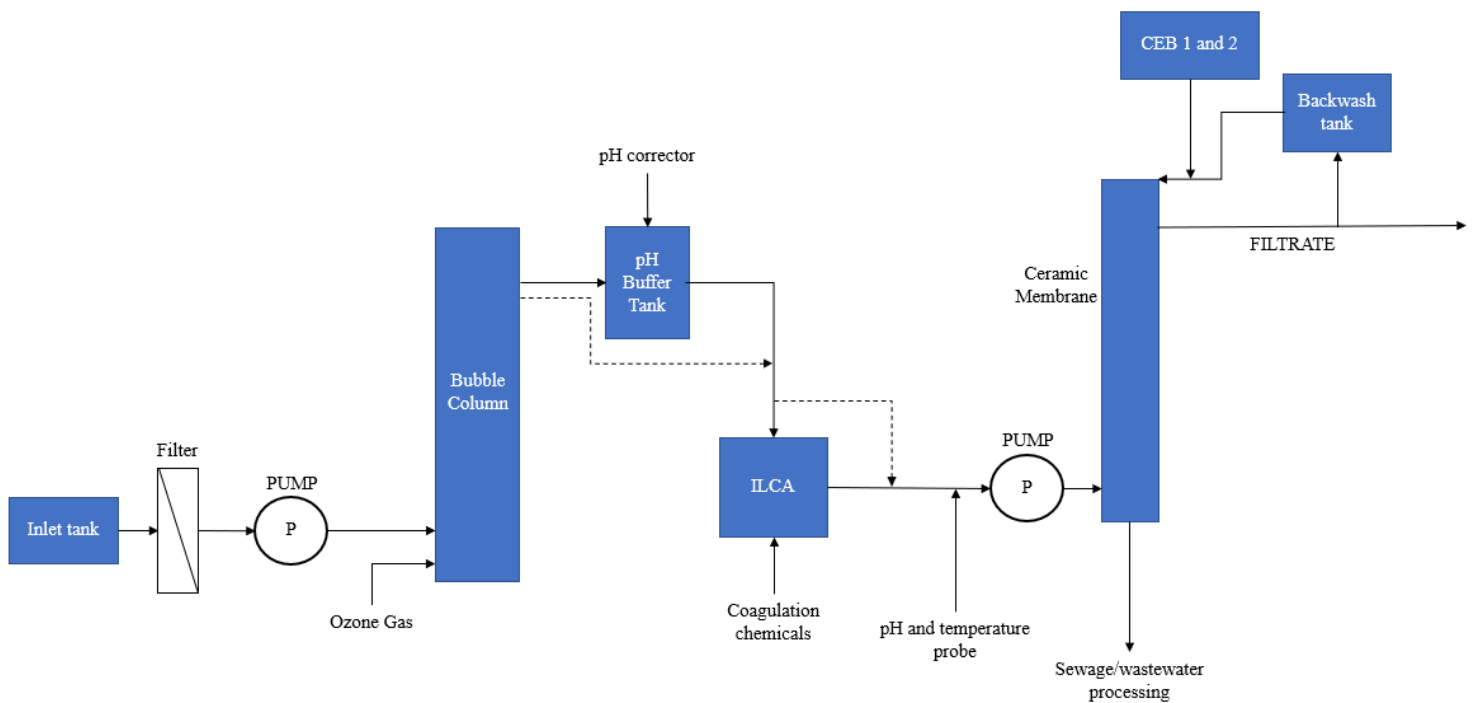


Figure 9: A flow diagram of the C0.4 pilot plant.

Table 2: The HRTs in the C0.4 pilot depending on the configuration of the pilot.

Pathway	HRT (Minutes)
Bubble Column	15
Bubble Column + pH Buffer Tank	17
Bubble Column + Coagulation Tank	20
Bubble Column + pH Buffer Tank + Coagulation Tank	22

The ozone treats the secondary wastewater effluent using a 50 L bubble column. A WEDECO OCS Modular 4HC was used to generate ozone which has a maximum production capacity of 4 g/L and pressure of 50 kPa. To generate oxygen for the ozone generator, an Air Sep by Topaz was used to draw ambient air in to separate and concentrate the oxygen gas to produce ozone gas (White, 2019). The 50 L bubble column acted as a contact chamber between the wastewater (entering from the top) and the ozone (entering at the bottom) to allow for the removal of organic matter and pharmaceuticals already present in the wastewater. The ozone residual was then measured at the end to determine the amount of “free” ozone available for the next processes (Ouma, 2021).

To clean the membrane, five different processes were used – normal backwash, CEB 1 and 2, and ozone and acid CIP. The normal backwashes and CEBs were completed between each filtration cycle (25 minutes) while the pilot ran, and the CIPs were completed for routine maintenance different between experiments. Table 3 below shows the details of the normal backwash and CEBs. During the normal backwashes, filtrate water was forced through the membrane at a pressure of 4.5 bar for 8 seconds. During the CEBs, 1.25 L of the chemical was pumped through the membrane at 18 L/h for 240 seconds and soaked for 230 seconds. To remove the chemicals, an air compressor was used at 4.5 bar. The backwashes followed a 4:1:4:1, where four normal backwashes occurred, then CEB 1, then 4 more normal backwashes, and finally CEB 2 (Ouma, 2021).

Table 3: The backwash cycle for the C0.4 Pilot.

Backwash Type	Frequency	Chemical	Concentration
Normal	4	Filtrate	N/A
CEB 1	1	NaOCl	100 mg/L
Normal	4	Filtrate	N/A
CEB 2	1	H ₂ O ₂ and HCl	100 mg/L

The acid and ozone CIP were completed to formally clean the membrane before a new experiment, and after the membrane pressure reached 200 kPa at 10°C and it fouled out. The acid CIP used 100 L of tap water and 2 kg of citric acid and is pumped through the membrane to remove any foulants for approximately three hours. The membrane was then flushed with tap water to remove the citric acid and ready for the ozone CIP (Ouma, 2021). The ozone CIP used a gas concentration of 100 g/Nm³ into the bubble column filled with tap water to clean the membrane. The ozone CIP lasted approximately two hours, and normal backwashes were completed manually to remove any foulants. Once the pressure in the membrane was around 0.3 – 0.4 bar, one final normal backwash was completed, and the pilot was ready for use again (Gouveia, 2021). All flux tests completed were over a period of 24 hours due to operational constraints. Figure 10, Figure 11, Figure 12, Figure 13 are photos of the C0.4 pilot plant.



Figure 10: The front side of the CO.4 pilot that houses every component except for the ozone generator.



Figure 11: The back of the pilot plant that houses the electrical controls.



Figure 12: The front of the ozone generator with the bubble column in the background.



Figure 13: The back of the ozone generator with the electrical controls.

4.1.3 *Het Waterlaboratorium in Haarlem*

HWL is located northwest of downtown Haarlem and is the company that PWNT uses for all water quality analysis. They also house the bench scale ozone bubble column also used by Bram Delfos and Meghan White who interned with PWNT in 2018/2019.

4.1.3.1 Ozone Bench Scale

The ozone bench scale resides in a hooded bench and runs as a semi-batch system, seen in Figure 14 below. To use the setup, the bubble column reactor is filled with 6 L of wastewater effluent, and the ozone gas is continuously fed into the bubble column for a specific time which can be converted into an ozone dose. The water is also continually circulated throughout the bubble column using a Jabsco DS-M series peristaltic pump (Delfos, 2019). Figure 15 shows the flow chart of the specifics in the ozone bench scale.



Figure 14: The ozone bench scale experimental equipment.

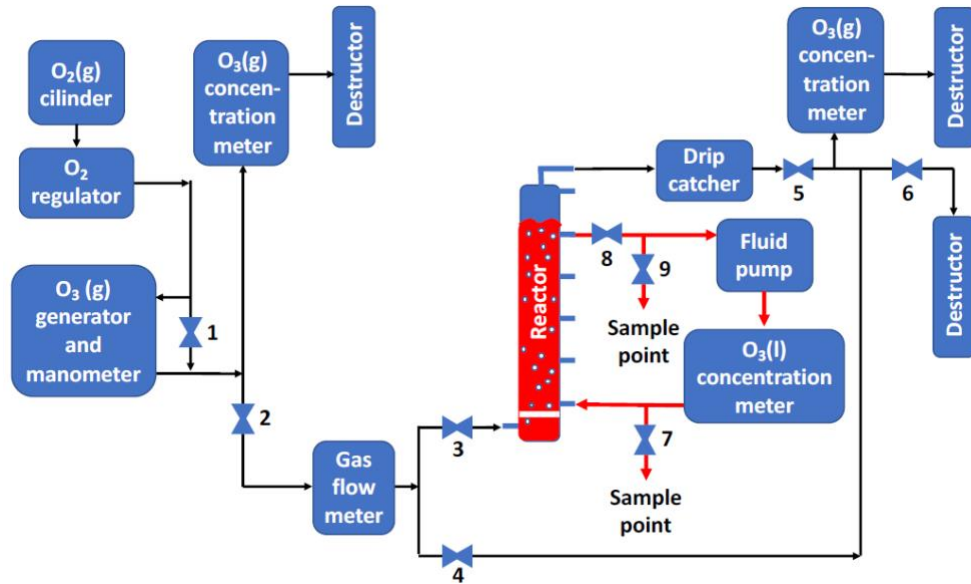


Figure 15: The flow diagram of the ozone bench scale (Delfos, 2019).

Instead of using ambient air to generate ozone, there is a pure oxygen tank to the left of the hooded bench attached to an air-cooled ozone generator (WEDECO ozone generator, Modular 4 HC series). The ozone gas generated is measured by concentration (Ozone Analyzer BMT 964, C-300) and flow (ABB FAM3255 metal cone gas flow meter). To monitor the gas balance, the gas concentration in and out are both measured using the BMT yellow electronic boxes in Figure 14 and the values are recorded electronically as well. The ozone residual in the bubble column is also recorded digitally using a Hach Orbisphere 410A with C1100 Ozone sensor O_3 .

4.1.3.2 Water Quality Analysis

HWL is where the advanced water quality analysis occurred. Samples from the experiments were periodically sent out to be evaluated for the following water quality parameters,

- UVT scan (200 – 700 nm)
- Turbidity
- Ammonium
- COD
- BOD
- pH

- Nitrate
- Nitrite
- Bromide
- Bromate
- DOC
- Fe³⁺ total
- 11 target pharmaceuticals, identified by STOWA



Figure 16: A set of sample bottles from HWL used for water quality analysis.

4.1.4 Water Matrix

The raw water used for each experiment came from the HHNK WWTP located in Wervershoof, North Holland. The wastewater entering HHNK Wervershoof comes from the surrounding villages and is treated with bar screening, grit removal, biological treatment (anoxic and anaerobic vessels), secondary clarification, and chlorination. Each step is part of the typical wastewater treatment process used within wastewater facilities (Farley, 2018). Table 4 below shows the raw water characteristics from September 2021 to December 2021.

Table 4: The raw water characteristics at HHNK Wervershoof from August to December 2021.

Parameter	Range	Average	Units
Turbidity	0.58 – 3.05	1.14	FNU
UVT ₂₅₄	50.20 – 58.30	54.28	%
UVT ₄₂₀	93.30 – 96.10	94.41	%
pH	6.70 – 7.60	7.12	N/A
Temperature	5.00 – 22.00	15.99	°C
DOC	6.03 – 10.13	8.63	mg/L C
Bromide	183.80 – 270.70	219.47	µg/L Br

4.2 Procedures

All methods for this research were created from established PWNT experimental procedures.

4.2.1 Jar Tests Using Ozonated Wastewater

1. Filled six jars with 1.5 L of RWZI ozonated wastewater stored in the fridge
2. Placed the jars in a warm water bath to reach 20°C
3. Set aside RWZI ozonated wastewater sample for testing later
4. Prepared coagulant doses (0, 5, 10, 15, 20, 25 mg/L Fe³⁺) (see Table 12 in Appendix 2.1)
5. Programmed the sequential settings for the jar tester (see Appendix 1.2.1)
6. Collected samples of acid/base chemicals
7. Turn on and place jars in jar tester
8. Added coagulant dose and pH adjustment (rinsed with Milli-Q water to get residual)
9. Started jar tester at 220 RPM for 1 minute (rapid mixing)
10. Jar tester automatically switched to 20 RPM for 20 minutes (slow mixing)
11. Continually monitored pH in all six jars and adjusted the acid/base chemicals as necessary
12. Turned off jar tester after 20 minutes and began settling for 30 minutes
13. Measured pH at the end of settling

14. Collected samples from each jar gently from a few inches below the surface
15. Analyzed samples for total iron, UV₂₅₄ and 420, and turbidity (see Appendix 1.4, 1.5, and 1.6)
16. Clean up lab

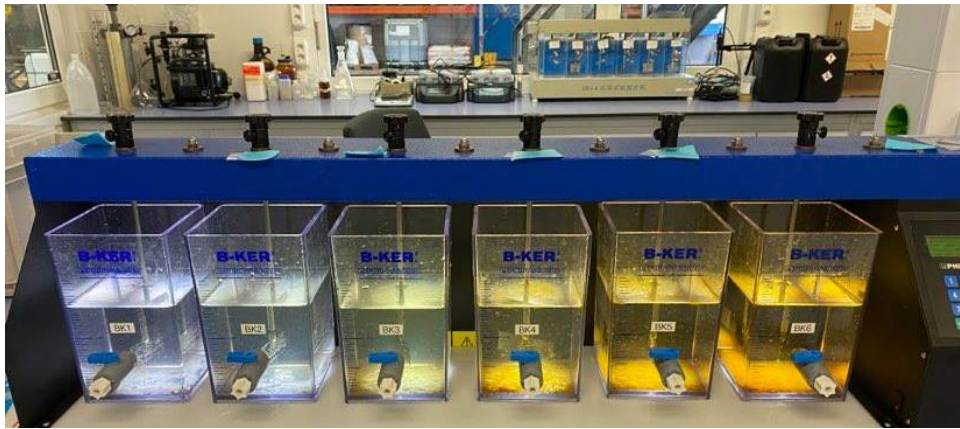


Figure 17: A Phipps and Bird jar tester during settling.

4.2.2 C0.4 Pilot

To run the C0.4 pilot, the bubble column, buffer tank, pH chemical tank, coagulant chemical tank, and CEB1 and 2 tanks must be filled. The pilot will not run if these tanks are not filled. The next step is to turn on the pilot, which will give power to the ozone generator that can also be turned on. Once the ozone settings are set, the wastewater flow through the membrane can be turned on and the pilot will run automatically based on the programmed settings. A panel on the back of the pilot is there to actively monitor the flux, TMP, and temperature during each experiment. To analyze the data from the pilot, the data is extracted from the pilot and imported into excel using the program, Readwin2000. The exact steps to run the C0.4 pilot can be found in appendix 4.1.

4.2.3 *Ozone Bench Scale*

To run the ozone bench scale, first turn on the ozone generator and turn the correct valves so that the bubble column is bypassed, and the ozone gas flows through both ozone concentration meters and to the destructors. The ozone gas should bypass the bubble column until stabilized, roughly 30 minutes. While the ozone gas is stabilizing, the bubble column must be filled with 6 L of wastewater effluent at room temperature (20-22°C) and the pump turned on to circulate the water through the tubing. Next, the computer for the bench scale is turned on, and the timing between the two concentration meters and dissolved ozone meter should be synced to each other.

To run an experiment, the loggers should be started on the computer and the correct valves should be open/closed to direct the ozone into the bubble column reactor. Finally, a timer should be set to keep track of exposure time in the bubble column.

When the timer is done, take the appropriate samples and turn the valves to bypass the bubble column again from the ozone gas. After stopping the electronic logging, the bubble column should be cleaned, and the tubes can be flushed with fresh air. The exact steps to run the ozone bench scale can be found in appendix 4.1.

Chapter 5

5. Results

Over the course of 6 months, multiple experiments were completed at a bench and pilot scale level. Each experiment built upon the theme of optimizing the process train of ozonation, coagulation, and CMF for the reuse of secondary wastewater effluent.

5.1 Ceramic Microfiltration Improvement

Past PWNT interns Meghan White (UNH, 2019) and Marvin Ouma (Wetsus Academy, 2021) both completed internships working with the C0.4 pilot in Wervershoof. White was able to conclude that using ozonation and coagulation separately had a positive effect on ceramic membrane performance (White, 2019). Ouma was able to determine that using ozonation and coagulation in sequence also had a positive effect on the ceramic membrane performance and resulting water quality (Ouma, 2019).

5.1.1 No Pretreatment on the Ceramic Membrane

No pretreatment on the ceramic membrane means that the secondary wastewater effluent from HHNK Wervershoof is flowing directly into the ceramic membrane in the pilot. Both White and Ouma showed that the critical flux with no pretreatment is 125 LMH (White, 2019) (Ouma, 2021). Throughout the study, 125 LMH will act as the experimental control value and flux comparisons after pretreatment is incorporated (ozonation and coagulation) will be done to characterize membrane performance.

5.1.2 Coagulation Pretreatment on the Ceramic Membrane

The coagulant used at the pilot is FeCl_3 . Both White and Ouma carried out jar tests with different coagulant doses to determine the optimal dose for UVT_{254} removal. White concluded

that using a coagulant dose of 6 mg/L Fe^{3+} resulted in a critical flux of 195 LMH. pH adjustment was not possible during her internship (White, 2019).

Ouma completed jar tests using raw HHNK Wervershoof effluent and found the optimal dose to be 10 mg/L Fe^{3+} . On the pilot, he tested 10 mg/L Fe^{3+} with two different pH's, 6.8 and 8.3. Two different pH's were chosen because of the different coagulation mechanisms associated with them. At pH 6.8, adsorptive coagulation occurs, and at pH 8.3, sweep coagulation occurs (depicted in Figure 6). His experiments determined that with a 10 mg/L dose of Fe^{3+} and a pH of 6.8, the critical flux was 200 LMH. When running the pilot at a pH of 8.3, the critical flux was 175 LMH.

Using coagulation with and without pH adjustment as pretreatment increased the ceramic membrane performance significantly. Without pH adjustment, the critical flux increased by 70 LMH, and with a pH adjustment to 6.8, the critical flux increased by 75 LMH. At pH 8.3, the critical flux increased by 50 LMH. Having a more neutral pH (6.8) resulted in a better membrane performance because the ceramic membrane prefers neutral pH conditions due its isoelectric point (Jafari, 2021). Using a pH of 6.8, the flux increased more than using a pH of 8.3, making it a better membrane performance.

5.1.3 Ozonation Pretreatment on the Ceramic Membrane

Ozonation pretreatment was also completed by Ouma on the C0.4 pilot. He completed critical flux tests using different ozone doses – 10, 15, and 20 mg/L O_3 with the results outlined in the Table 5 below.

Table 5: The ozone pretreatment critical flux results using three different doses.

Regime	Dose (mg/L O ₃)	Residual Before CMF (mg/L O ₃)	Critical Flux (LMH)	Sustainable Flux (LMH)
1	10	0.01	125 †	100 †
2	15	0.30	200 †	150 †
3	20	0.66	275*	250*

Notes:

† Marvin Ouma, 2021

* Appendix 3.5

Compared to no pretreatment, an ozone dose of 10 mg/L O₃ did not cause a higher critical flux. Increasing the ozone dose to 15 mg/L O₃ resulted in a higher critical flux. This was also observed tested for an ozone dose of 20 mg/L O₃. This is because there is a measurable ozone residual before the membrane. Once an ozone residual is quantifiable before the ceramic membrane, the critical flux increases significantly, from 125 to 200 to 275 LMH. Results from the third ozone dose regime can be found in appendix 3.5.

5.1.3.1 Ozone Calibration Curve

An ozone calibration curve was created on the C0.4 pilot to determine the ozone residual before the membrane as a function of the ozone dose. While the calibration curve will change depending on the DOC value from the wastewater effluent, the curve can still serve as a basis for what ozone residual to expect when using the C0.4 pilot. Figure 18 and Table 6 below shows the process conditions and ozone generator settings for the calibration curve.

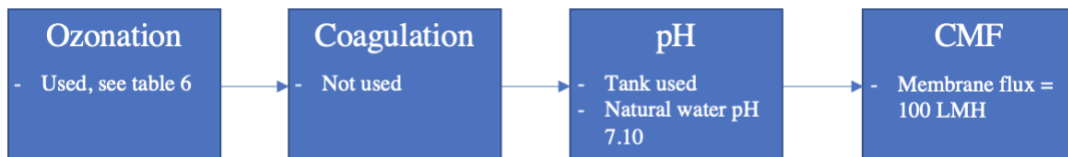


Figure 18: The process conditions for the ozone calibration curve.

Table 6: The ozone generator settings for the ozone calibration curve.

Gas Flow Rate (L/h)	O ₃ Gas Concentration (g/Nm ³ O ₃)	O ₃ Dose (mg/L O ₃)	DOC (mg/L C)	O ₃ /DOC
40	95	19	8.75	2.17
35	107	18.7		2.14
30	118	18		2.02
25	129	16		1.84
20	147	15		1.68
15	165	12		1.41
10	199	10		1.14

To generate the ozone calibration curve, the pilot water flow, ozone generator power setting, and bubble column HRT remained the same. To change the ozone dose, the gas flow rate was adjusted, and as a result the ozone residual also changed. To measure the ozone residual, accuvac ampules were used and duplicate measurements were taken for accuracy.

Figure 19 shows the calibration curve with ozone dose on the x-axis and ozone residual before the membrane on the y-axis.

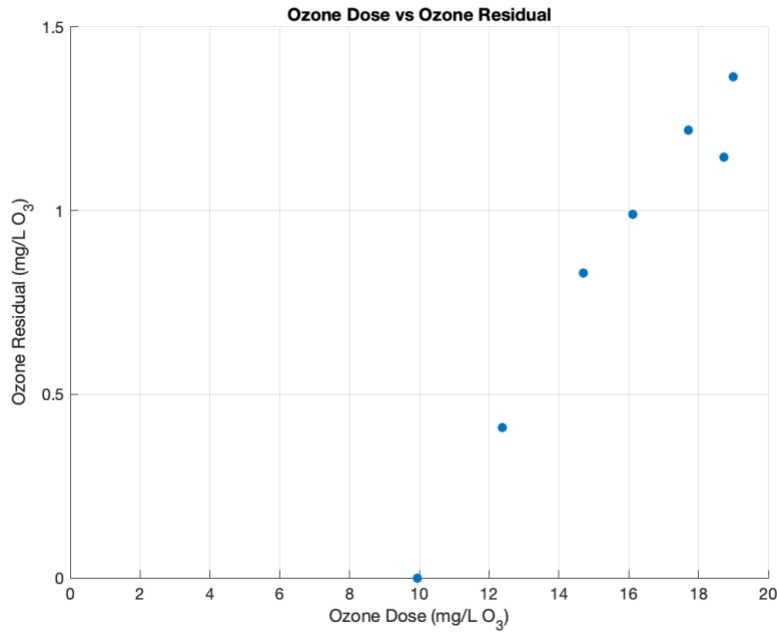


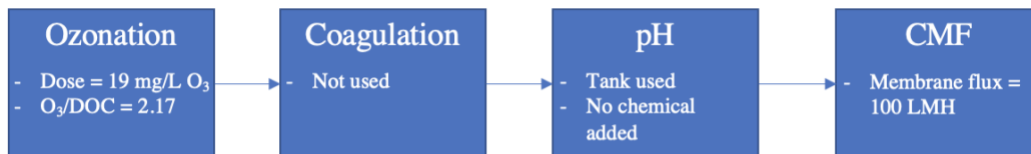
Figure 19: The ozone residual calibration curve generated using the C0.4 pilot.

No ozone residual is observed for O₃ doses up to 10 mg/L. For higher O₃ doses, the ozone dose vs residual is linear apart from dose 18.7 mg/L O₃. This calibration curve will serve as a baseline in the next experiments for which ozone residual can be expected before the ceramic membrane.

5.1.3.2 Long and Short Retention Time

An ozone residual test was completed to determine how the HRT of the pilot affects the ozone residual before the membrane. In the C0.4 pilot, there are different tanks that can be bypassed, altering the HRT (see Table 2). Two different scenarios were tested during this experiment, seen in Figure 20. Scenario one was typically used when just ozone is the pretreatment, and scenario two was used when ozone and coagulation are pretreatment for the ceramic membrane.

Scenario 1: HRT = 17 minutes



Scenario 2: HRT = 22 minutes

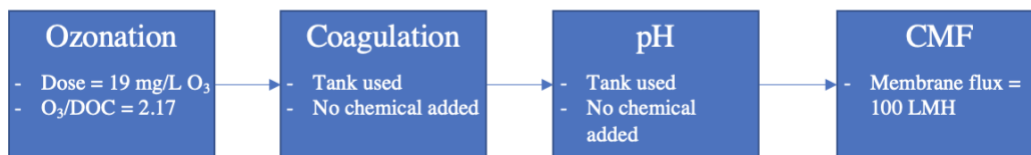


Figure 20: The two scenarios used with different HRTs in the C0.4 pilot.

Based on the pilot feed flow of 200 L/h, it was calculated that the HRT for scenario one is 17 minutes. With the coagulation tank in use in scenario two, it adds an extra 5 minutes to the HRT approximately (Gouveia, 2021). Figure 21 below shows the results with and without the coagulation tank.

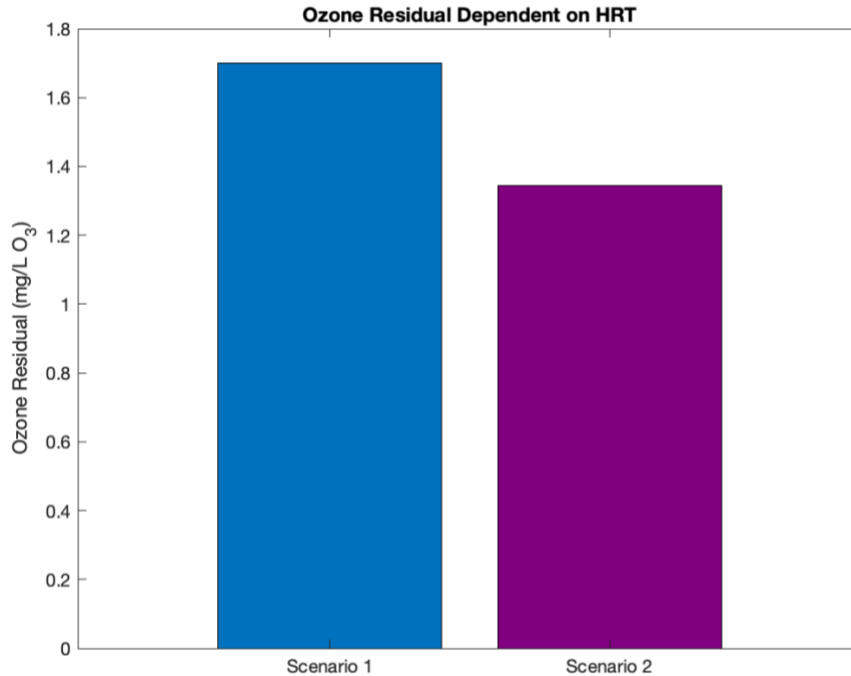


Figure 21: The ozone residual before the ceramic membrane in each scenario.

It is clear from Figure 21 that when the coagulation tank is in use in scenario two, the ozone residual before the ceramic membrane decreases. For this experiment, it decreased by 0.35 mg/L O₃. Using the coagulation tank resulted in a lower ozone residual before membrane because a longer HRT means more reaction time between the ozone and secondary wastewater effluent. These results are only valid for the conditions in Figure 20 and the change in ozone residual with and without the coagulation tank will differ between ozone doses.

The amount of DOC in the secondary wastewater effluent affects the ozone removal rate and remaining residual. With a consistent ozone dose, a higher DOC means that there are more organic compounds than “usual” that the ozone and OH radicals will react with. After the reactions are complete, there will be a lower ozone residual because there was more organic compounds in the water, and less free ozone. (Papageorgiou et al., 2017). For the HHNK Wervershoof WWTP, the DOC ranges between 6 and 10 mg/L C. Having an average DOC value

of 8.75 mg/L C means that there is a significant amount of DOC (for HHNK Wervershoof) in the water during this experiment.

5.1.4 Ozonation and Coagulation Pretreatment on the Ceramic Membrane

Ozonation and coagulation pretreatment was also completed by Marvin on the C0.4 pilot. He completed critical flux tests using a 20 mg/L O₃ dose, 10 mg/L Fe³⁺ coagulant, and at a pH of 6.8 Marvin was able to determine a sustainable flux of 250 LMH.

5.1.4.1 High Ozone Dose and Coagulation

A critical flux test was completed to determine the ceramic membrane's limits using coagulation, pH adjustment, and a high O₃/DOC ratio, seen in Figure 22. A high O₃/DOC ratio was used to evaluate the extreme possibilities when combining ozone and coagulation before the ceramic membrane. The HHNK Wervershoof wastewater temperature for all experiments (200-275 LMH) ranged between 21-22.5°C.

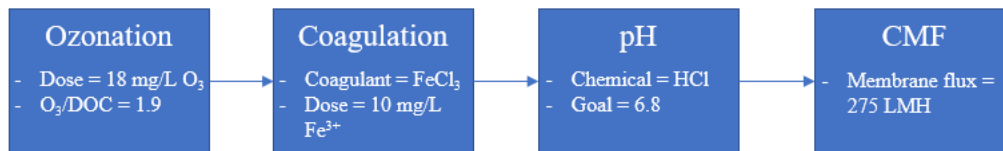


Figure 22: The process train for critical flux tests with ozone and coagulation as pretreatment.

Figure 23 shows the TMP profile from the critical flux test at 275 LMH. On the x-axis is time and on the y-axis is TMP at 10°C. Because the TMP exceeds 200 kPa at 10°C before the 24-hour run is completed, critical flux is 275 LMH. The ozone residual measured before the membrane was 0.60 mg/L O₃, decreasing by 0.30 mg/L O₃ when just ozone was in use.

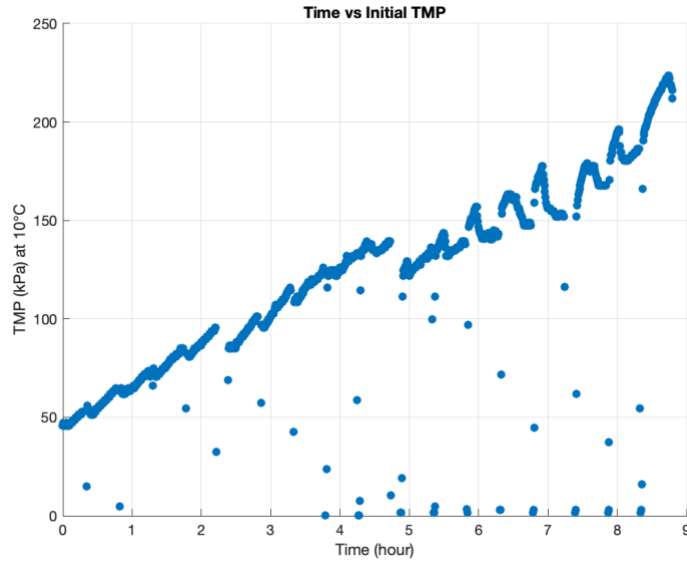


Figure 23: The TMP profile using ozone and coagulation as pretreatment at 275 LMH.

During the 200 and 250 LMH experiments, minimal fouling was observed but at 275 LMH, the fouling rate increased significantly. One reason for this could be reaching the pump's working limit. Figure 24 below shows the experimental TMP and flux data on the y-axis and time on the x-axis.

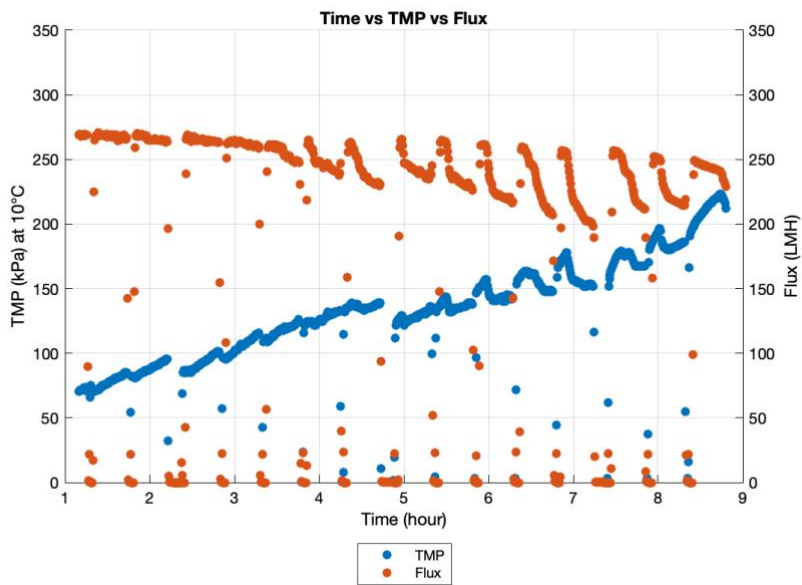


Figure 24: The experimental TMP and flux vs time at 275 LMH on the C0.4 pilot.

Initially the flux starts at 275 LMH, the setting for the experiment. However, as irreversible fouling begins to accumulate on the membrane, the TMP increases, and the flux slowly decreases. The higher pressure in the membrane shows the pump struggling to maintain the set LMH and after the 5-hour mark, the flux continually decreases until the 9-hour mark when the maximum TMP is reached. With a pH of 6.8, ozone residual of 0.60 mg/L O₃, and a coagulation dose of 10 mg/L Fe³⁺, the critical flux is 275 LMH.

5.2 Pharmaceutical Removal Analysis

In total, HWL analyzes 64 pharmaceuticals for each sample sent in. For the figures in section 5.2, 11 target pharmaceuticals identified by the Dutch Ministry of Infrastructure and Water Management. According to STOWA regulations, 70% of seven out of the 11 target pharmaceuticals must be removed from the wastewater treatment effluence before releasing back into a surface water source (Stichting toegepast onderzoek waterbeheer, 2020). Appendix 3.7 contains the graphs showing all 64 pharmaceutical results for the full picture.

5.2.1 6.5 mg/L O₃ Dose and Coagulation

Water quality analysis was completed using ozonation, coagulation, and pH correction to have data using an O₃/DOC ratio that is commonly found in WWTPs. The exact process train can be seen in Figure 25.

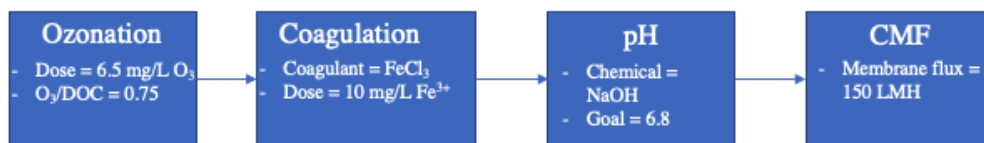


Figure 25: The process train for the water quality analysis with a 6.5 mg/L O₃ dose.

Table 7 below shows the key water quality parameters measured by HWL. With coagulation, the final turbidity is very minimal, and the pilot effluent water has the same UVT₂₅₄ (%) measured value using a dose of 10.5 mg/L O₃ (section 5.2.2).

Table 7: The water quality results using an O₃/DOC of 0.75, coagulation, and a pH of 6.8.

	Raw Water	After CMF
Bromide (µg/L Br)	203.9	207.1
Bromate (µg/L BrO ₃)	<1.00	<1.00
Turbidity (FTU)	1.04	<0.03
Temperature (°C)	11.7	
UVT ₂₅₄ (%)	53.0	89.0
UVT ₄₂₀ (%)	94.0	98.0

Figure 26 shows the pharmaceutical analysis completed for this experiment. On the x-axis is each target pharmaceutical, and on the y-axis is the percentage removed.

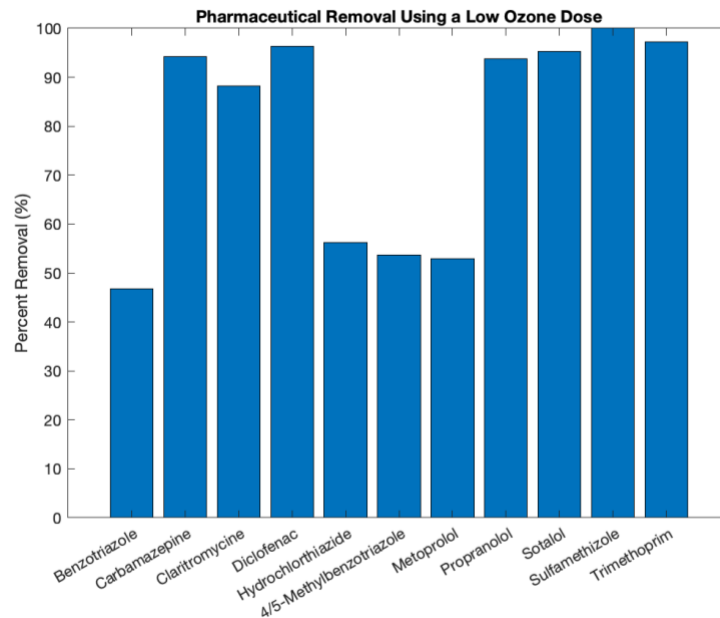


Figure 26: The pharmaceutical removal percentage using an O₃/DOC of 0.75, coagulation, and a pH of 6.8

Seven out of the 11 compounds had a 90% removal or higher and benzotriazole, hydrochlorothiazide, 4/5-methylbenzotriazole, and metoprolol all removed 55% or less of the

initial amount in the raw water. While this follows STOWA regulations, a higher O_3/DOC ratio before the membrane is required for all 11 target compounds to reach at least a 90% removal for wastewater reuse. Sulfamethizole had a 100% removal because there was none in the raw water to start. From these results, it can be concluded that an ozone dose of 6.5 mg/L O_3 will remove the pharmaceuticals in accordance with STOWA regulations, and a higher dose is required for wastewater reuse, the overall goal of the project.

5.2.2 10 and 14 mg/L O_3 Dose and Coagulation

Two different experiments were completed to observe how the ozone dose affects the pharmaceutical removal. The process train for each experiment can be seen in Figure 27. Ozone doses of 10.5 and 14 mg/L O_3 were chosen to align with the critical flux experiments using ozone only as pretreatment before the ceramic membrane.

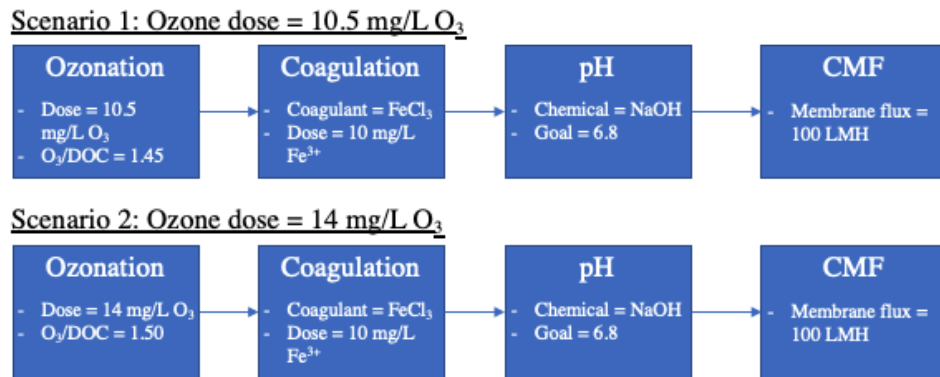


Figure 27: The process train for the two different ozone doses.

Table 8 below shows the water quality analysis results from the two different ozone doses. The raw water quality for each experiment remained similar, and the UVT_{254} (%) improvement was higher with the increased ozone dose. While the raw water DOC also increased from scenario one to two, the O_3/DOC ratio remained similar because of the increase in ozone dose.

Table 8: The analysis results from the low and high ozone residual experiments.

	Scenario 1		Scenario 2	
	Raw Water	After CMF	Raw Water	After CMF
Ozone Dose (mg/L O ₃)	10.5		14	
O ₃ /DOC	1.45		1.5	
Bromide (mg/L Br)	183.8	167.2	270.7	220.4
Bromate (mg/L BrO ₃)	0.1	20.48	0.09	43.64
Turbidity (FTU)	0.68	0.09	2.31	0.12
Temperature (°C)	17.6		18.2	
UVT ₂₅₄ (%)	61.1	88.3	54.8	85.7
UVT ₄₂₀ (%)	95.7	99.5	93.8	99.6

Figure 28 depicts the pharmaceutical analysis that was also completed for each experiment to see how the ozone dose affects the removal. The difference in removal between the two doses tested is minimal. The biggest percent difference between the ozone doses was for benzotriazole, at a 2% change. This leads to the conclusion that using a dose of 10.5 mg/L O₃ follows STOWA regulations which state that 70% of the seven out of the 11 target pharmaceuticals must be removed from the influent water. It also concurs with the conclusion from section 5.2.1 that an ozone dose higher than 6.5 mg/L O₃ will achieve the necessary removals for wastewater reuse.

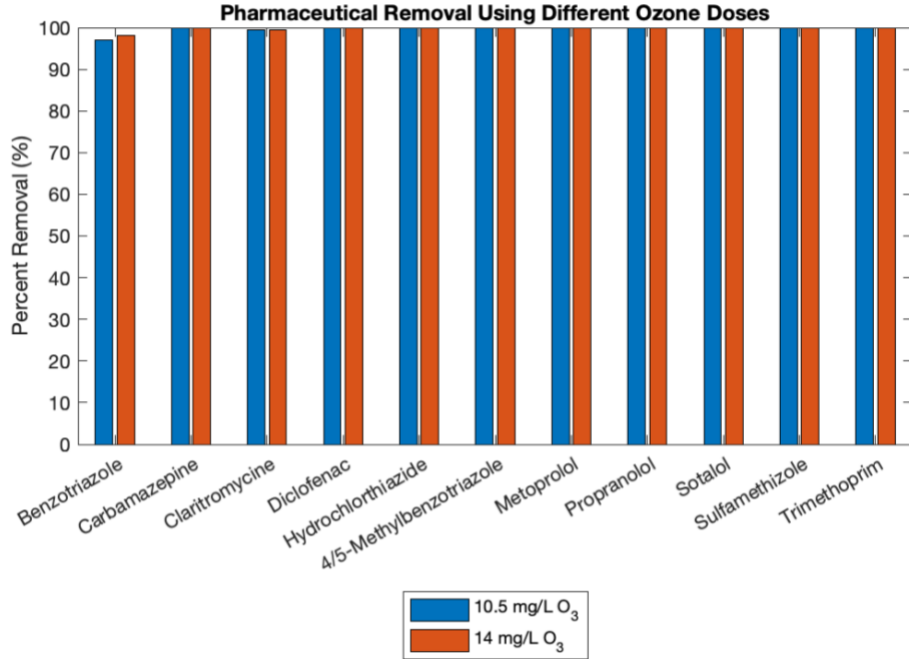


Figure 28: The percent removal of pharmaceuticals with different ozone dosages.

5.2.3 High Ozone Dose and Coagulation

Water quality analysis was also completed using a high ozone dose and O₃/DOC ratio to see the opposite end of the spectrum from section 5.2.1. A dose of 18 mg/L O₃ was chosen because it was also the highest ozone dose used to test ceramic membrane performance (see appendix 3.5). The coagulation dose and pH remained the same. The exact process train and conditions can be seen in Figure 29.

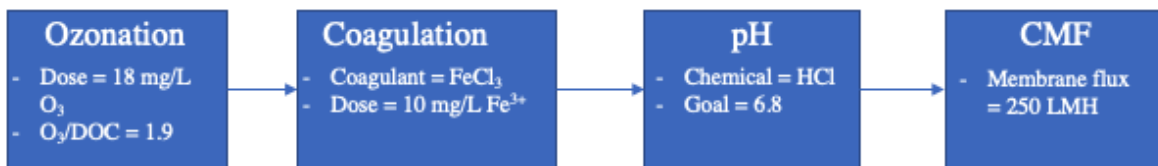


Figure 29: The process train for the water quality analysis using ozonation and coagulation.

Table 9 below shows the water quality analysis results using ozonation and coagulation as pretreatment. Unfortunately, there was an unknown error in the HWL analysis for bromide and

bromate, so those results are not included. The UVT₂₅₄ (%) measurements between the high dose of 18 and the low dose of 6.5 mg/L O₃ are the same, 89%.

Table 9: The water quality analysis results using ozonation and coagulation as pretreatment.

Parameter	Raw Water	After CMF
Turbidity (FTU)	0.71	<0.03
Temperature (°C)	21	
UVT ₂₅₄ (%)	53.0	89.0
UVT ₄₂₀ (%)	93.0	99.0

The resulting target pharmaceutical analysis results shown in Figure 30, with each pharmaceutical listed on the x-axis and the percent removal on the y-axis.

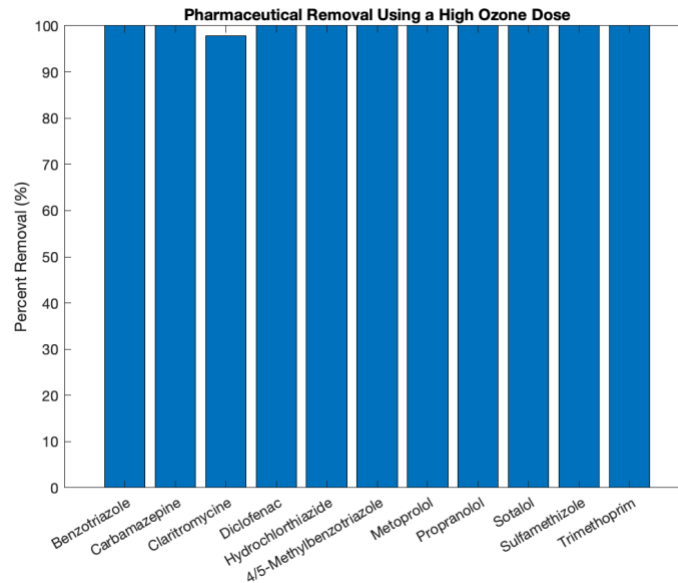


Figure 30: The pharmaceutical removal percentage using an O₃/DOC of 1.9, coagulation, and a pH of 6.8.

Using a higher ozone dose, an almost 100% removal from all 11 target pharmaceuticals was achieved. 10 out of the 11 target compounds had a 100% removal, with claritromycine at a 98% removal. In comparing Figure 28, Figure 26 and Figure 30, it can be concluded that a dose of 6.5 mg/L O₃ is necessary to abide by the STOWA regulations, and a higher dose will achieve a 95% or higher for the target pharmaceuticals present in the HHNK Wervershoof wastewater.

5.3 Bromate Formation during Ozonation and Advanced Oxidation Processes

5.3.1 Bromate Formation during Ozonation

The disadvantage of using ozonation for wastewater treatment when bromide is present is the formation of bromate. A series of experiments were completed using an ozone bench scale equipment at HWL to find the required weight ratio of H_2O_2 to O_3 to inhibit the formation of bromate.

The first step was to analyze the bromate formation as a function of ozone use. Six different experiments were run using RWZI effluent collected in November 2021 ($\text{DOC} = 8.87 \text{ mg/L C}$). For each experiment, a different ozone dose was applied – 10.7, 14.6, 20.3, 24.7, 26.3, and 31 mg/L O_3 . Figure 31 below shows the ozone dose on the x-axis, bromate formation on the primary y-axis, and ozone residual on the secondary y-axis. To calculate the ozone uptake time for the ozone dose, the ozone uptake curve and sample excel sheet can be found in appendix 3.3.

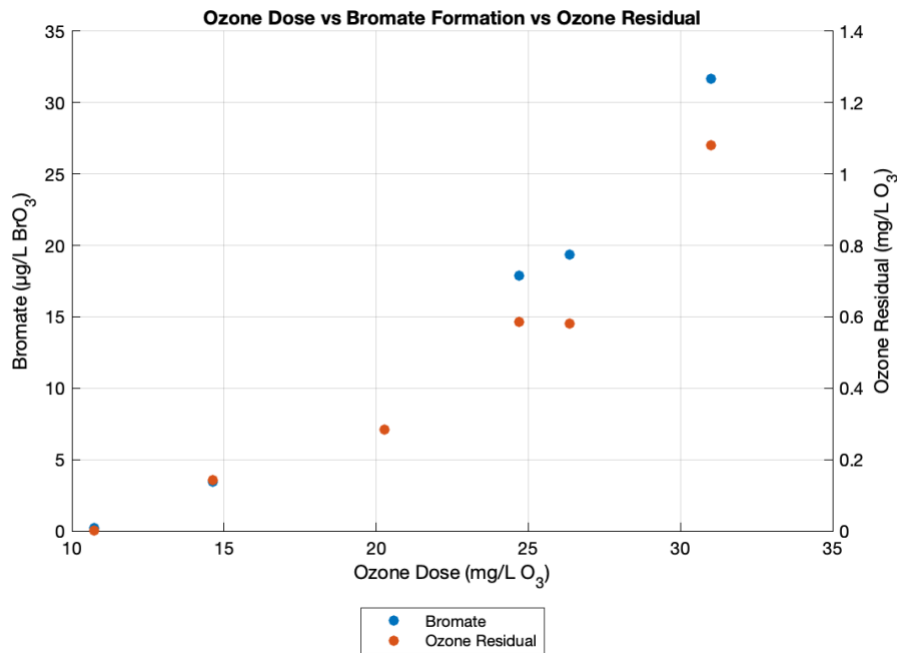


Figure 31: The bromate formation and ozone residual from each ozone dose.

The bromate formation and dissolved ozone residual both follow a linear formation, with 31.65 $\mu\text{g/L BrO}_3$ and 1.08 mg/L O_3 as the maximums. With no ozone residual, the bromate formation will be minimal and close to 0 $\mu\text{g/L BrO}_3$. Based on the ozone formation from Figure 31, the ozone dose of 24.7 mg/L O_3 was chosen for further testing with hydrogen peroxide.

5.3.2 Bromate Formation with Advanced Oxidation Processes

After graphing the relationship between bromate and ozone dose, the next step was to choose one of the ozone doses with significant bromate formation and add H_2O_2 to the water matrix. The ozone dose selected was 24.7 mg/L O_3 . Figure 32 below shows the bromate formation and dissolved ozone residual after adding different amounts of H_2O_2 to the reactor in proportion to the ozone dose. The ratios tested ranged from 2:1 to 0.25:1 $\frac{\text{H}_2\text{O}_2}{\text{O}_3}$. On the x-axis is the $\frac{\text{H}_2\text{O}_2}{\text{O}_3}$ ratio, the primary y-axis is the bromate formation and the secondary y-axis is the ozone residual.

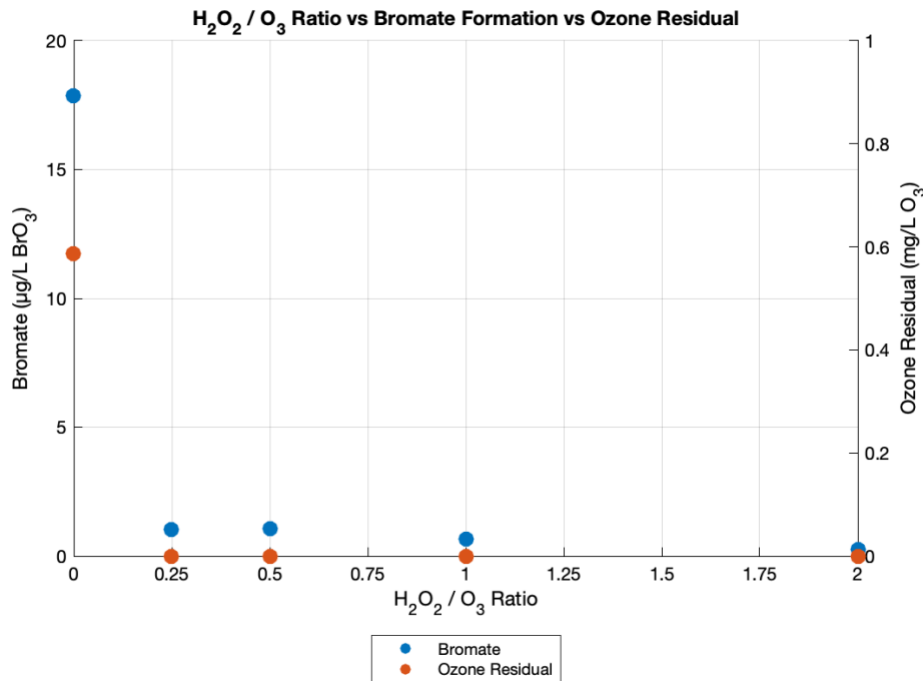


Figure 32: The bromate formation and ozone residual from each $\frac{\text{H}_2\text{O}_2}{\text{O}_3}$ ratio.

Similar to the bromate formation and ozone residual relationship in Figure 31, when the dissolved ozone residual is 0 mg/L O₃, the bromate formation is also very minimal. With no H₂O₂ added, a dose of 24.7 mg/L O₃ forms 17.86 µg/L BrO₃. With a ratio of 2:1 $\frac{H_2O_2}{O_3}$, the minimum amount of bromate formed is .24 µg/L BrO₃.

As less H₂O₂ is added, the bromate formation increases even though the residual ozone remains very low. The role of H₂O₂ in wastewater with ozone is to reduce the concentration hypobromite and residual ozone formed in the process of converting bromide to bromate. As a result, the final bromate concentration also decreases. However, some bromate is still formed even though the ozone residual is 0 mg/L O₃ because the concentration of residual ozone was not decreased fast enough with the lowering of the $\frac{H_2O_2}{O_3}$ ratio (Kruithof, 2021).

Based on Figure 31 and Figure 32, it can be concluded that the ozone residual can act as an indicator for how much H₂O₂ is needed to prevent the formation of ozone. The lower the ozone residual, the less H₂O₂ is needed. In addition, Figure 32 supports the conclusion made in the previous section, with no ozone residual, the bromate formation will be close to zero.

Chapter 6

6. Discussion

6.1 Introduction

The main objective of this research is to evaluate the ceramic membrane performance and resulting water quality with the pretreatment of ozonation and coagulation with ferric chloride as the coagulant. The research was completed using the bench scale ozone at HWL and a secondary wastewater effluent pilot in Wervershoof. The focus of this research was optimizing ozonation, the first step of pretreatment. This was done by evaluating the ceramic membrane's performance in terms of critical flux, pharmaceutical removal, and mitigating the formation of bromate, a toxic by-product.

6.2 Pretreatment Effect

6.2.1 Critical Flux Enhancement

Table 10 below shows a summary of the critical flux experiments conducted on the C0.4 pilot using no pretreatment and ozonation and coagulation individually and together.

Table 10: A summary of the critical flux test results using the C0.4 pilot.

Pretreatment Process	Dose	Residual	pH	Critical Flux
No Pretreatment (Natural Water)	N/A ♦	N/A	Natural Water	125
Coagulation	6 mg/L Fe ³⁺ ♣	N/A	Natural Water	195
	10 mg/L Fe ³⁺ ♦	N/A	6.8	200
	10 mg/L Fe ³⁺ ♦	N/A	8.3	175
Ozonation	10 mg/L O ₃ ♦	0.01 mg/L O ₃ ♦	Natural Water	125
	15 mg/L O ₃ ♦	0.33 mg/L O ₃ ♦	Natural Water	200
	20 mg/L O ₃ *	0.66 mg/L O ₃	Natural Water	275
Coagulation and Ozonation	10 mg/L Fe ³⁺ 18 mg/L O ₃	0.60 mg/L O ₃	6.8	275

Notes:

♣ Meghan White, 2019

♦ Marvin Ouma, 2021

* Appendix 3.5

From experimenting with no pretreatment to using coagulation and ozonation, the critical flux increased by 150 LMH, a significant amount. Using a high dose of ozone gives the same critical flux reached with ozone and coagulation. With the smallest dose of ozonation tested, 10 mg/L O₃, the critical flux remained the same as if there was no pretreatment. This is because there was also no measurable ozone residual before the membrane during this experiment, concurring with previous results and Schlichter et al. 2004, that state an ozone residual is necessary for improved membrane performance improvement by ozone pretreatment only.

6.2.2 Water Quality Improvement

Table 11 below summarizes the water quality results from the critical flux tests shown in Table 10.

Table 11: A summary of the water quality results from the critical flux tests.

Pretreatment Process	Dose	pH	Sampling Point	UVT ₂₅₄ (%)	UVT ₄₂₀ (%)	Turbidity (FTU)
No Pretreatment	N/A ♦	Natural Water	Raw Water	53.1	93.8	0.56
			Before CMF	53.1	93.8	0.56
			After CMF	54.9	94.5	0.05
Coagulation	6 mg/L Fe ³⁺ ♣	Natural Water	Raw Water	N/A	N/A	N/A
			Before CMF	N/A	N/A	N/A
			After CMF	N/A	N/A	N/A
	10 mg/L Fe ³⁺ ♦	6.8	Raw Water	50.3	93.6	0.88
			Before CMF	64.1	96.9	10.4
			After CMF	64.0	96.7	0.01
		8.3	Raw Water	N/A	N/A	N/A
			Before CMF	N/A	N/A	N/A
			After CMF	N/A	N/A	N/A
Ozonation	10 mg/L O ₃ ♦	Natural Water	Raw Water	46.9	92.2	0.78
			Before CMF	62.7	97.8	0.53
			After CMF	64.8	99.7	0.06
	15 mg/L O ₃ ♦	Natural Water	Raw Water	46.9	93.0	0.51
			Before CMF	73.0	98.3	0.40
			After CMF	77.0	99.6	0.06
	20 mg/L O ₃ *	Natural Water	Raw Water	53.9	93.7	0.75
			Before CMF	82.1	99.0	0.76
			After CMF	84.2	99.6	0.13
Coagulation and Ozonation	10 mg/L Fe ³⁺ 18 mg/L O ₃	6.8	Raw Water	53.0	93.0	0.70
			Before CMF	85.0	99.0	16.1
			After CMF	89.0	99.0	0.01

Notes:

♣ Meghan White, 2019

♦ Marvin Ouma, 2021

* Appendix 3.5

Using no pretreatment, the resulting UVT₂₅₄ (%) improvement is very minimal, 2%. Once coagulation and ozonation are added separately and in sequence, the water quality significantly improves. When coagulation is added as pretreatment, the UVT₂₅₄ and turbidity improves and when ozonation is added, the UVT₂₅₄ and UVT₄₂₀ increases as a function of ozone dose. When

ozonation and coagulation are both used as pretreatment, the resulting water quality is much better than with no pretreatment. Comparing the no pretreatment with the ozonation and coagulation pretreatment after CMF water, the UVT_{254} (%) increases by 35%, the UVT_{420} (%) increases by 4.5%, and the turbidity improves by 0.04 FTU. With both pretreatment processes before the ceramic membrane, the resulting water quality is the best out of all the runs.

6.2.3 O₃/DOC Influence

The O₃/DOC ratios chosen for each experiment on the C0.4 pilot ranged from 0.75 to 3.49 O₃/DOC. In Germany and Switzerland, the typical ratio for pharmaceutical control in their full scale WWTP with ozone treatment is 0.60 O₃/DOC (Kompetenzzentrum Spurenstoffe-BW, 2021). A low ratio is 0.30 – 0.40 O₃/DOC, and for wastewater reuse, a high ratio is over 1 O₃/DOC. To optimize membrane performance, a really high ratio is required, 1.5 O₃/DOC. Furthermore, the goal of ozonation in the EU is just for pharmaceutical degradation, their aim is not for membrane flux enhancement and wastewater reuse (Spruijt, 2021).

The higher O₃/DOC ratios were chosen for the pilot in Wervershoof to achieve the experimental conditions wanted in each test. For example, a high ozone dose was needed to have a measurable ozone residual before the membrane, and a low ozone dose for no ozone residual. This results in a high and low O₃/DOC ratio depending on the DOC in the water which is dependent on the rainfall. Because the wastewater at HHNK Wervershoof is treated outside, when it rains, the water is more diluted which results in a lower DOC, and vice versa during dryer weeks. In addition, the hydraulics in the C0.4 pilot are not optimized to achieve high ozone residuals just before the membrane due to the long contact time between ozonation and the membrane (extending piping and coagulation components).

6.3 Comparison of Ozone Doses for Membrane Performance and Pharmaceutical Removal

From section 5.1.3, it was concluded that for membrane performance improvement (measured via flux), an ozone residual before the membrane is required on the C0.4 pilot. Out of the ozone doses tested in this study, this translates to a minimum ozone dose of 15 mg/L O₃. In section 5.2, experiments measuring pharmaceutical removal with different ozone doses concluded that a minimum dose of 6.5 mg/L O₃ or less is required for Dutch regulations set by STOWA. Because the overall goal of this project is wastewater reuse, a higher pharmaceutical removal percentage is desired and was achieved by using a dose of 10.5 mg/L O₃. Using a dose of 10.5 mg/L O₃ resulted in all 11 target pharmaceuticals to be 95% or higher removed. However, with a dose of 10.5 mg/L O₃, the ozone residual was 0.05 mg/L O₃. This is a barely measurable ozone residual that will not help the membrane performance improve.

To optimize the C0.4 pilot, the selected operating conditions should allow the pilot to run at a high flux and produce water that has a high removal of the target pharmaceuticals. In order to achieve this, the ozone dose should be at least 15 mg/L O₃. From the experiments completed in this study, the pharmaceutical removal of all 11 target compounds will abide by STOWA regulations and be suitable for (see Figure 28). In addition, the membrane performance will improve from using no pretreatment (raw HHNK Wervershoof wastewater) to a steady sustainable flux of 150 LMH (see Table 5). If a higher membrane flux is desired, experiments showed that using an ozone dose of 18 - 20 mg/L O₃ will allow the membrane to treat more water over the same period of time. In conclusion, the minimum ozone dose required for improved ceramic membrane performance also overlaps with the ozone dose required for pharmaceutical removal regulations according to STOWA and wastewater reuse goals.

6.4 Bromate Formation via Advanced Oxidation Processes

6.4.1 Comparison with Previous PWNT Intern Research

Bram Delfos, a PWNT Intern in May 2019, also experimented with bromate formation via AOP with the same ozone bench scale, using H_2O_2 as well. His results are showed in Figure 33 below, in the orange boxes and yellow triangles. Figure 33 shows dissolved ozone (residual) on the x-axis and bromate formation on the y-axis.

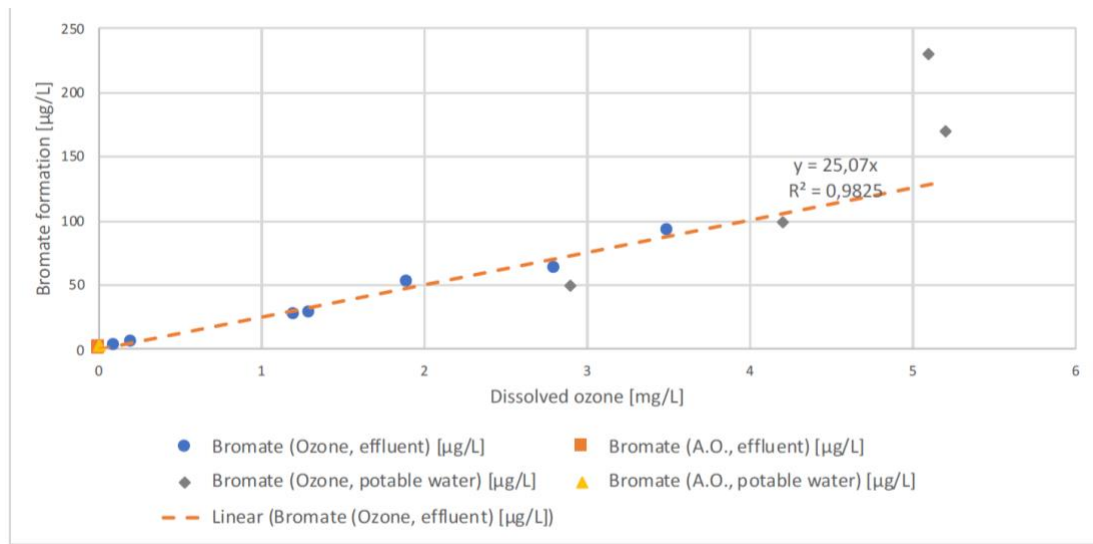


Figure 33: Delfos's bromate formation as a function of ozone residual (Delfos, 2019).

Delfos used a 4:1 $\frac{H_2O_2}{O_3}$ ratio, based on past drinking water experience (see section 6.4.2).

By adding four times the amount of H_2O_2 , Delfos was able to prevent all the formation of bromate. His results also concurred with the conclusions made in sections 5.3.1 and 5.3.2. Supported by the blue circles in Figure 33, with the smaller the dissolved ozone residual, the lower the amount of bromate formed. In addition, the dissolved ozone residual can act as an indication for how much hydrogen peroxide to add for a bromate formation below the limit.

6.4.2 Bromate Formation and Advanced Oxidation Processes using Surface water

In 2000, PWN conducted a feasibility study using ozone at their surface water plant Andijk for pesticide control. H_2O_2 was added to restrict the formation of bromate in the presence of bromide. Figure 34 shows the $\frac{H_2O_2}{O_3}$ ratio on the x-axis and bromate formation on the y-axis.

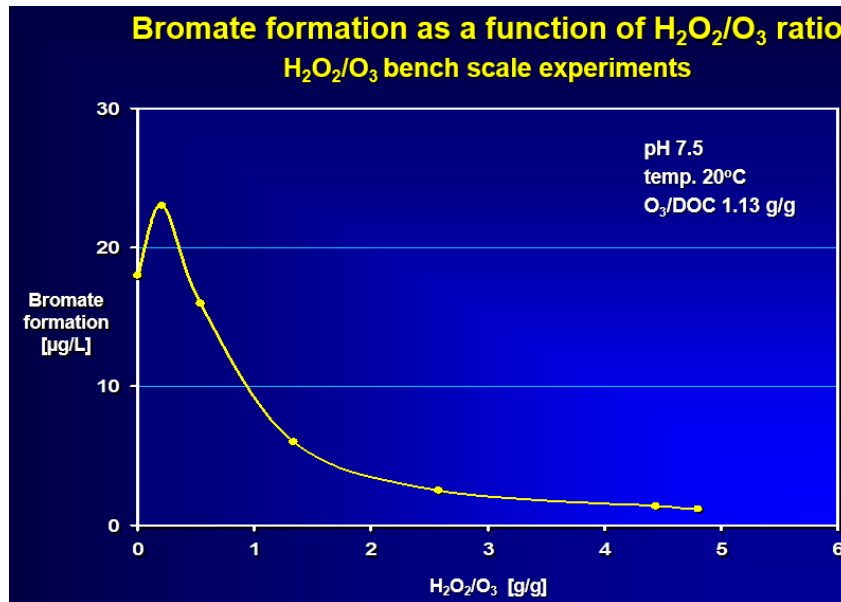


Figure 34: The bromate formation using H_2O_2 on surface water from PWN (Kruithof et al., 2000).

With the experimentation of many $\frac{H_2O_2}{O_3}$ ratios, it is clear that a large amount of H_2O_2 is needed to have a low bromate formation. With the smallest ratio tested, 0.25:1 $\frac{H_2O_2}{O_3}$, 23 $\mu\text{g/L}$ BrO_3 was formed with PWN surface water as the water matrix (higher than the 18 mg/L BrO_3 tested without the H_2O_2 addition). In comparison to Figure 32, using a 0.25:1 $\frac{H_2O_2}{O_3}$ ratio, a little over 1 $\mu\text{g/L}$ BrO_3 was formed using HHNK Wervershoof wastewater as the water matrix. The 0.5 $\mu\text{g/L}$ BrO_3 maximum limit could not be reached (in 2000) (Kruithof et al., 2000). In

wastewater, a 0.25:1 $\frac{H_2O_2}{O_3}$ ratio is sufficient for preventing the formation of bromate, and results in bromate measurements under the world average level of 10 $\mu\text{g/L BrO}_3$ (Cotruvo, 2013).

A much lower $\frac{H_2O_2}{O_3}$ ratio is expected in wastewater treatment effluent compared to surface water because of the organic content and the ozone demand for each water matrix. The DOC concentration in wastewater is much higher than surface water. With more organic content in wastewater, there is more to react with in addition to bromide, and it is less likely that the ozone will dissolve as a residual. Therefore, less peroxide is needed compared to surface water. In addition, the ozone demand is low for surface water, resulting in a higher ozone residual and the need for more peroxide (Spruijt, 2021).

6.4.3 Bromate Formation at a Lower Temperature

The PWN study (section 6.4.2) also observed the bromate formation at 5°C, the results in Figure 35 below. On the x-axis is the $\frac{H_2O_2}{O_3}$ ratio and bromate formation on the y-axis.

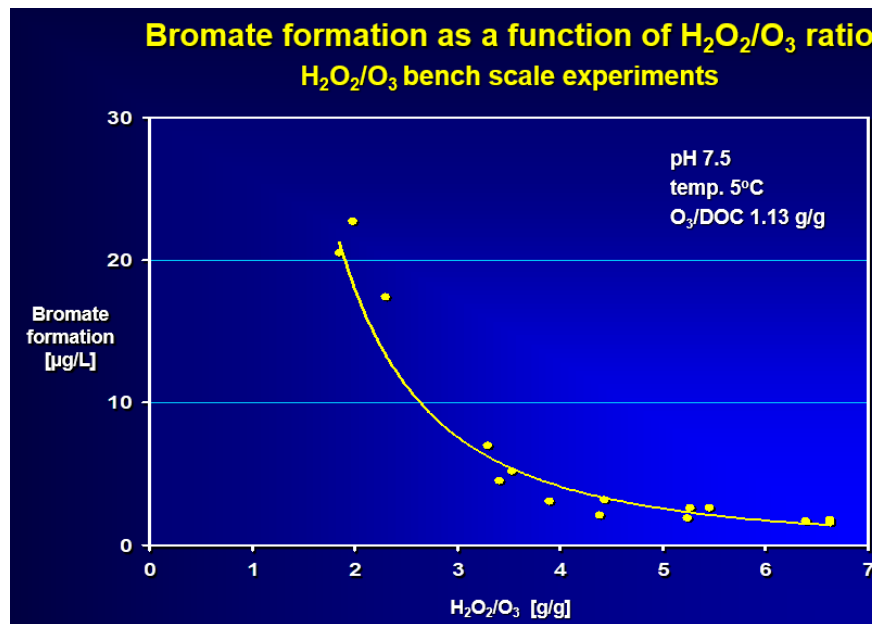


Figure 35: The bromate formation on surface water at 5°C (Kruithof et al., 2000)

In comparing the bromate formation between Figure 34 and Figure 35, more bromate is formed at lower temperatures. At a $2 \frac{H_2O_2}{O_3}$ ratio, the bromate formed at 20°C is 4.5 µg/L BrO₃ and at 5°C, there is 18 µg/L BrO₃ formed. This pattern follows for each $\frac{H_2O_2}{O_3}$ ratio tested and leads to the conclusion that bromate formation increases with decreasing water temperature.

Chapter 7

7. Conclusion and Recommendations

This chapter summarizes the results and discussion from chapters 5 and 6. It also gives recommendations for future work with this project to the next PWNT intern or professional who works on the project.

7.1 Conclusion

The purpose of the research was to use ozonation and coagulation as pretreatment for CMF with secondary wastewater treatment as the water matrix in the pilot. Experiments were carried out at a bench and pilot level. At a pilot scale, critical flux tests were completed that experimented with ozone doses and residuals measured before the membrane. From these experiments, it was observed that having a measurable ozone residual before the membrane resulted in a better membrane performance as compared to no pretreatment. In addition, an ozone residual is more important for membrane flux enhancement than NOM removal by ozonation. In regard to pharmaceutical removal according to STOWA regulations, it was determined that an ozone dose of 6.5 mg/L O₃ successfully removed 70% or more of the 11 target compounds. However, for wastewater reuse, a higher dose will achieve the higher pharmaceutical removal necessary. Bench scale tests using ozone were completed to experiment with the formation of bromate and mitigating it with the addition of hydrogen peroxide. The results showed that an ozone residual can act as an indicator for how much hydrogen peroxide to add to mitigate the formation of bromate. Based on these results, it was concluded that the combination of ozone and coagulation leads to good membrane performance and water quality.

7.2 Recommendations for Future Work

A bulleted list of recommendations has been compiled based on the research completed in the report for the next phase of the wastewater project with the C1 pilot.

- Rerun the ozone pretreatment at the same conditions used in the C0.4 pilot on the C1 pilot to demonstrate the observed results can be scaled up with higher flows.
- Apply hydrogen peroxide to the C1 pilot water to observe how the bromate formation changes in relation to the ozone residual measured before the ceramic membrane.
 - Use the ozone residual sensor as a monitoring tool for predicting how much hydrogen peroxide to add.
- Rerun experiments listed in appendix 3 that had equipment malfunctions which affected the results on the C1 pilot.

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Appendices

1. Supplemental Materials and Procedures

1.1 Coagulant Dose

1.1.1 *Materials*

- Milli-Q water
- 40% FeCl₃ chemical
- Glass beaker
- Stir bar and stir plate
- Pipette and pipettor

1.1.2 *Procedure*

1. Filled glass beaker with 45 mL of Milli-Q water
2. Added stir bar to glass beaker and placed on stir plate (turn on)
3. Added 0.80 mL of 40% FeCl₃ into the glass beaker
4. Kept stir bar moving for the duration of the experiment

1.2 Phipps and Bird Sequential Settings

1.2.1 *Procedure*

1. Turned on machine
2. Pressed “4” to program memories
 - a. M1 = 220 RPM for 1 minute
 - b. M3 = 20 RPM for 20 minutes
3. Pressed “back” two times
- ** To use sequential mode,
4. Pressed start
5. M1 (rapid mixing) began, alarm beeps when it ends
6. M2 (flow mixing) automatically began after M1 ends
7. Alarm for M2 went off, pressed “stop” so paddles stopped moving to begin settling

1.3 Phipps and Bird Continuous Settings

1.3.1 *Procedure*

1. Turned on machine

2. Pressed “1” for continuous mode
3. Typed in 220 RPM for rapid mixing
4. Pressed “enter” and “start” and ran for 1 minute
5. Pressed “stop”
6. Typed in 20 RPM for slow mixing
7. Pressed “enter” and “start” and ran for 20 minutes
8. “Pressed “stop” and began settling

1.4 Hach LCK 321 Fe³⁺

1.4.1 Procedure

1. Gathered six sample viles from the fridge
2. Uncapped and filled each vile with 2 mL of jar sample
3. Inverted 3 times and let sit for 15 minutes
4. Turned on Hach DR6000
5. Selected “barcode programs”
6. Cleaned and inserted the vile into Hach DR6000
7. Closed the lid and recorded the result

1.5 Hach DR6000 Spectrophotometer

1.5.1 Procedure

1. Turned on machine
2. Selected “single wavelength”
3. Selected “more” and “λ” (lambda) symbol
4. Specified the wavelength (254 or 420)
5. Selected “ok” and inserted zero sample cuvette
6. Poured sample into cuvette and cleaned it with a wipe
7. Inserted sample into machine, closed lid, and selected “read”
8. Recorded result
9. Repeated steps 6 through 8 for other samples
10. Repeated steps 3 through 9 for another wavelength

1.6 Hach 2100Q IS Turbidity Meter

1.6.1 Procedure

1. Turned on machine

2. Selected “verify cal” to calibrate the machine using supplied samples from the manufacturer
3. Filled sample bottle with jar sample and cleaned off using a wipe
4. Inserted sample bottle and closed the lid
5. Selected “read” and recorded result
6. Repeated steps 3 through 5 for the other samples

1.7 CO₂ Cover

1.7.1 *Gap for Paddle*

1.7.1.1 Procedure

1. Filled four jars with 1.5 L of RWZI wastewater stored in the fridge
2. Placed the jars in a warm water bath until the wastewater temperature reached 20°C
3. Prepared coagulant dose (see Appendix 1.1)
4. Programmed the sequential settings for the jar tester (see Appendix 1.2)
5. Inserted jars into jar tester
6. Covered two jars with parafilm, leaving a gap for the propeller (see Figure 36)



Figure 36: A covered and uncovered jar using parafilm.

7. Added coagulant dose to two jars, one covered and one uncovered
 8. Started mixer for 1 minute on 220 RPM and measured pH
 9. Mixer automatically changed to 20 RPM for 20 minutes and continued to measure pH
 10. Stopped jar tester and began settling for 30 minutes and continued to measure pH
 11. Turned off jar tester and cleaned up lab
- ** The parafilm was folded back to insert pH meter into the jar, and the jar was covered after the measurement was taken.

1.7.2 Fully Covered

1.7.2.1 Procedure

The procedure from CO₂ covered was also used for CO₂ fully covered experiment, with three changes. In step 1, the RWZI wastewater was filled to the brim of the jar. In step 5, a stir bar and plate were used instead of the jar tester. Finally, in step 6, the parafilm was stretched over the entire jar with no gaps.



Figure 37: A fully covered jar using parafilm and filled with RWZI wastewater to the brim.

1.8 Base Titrations

1.8.1 Procedure

1. Filled two jars with 1.5 L of RWZI wastewater stored in the fridge
2. Placed the jars in a warm water bath until the wastewater temperature reached 20°C
3. Prepared coagulant dose (0 and 5 mg/L Fe³⁺) (see Appendix 1.1 and Appendix 2.1)

4. Programmed the continuous settings for the jar tester (see Appendix 1.3)
5. Inserted the jars into jar tester
6. Added add the amount of coagulant dose into the jars
7. Started the jar tester to continually run at 50 RPM
8. Slowly added the 25% NaOH base at 30 μL increments and let the pH stabilize in between doses
9. Recorded the amount of the 25% NaOH base it took to reach a pH of 6.8
10. Continued to add the 25% NaOH base at 30 μL increments and allowed the pH to stabilize until a pH of 8.3 was reached
11. Repeated steps 1 – 3 and steps 5 – 10 for the remaining 4 coagulant doses (10, 15, 20, 25 mg/L Fe^{3+})
12. Turned off jar tester and cleaned up lab

2. Supplemental Calculations

2.1 FeCl_3 to Fe^{3+} Doses

Table 12 below shows the conversion from FeCl_3 to Fe^{3+} for the jar tests.

Table 12: The conversion from FeCl_3 to Fe^{3+} concentrations.

Coagulant Dose as FeCl_3 (mg/L)	Coagulant Dose as Fe^{3+} (mg/L)	Volume of 1% of 1,000 FeCl_3 solution (mL)
0	0.00	0
15	5.16	2.25
30	10.32	4.5
45	15.48	6.75
60	20.64	9
75	25.80	11.25

3. Supplemental Results

3.1 Base Titrations

The acid/base titrations were completed to determine the amount of acid or base added to each jar to reach a pH of 6.8 or 8.3 during the jar testing experiments. Because the coagulant, FeCl_3 , is known to decrease pH due to the increase in alkalinity consumption, only base titrations

were used to increase the pH (Gebbie, 2006). The RWZI wastewater used was collected in April 2021.

Table 13 below shows the amount of 25% NaOH base needed to raise the pH to the required 6.8 and 8.3. As expected, the amount of 25% NaOH base required increased with the coagulant dose in each jar. These values were used as a reference for the jar testing experiments. Because ozone would not affect the pH, regular wastewater was used as the source water (Spruijt, 2021). 10% HCl acid titrations were not completed because the starting pH was below the lowest goal pH.

Table 13: The amount of 25% NaOH needed to reach pH 6.8 and 8.3.

Fe³⁺ Dose	Total NaOH Added (µL)	Initial pH	Final pH
0	50	6.7	6.8
5	70	6.7	
10	80	6.7	
15	100	6.4	
20	110	6.4	
25	230	6.4	
0	190	6.7	8.3
5	200	6.7	
10	260	6.7	
15	280	6.4	
20	300	6.4	
25	350	6.4	

3.2 CO₂ Cover

The purpose of the CO₂ cover experiment is to see if the dissolving CO₂ from the air into the wastewater affected the pH during the experiments. As the wastewater absorbs the CO₂, the pH decreases and the water in each jar becomes more acidic (NOAA, 2020). The RWZI WWTP effluent used for this experiment was collected on April 6th, 2021. A second CO₂ cover

experiment was completed using a stir bar and plate instead of a Phipps and Bird jar tester to fully cover the jar with parafilm and compare results.

Figure 38 and Figure 39 below show the change in pH over a 51-minute period between two different CO₂ cover experiments. On the x-axis is time in minutes and on the y-axis is the pH. Each line represents a different jar, and the Fe³⁺ coagulant dose was 10 mg/L. In Figure 38, while the pH did fluctuate throughout the experiment, the deviation in pH was not significant enough to use parafilm in future jar testing experiments. Figure 39 shows the effect of CO₂ on wastewater using a fully covered jar filled to the brim. Between the two Fe³⁺ dosed jars, the uncovered jar slowly decreased in pH over time whereas the covered jar maintained a consistent pH throughout the 51-minute period.

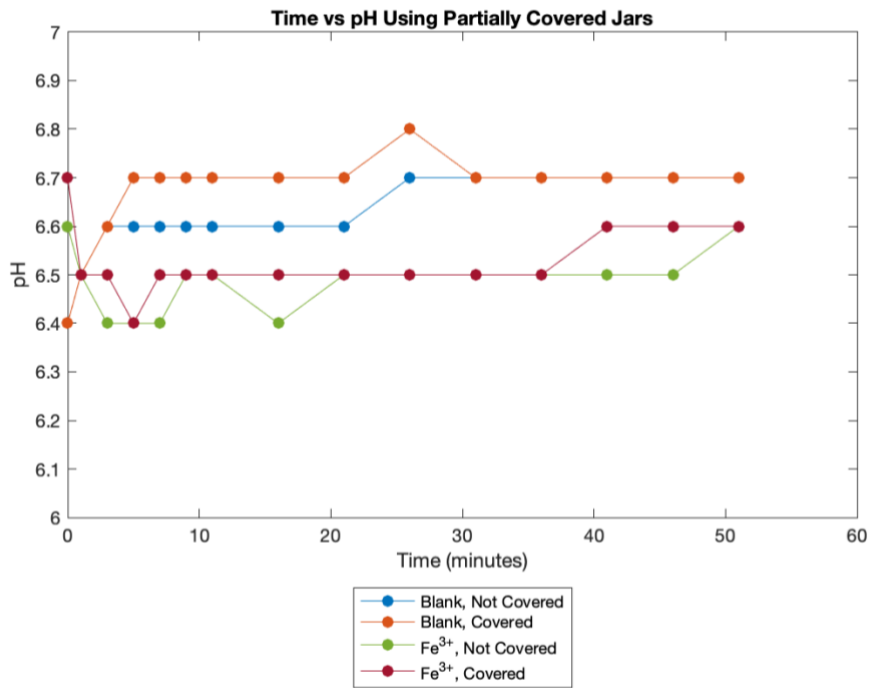


Figure 38: A graph showing the comparison of pH between four partially covered jars.

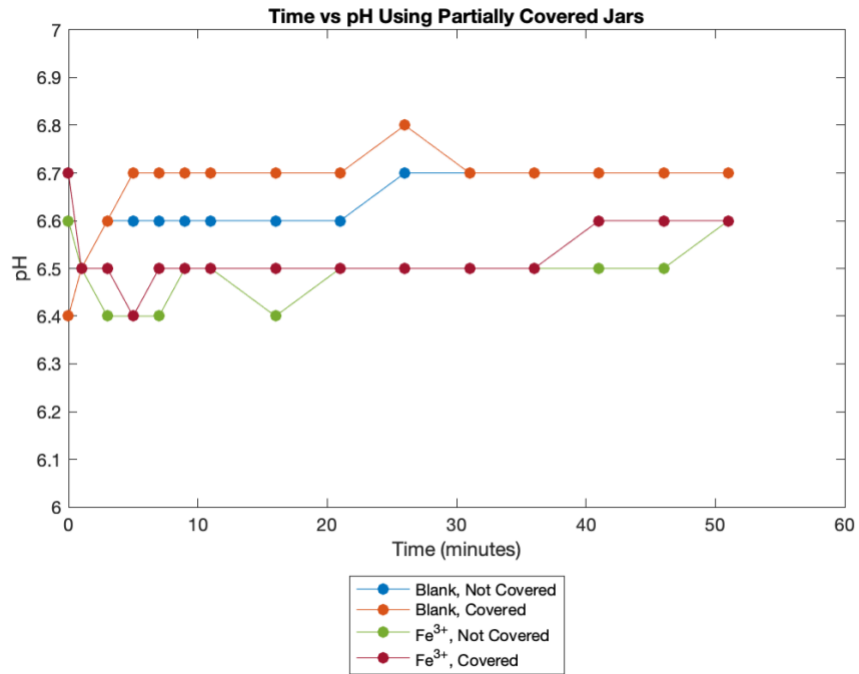


Figure 39: A graph showing the comparison of pH between four fully covered jars.

3.3 Ozone Uptake Curve

Figure 40 below shows the ozone demand curve generated at the ozone bench scale at HWL. It was used to calculate the time to expose the raw water to ozone, represented by the ozone dose.

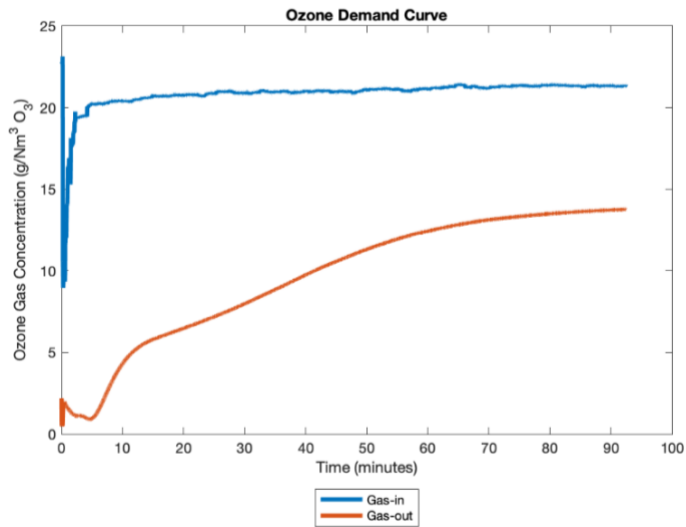


Figure 40: The ozone demand curve created at the HWL ozone bench scale.

Figure 41 below shows a sample excel sheet used to generate the ozone demand curve in

Figure 40.

	B	C	D	E	F	G	H	I	J
1	Time	Gas-in concentration (g/Nm3 O3)	Time	Gas-out concentration (g/Nm3 O3)	Gas Concentration Difference (g/Nm3)	Flow (mg/s)	Total uptake of ozone [mg O3] Accounts for the gas conc. Difference	Incoming flow (mg/s)	Incoming cumulative [mg] Not accounting for the gas out loss
2									
3					=C3-E3	=F3*(1/120)*(46/50)	=G3+H2	=C3*(1/120)*(46/50)	=I2+I3
4					=C4-E4	=F4*(1/120)*(46/50)	=G4+H3	=C4*(1/120)*(46/50)	=I3+I4
5					=C5-E5	=F5*(1/120)*(46/50)	=G5+H4	=C5*(1/120)*(46/50)	=I4+I5
6					=C6-E6	=F6*(1/120)*(46/50)	=G6+H5	=C6*(1/120)*(46/50)	=I5+I6
7					=C7-E7	=F7*(1/120)*(46/50)	=G7+H6	=C7*(1/120)*(46/50)	=I6+I7
8					=C8-E8	=F8*(1/120)*(46/50)	=G8+H7	=C8*(1/120)*(46/50)	=I7+I8
9					=C9-E9	=F9*(1/120)*(46/50)	=G9+H8	=C9*(1/120)*(46/50)	=I8+I9
10					=C10-E10	=F10*(1/120)*(46/50)	=G10+H9	=C10*(1/120)*(46/50)	=I9+I10
11					=C11-E11	=F11*(1/120)*(46/50)	=G11+H10	=C11*(1/120)*(46/50)	=I10+I11
12					=C12-E12	=F12*(1/120)*(46/50)	=G12+H11	=C12*(1/120)*(46/50)	=I11+I12
13					=C13-E13	=F13*(1/120)*(46/50)	=G13+H12	=C13*(1/120)*(46/50)	=I12+I13
14					=C14-E14	=F14*(1/120)*(46/50)	=G14+H13	=C14*(1/120)*(46/50)	=I13+I14
15					=C15-E15	=F15*(1/120)*(46/50)	=G15+H14	=C15*(1/120)*(46/50)	=I14+I15
16					=C16-E16	=F16*(1/120)*(46/50)	=G16+H15	=C16*(1/120)*(46/50)	=I15+I16
17					=C17-E17	=F17*(1/120)*(46/50)	=G17+H16	=C17*(1/120)*(46/50)	=I16+I17
18					=C18-E18	=F18*(1/120)*(46/50)	=G18+H17	=C18*(1/120)*(46/50)	=I17+I18
19					=C19-E19	=F19*(1/120)*(46/50)	=G19+H18	=C19*(1/120)*(46/50)	=I18+I19
20					=C20-E20	=F20*(1/120)*(46/50)	=G20+H19	=C20*(1/120)*(46/50)	=I19+I20
21					=C21-E21	=F21*(1/120)*(46/50)	=G21+H20	=C21*(1/120)*(46/50)	=I20+I21
22					=C22-E22	=F22*(1/120)*(46/50)	=G22+H21	=C22*(1/120)*(46/50)	=I21+I22
23					=C23-E23	=F23*(1/120)*(46/50)	=G23+H22	=C23*(1/120)*(46/50)	=I22+I23
24					=C24-E24	=F24*(1/120)*(46/50)	=G24+H23	=C24*(1/120)*(46/50)	=I23+I24
25					=C25-E25	=F25*(1/120)*(46/50)	=G25+H24	=C25*(1/120)*(46/50)	=I24+I25
26					=C26-E26	=F26*(1/120)*(46/50)	=G26+H25	=C26*(1/120)*(46/50)	=I25+I26
27					=C27-E27	=F27*(1/120)*(46/50)	=G27+H26	=C27*(1/120)*(46/50)	=I26+I27
28					=C28-E28	=F28*(1/120)*(46/50)	=G28+H27	=C28*(1/120)*(46/50)	=I27+I28
29					=C29-E29	=F29*(1/120)*(46/50)	=G29+H28	=C29*(1/120)*(46/50)	=I28+I29
30					=C30-E30	=F30*(1/120)*(46/50)	=G30+H29	=C30*(1/120)*(46/50)	=I29+I30
31					=C31-E31	=F31*(1/120)*(46/50)	=G31+H30	=C31*(1/120)*(46/50)	=I30+I31
32					=C32-E32	=F32*(1/120)*(46/50)	=G32+H31	=C32*(1/120)*(46/50)	=I31+I32
33					=C33-E33	=F33*(1/120)*(46/50)	=G33+H32	=C33*(1/120)*(46/50)	=I32+I33
34					=C34-E34	=F34*(1/120)*(46/50)	=G34+H33	=C34*(1/120)*(46/50)	=I33+I34
35					=C35-E35	=F35*(1/120)*(46/50)	=G35+H34	=C35*(1/120)*(46/50)	=I34+I35
36					=C36-E36	=F36*(1/120)*(46/50)	=G36+H35	=C36*(1/120)*(46/50)	=I35+I36
37					=C37-E37	=F37*(1/120)*(46/50)	=G37+H36	=C37*(1/120)*(46/50)	=I36+I37
38					=C38-E38	=F38*(1/120)*(46/50)	=G38+H37	=C38*(1/120)*(46/50)	=I37+I38
39					=C39-E39	=F39*(1/120)*(46/50)	=G39+H38	=C39*(1/120)*(46/50)	=I38+I39
40					=C40-E40	=F40*(1/120)*(46/50)	=G40+H39	=C40*(1/120)*(46/50)	=I39+I40
41					=C41-E41	=F41*(1/120)*(46/50)	=G41+H40	=C41*(1/120)*(46/50)	=I40+I41

RAW DATA

Figure 41: A sample excel sheet to generate an ozone demand curve.

3.4 High and Low Ozone Residual

Four different critical flux tests were completed to determine how the ozone residual before the membrane affects the ceramic membrane performance. Four different ozone residuals and two different ozone doses and fluxes were tested with two different C0.4 pilot configurations. The process train for the experiments can be seen in Figure 42 below. Without the coagulation tank and pH buffer tank (scenario two and four), the HRT is 15 minutes. In scenario one and three with the inclusion of both tanks, the HRT increases to 22 minutes. Unfortunately, there was a lab error, and the DOC measurement during the experiments is unknown.

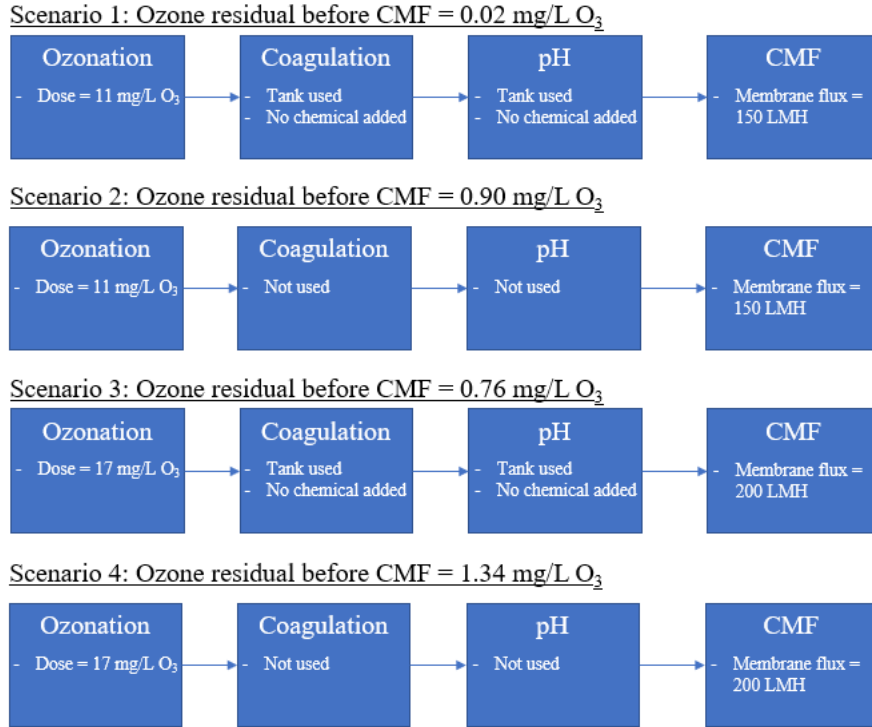


Figure 42: The process train for the critical flux experiments with different ozone doses and residuals.

Figure 43 below shows the TMP profile for scenario one and two. Figure 44 shows the TMP profile for scenario three and four. For both graphs, on the x-axis is time and on the y-axis is TMP at 10°C.

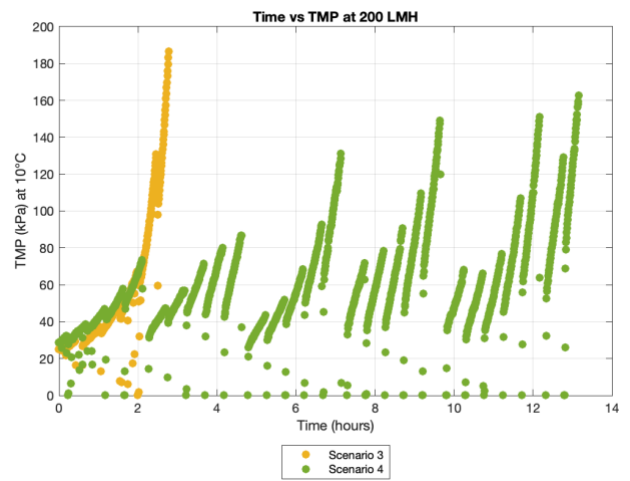
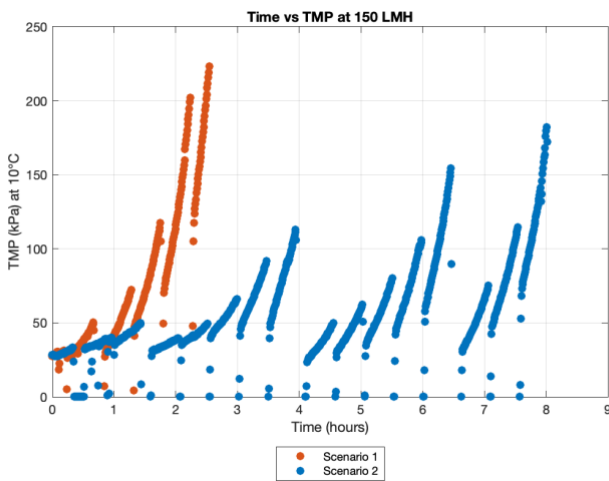


Figure 43: The TMP profile for an ozone dose of 11 mg/L O₃ using a short and long HRT.

Figure 44: The TMP profile for an ozone dose of 17 mg/L O₃ using a short and long HRT.

Both scenarios one and three had longer HRTs and smaller ozone residuals, and both also reached the maximum TMP significantly earlier than scenarios two and four with the short HRT and higher ozone residual before the membrane. Scenario four with the highest ozone residual before the membrane ran for the longest time at the highest membrane flux, 250 LMH. This leads to the conclusion that having an ozone residual before the ceramic membrane improves the membrane's performance.

However, none of the four critical flux experiments were able to run for the full 24-hours. This is because of the cold temperature of the water. Measured by the pilot, the water temperature for the four experiments ranged from 2 to 14°C, and averaged at 6.65°C. The temperature of the water changes the viscosity of the water, which affects the calculation correcting the TMP to 10°C. During these experiments, there also was an unknown malfunction of the equipment, and they should be rerun to confirm the conclusions made in this study in future work.

3.5 High Ozone Dose

Critical flux tests using ozonation as pretreatment were completed to observe how a high dose of ozone affects the ceramic membrane. The exact process train can be seen in Figure 45.

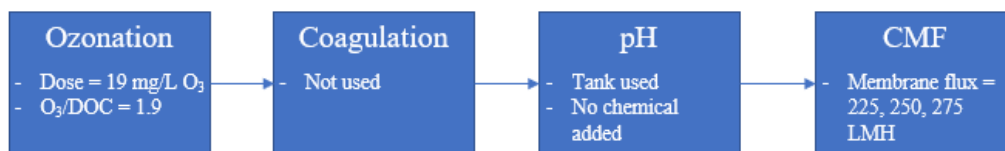


Figure 45: The process train for the critical flux experiments with ozonation as pretreatment.

Marvin Ouma was able to find a sustainable flux of 227 LMH using the same pilot settings in July 2021. Figure 46 below shows Marvin’s results at 227 LMH and results from a 225 LMH run in September 2021. On the x-axis is time and on the y-axis is the initial TMP. Table 14 also shows a comparable water quality analysis.

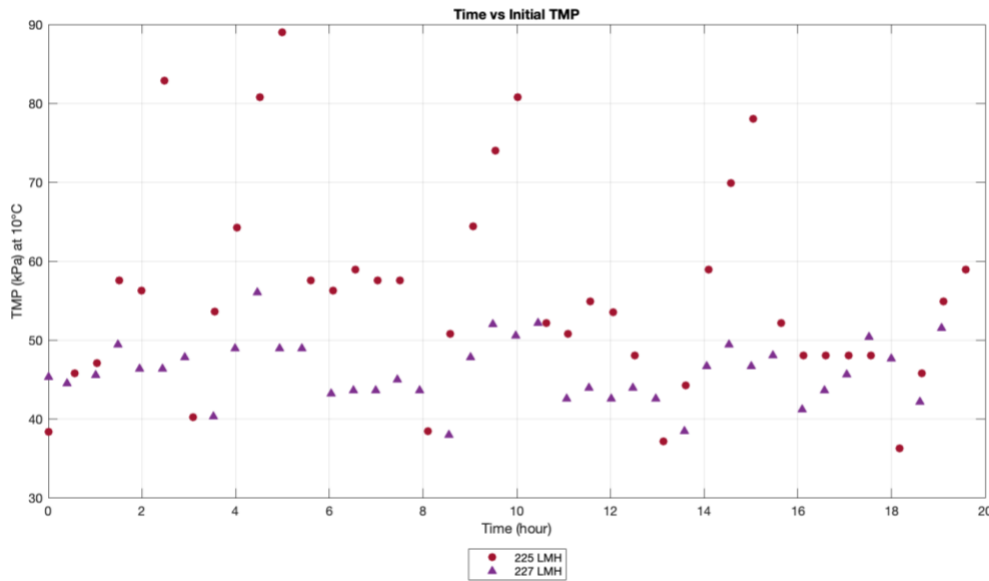


Figure 46: The initial TMP from 225 LMH and 227 LMH using ozonation as pretreatment.

Table 14: The water quality from 225 and 227 LMH using ozonation as pretreatment.

	Water Quality Parameter	225 LMH	227 LMH
Raw water	Temperature (°C)	21.8	22.4
	pH	7.6	7.39
	Flow rate (L/h)	200	200
	UVT ₂₅₄ (%)	51	50
After ozonation	UVT ₂₅₄ (%)	83	74.7
	UVT ₄₂₀ (%)	99	96.9
After CMF	UVT ₂₅₄ (%)	85	78.4
	UVT ₄₂₀ (%)	100	98.7

The experiment started at 225 LMH to make sure the water quality and membrane performance was similar from July to September. The TMP profile in Figure 46 remained similar, despite the higher initial TMP peaks observed during the 225 LMH run. The water

quality parameters in Table 14 are also similar, with the exception of the UVT_{254} values. Based on Figure 46 and Table 14, 225 LMH was determined to still be a sustainable flux, and the flow through the membrane was increased after 20 hours of observation.

Figure 47 shows the TMP profile for 225, 250 and 275 LMH all completed in September 2021. On the x-axis is time and on the y-axis is TMP at 10°C. After 48 hours of running, the C0.4 pilot exceeded 200 kPa during a flux of 275 LMH.

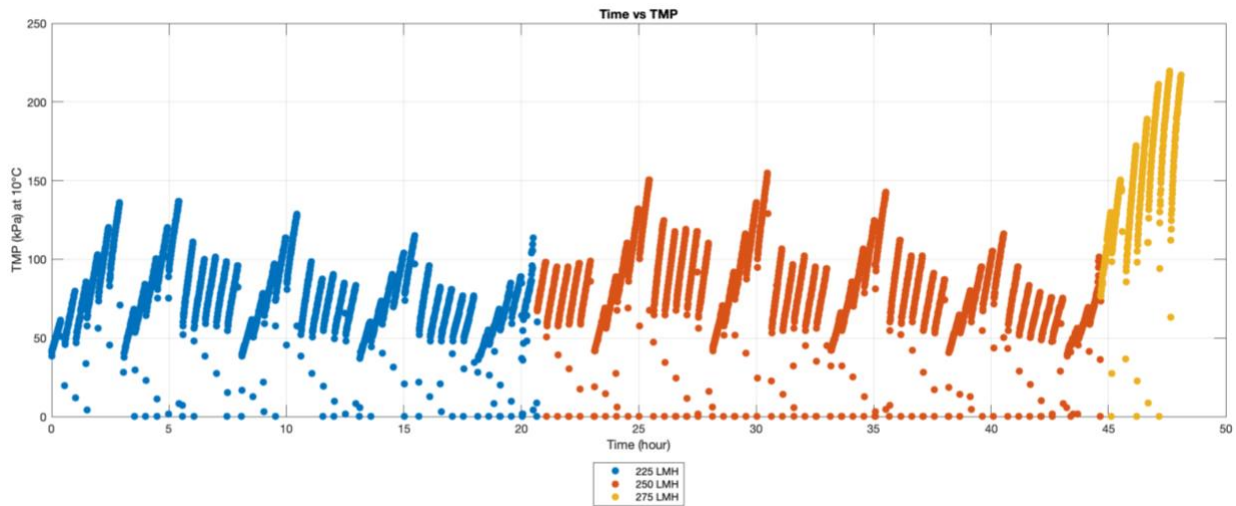


Figure 47: The TMP profile for 225, 250, and 275 LMH using an 19 mg/L O_3 dose.

Figure 48 below shows the initial TMP profiles for 225, 250, and 275 LMH. On the x-axis is time and on the y-axis is the initial TMP at 10°C. The fouling rate for each graph is in Table 15.

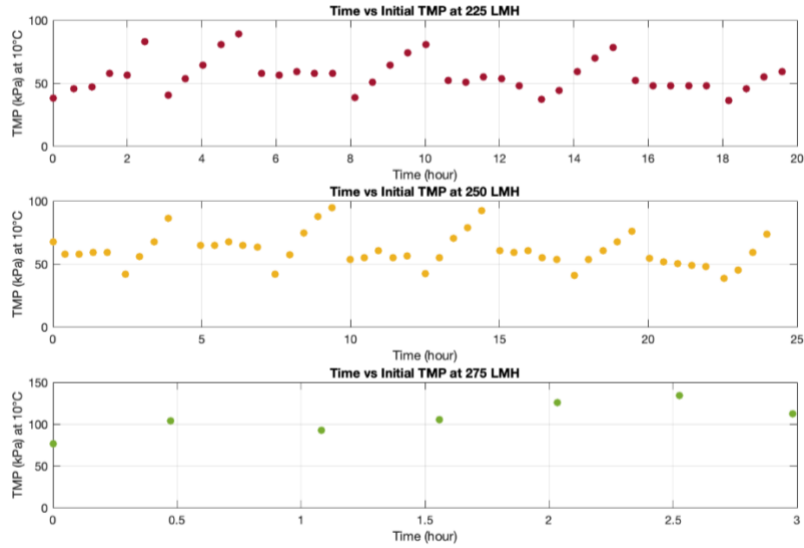


Figure 48: The initial TMP profile for 225, 250, and 275 LMH using a 19 mg/L O₃ dose.

Table 15: The fouling rate for each experiment using ozone as pretreatment.

Flux (LMH)	Fouling Rate (kPa/day)
225	-6.24
250	-12.00
275	345.60

While there are several initial TMP peaks in Figure 48, the fouling rate remains negative for 225 and 250. Once the membrane flow increases to 275 LMH, the fouling rate increases above the recommended 3 kPa/day by PWNT (Ouma, 2021). The fouling rates for 225 and 250 LMH are negative, which is unexpected for critical flux tests. This pattern also occurred in Meghan White’s work using the same C0.4 pilot, at a similar high ozone dose and membrane flux (White, 2019). The steep increase in the initial TMPs occurs every 5 runs, meaning that one of the CEB’s is affecting the TMP profile. More research and tracking of the backwash cycles is needed to understand why this occurs. For this thesis, the CEB heavily influences the TMP profile, and 275 LMH cannot confidently be concluded as the critical flux under the conditions presented in Figure 45.

Another important observation to note from Figure 48 is the increasing initial TMP at the beginning of each run for each flux. At 225 LMH, the initial TMP is 38 kPa at 10°C. This is the starting TMP after a CIP. At the beginning of 250 LMH, the first recorded TMP increases to 67 kPa, and at the start of 275 LMH, the first recorded TMP is 76 kPa, both at 10°C. Because no CIP was completed between the increase from 225 to 250 LMH, and 250 to 275 LMH, the membrane still had foulants within it from the previous run. This also impacted the results. Ideally in critical flux experiments, the membrane should be as clean as possible before testing the performance of it. Future critical flux experiments on the C1 pilot should include a rerun of a high ozone dose with a clean membrane for each flux.

3.6 Jar Tests Using Ozonated Wastewater

The next phase of the wastewater reuse project at HHNK is constructing and commissioning a larger pilot, the C1 pilot. This new pilot has a 25 m² METAWATER ceramic membrane and uses venturi dispersion ozonation and ILCA to treat the secondary wastewater effluent (Spruijt, 2021).

The purpose of the jar tests was to determine the optimal coagulant dose and pH for the C1 pilot using ozonated wastewater (10 mg/L O₃ dose) from HHNK Wervershoof in August 2021. The coagulant used was FeCl₃, and NaOH and HCl were used to increase and decrease the pH to 8.3 and 6.8 accordingly. Two different pH's were chosen due to the coagulation mechanisms associated with them. At pH 6.8, adsorptive coagulation occurs, and at pH 8.3, sweep coagulation occurs (depicted in Figure 6). Figure 49 below depicts the results from the jar test experiments with the Fe³⁺ dose on the x-axis and the measured UVT₂₅₄ (%) on the y-axis.

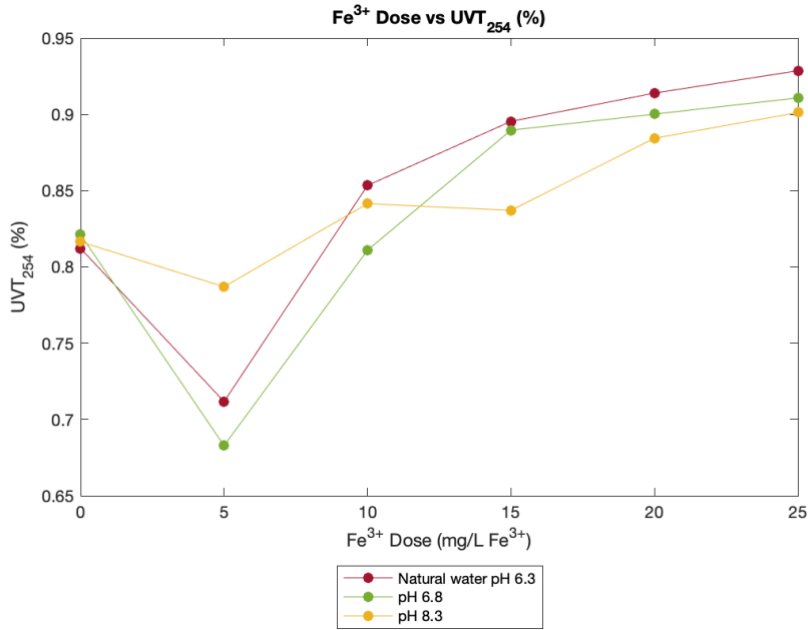


Figure 49: The UVT_{254} (%) results from all three jar test experiments.

In Figure 49, the UVT_{254} (%) values were significantly lower using a coagulation dose of 5 mg/L Fe^{3+} and then increased as the coagulation dose. In 2010, Baghvand et al. also observed this and concluded that it can be attributed to low initial turbidity values which are harder to coagulate due to low concentrations of stable particles. They also did jar testing using $FeCl_3$ as the coagulant, but their lowest turbidity was 1 NTU in their sample water. Table 16 below shows the initial turbidity values for the results depicted in Figure 49. The initial turbidity in the sample water is significantly lower than Baghvand et al.'s.

Doses of 10, 15, 20, and 25 mg/L Fe^{3+} increased UVT_{254} (%) values from the 5 mg/L Fe^{3+} dose which has a significantly lower UVT_{254} (%) value than the rest. Doses 15, 20 and 25 mg/L Fe^{3+} have similar UVT_{254} (%) values, both at pH 6.3 (natural water), 6.8, and 8.3.

Table 16: The initial turbidity values from the jar tests completed in August 2021.

pH	Initial Turbidity (FTU)
Natural pH 6.3	9.05
6.8	6.50
8.3	4.27

To determine the optimal pH, the ideal conditions for the ceramic membrane were taken into consideration, which has a preference of pH 7.0 to 7.5 because of its isoelectric point (Jafari, 2021). Because the UVT_{254} (%) values from the jar tests were also slightly higher using a lower pH, the optimal pH is 6.8. To determine the optimal coagulant dose, the change in UVT_{254} (%) was calculated between each test shown in Table 17 below.

Table 17: The change in UVT_{254} (%) between tests with a pH of 6.8.

Dose (mg/L Fe^{3+})	UVT_{254} (%)	pH	Dose Change (mg/L Fe^{3+})	UVT_{254} Change (%)
0	82%	6.8	0 to 5	-14
5	68%			
10	81%		5 to 10	13
15	89%		10 to 15	8
20	90%		15 to 20	1
25	91%		20 to 25	1

Going from a dose of 0 to 15 mg/L Fe^{3+} showed significant change between the UVT_{254} (%) results. However, from a dose of 15 to 20, and 20 to 25 mg/L Fe^{3+} , the UVT_{254} (%) increased at a change of 1% between each dosage. Quantitatively, 15 mg/L Fe^{3+} is the optimal coagulation dose using ozonated wastewater based on UVT_{254} (%) removal.

However, it is important to also consider what the ceramic membrane needs for optimal operation and the economic aspects as well. Too much $FeCl_3$ on the membrane can negatively affect the performance and result in a lower the critical flux. 10 mg/L Fe^{3+} should also be

considered and remain an option for testing in the C1 pilot once the coagulation optimization runs begin.

3.7 All 64 Pharmaceuticals Graphed

Figure 51, Figure 52, and Figure 53 show the pharmaceutical removal of all 64 pharmaceuticals that HWL analyzes. Following the conclusions made in section 5.2, a high ozone residual is needed for adequate removal.

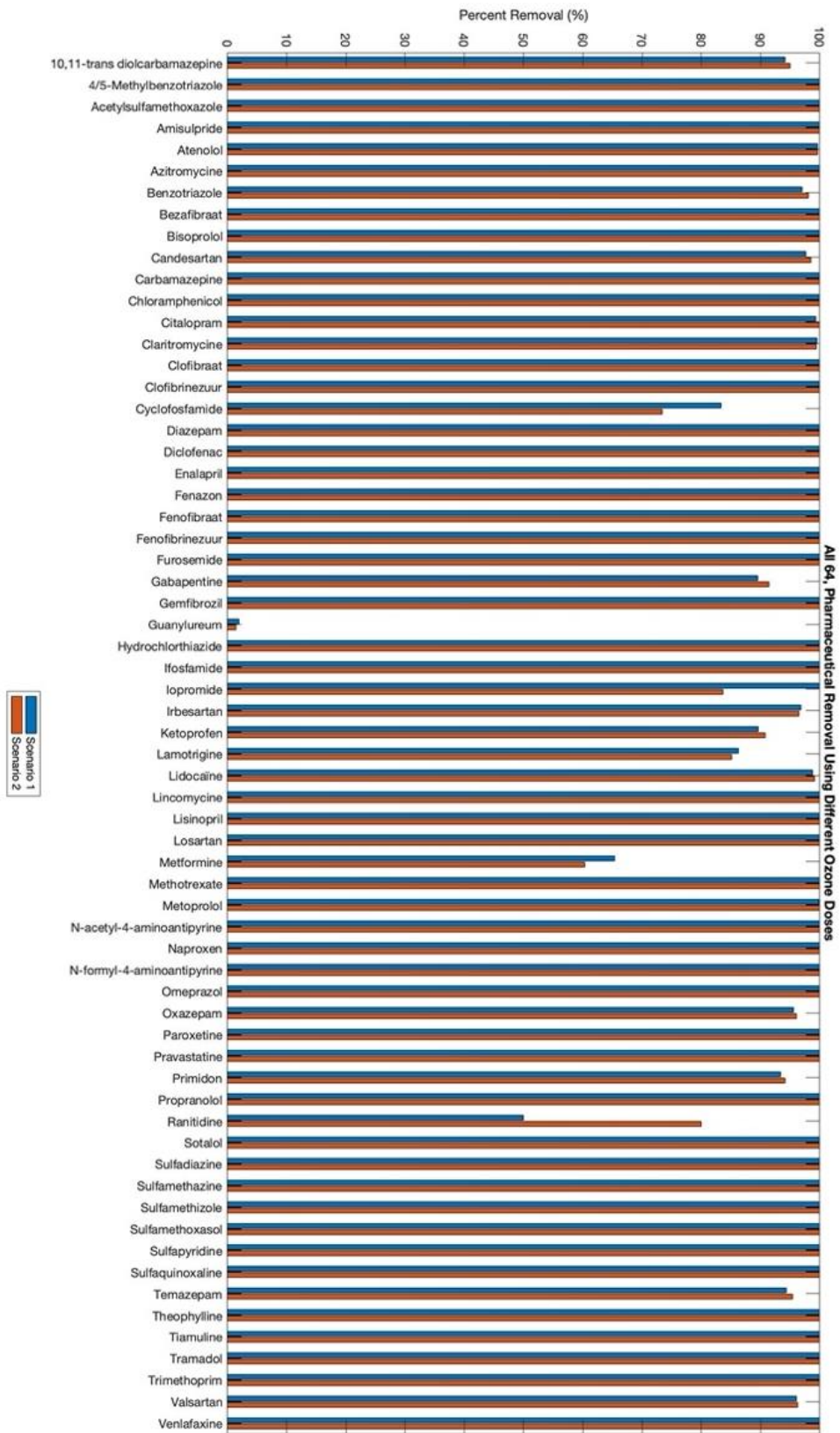


Figure 50: The removal of all 64 pharmaceuticals using different ozone doses.

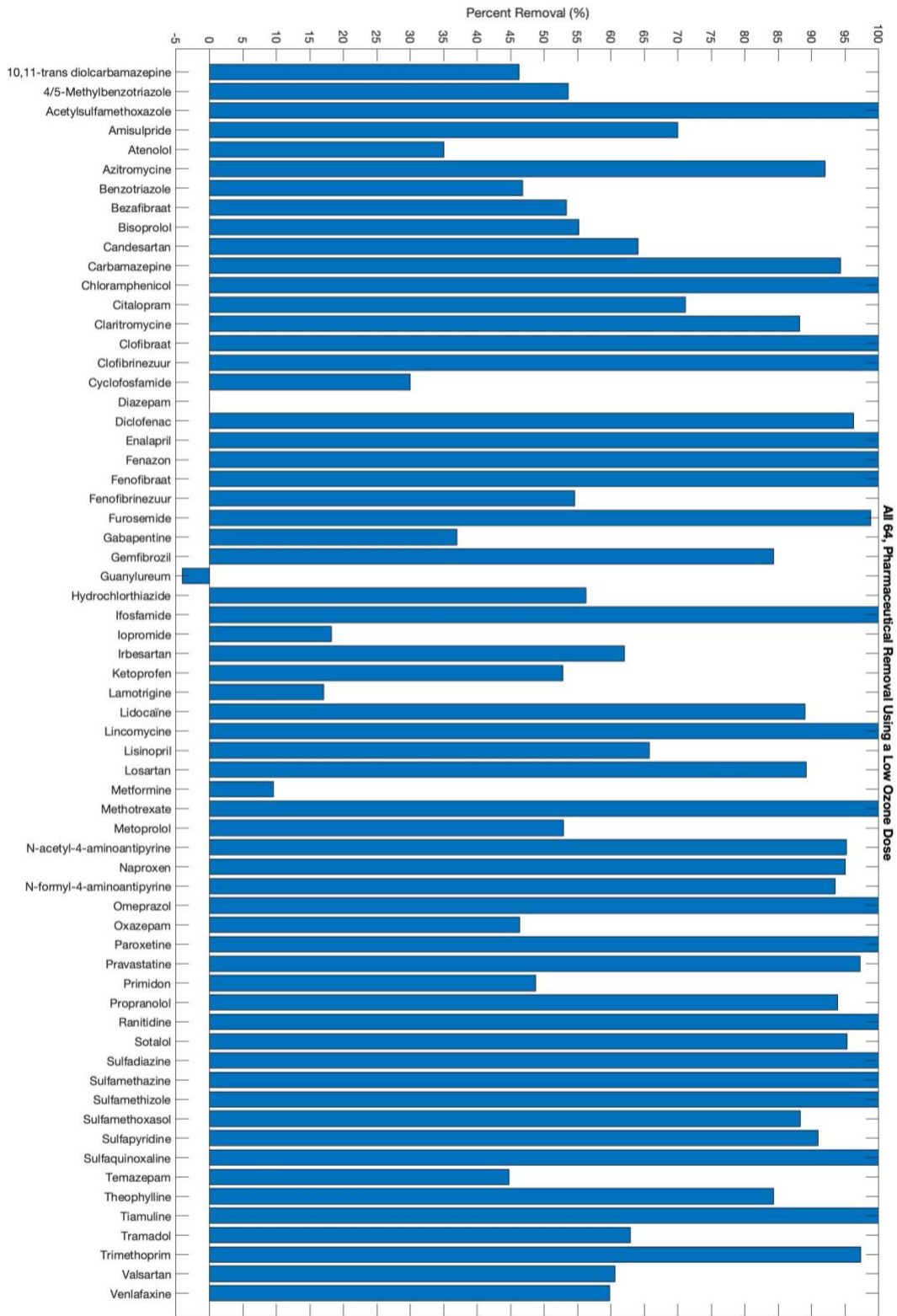


Figure 51: The removal of all 64 pharmaceuticals using a low ozone dose.

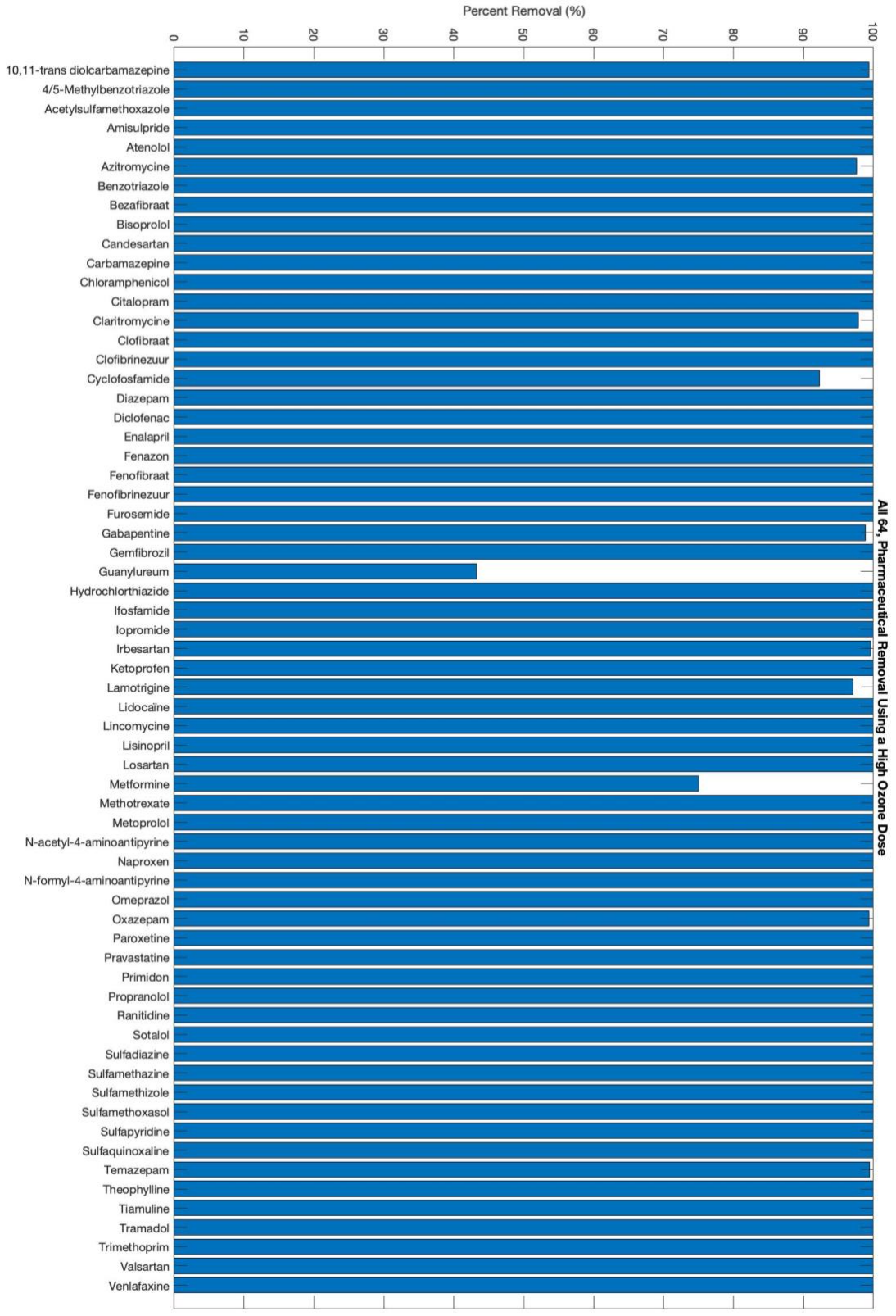


Figure 52: The removal of all 64 pharmaceuticals using a high ozone dose.

4. Manuals

4.1 Ozone Bench Scale

Compiled by Bram Delfos (2019) and Nicola Elardo (2021/22)

Start up:

1. Verify the reactor and tubing is clean
2. Fill the reactor with 6 L of the intended water matrix, make sure valves 7 and 9 are closed
 - a. Fill the 5 L beaker with the water matrix, and put the valve 9 tubing into the beaker
 - b. Turn the pump switch to the left and close valve 8
 - c. Open valve 8 and close valve 9 when finished
3. Start the pump at 1185 to circulate the water in the reactor (pump switch to the right)
 - a. If spiking or adding H₂O₂ to the water matrix, add at step 3 and circulate for proper mixing
4. Verify that valve 1 is closed
5. Turn on the ozone generator's main power switch, reset any alarms by pressing the blue button in the middle row on the far left
6. Open the oxygen cylinder and regulator valve
7. Reset both ozone concentration BMT's with the zero button
8. Start the ozone generator bypassing the reactor, running director to the BMT concentration meters and then to the destructor, ensure the manometer is at 0.5 barg
 - a. Run for at least 30 minutes until stable
 - b. Valve 1 closed, 2 open, 3 closed, 4 open, 5 closed, 6 closed
 - c. Check for ozone leakages during stabilization period
9. Link the laptop to the ozone gas and dissolved ozone meters
10. Verify the time settings on all meters are identical to the second
11. Start experiment

Run experiment:

1. Start logging both the meters on the laptop
 - a. "Save as" the file for the BMT program before logging for each experiment
2. Ensure the lid is on the reactor securely
3. Redirect the ozone from the concentration meters to the reactor
 - a. Valve 5 open, valve 3 open, valve 4 closed
4. Verify the pressure is still 0.5 barg, flow is 30 L/h, and concentration in is 20 g/Nm³
5. Start a timer immediately for ozone exposure time
6. 10 seconds before exposure time is over, open valve 9 to fill the sample tube
7. Take the sample
8. Stop logging on both the meters on the laptop
9. Copy and paste dissolved ozone into an excel sheet, the BMT data is automatically saved
10. Clean the lab

Cleaning the lab:

1. Verify valve 3 is closed
2. Turn the ozone generator system off
3. Open the reactor lid carefully (it's pressurized)
4. Flush the system with oxygen (0.5 barg)
 - a. Valve 1 open, 2, open, 3 closed, 4, open, 5 open, 6 closed to flush the bypass
 - b. Valve 4 closed, 3 open to flush the reactor
 - c. Valve 3, 2, 1 (in that order) closed after flushing
5. Close the oxygen cylinder and regulator
6. Empty the water matrix out of the reactor
 - a. Open valve 9, close valve 8 and turn the pump switch to the right
 - b. Have a beaker with valve 9 tubing to collect the effluent
7. Remove the reactor from the hooded bench and rinse in the sink
 - a. Use the brush to remove any gunk on the sides of the reactor
8. Flush the tubing with demineralized water
 - a. Place the tube labeled "water tubing" in a beaker with demi water
 - b. Place the tubing from valve 9 in an empty beaker
 - c. Turn on the pump to the right and run with demi water
 - d. Leave the tubing filled demi water
9. Place the empty reactor back in the hooded bench, reattach the tubing and close the hood

Misc. notes

- Verify the time settings for the BMT on the computer
- Verify the time settings on the dissolved oxygen meter on the monitor
 - ID: 1007
 - Password: 1234
- To start logging on the BMT, select options, log, start
- To start logging on the dissolved oxygen meter, open the Orbisphere program and it logs automatically
- When sampling, on the ozone demand curve the sample moment will be visually seen on the graph

4.2 C0.4 Pilot

Compiled by Meghan White (2019), Marvin Ouma (2021), and Nicola Elardo (2021/22)

Overview:

The PWNT Pilot in Wervershoof is a secondary effluent reuse system that consists of ozonation, ICLA, and ceramic membrane microfiltration. The secondary effluent is attached to

the system through the use of a filter where it is then exposed to pre-ozonation. After pre-ozonation the water goes through the static mixer, where some of the secondary effluent is recirculated through pre-ozonation. The secondary effluent then goes through the coagulation pretreatment unit, which consists of two tanks. Following coagulation, the influent water goes through the ceramic membrane where the filtrate goes through an activated carbon filter prior to being released into the environment.

Misc. Notes:

- HV-36
 - OPEN = going to bypass the CMF
 - CLOSED = to CMF, also close for a backwash
- To start a manual normal backwash, change the timings on the back of the pilot. Make sure to change them back to the original settings after. To bypass a CEB 1 or 2, shorten all the times in that section, and then the step 1 in normal backwash.
- Make sure T-05 is receiving overflow before starting a backwash
- Open AV-03 to bypass the membrane
- When running, pumps 3, 4, and 7 are open
- In HachDR600 when measuring the dissolved ozone, put the sample ampule in to “zero” the machine, and then put the blank in for the sample measurement. The blank should be darker than the sample when filling the ampule
 - To dilute the O₃, only dilute 2x, hard to do
 - The limit of the accuvac ampule is 1.50 mg/L
- Steps on the back screen of the pilot
 1. Filtration time
 2. –
 3. Dosing chemicals
 4. Resting/soaking
 5. Backwash of 8 seconds
 6. –
 7. Filling up the backwash vessel
- When the O₃ sensor goes off on the front of the pilot, the entire pilot shuts down
 1. Close the white tube valve from the generator to the bubble column
 2. Wait for the O₃ generator to shut off
 3. Void the error on the pilot and turn it back on
 4. When the O₃ generator turns back on, reopen the valve
- To manually fill the backwash vessel
 1. Open valve 6
 2. Left the white lever up at the top of the backwash vessel
 3. Insert tap water hose into the tap above the white lever (its messy)

4. Close the white lever and valve 6 when filled
- When inserting the compact disk, make sure the eject button is fully in
 - Whenever the power switch is completely off, the date resets
 - Check daily!
 - “Zero” the BMT ozone concentration sensor before testing the concentration each time
 - Blow air into the tubing to lower the concentration before zeroing if necessary
 - To see the concentration in the BMT, adjust the gas flow on the BMT knob, not on the gas generator
 - Make sure FI-03 and 02 have water in them
 - If not, then there is extra pressure/air in the system
 - Open HV-36 to release the air chose after
 - MAKE SURE HV-36 and 35 are both closed before the backwash begins
 - Good to open HV-36 each day to release any extra pressure
 - When setting the ozone dose, better to have a higher flow rate and a lower concentration
 - Bigger ozone bubbles are wanted in the column

Startup of Pilot:

Filling Secondary Effluent Tank:

1. Ensure that the pump is on for the pilot by asking someone at HHNK in their group office.
2. Open hydrant for the secondary effluent using the rusted metal apparatus. To do this, turn the orange valve located in the ground next to the hydrant in the counterclockwise direction.
3. Next, open the valve on the hydrant with the piping attached to it by turning it in the counterclockwise direction.
4. Since the first round of water entering the tank is relatively foul, leave the valve that allows water to exit at the bottom of the secondary effluent tank open for about 30 minutes before closing it and filling the tank.
5. Once the tank is filled, some of the secondary effluent will start flowing out of the overflow pipe. Once this starts occurring, adjust the hydrant valve to prevent the tank from overflowing. Once this is done, the secondary effluent is able to be used as the feed water for the pilot system.
6. To allow the secondary effluent to be the feedwater source for the pilot, attach the secondary effluent hose to the filter. Make sure the filter is cleaned before starting a new test.

Turning on the Pilot:

1. Attach the hose for the influent feed water, which is usually secondary effluent or tap water. This is done by pulling the orange clip down on the hose and pushing to into the inlet of the pilot until a clicking noise is heard.
2. Turn the black switch to the upright position located on the back of the membrane portion of the installation to start up the pilot, labeled “start installation”
3. Next, turn on the ozonation.



Figure 53: The back control panel on the ozone generator in the CO.4 pilot.

Table 18: The function of each ozone generator knob.

Label	Name	Function
1	Main switch	Used to power on the control system for ozone generation
2	Power production knob	To regulate the output power to the ozone generation. User can select desired power output from 0-10. When in use, knob No. 3 <u>MUST</u> be on off mode.
3	System set point	Used when external signal is incorporated, otherwise this knob <u>MUST</u> be <u>off</u> mode when knob No.2 is in use.
4	Pressure gauge	Provides the manometric pressure reading. This system operates under max pressure of 0.5 Bars.
5	Pressure regulator	Used to adjust the pressure in the system
6	Ozone system switch	Used to initiate ozone production.
7	Release	Pressed to release the malfunction red lights
8	Gas flow meter	Adjust the ozone gas flow rate. The system can measure flow rate in the range 10-140 L/h
9	Malfunction	This red light automatically turns on when the system is powered. This malfunction signal is removed when by pressing the release knob No. 7
10	Ozone release signal	This knob signals the release of ozone. It is accompanied by a sound from the ozone generator. This knob is automatically started after the BMT ozone analyzer has completed warming up and ready for use.

11	Injector pump	This green light is always on when the injector pump is fully in operation
12	Control voltage	This white light is automatically turned on when powered with correct voltage.
13	BMT 964 Ozone analyzer	Used to measure the ozone concentration in the gas phase. The machine gives readings in g/Nm ³ . The maximum measurables by BMT 964 is 300 g/Nm ³

4. Inspect all the gas path tubing to ensure they are correctly fitted to ensure no leakages. Also, check for possibility of water which might have accidentally entered the ozone gas tubes. Air from the compressor can be used to expel any water in the tubes. When performing this, it is advised to throttle the air released from the compressor to avoid using high pressures that can cause damage to the system.
5. Turn on main switch labelled 1 above.
6. Release the malfunction alert by pressing tab labelled 7.
7. Turn the ozone on by turning tab 6 to the right.
8. Adjust the power output (tab 2) and gas flow (tab 8) as desired.
9. Open the blue valves tube from the ozonation to the bubble column to allow ozone into the pilot.

Common Problems during Pilot Startup:

1. Buffer tank (T-01) is empty
 - To fix the empty buffer tank, allow tap water to flow through the system prior to turning on system. Once the buffer tank is filled to an appropriate level, turn on the pilot and hit the accept storing button on the back of the ceramic membrane portion of the pilot.
2. CEB1 or 2 levels are low
 - Refill the CEB1 and CEB2 tanks, directions in chapter 4
3. TMP exceeds 2 bars.
 - Release the pressure directly before the ceramic membrane by opening the spout and letting the water out. Then press the release button on the back of the pilot to resolve the error.

Running the Pilot:

Adjusting the Inlet Flow:

The inlet flow can easily be adjusted by turning the black dial at the front of the ozonation above in inlet water hose.

Adjusting the Flow through the Ceramic Membrane:

The flow through the ceramic membrane can be adjusted using a dial found inside the panel. The panel can be opened by using the key located right next to it. The dial is located in the upper right-hand corner. To increase the flow, turn the dial to the right, and to decrease the flow turn the dial to the left. The dial is extremely sensitive.



Figure 54: The interior and exterior of the pilot's control panel.

Adjusting the Ozone Concentration:

The ozone gas concentration can be adjusted using the dial labeled #2 (ozone production) located on the back of the ozonation portion of the pilot. To adjust the gas concentration, the dial must be unlocked, which is done by moving the switch on the side of the dial to the upright position. The dial can then be moved to the right to increase the concentration or to the left to decrease the concentration. Once the dial is set to the appropriate level, the dial should be locked again by moving the switch on the side of it to the right.

A black gas meter located on the top of this portion of the pilot will display the ozone gas concentration going into the water. Give the system time to adjust to the ozone gas concentration. It should usually take around 30 minutes to stabilize. Disconnect the tube running

from the ozone generator to the bubble column and directly connect it to the ozone concentration gas meter.

It is recommended to do test the ozone concentration before starting the experiments. Get some fresh air after.

Filling the CEB1 Vessel (Base):

The thirty-five-liter CEB1 vessel contains a 100-ppm hypochlorite solution. The system will shut down when the level of this solution is only at ten liters. In order to fill up this vessel, unscrew the black cap and then pour 10 liters of RO water into vessel. A 150 gram/liter sodium hypochlorite solution is added. If the sodium hypochlorite solution is actually 150 gram/liter, then 6.80 milliliters of this solution needs to be added to the vessel for every 10 liters of water.

To test free chlorine,

1. Get .5 mL of CEB1, fill to 10 mL (diluted 20 times)
2. Add reagent to the solution and shake
3. Add the sample to the 1 cm cuvette
4. Use the DR600 and favorite programs to measure the free chlorine
5. Aiming for 100 (or 5 with dilution)
6. Add more sodium hypochlorite to achieve the measurement if necessary

Filling CEB2 Vessel (Acid):

The thirty-five-liter CEB2 vessel is filled with a 100-ppm peroxide solution. The system will shut down when the level of this solution is only at ten liters. In order to fill up this vessel, the black cap is unscrewed and 10 liters of RO water is poured into the vessel. Next, 2.90 milliliters of a 35 percent peroxide (H₂O₂) solution are added followed by 40 milliliters of a 10 percent hydrogen chloride (HCl) solution. The pH of CEB2 should be around 2, so add more HCl if necessary. Check the pH of the HCl before starting to make sure it is below 2.

Filling the pH and coagulant tank:

Use the dilution equation, see below, to determine the amount of RO to concentrated chemical to add. Even though the tanks can hold 7 L, usually 6 L of RO is maximum and the rest is filled with the chemical.

$$C_1V_1 = C_2V_2 \qquad \text{Equation 8}$$

Where: C = Concentration

V = Volume

Shut Down of the Pilot:

Turning off the Pilot System:

1. Turn off the ozone generator
2. Close the blue valve on the ozone tube to the bubble column
3. Turn off the influent feed water pump by unplugging it
4. Shut off the membrane portion of the installation by turning the switch labeled “start install”
 - a. The power can be completely cut off from the pilot, but this resets the date each time back to January 1st, 1970.

Cleaning the membrane – Acid CIP:

1. Start with a normal backwash
2. Put pump into citric acid tank, make sure the tank is closed at the bottom
3. Weigh out 2 kg of Citric Acid and 100 L of tap water to put into citric acid tank
4. Connect pump tube to the bottom valve behind the coagulant container, HV-27
5. Open AV-001
6. Undo bubble column tube from pilot, #3 to drain the bubble column on left side of pilot
7. Connect #2 tube to citric acid tank on left side of pilot
8. Drain T-01
9. Open HV-36 and AV-003 to drain water out of the membrane. Close AV-003 after.
10. Open valve that hose is connected to in step 3, HV-27
11. Plug in pump to outlet and start it
12. Let water with HV-36 open to flow for ~3 minutes
13. Open HV-35
14. Close HV-36 until FI-02 regulates at 200 (adjust as necessary)
15. Run for ~ 3 hours
 - a. On metal spout, should be around 1.4 and on the back of the pilot, should be around 1.8 bar
16. After the membrane is clean...
 - a. Switch off pump
 - b. Close all valves in front that were open (AV-001, 27, 36 and 35)

- c. End with a normal backwash

Cleaning the Membrane – Ozone CIP:

1. Plug the tap water into the O3 generator (main inlet into pilot)
2. Fill the bubble column up to fill up the buffer tank
3. Turn on the pilot
4. Void the error on the pilot caused by the buffer tank not being filled
5. Make sure all orange pumps are closed
6. Complete a normal backwash (if not already done from the acid CIP)
7. Bypass the coagulation tank (close HV- 04, 06, 23) but remember to open back up when completed
8. Turn on the ozone generator
 - a. Power = 100%
 - b. Flow = 40 L/h
9. Let the highly ozonated tap water run through the pilot, occasionally open HV-36 to release pressure and extra air in the system
10. Perform the CIP for ~1.5 hours, can do manual backwashes or let the pilot do them every ~26 minutes until the membrane is clean
 - a. PT-01 should be around .5
 - b. The TMP should be in the range of 0.3 to 0.4 bar
11. End with a normal backwash and shut everything off

Analyzing the Pilot Data:

1. To obtain the data from the pilot system, go to the RSG30 monitor by Endress+Hauser located on the back of the ceramic membrane portion of the pilot.
2. Insert the compact disk into the pilot, this takes some finagling.
 - a. Also, a USB type B (male) cord can be used by plugging into the computer (much easier!)
3. Next, press on events and go to the compact disk functions. Make sure to update the compact disk first and then safely eject the compact disk.
4. Once the compact disk has been removed, put the disk into the diskette reader located at the pilot and then plug the reader into your computer.

Readout the data:

1. Open the ReadWin 2000 program on your laptop and have the diskette reader plugged in as well with the compact disk from the pilot monitoring system in it.
2. Click on the header titled read out.
3. Choose the option titled readout measured values using diskette. This action should result in box opening asking you to select a drive (double check which one in the file explorer).
 - a. If a USB type B (mal) was used, select readout measure values using interface/modem
4. Once the correct drive is selected press ok and the data should be saved. A window will show up once the data is saved asking if you would like to delete the data off the diskette, do not delete the data.

Export the data into an excel file:

1. Click on the header titled extra.
2. Select the option titled export measured values.
3. A window will pop up titled export measured values: select unit. Click on Ecograph T. This will prompt another window.
4. In the export measured values window, go to the portion titled display values, and determine the time period that you want. In the analogue values portion of the window, average and instantaneous value should be selected. Once these steps are completed, press continue.
5. A window dealing with channel selection will now appear. In the display channels column, you want to have Group 1 (GP1): FIT-01, Group 1 (GP1): PT-01, Group 1 (GP1): PT-02, Group 1 (GP1): PT-03, Group 1 (GP1): QIT-01 t, and Group 1 (GP1): QIT-01/O3 to be located under this column. Once they are all under display channels, press continue.
6. A window dealing with the setup of the file will then pop up on the screen. Under file type, select text file (*.xls), For data, select replace existing, and with regards to tabular, select text in inverted commas and export status. Lastly for decimal character and format operating time, select decimal point and 0000h00:00, respectively. Once these settings are chosen, press ok.
7. One final window will now pop up, asking for a file name and the location for the file to be saved. Upon completion of this final step, press save and your data will be exported as an excel file. The file can then be opened and analyzed.