FEASIBILITY OF *M. OLEIFERA* AS A COAGULANT AND ITS EFFECTS ON DOWNSTREAM ULTRAFILTRATION

By

Andrea Vera

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ABSTRACT

In recent years, plant-derived coagulants have been proposed as alternatives to traditionally used chemical coagulants, such as aluminum sulfate (alum) and ferric chloride. *Moringa oleifera* (*M. oleifera*) is a tree that is cultivated in many regions of the world (Central America and the Caribbean, parts of South America, Africa, South and Southeast Asia, parts of Oceania), including regions of water scarcity. *M. oleifera*'s seeds can be processed to extract a coagulant that has been demonstrated to be effective in removing suspended materials from various water types of practical importance. The goal of this thesis is to explore the feasibility of using *M. oleifera* for coagulation as pretreatment for ultrafiltration (UF). The present work employs two types of water (high and low turbidity) and uses alum as baseline comparison.

The study first compared coagulation performance of *M. oleifera* with that of alum, identified optimal coagulant doses for each, and subsequently used *M. oleifera*-derived coagulant to treat feed water for UF. Permeate flux was measured before and after membrane filtration a well as after simulated hydraulic cleaning of the membrane. Flux recovery ratio (FRR) was used as a quantitative metric of membrane cleaning efficiency, while hydraulic resistances (of the membrane and of the fouling layer) were used to characterize the extent of fouling. Residual total organic carbon (TOC) was measured after coagulation-flocculation-settling treatment with *M. oleifera* and after subjecting this water to UF.

M. oleifera was found to be comparable to alum in terms of turbidity reduction for high turbidity water but was more effective than alum in reducing turbidity in low turbidity water. Water treated with alum initially fouled the UF membrane quickly and tapered off into gradual fouling; in contrast, *M. oleifera* gradually fouled the UF membrane throughout filtration. For low turbidity applications, initial findings suggest that, while a higher FRR can be achieved with *M. oleifera* than alum, there is no significant benefit to fouling achieved by the addition of a coagulant. However, the presence of organics, regardless of origin, seem to result in fouling that is more difficult to address with hydraulic cleaning. UF effectively removed residual organics introduced by *M. oleifera* for low turbidity water, but insufficient TOC removal was observed for the higher doses required to treat high turbidity water during CFS. The results suggest that for low turbidity feeds, coagulation with *M. oleifera* is a viable pretreatment for downstream UF.

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TABLE OF CONTENTS

LIST OF ABBREVIATIONS

CFS	Coagulation, flocculation, settling
TOC	Total organic carbon
DBP	Disinfectant byproduct
MCL	Maximum contaminant level
THM	Trihalomethane
NOM	Natural organic matter
HAA5	Haloacetic acids
UF	Ultrafiltration
FRR	Flux recovery ratio
RPM	Revolutions per minute
NWOWTP	Northwest Ottawa Water Treatment Plant
MGD	Million gallons per day
DI	Deionized
LOD	Limit of detection
LOQ	Limit of quantification
SOP	Standard operating procedure
PES	Polyethersulfone
TMP	Transmembrane pressure

CHAPTER 1: AN INTRODUCTION TO THE STUDY

Introduction

As the human population continues to grow and the cost of water treatment increases, it becomes increasingly important to find alternatives to traditional methods of water treatment that help provide communities with safe and clean water. A common indicator of contaminated water is turbidity. A measure of the cloudiness of water, turbidity is caused by suspended solids in water; turbidity-causing materials can be introduced into water by a broad range of processes including soil weathering, nutrient runoff from agricultural fields, urban runoff, atmospheric deposition, and wastewater discharge. Many of these processes also contribute to microbiological contamination of water. There are several methods with which suspended particles can be removed from water and turbidity can be reduced, including coagulation-flocculation-settling (CFS). While many water treatment processes traditionally utilize chemical agents, natural alternatives have come to be evaluated as alternatives that could potentially address the limitations of chemical agents (see Coagulation, flocculation, settling and naturally derived coagulants) (Koul et al., 2022).

Coagulation, flocculation, settling and naturally derived coagulants

The three steps of CFS are commonly applied in water treatment facilities to remove colloidal suspensions from water. Coagulation, also referred to as rapid mix, aims to chemically destabilize those colloidal suspensions through charge neutralization, and this is typically achieved with the addition of a chemical coagulant, such as aluminum sulfate (alum) or ferric chloride (ferric). During flocculation, or slow mix, flocs form as the previously destabilized particles aggregate. If necessary, this stage can be aided by the addition of a polymer (such as a polyelectrolyte with a charge when it dissociates in water) to improve floc formation for optimized filtration, especially in the case of direct filtration (Ratnavaka et al., 2009). The flocculation and sedimentation processes can be aided by ballast, commonly microsand, that increases floc density and encourages settling (Crittenden et al., 2012). The final stage is referred to by many names (settling, sedimentation, decantation, clarification) and allows for the flocs to settle out to be separated from the water (Ihaddaden et al., 2022).

A recent focus of research within the process of CFS in water treatment has been on naturally derived coagulants, sometimes called bio-flocculants or bio-coagulants (called natural coagulants in this thesis). Natural coagulants are alternatives to traditional chemical coagulants utilized in water treatment process. As their name suggests, they can be derived from organic compounds, ranging from plant seeds to shrimp shells, and can originate from microbes, plants, or animals. Because chemical coagulants can be expensive, toxic, produce harmful waste, or alter the pH of the water being treated, the applications of natural coagulants have been explored in both wastewater and water treatment processes. Natural coagulants have been found to be safe and cost-effective, reduce deleterious effects on the environment, maintain the pH of the water being treated, and typically generate lower volumes of sludge (Koul et al., 2022) (Holmes et al., 2023).

While natural coagulants provide an alternative to chemical coagulants because of their reduced effect on water pH and reduced dependence on dose to be effective, the introduction of organics into drinking water during treatment is not without concern. TOC isn't itself inherently harmful to human health, but the presence of organics in water is problematic during disinfection since it can lead to the formation of carcinogenic disinfectant byproducts (DBPs) (Rook, 1974). The EPA enacted the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rule to address this issue two different ways: the first directly limiting concentrations of DBPs in finished drinking water with maximum contaminant levels (MCLs) and the second establishing TOC removal requirements depending on source water alkalinity and TOC to prevent DBP formation (USEPA, 2010).

Trihalomethanes (THMs) are a group of DBPs – including chloroform, bromodichloromethane, dibromochloromethane, and bromoform – that form because of reactions between chlorine, used in disinfection processes, and natural organic matter (NOM) (Li & Mitch, 2018). In fact, many of the compounds in naturally derived coagulants that might be introduced into treated water, such as carbohydrates and proteins, are precursors to the formation of Haloacetic Acids (HAA5), in addition to THMs. There is also the potential for color or odor problems resulting from the addition of natural coagulants (Okoro et al., 2021). Thus, further evaluation of natural coagulant performance and the downstream effects resulting from the introduction of organics into water treatment trains should be conducted to understand all the implications of using natural coagulants instead of (or in addition to) their chemical counterparts.

Moringa oleifera

Moringa oleifera (*M. oleifera*) has been dubbed the "miracle tree" because of its various benefits, medicinal and beyond. While it can be found in nearly all tropical and subtropical regions around the world, its origins lie in India, Southeast Asia, and the Arabian Peninsula. Belonging to a family of thirteen species, *M. oleifera* stands out because of its capacity to resist drought. Thus, it grows in many water-scarce areas. Beneficial uses have come from almost all parts of the tree: many nutritional benefits come from its leaves, and its bark, roots, and flowers have all been used in the treatment of a variety of medical conditions (Pareek et al., 2023).

Most recently, researchers have been investigating applications of *M. oleifera* seeds in water treatment by deriving a natural coagulant from its seeds. As a coagulant extraction, it primarily consists of proteins, fats, and carbohydrates from the *M. oleifera* seeds, and it was found that the coagulating agent, meaning the charge-neutralizing portion of the coagulant extraction, was the proteins dissolved in water, confirming earlier proposals for the active agents in coagulation (Ndabigengesere et al., 1995).

Objectives

The purpose of this thesis is to expand upon the evaluation of the use of *M. oleifera* seeds in the derivation of a coagulant for drinking water treatment and the potential downstream effects of introducing organics during the treatment process. There are three objectives:

1. To evaluate the performance of *M. oleifera* as a coagulant compared to that of alum for both high and low turbidity waters. Optimal coagulant dose and turbidity reduction will be the primary considerations in this assessment.
2. To evaluate the performance of ultrafiltration (UF) in the removal of organics from water treated by CFS with *M. oleifera* and assessing the contribution of organics in the CFS effluent on membrane fouling following downstream ultrafiltration. This will be represented by flux as a function of both time and permeate volume.

3. To assess the feasibility of UF in addressing the introduction of organics into water treated with *M. oleifera* during CFS. The balance between intrapore fouling and cake formation determines the ease with which hydraulic cleaning can restore permeate flux. This will be indicated by simulated hydraulic cleaning tests and subsequent calculation of the flux recovery ratio (FRR) and a characterization of fouling resistances.

With these objectives in mind, four hypotheses are put forward in this thesis:

1. A *M. oleifera*-derived coagulant is comparable to aluminum sulfate in terms of turbidity reduction with little effect on water pH, but it will introduce organics during coagulation.
2. UF removes *M. oleifera*-derived residual organics introduced during coagulation.
3. Membrane fouling by organics will limit productivity of the CFS-UF process. Membrane fouling by residual organics determines the tradeoff between UF permeate quality (e.g. residual organics, other micropollutants) and product water flux.
4. The feasibility of *M. oleifera* as a coagulant depends on the ease with which the membrane can be cleaned. Appropriate selection of membrane pore size (in the case of UF – molecular weight cutoff) helps limit intrapore fouling to facilitate inexpensive hydraulic cleaning of membranes.

CHAPTER 2: COAGULATION, FLOCCULATION, AND SETTLING

Introduction

In the first phase of this work, jar tests were used to simulate the CFS process, comparing the performance of *M. oleifera* to that of alum for both high and low turbidity waters. For each coagulant, a range of doses was applied to the raw water and a functional optimal dose was determined based on the highest percent reduction in turbidity achieved in both the high and low turbidity water. Alongside coagulant performance, the tradeoffs associated with the use of each coagulant were also evaluated: pH in the case of alum and residual TOC in the case of *M. oleifera*.

Materials and Methods

Preparation of alum and M. oleifera-derived coagulants

A stock solution of 0.012 M alum ($Al_2(SO_4)_3$) (Spectrum Chemical) solution was prepared and utilized for dosing during the experiments (see APPENDIX A: PREPARATION OF ALUM STOCK SOLUTION). *M.oleifera* seeds were purchased from Paisley Farm and Crafts in Appalachia, VA. Using the methods developed by Murali et al. (2022), the seeds were removed from their outer shell, and the kernels were ground up using a mortar and pestle. The powdered and fragmented seeds were sorted according to particle size using a stack of sieves, ranging in size from 150 µm to 1.18 mm. Murali et al. (2022) found that seed fragments in the particle size range of 300 to 600 µm were easy to consistently produce while also being effective in coagulation. All seed fragments from the 300-µm sieve were collected, while all other seed fragments larger than 600 µm were set aside for another round of powdering. Seeds fragments can be repeatedly powdered until they start to become sticky, after which they must be discarded.

To prepare the coagulant extract, 2.5 g of the selected fraction of seed fragments was mixed in a blender (Osterizer 6630) on “blend” setting with a 10 mM NaCl solution for 10 minutes. The mixture was subsequently vacuum-filtered through a 0.45 μm mixed-cellulose ester membrane to remove any seed fragments. Murali et al. reports that this process yields an approximate extraction ration of 10 g of *M. oleifera* seeds per liter, which would require a dosage of approximately 30 mL to treat 1 L of water. *M. oleifera* dose was quantified in terms of mg TOC/L for increased accuracy in reporting (APPENDIX B: *M. OLEIFERA* EXTRACTION TOC AND CALCULATION OF DOSE).

Jar test procedure and preparation of synthetic feed water

All jar tests were conducted using a jar tester (model 7790-960, Phipps & Bird) with six, 2-L square jars. Jars with square cross sections do not have a steady velocity gradient like jars with cylindrical cross sections (Pivokonský et al., 2022), resulting in much more turbulent and complete mixing and the consequential formation of larger and more compact floc (He et al., 2019). Each jar test followed the typical three-step procedure utilized in CFS applications: 1) coagulation for 1 min at 100 revolutions per minute (rpm), 2) flocculation for 40 minutes at 30 rpm, and 3) settling for 120 min with no mixing. Murali et al. previously determined that a flocculation period of 40 min was significantly more effective than 20 min and more or just as effective as 60 min. Additionally, Murali et al. found that 30 rpm produced the highest percent removal of turbidity. Thus, flocculation was operated for 40 min at 30 rpm. This procedure was the same regardless of coagulant used (alum or *M. oleifera*-based). The transition from flocculation to settling included removing the impellers from the jars to prevent the accumulation of floc on them as opposed to the bottom of the jars (Murali et al., 2022).

Feed water

Two different feed waters were used for jar tests. High turbidity water, which was represented with a synthetic feed water, and low turbidity water, which was represented by water collected from the influent of the Northwest Ottawa Water Treatment Plant (NWOWTP) in Grand Haven, Michigan.

NWOWTP provides water to Grand Haven, Michigan, and some of the surrounding communities, delivering more than 2.4 billion gallons of water to its more than 40,000 customers in 2022 (Northwest Ottawa Water System, 2022). The plant has a capacity of 23.25 MGD and will treat from 3.5 to 5.5 MGD in the winter to 13 to 16 MGD in the summer. The plant is unique in that it collects water from buried intakes off the shore of Lake Michigan. The intake pipes are buried beneath the sand on the bottom of Lake Michigan, 12 to 15 feet below the water surface, acting as pre-filtration for the plant and an additional layer of gravel to prevent intake of sand.

Because of this setup, no pre-chlorination is required, influent water to the plant is of low turbidity, and water quality is very consistent from one day to the next. Typical influent turbidity is ~ 0.06 NTU. With an alum dose ranging between 2.2 to 3 mg/L, one of the goals of the treatment process is to reduce the turbidity by 50 percent (Van Oeveren, 2023).

The plant uses a nontraditional filtration setup: water enters the coagulation chamber where coagulant is added, and rapid mix is initiated. The water then flows to the flocculation chamber and is subsequently fed directly to the filter beds. The plant utilizes eight, 52-inch-deep bed anthracite coal filters, one of which is offline each day. The media eventually needs to be replaced to ensure that grain size is sufficiently large (Van Oeveren, 2023).

Water was collected on September 9, 2023, and October 6, 2023, from the influent to the plant to be used in CFS and filtration tests. This water was utilized not only to represent low turbidity waters, but also to investigate the potential for the application of naturally derived coagulants and/or UF in direct filtration plants.

To represent high turbidity water, a synthetic feed water was prepared in the lab. A 15 g/L stock aqueous solution of kaolin clay (Spectrum Chemical) was stirred for at least 24 hours prior to conducting a jar test to ensure that the clay particles are completely hydrated. To each jar in the jar test apparatus, 20 mL of stock solution was added, and the remainder of the jar volume (1980 mL) was filled with deionized (DI) water to dilute the stock solution, producing a synthetic feed water with an initial turbidity of approximately 225 NTU. Each jar was prepared in this same way and allowed to mix at 100 rpm for at least 30 minutes prior to the addition of the coagulant to ensure complete combination of the stock solution and DI water.

Effluent characterization

The CFS effluent was characterized in terms of pH (Accumet Basic AB15 pH meter, Fisher Scientific) and turbidity (2100 Turbidimeter, Hach). TOC (OI Analytical TOC 1030, Xylem) was also measured when *M. oleifera*-derived coagulant was utilized.

pH – As an important indicator in water treatment, pH was measured for both the CFS influent and effluent to illustrate the effect of the addition of the coagulant on the pH of the water. Alum as a coagulant is known to reduce pH in treated water, while *M. oleifera* as a coagulant has demonstrated little effect on pH (Koul et al., 2022). Significant effects on pH could present challenges in the greater scheme of water treatment. The physicochemical properties of water the water treatment plant influent are extremely important to the success of water treatment processes since many stages of treatment are chemically dependent. A small shift in pH in either direction can dramatically change the state in which dissolved ions exist, rendering a process designed to operate under certain pH conditions ineffective (Crittenden et al., 2012). Conversely, pH control can be used to our advantage during water treatment. For example, coagulation can be optimized through pH adjustments, since pH affects particle surface charge (Naceradska et al., 2019).

Turbidity – Like pH, turbidity was measured for the feed water and the CFS effluent. Approximately 30 mL samples were collected from each jar using the built-in sample ports for analysis. Each sample port was flushed prior to effluent sample collection to avoid contamination by higher-turbidity water that the port was in contact with at an earlier stage of the experiment.

TOC – While there was no expectation of the presence of organics in the synthetic feed water (clay-water suspension) until after the addition of the *M. oleifera*-derived coagulant, samples were collected for TOC analysis before and after CFS for both high and low turbidity water to accurately quantify the organics in the effluent due to the addition of *M. oleifera*. A calibration was performed using 1 ppm, 10 ppm, and 100 ppm TOC standards (see APPENDIX C: PREPARATION OF TOC STANDARDS) prior to the collection of measurements.

For waters treated with alum, turbidity and pH were measured before and after CFS. TOC did not have to be measured when the added coagulant was alum, an inorganic chemical. To quantify the addition of organics by the natural coagulant, TOC was measured in addition to turbidity and pH for waters treated with *M. oleifera*.

Determining optimal coagulant dose

In the identification of an optimal coagulant dose for this synthetic feed water, one of the six jars was always operated without the addition of a coagulant to control for the natural sedimentation of suspended particles. The other five jars were assigned increasing coagulant doses, and all jars were operated according to the jar test procedure described in the previous section, *Jar test procedure and preparation of synthetic feed water*. After quantifying the turbidity of both the feed water and the CFS effluent, residual turbidity as a percent of the initial turbidity was calculated. When plotted as a function of coagulant dose, the minimum in the plotted curve was selected as the optimal dose because it achieved the highest removal. This value was solved for by fitting a curve to the data and extracting the minimum value from the plot. If there was not a statistical difference for this value for a certain range of doses, this method was used to identify a functional optimal dose for the generation of filtration feed water (see Filtration procedure and membrane flux) and the range within which the optimal dose exists was identified.

Results and Discussion

A range of coagulant doses for alum and *M. oleifera* was utilized to determine the optimal coagulant dose for high and low turbidity feed waters. This range was different for each influent quality scenario because different turbidities require different coagulant doses.

Because of the known effect of alum on the pH of the water being treated, residual turbidity and pH were plotted as functions of alum dose. Little effect on pH was observed with the application of *M. oleifera*, so residual turbidity and TOC were plotted as functions of *M. oleifera* dose. In the case of high turbidity water, final TOC was plotted due to the lack of TOC in the initial samples. Thus, final TOC was an accurate representation of the TOC that could be associated with the addition of *M. oleifera*. Conversely, residual TOC was plotted for low turbidity water because TOC was consistently observed in the NWOWTP water samples prior to the addition of *M. oleifera*.

Low turbidity water

The initial turbidity of the low-turbidity water was on average 0.24 ± 0.09 NTU. While still a very low turbidity for surface water, this turbidity is significantly larger than the influent turbidities observed at NWOWTP daily. It is suspected that the collection of the water from a sink at the plant into 80-L carboys and the transfer into the jars with residual clay particles for testing resulted in a small amount of cross-contamination that resulted in the increased levels of turbidity.

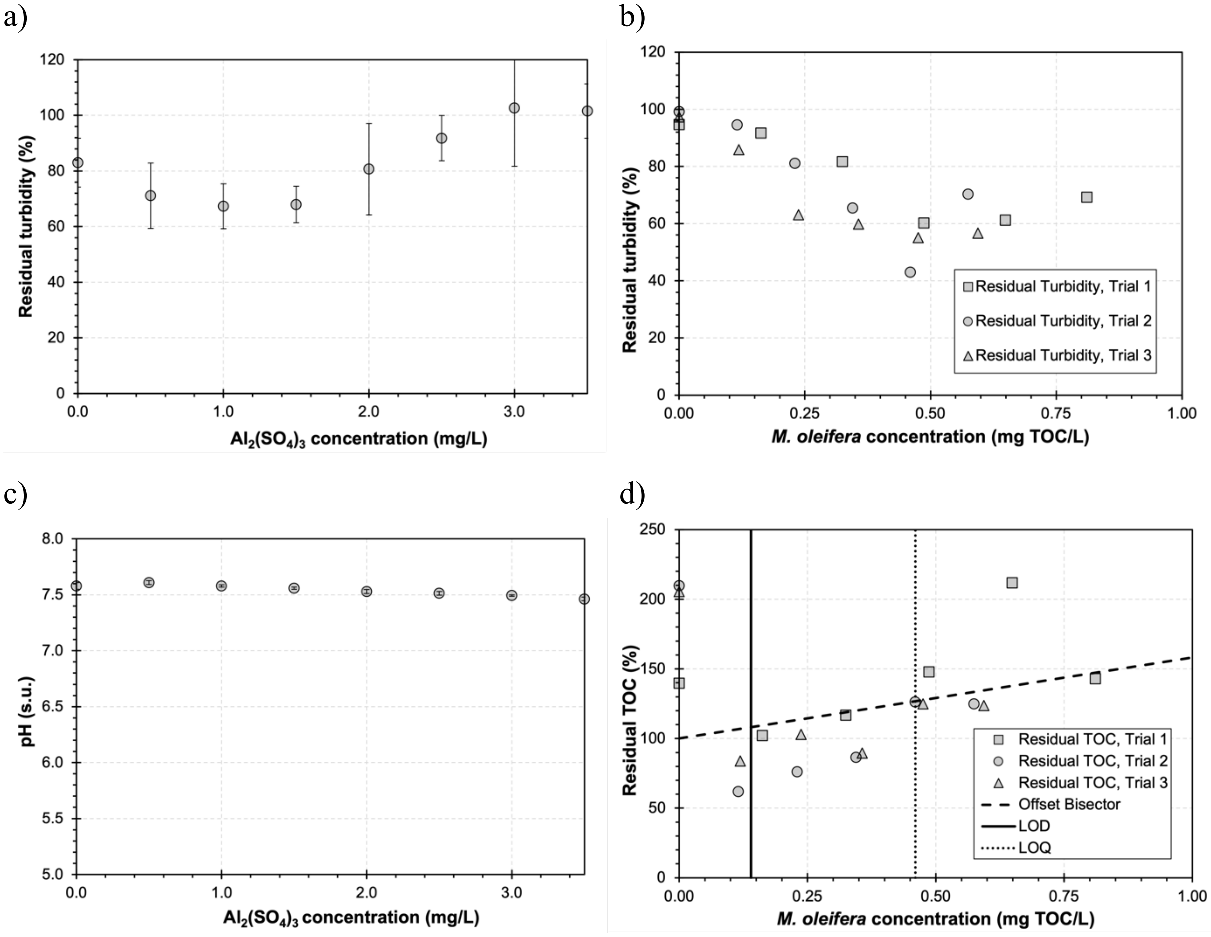


Figure 1. For low turbidity water with an average initial turbidity of ~0.24 NTU and average initial TOC of ~1.7 mg/L, a) residual turbidity as a function of alum dose, b) residual turbidity as a function of M. oleifera dose, c) pH as a function of alum dose and d) residual TOC as a function of M. oleifera dose with limit of detection (LOD) and limit of quantification (LOQ) identified. Error bars in a) and c) represent standard deviation from triplicate samples.

An array of 0 mg/L, 0.5 mg/L, 1.0 mg/L, 1.5 mg/L, 2.0 mg/L, 2.5 mg/L, 3.0 mg/L, and 3.5 mg/L of alum dosages was utilized to evaluate optimal alum dose in low-turbidity water. This range was initially selected based on the typical dose range of 2.2 to 3.0 mg/L used at NWOWTP. While there was no statistical difference within the range of doses from 0 to 2 mg/L, the functional optimal dose was selected by fitting a polynomial curve to the data in Figure D1a and Figure D1b (see APPENDIX D: IDENTIFICATION OF FUNCTIONAL OPTIMAL *M. OLEIFERA* COAGULANT DOSE) to identify the minimum value on the curve. The functional optimal dose was found to be 1.2 mg/L to reduce turbidity by approximately 36.5%. As expected, Figure 1c shows that pH decreased with an increase in alum dose.

The typical alum dose applied at NWOWTP is approximately 1.0 mg/L greater than the optimal dose identified for the water used in these experiments, even though it has a lower turbidity at the plant than what was measured in the lab. This slight discrepancy in dose could be attributed to slight differences in alum, the operating conditions of NWOWTP compared to the lab, the difference in scale of testing, or slightly altered water quality from cross-contamination in the lab.

An array of 0 mL, 0.25 mL, 0.5 mL, 0.75 mL, 1.0 mL, and 1.25 mL of *M. oleifera* was utilized to evaluate optimal *M. oleifera* dose in low-turbidity water. After conversion to the more exact measure of *M. oleifera* coagulant dose in terms of mg TOC/L (see APPENDIX B: *M. OLEIFERA* EXTRACTION TOC AND CALCULATION OF DOSE), the optimal dose could be identified. While there was no significant difference for the dose range of 0.40 to 0.53 mg TOC/L (see APPENDIX D: IDENTIFICATION OF FUNCTIONAL OPTIMAL *M. OLEIFERA* COAGULANT DOSE), the functional optimal dose was found to be 0.53 mg TOC/L to achieve a turbidity reduction of 47.8%, achieved by administering 1 mL of *M. oleifera* extraction to 2 L of water. Figure 1b shows the distribution of residual turbidity and residual TOC with the addition of *M. oleifera*. *M. oleifera* coagulant extract was more effective in reducing turbidity than alum, as reflected by turbidity removals at the determined functional optimal dose of 47.8% and 36.5%, respectively. Additionally, turbidity removal by *M. oleifera* was much closer to NWOWTP's treatment goal of 50% reduction.

Consistently higher residual TOC values were observed in the control samples compared to the samples to which *M. oleifera* coagulant extract had been added. However, the limit of detection (LOD) of the instrument, calculated to be 0.14 mg/L, indicates that any values in Figure 1d below the LOD should be disregarded (see APPENDIX E: LIMITS OF DETECTION AND QUANTIFICATION).

High Turbidity Water

The initial turbidity of the high turbidity water was on average 226.3 ± 24.5 NTU. An array of 0 mg/L, 1.0 mg/L, 2.0 mg/L, 3.0 mg/L, 4.0 mg/L, and 5.0 mg/L of alum was utilized to evaluate optimal alum dose in high turbidity water. This range was initially selected based on previous experiments conducted by Murali et al. (2022). There was no statistical difference observed for turbidity reduction within the range of doses from 3 to 4 mg/L, but a functional optimal dose was found to be 3.4 mg/L to achieve a turbidity reduction of ~ 81.0% (Figure 2a).

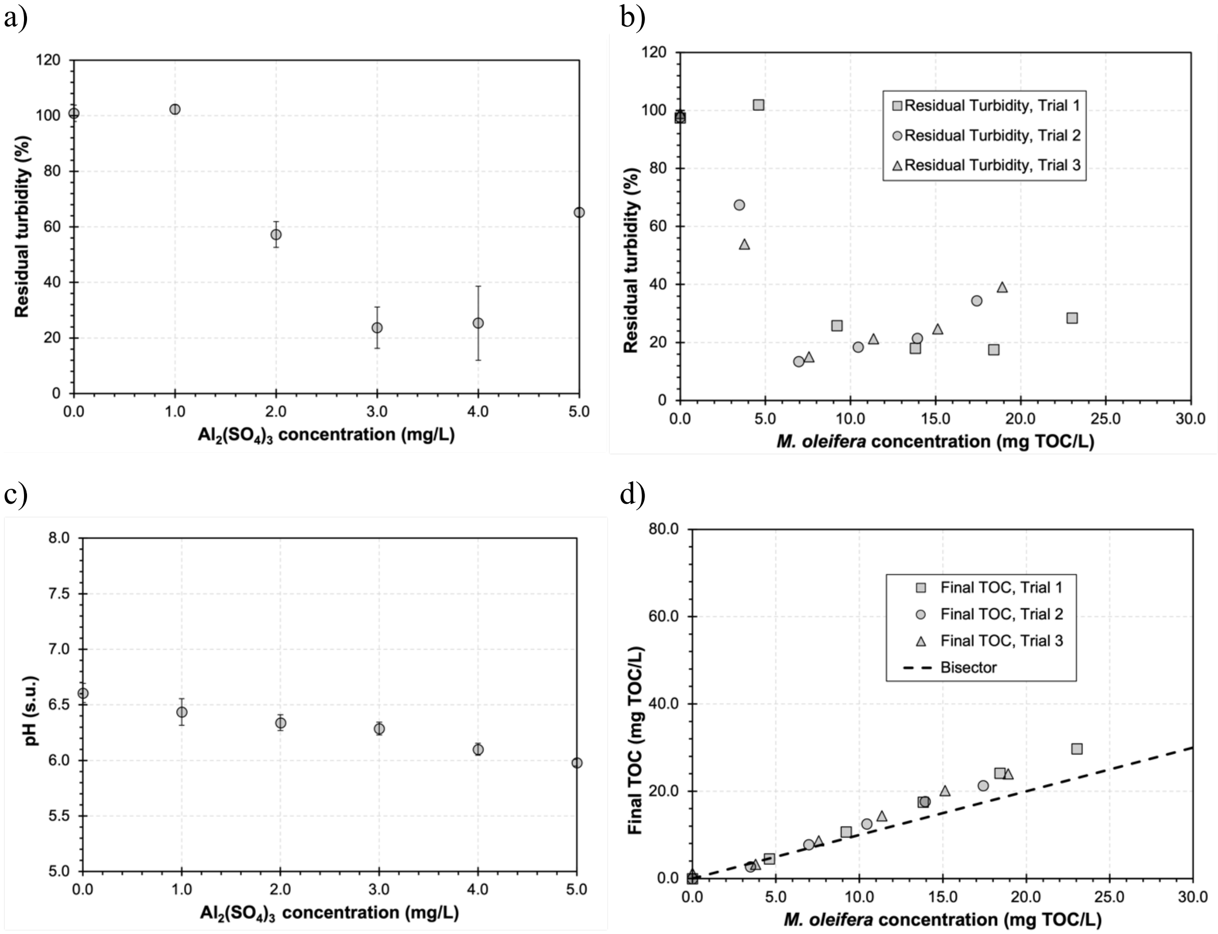


Figure 2. For high turbidity water with an average initial turbidity of ~226 NTU, a) residual turbidity as a function of alum dose, b) residual turbidity as a function of M. oleifera dose, c) pH as a function of alum dose and d) final TOC as a function of M. oleifera dose. Error bars in a) and c) represent standard deviation from triplicate samples.

An array of 0 mL, 10 mL, 20 mL, 30 mL, 40 mL, and 50 mL of *M. oleifera* doses was utilized to determine the optimal coagulant dose in high turbidity water. While there was no significant difference for the dose range from 7.9 to 15.8 mg TOC/L (see APPENDIX D: IDENTIFICATION OF FUNCTIONAL OPTIMAL *M. OLEIFERA* COAGULANT DOSE), the functional optimal dose was determined to be 11.9 mg TOC/L to achieve a turbidity reduction of ~ 80.8 % (Figure 2b), achieved by administering 30 mL of *M. oleifera* extract to 2 L of water.

A residual turbidity of ~ 20% was observed for high turbidity water treated with alum and *M. oleifera* coagulants alike, meaning their performances as coagulants were comparable. As the *M. oleifera* dose increases, the TOC of the treated water has a higher concentration of TOC than would be expected due to the addition of *M. oleifera* to water with no initial TOC. In other words, it was expected that the TOC of the treated water would be less than or equal to the TOC administered through *M. oleifera* dose, as represented by the bisector in Figure 2d, but TOC levels are observed to be slightly higher. Samples are filtered with a 0.45 μm filter prior to conducting TOC measurements. Thus, the *M. oleifera* extraction was filtered prior to TOC quantification. However, the extraction was not filtered in this way prior to its addition to the jars; samples to which *M. oleifera* coagulant was added were filtered after undergoing the CFS process. What is being observed could be a continuation of the extraction prior to CFS. In addition to extracting the coagulant by soaking in a salt solution (Okuda et al., 1999) as is done for this thesis, another way in which coagulant can be extracted is by simply soaking in water (Jahn & Dirar, 1979). Thus, the extended period in which volumes of up to 50 mL of *M. oleifera* extract are mixed with water and the higher-than-expected concentrations of TOC after CFS leads us to believe that the extraction of coagulant continued during experimentation, and the process of denaturing proteins of the *M. oleifera* seeds continued.

This trend, however, is not observed for low turbidity water in Figure 1d and could be due to the significantly smaller volume of *M. oleifera* coagulant extract added to each of the jars and the limit of quantification of the instrument. The doses of *M. oleifera* used to treat the low turbidity water were at or below 1.25 mL, significantly smaller doses than were used to treat the high turbidity water. Naturally, this means that there are also significantly less organics introduced into the water. In Figure 1d, it looks as though values above ~ 0.45 mg TOC/L follow the trend observed in Figure 2d, while values below ~ 0.45 mg TOC/L all fall below the bisector. This is hypothesized to be an anomaly observed because of the values being at or below the limit of quantification (LOQ) of the TOC instrument, calculated to be 0.46 mg/L. Thus, the values below the LOQ in Figure 1d don’t reliably demonstrate the removal of organics by *M. oleifera* (see APPENDIX E: LIMITS OF DETECTION AND QUANTIFICATION).

CHAPTER 3: MEMBRANE FILTRATION

Introduction

The second phase of this study aims to evaluate the feasibility of implementing ultrafiltration downstream of the pretreatment of water with *M. oleifera* during coagulation, flocculation and settling. Functional optimal doses determined in the previous chapter were used to produce two of four feed waters from both high and low turbidity waters, while the other two feed waters served as controls. The four feed waters were filtered through a dead-end filtration cell equipped with a UF membrane, and fouling was measured over time. Hydraulic cleaning of the membrane was simulated with a magnetic stirrer and DI water and flux was remeasured. Flux recovery ratio was used to characterize the efficiency of the hydraulic cleaning of the membrane, and membrane resistances due to reversible and irreversible fouling were used to characterize the extent of fouling.

Materials and Methods

Filtration procedure and membrane flux

Filtration was conducted using a Biomax® 50 kDa polyethersulfone (PES) UF membrane and a 50 mL Amicon stirring filtration cell. The stirring cell was fitted with 44.5 mm-diameter membranes. Three types of feed water were used for each filtration, each detailed in Table 1. They were selected for evaluation so that trends in fouling could be attributed to either the coagulant, or the effects of the CFS process alone, or the untreated water. The determination of the functional optimal coagulant dose for each coagulant for both high and low turbidity water informed the selection of coagulant dose to be used in subsequent filtration tests. Functional optimal doses determined in Chapter 2 were added to high or low turbidity water to produce the filtration CFS water.

Table 1. Feed waters utilized for ultrafiltration.

Feed Water	**Specifications**
Raw	High or low turbidity water prior to CFS (unaltered).
Control	High or low turbidity water put through the CFS procedure without the addition of the coagulant.
CFS w/ Alum	High or low turbidity water put through the CFS procedure with the addition of alum coagulant at its previously determined optimal dose.
CFS w/ *M. oleifera*	high or low turbidity water put through the CFS procedure with the addition of *M. oleifera* coagulant at its previously determined optimal dose.

To conduct membrane filtration tests, the feed water was placed in a pressurized dispensing vessel that was connected on one end to a compressed nitrogen tank and on the other end to the filtration cell, as pictured in Figure 3 and outlined in an additional schematic in Figure 4 for clarity. The permeate was collected in a glass beaker placed atop a mass scale.

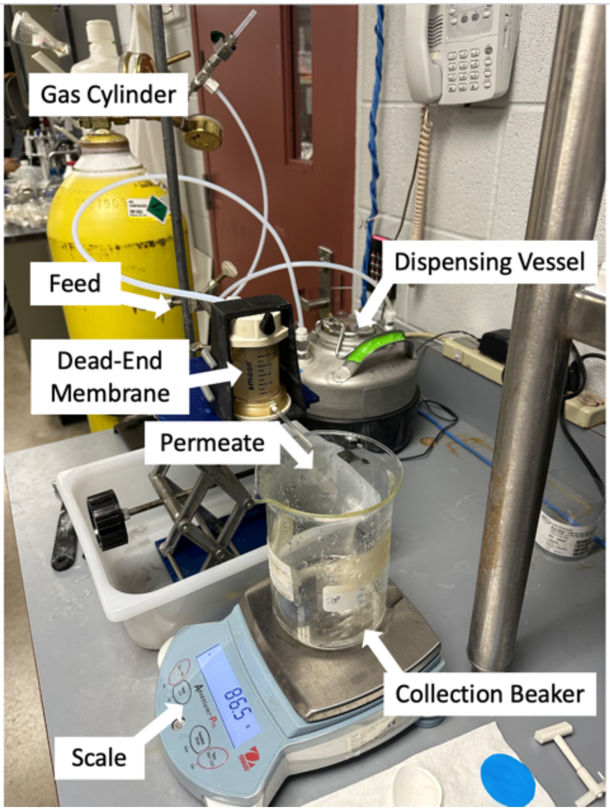


Figure 3. Filtration experimental setup.

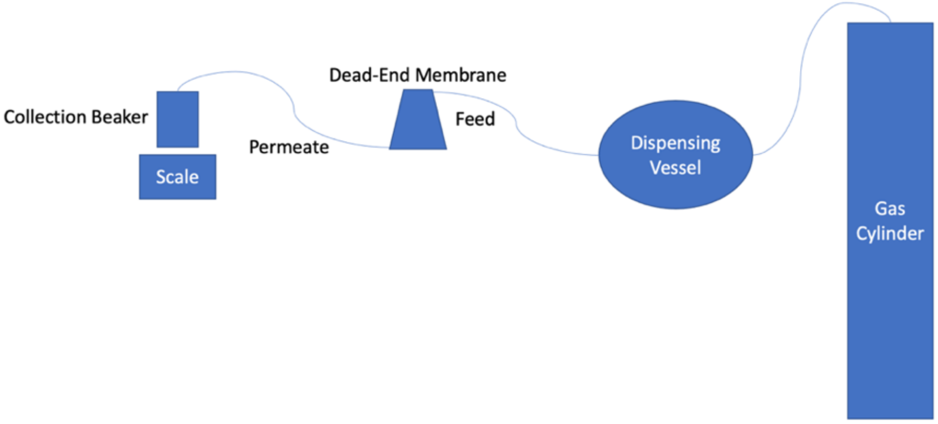


Figure 4. Filtration experimental setup schematic.

Each filtration test involved subjecting membranes to a 15-minute fouling period during which each feed water was filtered through a UF membrane with a transmembrane pressure of 20 psi. The total mass of permeate collected was recorded every 30 seconds, and each experiment was repeated in triplicate for each feed water. The change in mass and time for each measurement interval were calculated. The volume of permeate collected was calculated using the density of water at the measured temperature of 23°C (~ 0.998 g/cm^3). Permeate flux J was then calculated using Equation (1), where ΔV is the volume of permeate collected over a given time interval, Δt is the length of the time interval, and A_m is the membrane surface area. Membrane flux is the permeate flow per unit time per unit area of the membrane surface and is a useful metric for assessing membrane performance.

$$J = \frac{\Delta V}{\Delta t A_m} \tag{1}$$

Prior to each filtration, the membrane was compacted and conditioned so that any visible changes in flux during filtration of the feed waters listed above could be attributed to fouling by feed constituents rather than membrane compaction and conditioning, with no concern of confounding variables. This was achieved by first running DI water through the membrane at the maximum pressure of 40 psi for 20 minutes, ensuring that for the last five minutes the change in membrane flux every minute was less than 5% lower than the previous minute's flux (a value selected to indicate that the flux had stabilized). Next, DI water was run through the membrane at progressively increasing pressures (20 psi, 30 psi and 40 psi) for 5 min under each pressure. Every 30 seconds, the total mass of permeate collected was recorded. The average flux under 20 psi was used as an estimate of initial membrane flux.

$$J = \frac{\Delta P}{\mu R_m} \tag{2}$$

Considering the definition of membrane flux presented in Equation (2), a plot of the average flux as a function of each pressure condition $J/\Delta P$ the result is a line with a slope equal to $1/\mu R_m$. The initial membrane resistance R_m can be calculated from the slope using the viscosity of water (0.933 mPa·s) at 23°C, the temperature at which experiments were conducted.

Flux was plotted as a function of time and as a function of permeate volume (see APPENDIX F: CONSTRUCTION OF FLUX V. PERMEATE VOLUME PLOTS for more information on data manipulation). Each is helpful in illustrating different characteristics of the fouling process: flux as a function of permeate volume communicates how the quantity of filtered water produced changes between scenarios, and flux as a function of time is helpful when looking at the rate of change of flux.

Hydraulic cleaning procedure and flux recovery ratio

A common bottleneck in the application of membranes in filtration is fouling. Organics compounds are a known cause of adsorptive fouling of membranes and such fouling can be at least partly irreversible (Wang et al., 2023). Membrane fouling can be mitigated by pretreating feed water and removed by subjecting fouled membrane to hydraulic or chemical cleaning. However, fouling can never be completely avoided, so the removal of fouling agents by hydraulic cleaning is important in the application of UF membranes (Chang et al., 2016).

To simulate this cleaning process, the filtration cell was removed from the filtration setup after the completion of a 15-minute fouling cycle and was placed on top of a stir plate. Leaving the membrane inside of the cell, a magnetic stirrer was inserted into the cell, which was subsequently filled with 15 mL of DI water. The magnetic stirrer was spun at 200 rpm for 1 minute, and the water was removed from the cell. The post-hydraulic cleaning flux was then measured using DI water to prevent any further fouling. DI water was again run through the membrane at several values of the transmembrane pressures (20 psi, 30 psi and 40 psi) for 5 minutes under each pressure. Every 30 seconds, the total mass of permeate collected was recorded. The average flux under 20 psi was used as an estimate of membrane flux after hydraulic cleaning, as it was prior to fouling.

$$FRR = \frac{1 - \frac{J_F}{J_W}}{1 - \frac{J_F}{J_0}} \tag{3}$$

Flux recovery ratio (FRR) was calculated using Equation (3) where J_W is the flux after hydraulic cleaning, J_F is the flux after fouling, and J_0 is the initial membrane flux (see APPENDIX G: DERIVATION OF FLUX RECOVERY RATIO). By this method of calculation, FRR is representative of how much fouling is reversible, while the inverse represents how much fouling is irreversible. Compounds in water can foul membranes in different ways: adsorption to membrane pore walls, blocking of pore channels or openings, or deposition on the membrane surface. An understanding of the distribution of fouling agents on and within the membrane is important for evaluating how effective membrane cleaning will be (Tseng et al., 2022). A high FRR indicates that hydraulic cleaning was effective in removing the membrane cake and that the fouling agents were accumulating on the membrane surface rather than within the membrane pores.

However, FRR as defined in Equation (3) is purely a representation of the efficiency of membrane cleaning and does not communicate the degree to which the membrane was fouled. Thus, the portions of membrane resistance due to fouling that were reversible and irreversible were calculated (for equation definitions of membrane resistances see APPENDIX G: DERIVATION OF FLUX RECOVERY RATIO). This provides more information on the effect of the fouling observed during filtrations with different feed waters.

Results and Discussion

A constant transmembrane pressure (TMP) of 20 psi was applied during every filtration sequence, but slight differences in initial resistance and consequently initial flux were observed due to coupon-coupon variability in membrane permeability (i.e. variability in different cuts of the same membrane). The average initial flux was 178.3 ± 9.4 mL/m^2/sec with an observed range from 160.4 to 193.1 mL/m^2/sec. Because the same type of membrane was utilized throughout filtration experiments, TMP was fixed, and the initial flux showed only modest variability (coefficient of variation of ~ 5.3%), the permeate flux was normalized by its initial value (J_0) for ease of comparison.

It was hypothesized that waters treated with *M. oleifera* coagulant during CFS would result in increased fouling due to the presence of additional organics in the feed water. While individual points seem to illustrate that *M. oleifera* coagulant does contribute to greater fouling of the membrane after the filtration of similar volumes of water, the overall difference was not statistically significant for a single-factor ANOVA test with an alpha value of 0.05 (see APPENDIX H: STATISTICAL ANALYSIS RESULTS) in experiments with low turbidity water (Figure 5). Higher variation in flux was observed for low turbidity water treated with *M. oleifera* coagulants during CFS compared to the three other feed waters, as represented by larger standard deviations used in the construction of error bars. All feed waters similarly fouled UF membranes and produced comparable permeate volumes.

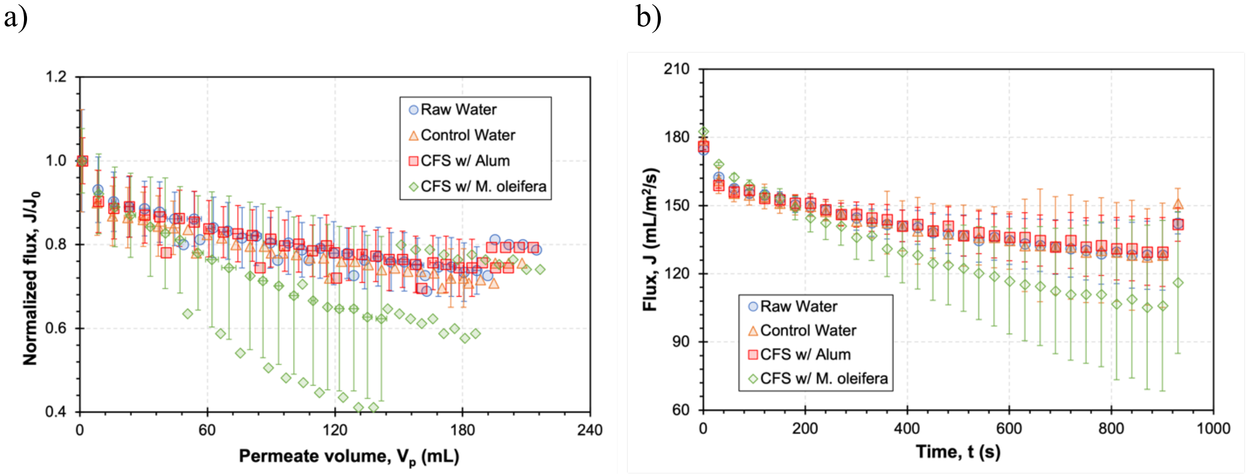
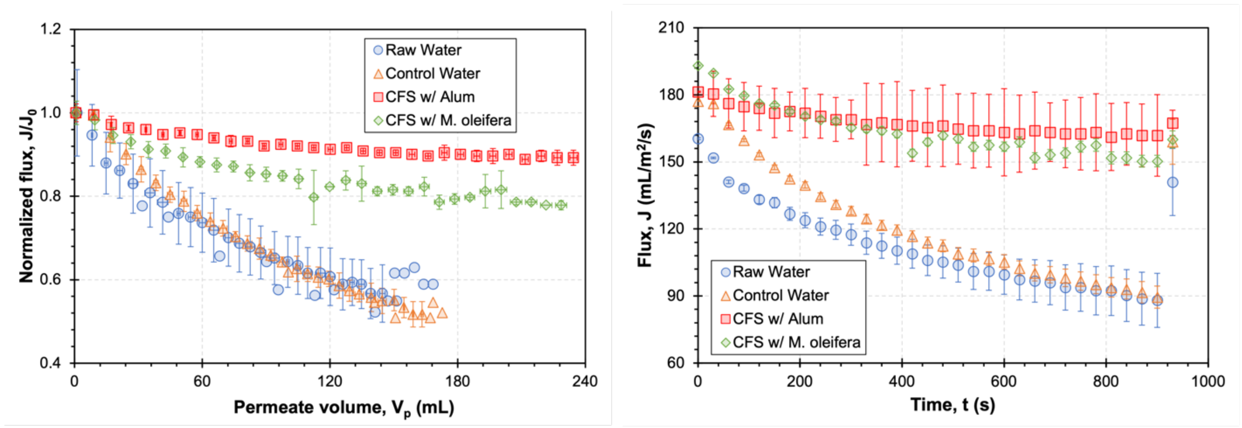


Figure 5. For four feed waters derived from low turbidity water a) Normalized flux (average initial flux of ~178 mL/m^2/s) as a function of permeate volume and b) flux as a function of time. Error bars in both graphs represent standard deviation from triplicate samples.

Instantaneous slope of the fouling trend illustrated in Figure 5b represents the rate of the change of flux. From visual inspection, in low turbidity water treated with alum, significant fouling occurs initially, as represented by a quick initial drop in flux. The slope then tapers off, as observed by a more gradual decrease in flux over time. Fouling by *M. oleifera*, on the other hand, occurs more gradually and consistently throughout the filtration period. This suggests that *M. oleifera* is continuously fouling the UF membrane. We also hypothesize that after the initial rapid fouling of the membrane by alum, the cake layer on the membrane is resulting in the continued but much more gradual decline in flux.

Membrane filtration is not usually feasible for source waters with high turbidity due to rapid fouling, but the interest lies in the relative effectiveness of coagulants as pre-treatment to reduce the rate of fouling of the membrane. Figure 6 shows that there was no observed difference between raw water and control water, but there was a difference between these two feed waters and water treated with a coagulant during CFS as pre-treatment. Greater permeate volume is produced and significantly less fouling is achieved during filtration with waters that have gone through pre-treatment by CFS, regardless of coagulant. However, high turbidity water treated with alum during CFS reduced fouling more than is observed for high turbidity water treated with *M. oleifera* coagulant during CFS.



a) b)

Figure 6. For four feed waters derived from high turbidity water a) Normalized flux (average initial flux of ~178 mL/m^2/s) as a function of permeate volume and b) flux as a function of time. Error bars in both graphs represent standard deviation from triplicate samples.

Figure 5a and Figure 5b both show that there is no significant difference in fouling potential between the four feed waters derived from low turbidity water. An interesting difference, however, is communicated between Figure 6a and Figure 6b. While there is no significant difference observed between the fouling potential of high turbidity water treated with alum or *M. oleifera* during CFS when looking at fouling as a function of time, there is a significant difference observed between the two coagulants when looking at fouling as a function of permeate volume.

Figure 5b and Figure 6b illustrate flux values achieved after hydraulic cleaning. For both high and low turbidity-derived feed waters, there is no statistical difference in the flux value achieved after hydraulic cleaning between feed waters. This suggests that the hydraulic cleaning procedure utilized in this study achieved the maximum reversal of fouling that was possible by physical removal. However, there is the possibility of higher post-cleaning flux if chemical cleaning were used instead of or in addition to hydraulic cleaning.

Flux recovery ratio contributes to an understanding of how any residual coagulant in water treated with CFS in addition to any remaining suspended particles interact with the membrane and contribute to its fouling. Figure 7 compares the FRR achieved after hydraulic cleaning of UF membranes used to filter four different feed waters derived from high and low turbidity waters. Based on the observed standard deviations, there was no difference between the FRR achieved for raw water, control water, and water treated with *M. oleifera* during CFS for low turbidity water. The use of alum during CFS, however, was observed to result in a significantly lower FRR than all other feed waters. For high turbidity water, no difference was observed between raw and control waters, nor was a difference observed between water treated with alum and *M. oleifera* coagulants during CFS, but a difference was observed between these two groups. This makes sense because when there are more particles suspended in the feed water that will accumulate on the surface of the membrane (as is the tendency for clay particles), the greater flux can be recovered by physically washing the membrane surface. High turbidity water treated with coagulants during CFS had significantly lower FRRs, averaging around 30% compared to FRRs for raw and control water averaging around 85%.

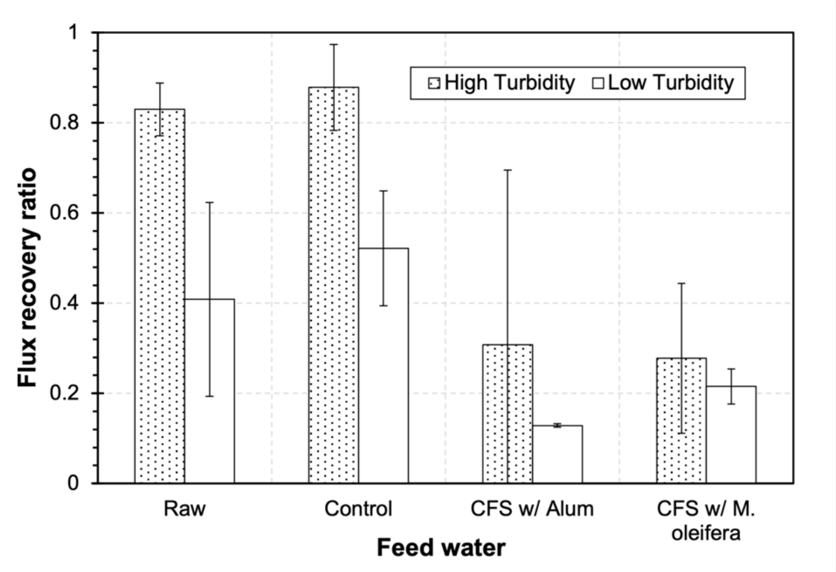


Figure 7. Flux recovery ratio for four feed waters derived from high and low turbidity waters. Error bars represent standard deviation from triplicate samples.

Differences in FRR were observed between raw and control feed waters derived from high and low turbidity water, but no difference was observed between FRR for high and low turbidity water treated with alum or *M. oleifera* during CFS. This suggests that the coagulants are removing the same particles from the water treated during CFS, resulting in a similar impact on what agents can (and can't) be removed from the membrane surface with hydraulic cleaning and, thus, the flux that can be recovered through cleaning. FRR alone, however, does not communicate the effect of the fouling observed. Figure 8 breaks down the total membrane resistance due to fouling into resistances due to reversible and irreversible fouling calculated from average flux initially, after fouling, and after washing. Because the raw and control waters were untreated, they were observed to have higher reversible resistances due to the presence of particles that were otherwise removed during CFS. In other words, the particles causing reversible fouling through deposition on the membrane surface are removed during CFS for both high and low turbidity waters.

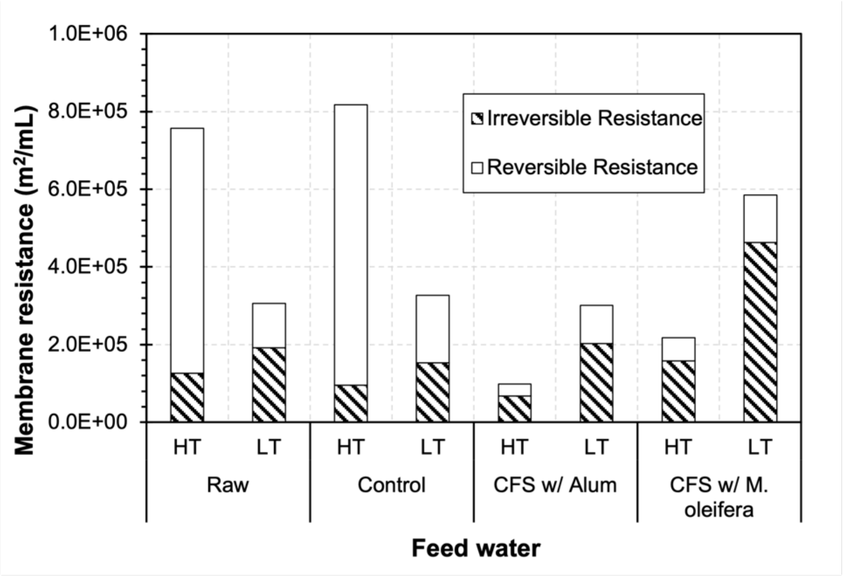


Figure 8. A breakdown of total membrane resistance due to fouling into reversible and irreversible fouling for high and low turbidity-derived feed waters calculated from the averages of triplicate trials.

Initial observations of FRR in Figure 7 for water treated with *M. oleifera* during CFS suggest that it is a better option for UF pretreatment than alum due to its higher FRR. However, Figure 8 shows higher irreversible fouling is observed for water treated with *M. oleifera*, regardless of initial turbidity, compared to water treated with alum. In fact, higher irreversible fouling is observed for all low turbidity-derived feed waters compared to their high turbidity counterparts, even though low turbidity raw and control feed waters had significantly lower pre-filtration turbidities. We suspect this can be attributed to the natural presence of organics in the low turbidity water from NWOWTP and the lack of organics in the synthetic high turbidity water (clay suspension). Organics in water seem to foul UF membranes in a way that is more difficult to be addressed with hydraulic cleaning. This study, however, did not evaluate whether chemical cleaning could address fouling by organics.

Figure 8 shows similar reversible and irreversible fouling for low turbidity raw water, control water, and water treated with alum during CFS. Contrary to the expectation that similar FRRs for these three feed waters would thus also be observed, Figure 7 shows that the water treated with alum during CFS had a lower FRR than the raw and control waters. This may be a result of the way in which alum in combination with any remaining suspended particles foul the membrane compared to the fouling by suspended particles themselves in the raw and control waters, but where similar reversible and irreversible resistances are observed, so should a lower FRR be observed.

On average, 68 ± 15% of TOC was removed by UF in low turbidity water treated with the functional optimal *M. oleifera* dose (see APPENDIX I: ULTRAFILTRATION TOC REMOVAL). When looking at the average initial TOC of the raw water (1.7 mg/L) and the average TOC after the UF of low turbidity-derived feed waters (1.3 mg/L), there is a ~ 24% removal of TOC from the raw water to the end of the treatment process, including the addition of *M. oleifera*. Based on the TOC removal requirements outlined by the EPA's Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rule, a raw water alkalinity of 116 mg/L as $CaCO_3$ (Northwest Ottawa Water System, 2022), NWOWTP would be required to remove 25% of TOC (USEPA, 2010). Even with the addition of a natural coagulant, it could still be feasible for the plant to meet TOC removal requirements.

An average of 9 ± 9% removal of TOC by UF was observed in high turbidity water with its corresponding functional optimal *M. oleifera* dose. Contrary to the expectation that a greater concentration of TOC would present the opportunity for greater TOC removal, UF would appear to be much more effective in removal of TOC introduced by the *M. oleifera* coagulant in low turbidity water compared to high turbidity water when comparing these removal percentages. However, a maximum removal of TOC for both high and low turbidity water reached a maximum at ~ 4 mg/L. Because the same range of removal of TOC was observed for feed waters derived from high and low turbidity water and treated with *M. oleifera* during CFS, ~ 4 mg TOC/L could be the maximum concentration of organics that can be removed by the UF membranes utilized in this study. Because there is a higher concentration of TOC in the high turbidity water after CFS since a greater volume of *M. oleifera* extract is required to treat the water during CFS, the TOC removed during UF make up a smaller percentage of the total TOC observed prior to UF compared to that of the low turbidity water treated with *M. oleifera* during CFS.

Conclusions

When considering the practical applications of *M. oleifera* derived coagulants in water treatment processes, we must think about commonly used water treatment trains (Table 2) and how a coagulant substitution might affect the rest of the treatment process. As previously mentioned, the presence of organics in water during disinfection can lead to the creation of carcinogenic DBPs. Since *M. oleifera* derived coagulants come from a seed with proteins and carbohydrates, it will have TOC content. Thus, it cannot be used in applications in which chlorination will be applied for disinfection unless an additional barrier to the organics is implemented. UF has been proposed as a potential barrier to residual organics in this study.

Table 2. Treatment configurations considered for the application of M. oleifera coagulants.

Water	**Coagulant**	**Filtration Mechanism**
High Turbidity	Alum	Membrane
	M. oleifera	
Low Turbidity	Alum	
	M. oleifera	
	None	

In the case of high turbidity water, this study suggests that, if membranes were to be implemented as a method of filtration and to achieve additional log removal of pathogens, pre-treatment with CFS prior to filtration would significantly reduce the fouling observed. However, selection of the coagulant utilized during CFS is important, as *M. oleifera* will result in greater fouling of the membrane than alum. Because both coagulants achieve the same removals of turbidity during CFS, it can be concluded that the residual coagulant within the water (as represented by residual TOC for *M. oleifera*) is the fouling agent resulting in a difference in fouling potential. Thus, alum would be preferred as pre-treatment during CFS for UF of high turbidity waters.

Low turbidity water is of more interest to this study, as it has more practical implications for scenarios in which membrane filtration would be implemented. In the case of low turbidity water, findings from this study suggest that there is no benefit in terms of effect on fouling from the use of a coagulant as pre-treatment for UF. While the addition of a coagulant prior to sand filtration or filtration with other media is helpful in promoting the adsorption of floc to the media, the addition of a coagulant, whether alum or *M. oleifera*, has shown no difference in fouling potential compared to the direct filtration of the raw water. In fact, a higher FRR was observed for UF membranes used for the filtration of the raw water directly compared to when the raw water was treated with alum during CFS. While UF removes approximately the percent TOC that is required by the Stage 1 and 2 Disinfectants and Disinfection Byproducts Rule after the introduction of *M. oleifera* coagulant as pre-treatment, there is no benefit CFS for low turbidity water prior to UF. This suggests that UF applications for low turbidity water are legitimate treatment configurations that will require low additional pre-treatment costs (i.e. no additional chemical pre-treatment requirements).

Complexities of Work

The interest in *M. oleifera* as a coagulant emerged, in part, as an opportunity for water treatment in resource constrained areas because of its capacity to grow in water-scarce areas. However, this research was performed within the context of our competitive economy in the United States, effectively evaluating how *M. oleifera* could be utilized within large-scale water treatment as a replacement for alum. Thus, there are a few considerations that should be made when continuing work with regards to utilizing *M. oleifera* to make water treatment more accessible.

Because water treatment is limited in terms of treatment steps in resource constrained areas and disinfection can't always be implemented, DBP formation isn't a principal risk to human health. If disinfection is utilized, solar disinfection is most accessible and doesn't warrant concerns for the formation of DBPs. The most immediate concern in these areas is having sufficient water supply to meet the needs of the community, so the chronic effects of DBPs also aren't a priority in terms of risk management. In the context of water scarcity, water is often stored in large tanks or cisterns prior to use. If water has been treated with *M. oleifera* and there are residual organics in the stored water, there is potential for regrowth of bacteria, especially since the coagulant extract consists of proteins and carbohydrates that could serve as food for them. A better metric of its feasibility for water treatment in water scarce areas could be regrowth potential and management.

The preparation of the *M. oleifera* coagulant extract as was prepared in the laboratory for this study is an impractical method for the extraction of coagulant locally unless all the necessary equipment is available. Rather than developing methods of extraction to improve efficiency in the laboratory (although useful if the goal is to develop a commercially marketable coagulant), simple, “at-home” methods for coagulant extraction should be tested for their effectiveness in turbidity reduction. For example, simply soaking seeds in seawater could be a simpler method of coagulant extraction, but this method should also be tested during water treatment to ensure it is still capable of neutralizing suspended particles.

Recommendations for Future Work

This thesis made progress towards achieving the goal of evaluating the use of *M. oleifera* seeds in the derivation of a coagulant for drinking water treatment and the potential downstream effects of introducing organics during the treatment process, but much work is still required to achieve it completely.

Natural coagulants can originate from several sources and can be produced in many ways, so they do not all have the same properties, nor do they behave the same during treatment. Molecular weight is of particular importance when it comes to the interaction between coagulant and the membrane. If the natural coagulant has a sufficiently low molecular weight, it can pass through the membrane and reduce fouling. However, this will put public health at risk with significantly increased risk of DBP formation. Higher molecular weight natural coagulants may have different effects on membrane fouling and the characteristics of the cake formed. Similarly, different types of membranes usually applied in water treatment (e.g. microfiltration) could be used to conduct the filtration tests with water that has been treated with *M. oleifera* during CFS.

Particles suspended in water are frequently 20 times smaller (usually even smaller) than the pore size of granular media used for filtration. Not only does the addition of a coagulant encourage the aggregation of particles so that they can settle out of water during clarification, but it also creates floc that, even if they remain smaller than the effective media pore size, can be physically removed and adsorbed as water moves through the depth of the filter bed (Ratnavaka et al., 2009) (Crittenden et al., 2012). Because the purpose of coagulants is also to condition particles in water to stick to granular filtration media, the interaction between *M. oleifera* and media during traditional sand filtration should be further explored. While this study evaluated the turbidity-reducing capacity of *M. oleifera* during CFS, it did not evaluate the interaction between the coagulant and different types of granular filters.

The interaction of *M. oleifera* coagulants with more traditionally used chemical coagulants should be further explored, especially concerning whether they enhance (additively or symbiotically) or reduce turbidity removal. This could offer the possibility of reducing chemical coagulant dose and increasing effectiveness by supplementing with a natural coagulant. The interactions between natural coagulants of different molecular weights (resulting from their simultaneous addition) could be interesting when looking at membrane fouling.

In response to observations made during experimentation, Table 3 summarizes the importance of experimental observations and proposed work that could be used to further explore the observed phenomena.

Table 3. Summary of proposed work based on observations made during the study.

Observation	**Importance**	**Proposed Work**
Relatively low FRR for low turbidity water treated with CFS and no significant difference in flux after hydraulic cleaning for high or low turbidity water.	Most of the fouling occurring from low turbidity water cannot be reversed by hydraulic cleaning.	Simulating chemical cleaning of membranes by applying sodium hypochlorite to membrane and calculating FRR.
Complete change in opacity of *M. oleifera* extraction after 2-3 hours (even if stored in refrigerator).	*M. oleifera* is only effective as a coagulant if it is used shortly after extraction. This is interesting when compared to the findings that *M. oleifera* proteins are stable in dried, powdered form up to 6 months in storage (Ndabigengesere et al., 1995).	Turbidity removals over time with fixed doses of *M. oleifera* extract allowed to sit before use.
An average pH of 6.2 was observed for the clay suspension compared to an average pH of 7.6 for the water from NWOWTP.	The alkalinity of the two waters was not quantified, and differences in alkalinities determine the consumption of pH and could impact the performance of coagulants in charge neutralization.	Conduct similar tests but with directly comparable water in terms of alkalinity. For example, the clay suspension could be produced with the raw water from NWOWTP instead of DI water.
Residual TOC higher than would be expected from the addition of *M. oleifera* is observed in samples after CFS.	It remains unknown (in the case of low turbidity water) if residual TOC is TOC naturally present in the water or TOC from *M. oleifera*.	Label M. oleifera carbon in a way that wouldn't interfere with CFS so that residual TOC can (or can't) be specifically attributed to *M. oleifera*.

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APPENDIX A: PREPARATION OF ALUM STOCK SOLUTION

For each desired alum concentration, an equivalent aluminum hydrate concentration was calculated using the mass ratio of the molecular weight of aluminum sulfate hydrate (630.49 g/mol) to that of aluminum sulfate (342.17 g/mol). The alum concentration (first column in Table A 1) was thus multiplied by the mass ratio of 1.84 to get the alum hydrate concentration (second column in Table A 2) that should be in the jars.

Table A 1. Calculation of alum stock solution doses.

Alum Concentration (mg/L)	Alum Hydrate Concentration (mg/L)	Alum Solution Dose (mL)
0	0.0	0
0.5	0.9	0.25
1	1.8	0.49
1.5	2.8	0.74
2	3.7	0.99
2.5	4.6	1.24
3	5.5	1.48
3.5	6.4	1.73
4	7.4	1.98
5	9.2	2.47

A dose volume to achieve an alum concentration of 50 mg/L was fixed at 25 mL so that the doses in the range of 0.0 mg/L to 5.0 mg/L would be in the range of 0 mL to 3 mL doses and inconsequential to the overall jar volume of 2 L. A mass balance of alum in Equation (A-1) inventories aluminum hydrate concentrations between the stock solution concentration C_s, concentration in the jar prior to the addition of coagulant C_j, and the total concentration in the jar after coagulant addition of the coagulant C_t. These concentrations are accounted for in the volumes of dosed coagulant V_d, the jar V_j, and the total volume after the addition of the coagulant $V_j + V_d$.

$$V_d C_s + V_j C_j = (V_j + V_d) C_t \tag{A-1}$$

Taking into consideration the fact that there is no alum hydrate in the jars prior to the addition of coagulant, we can reduce the initial mass of alum in the jars $V_j C_j$ to zero. Equation (A-1) can be simplified to solve for C_s, yielding Equation (A-2) which was used to solve for the stock concentration of 7.464 g/L aluminum sulfate hydrate.

$$C_s = C_t \left(\frac{V_j}{V_d} + 1 \right) \tag{A-2}$$

Once more beginning from Equation (A-1), the volume of aluminum hydrate stock to be added to each of the jars based on the desired alum concentration in each jar was solved for using Equation (A-3).

$$V_d = \frac{V_j}{{C_s}/{C_t} - 1} \tag{A-3}$$

Interpolation between values in Table A 1 yielded the dose in mL of alum stock solution for the optimal doses of 3.44 mL and 1.22 mL for high- and low-turbidity water, respectively, as presented in Table A 2.

Table A 2. Optimal alum dose conversions.

Optimal Alum Concentration (mg/L)	**Alum Solution Dose (mL)**
3.44	1.70
1.22	0.60

APPENDIX B: *M. OLEIFERA* EXTRACTION TOC AND CALCULATION OF DOSE

It is important to quantify the addition of *M. oleifera* according to a measure other than volume since the extraction process will not result in an identical coagulant extraction each time it is performed. This is also helpful in knowing how much TOC is being added per liter of water being treated that can then be compared to TOC values at points later throughout treatment (see APPENDIX C: PREPARATION OF TOC STANDARDS for calibration standard preparation). The *M. oleifera* extraction was prepared fresh before each jar test since, it was later discovered, that the extraction is not an effective coagulant if used several hours after preparation, even if stored in the refrigerator. This increases the likelihood that slightly different concentration of organics will be administered to the water being treated during each trial.

Thus, the TOC concentration in the *M. oleifera* extraction was measured with each jar test trial using two dilutions: 100x and 150x. Taking into consideration the dilution factor, the average of the two instrument responses for each dilution was computed and used to calculate the dose of *M. oleifera* coagulant for that trial. In Table C 1, each trial is labeled as high or low turbidity ("HT" or "LT," respectively), "MO" for *M. oleifera*, and the number corresponding to the trial number.

Table C 1. M. oleifera extraction TOC instrument responses.

Trial	Instrument Response (ppm)	Dilution	Extraction TOC (ppm)	Average (ppm)
LTMO1	13.4	100	1340	1300
LTMO1	8.4	150	1260	
LTMO2	10.7	100	1070	920
LTMO2	5.1	150	765	
LTMO3	9.2	100	920	950
LTMO3	6.5	150	975	
HTMO1	8.5	100	850	920
HTMO1	6.6	150	990	
HTMO2	4.3	100	430	700
HTMO2	6.4	150	960	
HTMO3	6.4	100	640	760
HTMO3	5.8	150	870	

Dose in terms of mg TOC/L was achieved by multiplying the administered dose in mL by the previously mentioned average TOC concentration (with appropriate unit conversions) and dividing by the volume of water in each jar test, 2 L.

APPENDIX C: PREPARATION OF TOC STANDARDS

TOC standards were prepared in the lab by creating an aqueous solution of glucose ($C_6H_{12}O_6$) with DI water. The total mass of carbon in glucose (72.1 g/mol) is 40% of the total mass of glucose (180.2 g/mol), so 1000 mg/L of glucose is equivalent to 400 mg/L of TOC. To prepare a TOC stock solution, 500 mL of 100 mg/L TOC solution was prepared with 125 mg of glucose. This solution was diluted by a factor of10 (1 mL stock solution plus 9 mL DI water) to produce a solution of 10 mg/L TOC. This solution was once more diluted by a factor of 10 (1 mL solution plus 9 mL DI water) to produce a solution of 1 mg/L TOC. Along with DI water, these three TOC solution standards were used in the calibration of the instrument.

APPENDIX D: IDENTIFICATION OF FUNCTIONAL OPTIMAL *M. OLEIFERA* COAGULANT DOSE

For the purposes of identifying a functional optimal dose of *M. oleifera* knowing that the dose in terms of mg TOC/L would not be the same for each fixed volume dose, a plot was constructed using by plotting residual turbidity as a function of the average mg TOC/L for each fixed volume dose. As illustrated in Figure D 1a and Figure D 1b, this allowed for the assignment of standard deviations to both residual turbidity and residual TOC in addition to the fitting of a polynomial curve for the identification of a minimum.

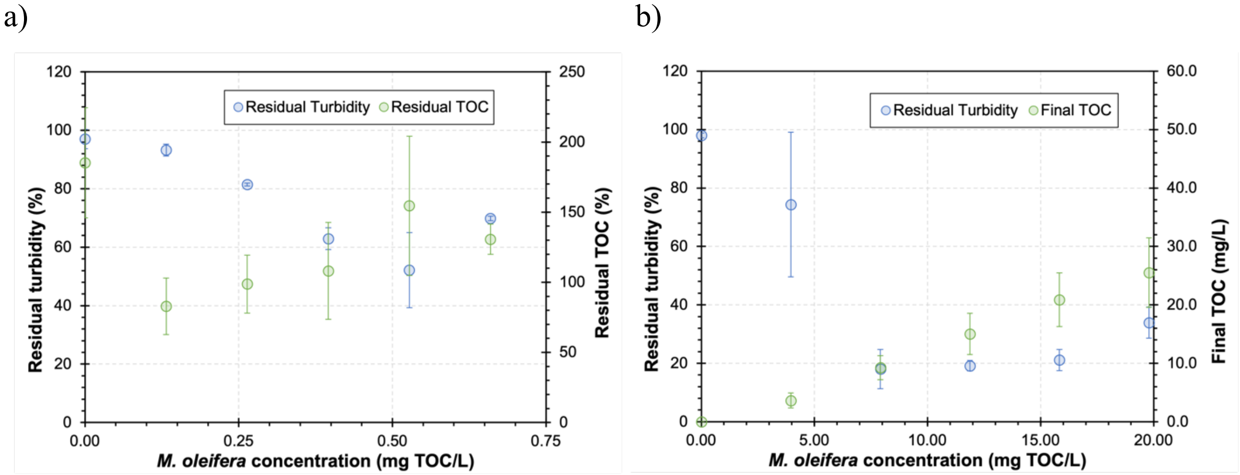

Figure D 1. a) Residual turbidity and residual TOC as a function of averaged M. oleifera dose (mg TOC/L) for low turbidity water and b) Residual turbidity and final TOC as a function of averaged M. oleifera dose (mg TOC/L) for high turbidity water. Error bars in both graphs represent standard deviation from triplicate samples.

APPENDIX E: LIMITS OF DETECTION AND QUANTIFICATION

Due to the use of very small *M. oleifera* coagulant extract doses, the limit of detection (LOD) and the limit of quantification (LOQ) of TOC were calculated in order to determine whether residual TOC values presented in the instrument response are reliable or possible.

Table E 1.Summary of the TOC instrument responses and the calculated standard deviations associated with each standard used in calibration.

Concentration (ppm)	**Average Area (counts)**	**Relative Standard Deviation, RSD (%)**	**Coefficient of Variation (CV)**	**Standard Deviation**
0	29278	1.4	0.014	409.9
1	38206	2.23	0.0223	852.9
10	117253	3.77	0.0377	4420
100	924465	3.42	0.0342	31620

Standard deviation values for each TOC standard used in calibration in Table E 1 were calculated by converting the relative standard deviation (RSD) from a percent to a decimal value, known as the coefficient of variation (CV). By rearranging the definition of the coefficient of variation in Equation (E-1), the standard deviation was obtained.

$$CV = \frac{\sigma}{\mu} \tag{E-1}$$

LOD and LOQ are defined in equations (E-2) and (E-3), respectively.

$$LOD = \frac{3 * standard\ deviation\ of\ lowest\ conc.in\ calibration}{slope\ of\ calibration\ line} \tag{E-2}$$

$$LOQ = \frac{10 * standard\ deviation\ of\ lowest\ conc.in\ calibration}{slope\ of\ calibration\ line} \tag{E-3}$$

The slope of the calibration line, calculated to be 8956 counts/ppm using values in Table E 1, and the standard deviation of the lowest concentration used in the calibration, calculated to be 409.9, were plugged into Equations (E-2) and (E-3) to obtain values of 0.14 ppm as LOD and 0.46 ppm as LOQ.

APPENDIX F: CONSTRUCTION OF FLUX V. PERMEATE VOLUME PLOTS

Permeate mass values were collected at fixed, 30-second time intervals, so the permeate volume can vary between the trials conducted for each feed water. This means that there is standard deviation for both flux on the y-axis and permeate volume on the x-axis. For each feed water, all the permeate volume measurements collected and their corresponding flux values for all three trials were combined, color-coded by trial, and sorted from smallest to largest permeate volume. Because standard deviation should be representative of variation within trials, the sorted values were separated into groups of three values, one from each trial, with similar permeate volumes. The average and standard deviation for both permeate volume and flux were calculated. Flux was normalized by J/J_0 and coefficient of variation was used for the addition of error bars (standard deviation divided by mean). Moving from smallest to largest permeate values, any outlying values that could not be easily grouped together were plotted as individual values as seen in Figure 5a and Figure 6a.

APPENDIX G: DERIVATION OF FLUX RECOVERY RATIO

This definition of flux recovery ratio was derived from the understanding that flux recovery is defined as the reversible membrane resistance R_{Rev} over the sum of the total membrane resistance due to fouling, which is a sum of reversible resistance and irreversible membrane resistance R_{Irrev} as seen in Equation (G-1). Because the irreversible and reversible membrane resistances are unknown, this definition was alternatively defined in terms of flux.

$$FRR = \frac{R_{Rev}}{R_{Rev} + R_{Irrev}} \tag{G-1}$$

Flux, in general, has been previously defined in Equation (2). This definition can be refined when looking at the flux at specific instances. Initial flux J_0 can be defined with TMP ΔP, water viscosity μ, and initial membrane resistance R_m in Equation (G-2).

$$J_0 = \frac{\Delta P}{\mu \cdot R_m} \tag{G-2}$$

Similarly, flux after fouling J_F in Equation (G-3) is determined by the total membrane resistance after fouling, which is the sum of R_m, R_{Rev}, and R_{Irrev}. Flux after washing J_W in Equation (G-4) is determined by R_m and R_{Irrev}, since hydraulic cleaning can reverse a portion of fouling.

$$J_F = \frac{\Delta P}{\mu \cdot R_{Total}} = \frac{\Delta P}{\mu \cdot (R_{Rev} + R_{Irrev} + R_m)} \tag{G-3}$$

$$J_W = \frac{\Delta P}{\mu \cdot (R_{Irrev} + R_m)} \tag{G-4}$$

Equations (G-2), (G-3), and (G-4) can be rearranged to solve and isolate the resistances, as seen in Equations (G-5), (G-6), and (G-7), respectively.

$$R_m = \frac{\Delta P}{\mu \cdot J_0} \tag{G-5}$$

$$R_m + R_{Rev} + R_{Irrev} = \frac{\Delta P}{\mu \cdot J_F} \tag{G-6}$$

$$R_{Irrev} + R_m = \frac{\Delta P}{\mu \cdot J_W} \tag{G-7}$$

A substitution of Equation (G-5) into Equation (G-7) yields Equation (G-8), which can be rearranged to solve for R_{Rev} in Equation (G-9).

$$R_{Rev} + \frac{\Delta P}{\mu \cdot J_W} = \frac{\Delta P}{\mu \cdot J_F} \tag{G-8}$$

$$R_{Rev} = \frac{\Delta P}{\mu \cdot J_F} - \frac{\Delta P}{\mu \cdot J_W} \tag{G-9}$$

The total resistance due to fouling, $R_{Rev} + R_{Irrev}$, is obtained by subtracting Equation (G-5) from Equation (G-6), yielding Equation (G-10).

$$R_{Rev} + R_{Irrev} = \frac{\Delta P}{\mu \cdot J_F} - \frac{\Delta P}{\mu \cdot J_0} \tag{G-10}$$

A substitution of Equations (G-9) and (G-10) into the initial definition of FRR in Equation (G-1), FRR can be defined in terms of J_0, J_F, J_W, ΔP, and μ. Equation (G-11) can be simplified as shown below because fouling tests are conducted while operating under a constant pressure, and the viscosity of water is characteristic at operating temperature.

$$FRR = \frac{R_{Rev}}{R_{Rev} + R_{Irrev}} = \frac{\frac{\Delta P}{\mu \cdot J_F} - \frac{\Delta P}{\mu \cdot J_W}}{\frac{\Delta P}{\mu \cdot J_F} - \frac{\Delta P}{\mu \cdot J_0}} = \frac{\frac{1}{J_F} - \frac{1}{J_W}}{\frac{1}{J_F} - \frac{1}{J_0}} = \frac{1 - \frac{J_F}{J_W}}{1 - \frac{J_F}{J_0}} \tag{G-11}$$

APPENDIX H: STATISTICAL ANALYSIS RESULTS

Table H 1. Summary of ANOVA single factor analysis for high turbidity feeds.

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HTRW	3	264.24623	88.082077	41.53841
HTCW	3	268.54292	89.514306	10.76921
HTCFSA	3	485.5256	161.84186	10.76921
HTCFSM	3	451.15210	150.38403	4.615379

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	13793.83	3	4597.9433	271.6969	2.1876E-08	4.06618055
Within Groups	135.38445	8	16.923057			
Total	13929.214	11				

Table H 2. Summary of ANOVA single factor analysis for low turbidity feeds.

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
LTRW	3	384.55346	128.18448	75.38452
LTCW	3	384.55346	128.18448	43.07687
LTCFSA	3	388.85014	129.61671	116.9229
LTCFSM	3	317.95481	105.98493	906.1527

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1161.152	3	387.05082	1.356244	0.3236315	4.0661805
Within Groups	2283.074	8	285.384281			
Total	3444.226	11				

Single factor ANOVA with an alpha value of 0.05 was utilized to obtain the following results to determine statistical differences between the four different high turbidity feeds and differences between the four different low turbidity feeds. Single factor was selected to evaluate the effect of one factor (the feed water pretreatment) on a response variable (membrane flux after fouling). A p-value of less than 0.05 indicates statistical significance, which is observed for the flux after fouling for feed waters derived from high turbidity water, but not for feed waters derived from low turbidity water.

APPENDIX I: ULTRAFILTRATION TOC REMOVAL

For high turbidity (“HTMO”) and low turbidity (“LTMO”) waters that were treated with the functional optimal dose of *M. oleifera*, the amount of TOC removed by the UF membrane during filtration and the percent of TOC removed (of the post-CFS, pre-filtration TOC concentration) are shown in Table I 1.

Table I 1. TOC removal by ultrafiltration.

Trial	**TOC Removed (mg/L)**	**% TOC Removed**
LTMO1	2.6	61%
LTMO2	4.6	85%
LTMO3	1.9	58%
HTMO1	2.9	18%
HTMO2	1.0	7%
HTMO3	0.1	1%