DEVELOPING INTEGRATED MEMBRANE PROCESSES FOR

INDUSTRIAL WASTEWATERS

ADVANCING INTEGRATED MEMBRANE FILTRATION PROCESSES FOR TREATING INDUSTRIAL WASTEWATERS WITH TIME VARYING FEED PROPERTIES

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the

Requirements of the Degree Doctor of Philosophy.

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TITLE: Developing membrane filtration processes for treating industrial wastewaters with time varying feed properties

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PAGES: xii, 231

Lay Abstract

Wastewaters sourced from industrial processes are considered 'tough-to-treat' due to high contaminant concentrations and time-varying compositional properties. Recent advancements in membrane technologies have demonstrate great promise in treating industrial wastewaters, however, these membranes often need to be integrated with other treatment technologies to overcome challenges with treating these wastewaters. This thesis aims to push the adoption of integrated membrane processes for treating highstrength industrial wastewaters. By utilizing advanced analytical techniques to investigate the effects of high contaminant loadings and variable feed properties on membrane processes, it was determined that screening tools are needed to rapidly design and optimize membrane process that are tailored to the properties of the wastewater. This thesis introduces a high-throughput and miniaturized screening platform that combines analytical centrifugation and filter-plate technology to holistically screen two-stage coagulation-filtration processes with little time and material requirements.

Abstract

Wastewaters that are produced by industrial processes are more challenging to treat than municipal wastewaters, primarily due to two reasons. Firstly, industrial wastewaters contain high concentrations of several different contaminants (e.g. metals, nutrients and organics etc.), which can be challenging for a single process to treat. Secondly, the compositional properties of the wastewaters can vary significantly as it is dependent on several upstream processes. Commercial membrane technologies have shown significant adoption in desalination and municipal wastewater treatment applications. Their favourable selectivity and tunable properties have garnered interest from both academia and industry to push these technologies into industrial wastewater treatment. Despite showing promising contaminant removal results, current studies have shown that fouling due to high contaminant loadings, and variable treatment efficacies due to feed property variations, limit the adoption of commercial membranes into these applications. Current research addresses these challenges through the new material development or surface modifications, however, there is a need to approach these challenges at a process level by integrating existing membrane technology into adaptive processes.

This thesis aims to advance the adoption of commercial membrane technology into 'tough-to-treat' industrial wastewater applications. Firstly, the effects of high contaminant concentrations and variable feed properties on membrane treatment is studied by using advanced techniques, such as gas chromatography – mass spectrometry, to resolve the composition of feed and permeate streams from membrane processes treating real wastewaters. It was determined that fast and efficient screening tools are required to optimize and adapt membrane processes to respond to this variability. This thesis then introduces high-throughput and miniaturized screening platform that combines analytical centrifugation with filter plate technology to rapidly optimize two-stage coagulation-filtration processes with an extremely low material and time requirement.

Acknowledgements

This five-year journey would not have been possible without the help and support of so many people along the way. First and foremost, I would like to show my sincerest gratitude to my supervisor, Dr. David Latulippe. Thank you for agreeing to be my thesis supervisor during the final year of undergraduate studies, and providing me with the opportunity to continue working with you into a Ph.D. I have learned so much from being a part of this lab, and I am forever grateful for the experience you have given me. I would also like to thank my two committee members, Dr. Robin Zhao and Dr. Michael Thompson. Thank you for agreeing to be a part of this journey with me, and providing so much valuable feedback over the years. I hope you were also able to gain something valuable from our time together.

A large theme of this thesis is industrial collaboration. I have been fortunate to have worked with two industrial partners that have provided invaluable industry expertise, granted access to their facilities, and provided financial support for the project. Firstly, I would like thank Sasha Rollings-Scattergood, Indranil Sarkar and Kevin Lutes from Anaergia. Thank you for all your support, advice and expertise you provided over the last three years. Next, I would like to thank Tom Maxwell, Jo-Ann Livingston, Milos Stanisavljevic, and Richard Mock from Aevitas, who supported me through the first two years of my Ph.D. I am particularly grateful to the team at Aevitas for allowing me to conduct a pilot scale study at their facility. Finally, I would like to acknowledge all the funding agencies that have provided financial support for these projects; the Natural Sciences and Engineering Research Council, Mitacs, the Ontario Graduate Scholarship program. Additionally, I would like to thank the Canada Fund for Innovation John R. Evans Leaders Fund for funding several key pieces of equipment I used throughout my research.

This research would not have been possible without the help of several knowledge experts that have assisted me with my research. Firstly, I would like to thank Dr. Kirk Green from the McMaster Regional Center for Mass Spectrometry for training me on gas chromatography – mass spectrometry, a technique that I used extensively in my early work. Next, I would like to thank Dr. Marta Prinz, Dr. Zeynel Beyandir, Dr. Medhi Keramane and Elna Luckham and the entire team at the Biointerfaces Institute that have trained me on several instruments. Finally, I would like to thank Dr. Sigrid Peldszus and Kirti Nemani from the University of Waterloo for their assistance with LC-OCD analysis.

I would show appreciation to Dr. Jake Nease, Dr. Charles de Lannoy and Dr. David Latulippe, for taking me on as a teaching assistant for their respective courses. I am so fortunate that I was able to be a teaching assistant for so many courses that I loved as an undergraduate student, and I am grateful for the opportunity to experience them from the teaching side. I hope that I had a positive impact on the course offering and the countless students I interacted with.

I am extremely grateful for all the senior Latulippe Lab members that supported me early on in my Ph.D. Thank you to Patrick, Evan, Karina, Salman and Amir for all the training and advice you have given me. Additionally, thank you to my colleagues Ian, Matthew and Satyam that have supported me in so many ways while we worked together. Your dedication to producing high quality work was inspirational to see, and motivated me to follow in your footsteps. Next, I would like to show my appreciation for all the undergraduate research assistants that I have mentored throughout my Ph.D. Thank you Nicole, Erica, Susie, Jacob, Brianna, Christophe, Yves and Jack for all the many contributions you have made to this research. I will always be grateful for the enthusiasm and willingness to learn that each of you showed, and I hope that you were able to gain something valuable from our time together. I wish you all the best with your future endeavours.

My time at McMaster was made so much better by the incredible support I had from the friends I had coming into this Ph.D., and all the new friends I made along the way. Your support outside the lab means so much to me. To Shashaank, Ali, Astawa, Marisa, Zanab, Nafiza and Faraaz, thank you for all the support and friendship you have shown me since we ended high school all those years ago. To the friends I made in undergrad and have stuck with me since, Alex, Deniz, Cassandra, Melissa, Jerome, Erik, Jamie and Logan. Our lives have taken us in so many different directions but I am so grateful that we always find the time for each other. Finally, to Emily, Oli, Joelle, Erika, Samin, Heather, Todd, Jake, Matt and Annika and all the other friends I have made while in Hamilton. All the friendsgivings, softball games, concerts and countless other social events we shared together kept me sane through these years, and I am so appreciative for all the memories we made together

Next, I would like to thank my core group of Latulippe Lab friends, who made my time at graduate school so much more special. To Claire, Scott, Nathan, Ryan, Ana, Sarah

R., Sarah A., Landon and Sam, thank you so much for all the incredible friendship and support you have shown me over the last few years. We became so close so fast, and I am so fortunate to have such a strong and tight support circle around me day in and day out. Beyond just the support you showed me in the lab, I am so grateful for all the camp trips, the ski trip, all the birthdays we celebrate, our overly competitive squash games, the Costco trips and even the late-night lab sessions we shared together. You all made me more excited for Mondays than Fridays because I got to come be with my favourite people. You are all such brilliant and talented people, and it inspired me to work that much harder. I am so proud of all your achievements and I can't wait to see where the next phase of life takes us.

Finally, to my parents Desiree and Millinda Premachandra, and sister, Shweta Premachandra, who taught me the value of hard work. Thank you for all the support, understanding and encouragement you have provided me during this period. I hope that through this achievement I have made you proud.

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List of Abbreviations & Symbols

Abbreviations

Abs.	Absorbance
AC	Analtical centrifuge
AD	Anaerobic digestate
CCC	Critical coagulant concentratin
CCD	Charge coupled device
CF	Coagulation-Flocculation
COD	Chemical oxygen demand
DCM	Dichloromethane
DI	De-ionized
DOC	Dissolved organic carbon
GC-MS	Gas chromatography - Mass spectrometry
НТ	High-throughput
HTMS	High-throughput and miniturized screening
HTPD	High-throughput process development
HTS	High-throughput screening
ICP-OES	Inductively coupled plasma - Optical emission spectroscopy
IWW	Industrial wastewater
LC-OCD	Liquid chromatography - Organic carbon detection
LHS	Liquid handling system

LMH	$L/m^2/h$
LMW	Low molecular weight
MF	Microfiltration
ML	Machine learning
MSTFA	N-methyl-N-(trimethylsilyl)trifluoroacetamide
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
NIR	Near infrared light
NOM	Natural organic matter
RO	Reverse Osmosis
SDL	Self driving lab
SSO	Source separated organics
TCMS	Chlorotrimethylsilane
TDS	Total dissolved solids
TMP	Transmembrane pressure
TOC	Total organic carbon
TSS	Total suspended solids
TSS	Total solids
UF	Ultrafiltration

Symbols

L _p	Permeability
Di	Diffusion coefficient for species i
Ci	Concentration of species i
μ	Dynamic Visosity
ψ	Applied Voltage
X	Distance
R	Gas constant
F	Faraday's constant
Т	Temperature
Т	Time
G	Gibbs free energy
Pc	Concentrate pressure
P _F	Feed pressure
P _P	Permeate pressure
J	Flux
K _B	Boltzmann constant
η	Kinematic viscosity
ζ	Zeta-potential
R	Hydraulic resistance
R	Fouling Index
V	Volume

Declaration of Academic Achievement

This Ph.D. thesis has been prepared as a sandwich thesis containing work previously published or prepared for publishing, as listed below:

- Chapter 2 is adapted from the manuscript "Treatment of complex multi-sourced industrial wastewater New opportunities for nanofiltration membranes". *Chemical Engineering Research and Design* 2021, 168: 499-509. https://doi.org/10.1016/j.cherd.2021.01.005. Experiments were primarily carried out by me, with assistance from N. Perna, S. O'Brien and J. McGivern.
- Chapter 3 is adapted from the manuscript "Development of a crossflow nanofiltration process for polishing of wastewater by-products from biogas production processes". *Journal of Water Process Engineering*. 50: 103197. https://doi.org/10.1016/j.jwpe.2022.103197. Experiments were primarily conducted by me, with the assistance of C. Michaud-Lavoie, B. Chester, and M. McClure. The LC-OCD work presented in this chapter was conducted by S. Peldszus and K. Nemani.
- Chapter 4 is adapted from the manuscript "High-throughput screening to evaluate optimum coagulation conditions via colloidal stability analysis". *Chemosphere*.341: 139798. <u>https://doi.org/10.1016/j.chemosphere.2023.139798</u>. Experimental work was primarily conducted by me, with assistance from Y. McKay and M. McClure.
- **Chapter 5** is adapted from the manuscript "Leveraging colloidal stability measurements to optimize the treatment of anaerobic digester centrate" that has been

prepared for journal submission. Experimental work was primarily carried out by me, with assistance from M. McClure.

• Chapter 6 is adapted from the manuscript "High-throughput and miniaturized screening pipeline for optimizing two stage coagulation-membrane filtration processes" that was prepared for journal submission. Experimental work was primarily conducted by me, with assistance from J. Ormsby and E. Langeitne-Wilkins.

Work presented in all chapters was completed under the supervision of D. Latulippe. The high-pressure cross-flow filtration system that was used in chapters 2, 3 and 5 was built and commissioned by R. LaRue.

Chapter 1

Introduction

Chapter 1 Introduction

1.1 Membrane Filtration

1.1.1 Introduction to membrane technology

Membranes are semi-permeable barriers that preferentially transport one chemical species over another, thereby enabling the separation of a multi-component mixture through a difference in the transport rate of individual species¹. Research in membrane science can be traced back to the late eighteenth century, however, the modern membrane was developed in the early 1960s by Loeb and Sourirajan, who developed a phase inversion technique for making anisotropic reverse osmosis membranes using cellulose acetate². This discovery kick-started the production of commercial membranes, and by the late 1980s, several membranes were available in a variety of materials, geometries and cut to be used in various commercial applications.

The three dominant driving forces in pressure driven membrane separations are pressure, concentration, and ion transfer, as shown in Figure 1.1. In the first regime, applied pressure on one side of the membrane induces viscous flow from a region of high to low pressure through a membrane containing pores. This is best described through Darcy's law (Eq. 2), where L_P is membrane permeability, P is the applied pressure, x is the membrane thickness and μ is the solution viscosity. This is the dominant transport process in pressure-driven membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)³. Diffusion is a spontaneous process that transports material from a region of high to low concentration and is best described through Fick's law (Eq. 3), where D_i and C_i are the diffusion coefficient (similar to permeability in Darcy's law) and concentration of species *i*. This is the dominant transport mechanism in diffusion-driven membrane processes such as pervaporation, membrane extraction, and membrane distillation⁴. Finally, ion transfer under a voltage gradient occurs in membranes containing charged surface groups. Like diffusion under a concentration gradient, ion transfer occurs under a concentration gradient but is also influenced by the magnitude of the voltage gradient (φ), and the valency of the ion (Z_i) being transported. This is best described by the Nernst-Planck equation (Eq. 4), which is an extension of Ohm's law. Here *F* is Faraday's constant (96485.3 C/mol e⁻), *R* is the gas constant (8.3145 J/mol K), and *T* is the temperature (in °K). This mechanism dominates in electrically driven membrane processes such as electrodialysis and electrophoresis^{1.4}. Both diffusion and ion transfer are spontaneous processes, meaning that transport occurs from a region of high to low Gibbs free energy ($-\Delta G$).

$$J = \frac{L_p}{\mu} \frac{dP}{dx} \quad (\text{Eq. 1.1}) \quad J_i = D_i \frac{dC_i}{dx} \quad (\text{Eq. 1.2}) \quad J_i = D_i (\frac{dC_i}{dx} + \frac{Z_i F C_i}{RT} \frac{d\varphi}{dx}) \quad (\text{Eq. 1.3})$$

The most prevalent industrial membrane processes are pressure-driven and have been applied extensively in municipal and industrial water treatment and purification².



Figure 1.1. Three primary regimes in membrane transport processes. The decrease in vertical height of species being transported under a diffusion or voltage gradient represents a decrease in Gibbs' free energy ($-\Delta G$). Figure adapted from¹

Synthetic membranes are made with materials such as polymers, glass, ceramic, liquids, and metals. Polymeric membranes are the most popular due to their tunable properties (such as pore size, surface charge, hydrophobicity, and component affinity) and flexibility which allows them to be packed into modules with a high packing density (large membrane filtration area in a small module volume)⁴. Common membrane polymers include polyvinylidene fluoride, polyether sulfone, polyamide, and polypropylene¹. The geometry of a membrane is known as a module. Spiral wound, tubular and hollow fiber geometries are commonly used due to their high packing density. Flat sheet membranes resemble a flat surface upon which filtration occurs and are used extensively in the lab and bench-scale membrane testing, however, it is rarely used industrially due to having a low packing density.

Pressure-driven membranes can be classified based on their pore size as MF, UF, NF, or RO. Macroporous membranes (MF and UF) rely on viscous flow and size exclusion to create separation, whereas microporous membranes (NF and RO) create

additional separation based on the solubility of a species within the membrane (diffusion) and charge group interactions between the membrane and component (charge exclusion). Table 1.1 compares membrane types.

Туре	Pore Size Range	Molecular Weight cut- off (Da)	Mechanism of Transport	Mechanism of Rejection	Examples of rejection
MF	$0.1-1 \ \mu m$	>100,000	Viscous flow	Size exclusion	Bacteria, cells, colloids
UF	2 – 10 nm	1000 – 500,000	Viscous flow, diffusion	Size exclusion	Biopolymers, viruses, small colloids, bacteria
NF	0.5 – 2 nm	400 - 500	Viscous flow, diffusion, ion transfer	Size exclusion, solubility, charge exclusion	Divalent salts, sugars, organic compounds
RO	Poreless	<200	Viscous flow, diffusion, ion transfer	Size exclusion, solubility	Monovalent salts

Table 1.1. Comparison of the four main membrane types¹.

1.1.2 Membranes in water and wastewater treatment

Membrane processes serve an important role in water and wastewater treatment due to their extensive treatment capacity⁵. The modern membrane was developed for water softening applications, where charged solutes such as sodium, chloride, magnesium, and calcium can be removed up to 99% with relatively low energy requirements compared to alternative technologies⁶. Membrane technologies play a critical role in modern drinking water and municipal wastewater plants, in part due to the reliability of the incoming feed properties that allow for processes to be developed and customized for the specific application. In Canada, membranes play an important role in drinking water treatment applications, where plants fitted with membrane technology
served 8% of the population in 2011, which amounts to ~383 million cubic meters of water filtered⁷. Municipal wastewater accounts for approximately 65% of wastewater entering wastewater treatment facilities entering Canada's sewer systems⁸. In municipal wastewater treatment applications, membranes bioreactors that combine membrane processes with biological processes (such as anaerobic and aerobic digestors), are used together to treat the high organics loading^{6,9}. However, increasing water consumption and strict discharge requirements have created a precedence to push this technology from drinking water and municipal wastewater treatment, in to "tough-to-treat" industrial wastewater treatment applications.

1.1.3 Membranes in "tough-to-treat" applications

The next frontier for membrane technology is in their application into "tough-totreat" industrial wastewater treatment applications. Industrial wastewaters are wastewaters that are produced from industrial process. These wastewaters account for approximately 18% of wastewater discharged into Canadian sewers⁸. Unlike municipal wastewater, which tends to have constant feed characteristics, industrial wastewaters have extremely high concentrations of a variety of contaminants⁹ (e.g., COD concentrations in the 1000 – 10000 mg/L range), and the volume and composition of these wastewaters can vary over time¹⁰. For facilities that produce industrial wastewater, the wastewater must either be treated on-site before being discharged into a sewer or be externally transported to a facility to a dedicated industrial wastewater treatment facility for treatment¹¹. Both methods can be challenging, for facilities that treat wastewater on site, federal regulations such as the *Wastewater Systems Effluent Regulations* put strict discharge limits on the quality of water that can be discharged into sewers¹². The regulations are becoming stricter as the demand for water increases, and are becoming increasingly difficult to achieve with conventional treatment technologies, such as bioreactors and settling tanks. Failure to comply with these regulations can lead to strict fines; for example, the City of Toronto fines \$100,000 per day when discharged sewage in non-compliant¹³. Secondly, for facilities that haul their wastewater to external treatment facilities, haulage can be extremely costly, and scales with the volume of wastewater produced and the frequency of shipments¹⁴.

1.1.2.1 Challenge 1: High concentrations of contaminants and membrane fouling

"Tough-to-treat" industrial wastewaters typically contain high concentrations of several different compounds⁹. Figure 1.2 shows a schematic of the different contamination sources that can be found in industrial wastewaters, and the technologies that are traditionally used to target these compounds. The high selectivity and tunable properties of membranes make them an attractive alternative to traditional technologies. Several studies have investigated the use of membrane technology for treatment of a variety of industrial wastewaters, such as mining, pharmaceutical waste, textile dyes, diary production. Table 1.2 summarises a few of these studies, and highlights the class of membrane used, the influent properties of the wastewater, and the level of treatment achieved via the membrane.

Table 1.2.	Examples	of MI	F, UF	and	NF	membr	anes	in	five	diffe	rent i	ndustrial
wastewater	applications	s. The	influe	ent a	nd	effluent	meas	sure	ments	of	select	quality
parameters are shown, along with the percentage removal.												

Wastewater Source	Class	Quality Parameters	Influent Concentration	Effluent Concentration (Removal %)	Reference
	NE	COD (mg/L)	240	20 (92%)	15
	NГ	TDS (mg/L)	2460	384 (82%)	
Pharmaceutical	NF	COD (mg/L)	4516	79 (98%)	16
		TDS (mg/L)	712	BDL (100%)	10
	NF	Conductivity (mS/cm)	4.6	0.4 (91%)	17
Mining		Sulfate (mg/L)	2620	168 (94%)	
winning	NF	Calcium (mg/L)	80	16 (98%)	18
		Sulfates (mg/L)	3500	126 (96%)	
	UF	COD (mg/L)	708	177 (75%)	
		Conductivity (mS/cm)	3.8	2.66 (30%)	19
I extile Dyes	NF	COD (mg/L)	2960	770 (74%)	
		Turbidity (NTU)	1500	7.4 (99.5%)	20
	MF	COD (mg/L)	1182	678 (43%)	21
Landfill		BOD (mg/L)	651	238 (63%)	
Leachates	NF	COD (mg/L)	500	100 (80%)	22
		SS (mg/L)	130	BDL (100%)	
	MF	COD (mg/L)	3256	3065 (6%)	23
.		Turbidity (FAU)	160	40 (75%)	
Dairy Wastewater	UF	COD (mg/L)	346	17 (95%)	24
		SS (mg/L)	111	11 (90%)	



Figure 1.2. Schematic of the types of contaminants present in industrial wastewaters, and the traditional technologies that are used to treat them. "Tough-to-treat" industrial wastewaters will typically have high concentrations of many of these contaminants, and several technologies need to be combined to fully treat these wastewaters.

Overall, membranes in these "tough-to-treat" applications have shown significant promise, however, the treatment efficacy depends on the type of membrane selected and the influent properties of the wastewater. One significant challenge that membrane processes face when treating wastewaters with high contaminant concentrations is membrane fouling. Fouling is a phenomenon in which particles that are being removed either adhere or 'cake' onto the membrane surface, which causes an increase in the resistance for filtration. This manifests as either an increase in the transmembrane

pressure (TMP) to maintain a certain permeate flux or a decrease in permeate flux to maintain a certain TMP, the former being the more common. Consequently, fouling decreases membrane productivity⁵. Fouling can be classified as 'reversible' if membrane productivity can be restored through physical cleaning methods, or 'irreversible' if the loss in membrane productivity cannot be regained or regained only through aggressive chemical cleaning. In reversible fouling, a cake layer of loosely bound foulants forms over the filtration surface to increase the resistance to filtration, whereas irreversible fouling results in the chemosorption of foulants onto the membrane surface and poreplugging. For non-porous and microporous membranes that rely on diffusion such as RO and NF, an important concept is concentration polarization. Here, the concentration of accumulated particles on the membrane surface is higher than that of the bulk fluid, causing back diffusion into the bulk under a concentration gradient²⁵. Crossflow filtration is better able to control concentration polarization as shear forces prevent the formation of a concentrated fouling layer ²⁶. The most common foulants that are found in membrane feed streams are best classified in review articles by Guo et al.⁵ & AlSawaftha et al.²⁷, and are summarized in Table 1.3.

	Colloidal Fouling	Organic fouling	Scaling	Biofoulants
General Description	Monodispersed insoluble suspensions in water that are classified by size as settleable solids (>100 μm), supra- colloidal solids (1 - 100 μm), dissolved solids (<10 Å)	A broad range of organic compounds with molecular weights ranging from 1,000 – 100,000 Da ⁵ . The largest fraction is hydrophobic (humic) acids that contain several aromatic groups and conjugated double bonds. The remaining fraction includes transphillic and amino acids, proteins, and carbohydrates, that contain more aliphatic carbons ⁵ .	Deposition of inorganic salts on the membrane surface. The most common scalants in membrane processes are carbonate, silica, sulfate, calcium, iron, and magnesium due to their ubiquity and low solubility ²⁸ .	Accumulation of microorganisms and their secretions on a membrane surface
Fouling Mechanism	Colloids that are similar in size to the pore size cause pore blocking, while larger colloids form a cake layer. Cake formation involves initial deposition, compaction into a tight skin layer, and gradual growth over the skin layer ²⁹ .	The hydrophilic fraction of NOM contributes most significantly to membrane fouling ^{30,31} , while large compounds of both hydrophobic and hydrophilic fractions contribute to reversible fouling ³² .	The concentration of salts during filtration leads to their solubility limit being exceeded, thereby causing these salts to precipitate and foul a membrane surface ³³ . The degree of scaling is dependent on both the concentration of the salt and its solubility in water.	Extracellular polymeric substances (EPS) secreted by microorganisms adhere to the membrane surface and leads to subsequent attachment (bioadhesion) followed by growth (multiplication) or organisms on the membrane surface ³⁴

Table 1.3. Description of the types of foulants found in membrane filtration processes and their mechanism of fouling.

1.1.2.2 Challenge 2: Time Varying Feed Properties

The second challenge associated with the treatment of industrial wastewaters is the prevalence of wastewaters with temporal variability in their feed properties. This can either be variability in the volumes of wastewater that are treated, the composition of wastewater, or seasonal variations in the temperature of the wastewater. Previous studies have explored the effect of feed variations on less "tough-to-treat" applications, such in surface water^{35–37}, municipal wastewater treatment^{38,39}, and seawater applications^{40,41}. Though the wastewaters used in these studies had lower contaminant concentrations as compared to industrial wastewaters, these studies have demonstrated the effect of feed variations on membrane processes. For example, Her et al. observed higher natural organic matter (NOM) fouling and salt precipitation when the dissolved organic carbon (DOC) and conductivity of the incoming feed of a surface water was higher⁴². Ayache et al. showed that seasonal variations in the nutrient loading of municipal wastewaters can affect the prevalence of biofouling on reverse osmosing membranes. Finally, Sui et al. studied how variations in the loading of specific pharmaceuticals affect MBR treatment³⁹. Higher pharmaceutical loadings observed in the summer months lead to an overall lower removal rate by MBR treatment. Additionally, certain pharmaceutical compounds such as carbamazepine and sulpiride were not removed via membrane treatment, and thus bulk removal of pharmaceuticals was lower when higher concentrations of those compounds were present.

A very limited number of studies have investigated the effects of feed variability on industrial wastewater samples. Silva et al. showed that variations in the ratio of COD/SO₄²⁻ in sulfate-rich wastewaters sourced from ethanol production led to variations in the performance of an MBR fitted with an UF membrane. Higher COD removal rates were observed when the ratio of COD/SO₄²⁻ was higher, and higher fouling was observed when the ratio was lower (higher sulfate concentration). Conversely, Farizoglu and Uzuner showed that extreme variations (COD ranging between 921 and 9004 mg/L over an eight-month period) in the influent organics loading of a dairy wastewater to a UF system had minimal impact on the treatment efficiency, however, a higher fouling rate was observed when the influent COD was higher⁴³. Though limited, these studies have shown the extent to which variable feed properties can affect the efficacy of membrane treatment processes.

1.2 Integrated membrane processes

A variety of solutions have been proposed to adapted membrane processes into "tough-to-treat" applications. This includes research at all levels of the membrane research pipeline, from novel membrane materials to fully integrated membrane systems⁴⁴. Currently, the majority of new membrane research is focused on developing polymers that have beneficial properties when cast into membranes. Very few of these materials ever move forward into viable membrane modules, and even fewer make it into commercial applications⁴⁴. There is a strong need for researchers to focus on taking existing membrane technologies that have already gone through the strenuous research and development cycle, and develop smart and integrated processes around them to treat industrial wastewaters⁴⁴.

Though many commercial membranes exist with high selectivity for several different contaminants, low membrane throughput caused by membrane fouling remains a significant challenge when pushing these technologies into "tough-to-treat" applications. Integrated membrane processes refer to how membranes interact with other treatment processes within a larger treatment train. These challenges can be overcome by integrating membranes with other treatment technologies.



Figure 1.3. (A) The research and development pipeline required to take a novel material and develop it into a viable membrane technology that can be used in full-scale applications. (B) The current number (1) and share (2) of papers focused on polymer, membrane material, module, and process research between 1980 and 2020, highlighting that the majority of current research is focused on polymer and material research. Reprinted with permission from Beuscher et al.⁴⁴ under Creative Commons license.

1.2.1 Multi-stage processes

Membrane processes are often coupled with other separation technologies such as disinfection, coagulation-flocculation, activated carbon, and media filtration to remove foulants before filtration. Typically, these processes are placed upstream of a filtration process to reduce the fouling propensity of membranes by removing larger contaminants. Disinfection prevents membrane biofouling by reducing the number of micro-organisms in the feedwater²⁷. Chloride is the most used disinfectant, however, UV-radiation and oxidizing biocides such as hydrogen peroxide are also used⁴⁵. Coagulation-Flocculation is a highly effective in removing turbidity and suspended solids before filtration. Coagulation-Flocculation before membrane filtration has been widely studied for MF^{46,47}. UF^{48,49}, NF^{50,51} and RO⁵² systems. Here, a coagulant (typically a positively charged metal ion) is used to destabilize colloidal suspensions via charge neutralization, and floc formation occurs once van der Waals forces overcome repulsive forces⁵³. Microflocs are then aggregated via the addition of a polymeric flocculant to form settleable macroflocs⁵⁴. Even though it is highly effective, it can be expensive to implement due to chemical costs and high plant footprint requirements as large reaction and settling tanks are required if in-line coagulation/flocculation is not used. Activated carbon, either as powdered (PAC) or granular (GAC) activated carbon, is used to adsorb DOC through van der Waals interactions between contaminants and the PAC/GAC granules⁵⁵. PAC/GAC has been widely studied as a membrane pretreatment technology and has shown to be effective in removing organic fractions from wastewater^{56,57}. Media filtration involves filtering the feed water before entering a membrane process and includes simple physical separation techniques such as sand filtration⁵⁸, adsorptive resins⁵⁶ and large pore-sized MF and UF membranes before NF/RO^{59,60}. Integrated membrane processes can be designed to solve the two central challenges associated with industrial wastewater treatment (high contaminant concentrations and variable feed properties).

1.2.2 High-throughput screening tools

Multistage processes improve the performance of downstream membrane processes by reducing the fouling propensity of the incoming feed. Several design considerations must be accounted for when developing these processes such that both processes are not only tailored to the wastewater that is being treated, but also that the operation of the membrane process does not operatessub-optimally due to changes made to the water properties by the pretreatment process. A common example of this is the use of coagulation pretreatment processes prior to membrane filtration. Coagulation processes effectively remove large colloids, such as NOM, that would otherwise foul membrane surfaces, however, the coagulant dosing needs to be carefully administered. Underdosing the coagulant can lead to significant colloidal fouling on membrane surfaces, whereas overdosing can lead to scaling as metallic precipitates deposit on membrane surfaces. This can be particularly challenging for processes that face significant feed variability, as the coagulant dose needs to be readjusted. Similarly, other processes pretreatment processes needed to be similarly adjusted to optimize downstream membrane processes.

Process screening is a method of rapidly designing and optimizing processes by using a smaller scale version of the industrial processes to rapidly evaluate the process under a variety of design parameters and process alternative at a bench or pilot scale. This

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is particularly beneficial when designing integrated membrane processes for 'tough-totreat' industrial wastewaters as operating parameters can be optimized for the particular wastewater being treated. Additionally, screening tools can be used to efficiently re-adjust those process variables when the influent properties change over time. Current screening tools that are used in wastewater treatment applications involve large bench scale equipment that allow practitioners to evaluate screening tools, however, the screening process with these technologies can be time-consuming and have a low throughput. This thesis focuses on high-throughput screening (HTS) for two-stage coagulation and filtration processes that enables rapid designing and optimization of these integrated processes.

1.2.2.1. Membrane HTS

The current standard for evaluating membrane processes involves using a labscale or pilot scale membrane module. An example of this is an 1812 spiral wound membrane module that fits a large membrane surface into a module that has an 18-inch length, and 1.2-inch diameter⁶¹. Another example of this is the use of a SEPA cell, which is high pressure filtration cell that evaluates flat sheet membranes with an ~140 cm² active surface area^{62,63}. These bench scale filtration technologies are often fitted into a bench scale filtration system that includes a tank to store several liters of wastewater, and a pump that can generate high pressure and crossflow rates. The stirred cell is another common screening tool that is used frequently in bioseparations applications. Here, a sealed vessel is filled with between 3 – 400 mL of liquid and filtered through a flat sheet membrane using pressured supplied through a gas source. A magnetic stirring apparatus is included inside the vessel to emulate crossflow filtration process where shear forces prevent deposits from forming on the membrane surface. Even though widely used in both practice and research, these technologies struggle with having a low-throughput (one membrane screened at a time) and long testing time (several hours per test to evaluate membrane fouling).

Several high-throughput and miniaturized alternatives have been presented in the literature that over come the challenges with standard bench scale filtration technologies. This includes systems that have parallelized several filtration systems to test several membranes simultaneously^{64–66}, or ultra-scaled down filtration cells ^{67,68} that can evaluate membrane performance with a low material requirement. Filter plates are a technology that is widely used in optimizing membrane processes (membrane adsorbers) in bioseparations applications. Here, the wells of a microplate are fitted with a membrane filter in which between 12 and 1536 different solutions can be filtered simultaneously⁶⁹. However, this technology is currently limited as these plates are typically fitted with the same membrane type. As such, only variations in the solutions being placed into the filter plate can be screened, and comparing membranes requires the use of multiple plates.



Figure 1.4. Examples of high-throughput or miniaturized membrane screening tools. (A) A miniaturized testing cell designed by O'Neal and Jensen that allows membrane performance to be evaluated with microliters of testing solution⁶⁷. (B) A parallelized flat-sheet membrane testing apparatus designed and built by Vandezande et al. that allows 16 membranes to be screened simultaneously65. Reprinted with permission from O'Neal and Jensen, and Vandezande et al. from Creative Commons license.

1.2.2.2 Coagulation HTS

Jar testers are widely used to optimize coagulation processes; however, these large systems have a low throughput (4 - 6 jars) and requires a large material requirement (1 - 2 L/jar). This can be challenging when several combinations of operating conditions must be screened (pHs, concentrations, coagulants etc.). Like membrane processes, several alternatives that address the material and time requirements of screening coagulation processes have been proposed in the literature. Technologies that have reduced the volume include coagulation screening in microwell plates^{70,71}, microfluidic devices⁷² and miniaturized mixing vessel⁷³. One such study has looked to reduce the experimentation time by introducing a novel spinning disc device, however, only one condition can be evaluated at a time⁷⁴.

1.3 Objectives and thesis outline

The goal of this thesis is to advance the adoption of membranes into "tough-totreat" applications, and do so by achieving two objectives. The first objective is to develop an understanding of how high strength industrial wastewaters with variable feed properties affect membrane processes by using state-of-the-art techniques to resolve the compositions of influents and effluents of membrane processes. The second objective is to develop an HTS tool that enables the rapid design and optimization of integrated membrane processes

Chapter 2 investigates the application of four commercially available nanofiltration membranes in the treatment of time-varying multi-sourced industrial wastewaters. Three batches of wastewater were sourced from industrial wastewater treatment plant that collects, blends and treats wastewater from various industries. As such, the influent properties vary daily depending on the volume and composition of the various wastewaters that are received. In this study, it was shown that batches with similar bulk properties (such as COD) have very different treatment efficacies when treated with these membranes. Gas chromatography-mass spectrometry (GC-MS) was used to fingerprint the composition of the membrane influents and effluents, and show that different compounds have different selectivity when filtered, and the overall removal was heavily dependent on the composition.

Chapter 3 investigates the application of nanofiltration membranes as a polishing treatment technology at the back end of a MBR that is treating dewatered digestate stream. Two batches of MBR permeate were sourced from a biogas generation facility

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and treated using three commercial nanofiltration membrane. This chapter investigated the trade-off between permeate recovery and quality that was observed across the three membrane processes, and investigated how the difference in upstream conditions (namely the concentration of ammonia) affected the removal performance of a downstream membrane process.

Chapter 4 aimed to demonstrate the use of analytical centrifugation as a viable HTS tool for rapidly developing and optimizing coagulation processes. Jar testing is an inefficient and material intensive coagulant screening tool, and current alternatives have either increased the throughput or reduced the material requirement for screening. Analytical centrifuges assess the stability of solutions by measuring the transmission of near-infrared light along a sample. Through this technology is primarily used for assessing the stability of formulated solutions in industries such as personal care products, paints, and food items, we demonstrated that this technology can be used to approximate the colloid stability of coagulated wastewater systems through an optics-based measurement. In this chapter, we use the AC to optimize the coagulation treatment solution conditions (pH and coagulant dose) for a single batch of wastewater with a low material and time requirement. Additionally, we demonstrate how the stability measurements via the AC can be used to compare coagulants and make process adjustments when faced with feed variations.

Chapter 5 builds upon the work presented in chapter 4 by using an analytical centrifuge to optimize a coagulation-flocculation pretreatment process prior to a downstream nanofiltration. Previous studies have shown that controlling the zeta-

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potential is important when selecting coagulant dosages prior to membrane filtration. However, zeta-potential measurements are not accurate for industrial wastewaters that have a high salt concentration. In this chapter, the liquid fraction of dewatered digestate was pretreated via coagulation-flocculation, and an AC was used to select three coagulant dosages based on measurements of instability index (undertreatment dose, a dose at the critical coagulant concentration, and an overdose). The selected doses were then used to pretreat a large volume of wastewater at each condition (10 L+) and filtered using a SEPA cross flow filtration cell fitted with a commercial nanofiltration membrane. The filtration results highlighted the importance of controlling the coagulant dose based on colloid stability, and the AC provides a viable method to achieve this for high salinity wastewaters.

Chapter 6 introduces a HTMS pipeline that screens integrated two-stage coagulation filtration processes in unison. This fills an important gap in the literature as current studies that are either developing or optimizing integrated coagulation-filtration screening processes often resort to slow and material intensive jar testing and bench-scale membrane equipment. Though several combinations of design considerations exist for both coagulation (e.g. pH, coagulant type, concentration) and filtration (e.g. membrane material, operating pressure) processes, the use of conventional screening technology limits the scope of the combinations of variables that can be tested. In this chapter a screening pipeline that combines analytical centrifugation for coagulant screening, and filter plate technology for membrane screening, was developed to screen both processes in unison. Additionally, elements of 'next generation' screening technologies were

adopted from the biomanufacturing industries by introducing elements of *miniaturization* (performing coagulation experiments and filtration experiments in microwell plates), *automation* (using a liquid handling system to perform all liquid transfer tasks), and rapid measurement techniques (using rapid absorbance-based techniques). In all, 648 combinations of coagulation-filtration experiments where six coagulants were screened at all combinations of nine concentrations and four pHs, with a AcroPrep filter plate fitted with 30K Omega ultrafiltration membranes.

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Chapter 2

Treatment of complex multi-sourced industrial wastewater—New opportunities for nanofiltration membranes

Chapter 2 Treatment of complex multi-sourced industrial wastewater—New opportunities for nanofiltration membrane

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Published work at the Chemical Engineering Research and Design journal. Reprinted with permission. Copyright© Elsevier 2021 https://doi.org/10.1016/j.cherd.2021.01.005

2.1 Abstract

Restrictions on the volume of organics discharged from industrial wastewater treatment plants has created an impetus to implement nanofiltration (NF) membrane technology at these facilities. However, NF membranes are rated based on simple performance metrics (e.g. permeability and salt rejection), not their capacity to reject organic content. In this study, three industrial wastewater (IWW) samples with varying concentrations (measured via COD) and compositions (analyzed via gas chromatographymass spectrometry) were filtered using four commercial NF membranes (NF90, TS80, NFS and NFX). The NF90 membrane demonstrated the best COD removal, however compositional differences between samples significantly influenced the magnitude of COD reduction, the permeate flux performance during filtration, and the measured hydraulic permeability and salt rejection before and after filtration. To investigate this further, separate solutions of commonly occurring chemical compounds (benzyl alcohol, 2-phenyl ethanol, pentanoic acid) were made with equivalent COD concentrations and filtered through the NF90 and NFX membranes. The NF90 membrane demonstrated significantly better COD removal for all three solutions. It was found that the NFX membrane achieved an increase in permeate flux during constant pressure filtration which was attributed to a "solvent activation" phenomena. These results serve as 'proof-ofconcept' that commercial NF membranes can significantly reduce the COD concentration of IWW, however, performance metrics that encompass both bulk and compositional properties must be adopted and standardized.

2.2 Introduction

Membrane-based processes play an integral role in the treatment of wastewater that is generated from a variety of industrial sources. It is anticipated that forthcoming stricter regulations related to environmental discharge standards will create an even greater demand for the usage of membrane-based processes. For example, the Canadian government has approved a new set of Wastewater Systems Effluent Regulations (WSER) that set stricter discharge limits for the facilities that treat and discharge over 150 billion liters of wastewater each year ¹. Industrial wastewater (IWW) will typically contain detectable amounts of organic compounds (e.g. glycols) with the possibility of very complex compositions depending on the exact industrial source ². Often the levels of these compounds, which is normally quantified using bulk property measurements such as chemical oxygen demand (COD), will preclude the use of biological treatment processes due to the associated toxicity and thus facilities rely on an assortment of physico-chemical techniques such as coagulation-flocculation, sand filtration, and activated carbon adsorption^{3, 4}. The use of pressure-driven membrane processes as a "polishing" step in the treatment of IWW is a promising strategy for facilities to meet the requirements of new effluent discharge standards ⁵.

Nanofiltration (NF) membranes were originally developed as a low-pressure alternative to reverse osmosis membranes for water softening applications ^{6, 7}. The overall performance of NF membranes is governed by the thin 'active layer' of polymer (typically polyamide) that is generated through interfacial polymerization, specifically a polycondensation reaction^{8, 9, 10}. The mechanism for organic solute and solvent transport through NF membranes is rather complex due to the combined effects of convection due to transmembrane pressure gradients, diffusion due to concentration gradients, and electrostatic repulsion effects^{11, 12}. Given the complex composition of IWW, it is very challenging to predict the treatment performance for a given NF membrane because the membrane manufacturers only report a few simple performance metrics, namely the permeability of water, rejection of common salts (typically sodium chloride and magnesium sulfate), and molecular weight cut-off (MWCO). The typical MWCO value for commercial NF membranes is the range of 200 to 500 Da, however the manufacturers provide no details on how these values were determined. Previous studies have shown that MWCO values are not well correlated with the removal of organic compounds ^{13, 14}; the transport of organic compounds through NF membranes is much more complex given the dependence on multiple properties including charge, hydrophobicity, and ionization constant ^{11, 15}. Furthermore, it is possible that certain chemical compounds present in IWW may swell the active layer of NF membranes and cause a permanent change in its structure in a similar manner to that reported for reverse osmosis membranes ^{16, 17, 18}. Understanding those effects that may occur simultaneously along with the more well known effects of membrane fouling is a challenge ^{19, 20, 21}.

In this study, we evaluated the performance of four commercial NF membranes as a "polishing" step for three IWWs of complex composition that were obtained from a specialized IWW treatment facility that receives daily deliveries of IWW that is generated from a variety of different industries. Thus, the composition of the incoming IWW varies considerably and yet the effluent from the facility must be continuously below the discharge standards for the local municipality. While there have been numerous studies that examined the use of NF membranes for treatment of IWW from a single source, to the best of our knowledge, there are no published studies related to this particular application of membrane technologies. Our comprehensive comparison included membrane productivity (via permeate flux measurements in constant pressure filtration), treatment efficacy (via COD rejection measurements), and membrane stability (via changes in salt rejection after the wastewater filtration test). In order to obtain detailed quantitative information on the composition of each IWW and the relative performance of each NF membrane in terms of rejection of specific chemical compounds, we analyzed the feed and permeate samples using gas chromatography-mass spectrometry (GC-MS); previous studies have a used a similar approach for the evaluation of treatment performance for other applications ^{22, 23, 24}. Based on the emerging trend towards use of NF membranes in so-called 'tough-to-treat' applications, it is our opinion that new performance metrics need to be adopted and standardized across industries and that the outcomes from this study lay the groundwork for that development.

2.3 Materials & Methods

NFS

NFX

2.3.1 Nanofiltration Membranes

Four commercially available flat-sheet polyamide NF membranes were purchased in large sheets and then precisely cut to fit within the bench-scale crossflow SEPA cell (Sterlitech). A summary of the membrane characteristics, as provided by the manufacturers, is presented in Table 2.1. These membranes were selected based on their previous and promising application in industrial settings – particularly for treatment processes involving a single-sourced wastewater (i.e. textile wastewater). The primary purpose of these membranes is for monovalent and divalent salt removal, however with niche industrial applications as stated by their respective manufacturers. For example, the NF90 can be used for nitrate, iron, and some organic molecule removal. Similarly, the NFS membrane is specialized for sulfate removal from flood injection wastewater produced by the oil and gas industry, while the NFX is rated for several industrial applications ranging from lactose demineralization to textile dye concentration. Finally, the TS80 membrane developed by Microdyn-Nadir can be used for the removal of uncharged organic solutes from wastewater.

	Mombrono ID	Membrane	Dated MWCO	Rated MgSO ₄	Rated NaCl
	Memorane ID	Manufacturer	Kaleu MWCO	Rejection	Rejection
	NF90	Dupont	200 – 400 Da	99.0%	90.0%
	TS80	Microdyn-Nadir	~150 Da	98.5 - 99.2%	80.0%

100 - 250 Da

150 - 300 Da

99.5%

99.0%

50.0 - 55.0%

40.0%

Table 2.1. Properties of NF membranes as provided by the manufacturers.

Synder

Synder

2.3.2 Bench-scale crossflow filtration system

A schematic of the filtration system used in this study is presented in Figure 2.1. A more detailed schematic which includes a "clean-in-place" tank, pressure gauges, pressure relief valves, and the rotameters used in the system is presented in Figure A.2 of the Supplemental Materials. In regular operation, a fluid (tap water, cleaning solution, wastewater etc.) is placed into the feed tank (T01) and pressurized using a Hydracell M03-S positive displacement pump (P01) then sent to the bench-scale crossflow SEPA cell (filtration area of 140 cm²). The concentrate and permeate are recycled back into the feed tank, with permeate samples collected periodically through a sampling port (V04). During filtration, the bypass valve (V02) was closed, the feed control valve (V01) was fully opened, and the trans-membrane pressure (TMP) was manually controlled to the desired fixed value using the concentrate control valve (V03). The three pressure gauges PG01, PG02, and PG03 were used to record the feed pressure, P_F , the concentrate pressure, P_C , and the permeate pressure, P_P , respectively; the TMP pressure was calculated from those recordings according to Equation (2.1).

$$P_{\rm TMP} = \frac{P_{\rm F} + P_{\rm C}}{2} - P_{\rm P} \tag{2.1}$$



Figure 2.1. Schematic of the bench-scale crossflow filtration system used in this study – see text for details and descriptions of the system components.

2.3.3 Membrane performance testing

Three IWW samples were acquired from a treatment facility that receives WW from approximately 100 different clients from chemical, food, automotive, and other industries. The samples been 'pretreated' using various physico-chemical processes (e.g. flocculation-coagulation, hydrogen peroxide with aeration, sand filtration) and were collected over a period of approximately three weeks to ensure diversity in their composition. In our lab, the samples were filtered using 0.45-micron filters (Whatman) and then analyzed to determine their respective COD, pH, and conductivity values. The COD was measured using the Hach 'high-range' COD testing kits according to the supplier's instructions. The pH and conductivity were measured using an HI5522 pH/conductivity meter (Hanna Instruments). Since the IWW is sampled at the end of the

existing process, it should be noted that there is virtually no suspended solids in the wastewater and the pH of wastewater is close to neutral (7.0 ± 0.2) due to pH adjustments made during the process. Table 2.2. shows the average measured COD and conductivity of each wastewater.

Table 2.2. Measured feed parameters of the wastewaters studied in this investigation. Average values and standard deviations for each parameter are based on 8 measurements for Wastewater A and 16 measurements for Wastewaters B & C.

Wastewater ID	COD (mg/L)	Conductivity (µS/cm)
А	1212 ± 92	4681 ± 275
В	2624 ± 144	1423 ± 32
С	2694 ± 83	1602 ± 84

To complement the testing done with the three real IWW samples, a select number of solutions containing just one chemical found in the IWW samples were created. The three compounds selected for this study were benzyl alcohol (>97.0%, VWR), 2-phenyl ethanol (>98.0%, TCI America), and pentanoic acid (>98.0%, TCI America). The theoretical oxygen demand (ThOD) was calculated for each compound to determine the mass required to make the required amount of solution in deionized water with an approximate COD of 1333-mg/L. After thoroughly mixing the solution, the actual COD was measured using the same Hach testing kits.

The hydraulic permeability of each NF membrane was measured before and after each filtration test. The permeate flux (J) of regular tap water through the membrane was determined via timed collection at transmembrane pressures (TMP) ranging from 4.14 bar

(60 psi) to 9.65 bar (140 psi) in approximate increments of 1.38 bar (20 psi). According to Equation (2.2), the permeability of the membrane was determined by conducting an ANOVA regression analysis of average permeate flux versus TMP.

$$L_P = \frac{J}{P_{\rm TMP}} \tag{2.2}$$

The salt rejection properties of each NF membrane were also measured before and after each filtration test. Solutions of either sodium chloride (99.5%+, Fisher Scientific) or magnesium sulfate heptahydrate (99.4%, Fisher Scientific) were prepared at concentrations of 2000 mg/L and then filtered in a crossflow configuration with constant recirculation for 30 minutes at a constant TMP of 7.58 bar (110 psi). The pressure and solute concentrations were selected based on manufacturer recommendations. After 30 minutes of filtration with recirculation, three feed and permeate samples were collected. The concentration of salt in those samples was determined from conductivity measurements (HI5522 pH/conductivity meter) and a wide-range calibration curve. Salt rejection values were determined via Equation (2.3):

$$R(\%) = \frac{c_f - c_p}{c_f} \times 100$$
(2.3)

where C_f and C_p are the average salt concentrations in the feed and permeate samples.

The wastewater was filtered through each membrane in a crossflow configuration at a constant TMP of 6.89 bar (100 psi). The wastewater was initially allowed to filter through the membrane with complete recirculation for 20 minutes; based on our preliminary work (results not shown) it was found that was sufficient time to reach steady
state conditions. Next, the permeate was collected in a non-recycle operation over a 2hour period with the permeate flux recorded every 20 minutes by measuring the time to filter 2-ml of permeate, with five measurements taken at each time interval. The normalized permeate flux was calculated via Equation (2.4) to compare the permeate flux at a given time (J_T) to the initial permeate flux (J_0).

$$J_{norm,T} = \frac{J_T}{J_0} \tag{2.4}$$

Two samples of the feed were collected at the start (t = 0) and end (t = 120) of the filtration period. COD measurements of the feed and permeate samples were used to calculate the COD percentage rejection according to Equation (2.5).

$$R_{COD}(\%) = \frac{(COD_{Feed} - COD_{Permeate})}{COD_{Feed}} \times 100$$
(2.5)

2.3.4 Gas chromatography-mass spectrometry analysis

The as-received samples of IWW and collected samples from the NF filtration experiments were analyzed as described below. Firstly, a 100 mL aliquot of each sample was acidified with ~2 mL of 1.0M hydrochloric acid (96.41%, LabChem) to reduce the pH to approximately 2.0. The solution was then placed into a separatory funnel along with 100 ml of ACS-grade dichloromethane (99.5%+, VWR) and continuously mixed through vigorous shaking for 3 minutes. After mixing, the organic-rich solvent phase at the bottom of the two-phase mixture was separated and filtered using ~5g of anhydrous sodium sulfate (99.1%, Fisher Chemical) to dehydrate the DCM layer. The solvent phase was then concentrated to a volume of 5-10 mL using a vacuum rotary evaporator with a

water bath set to 40°C (boiling point of DCM). Next, the solvent phase was further concentrated to 2 mL via nitrogen purging; that method allowed for better control of the final volume. Following concentration, it was necessary to perform chemical derivatization on the organic compounds that were extracted from the wastewater. The purpose of chemical derivatization is to facilitate separation in the GC column by reducing functional group polarities through trimethylsilylation, which entails replacing the functional group with a trimethylsilyl group ²⁵. To this end, a 25 µL aliquot of the pase was mixed with 25 µL of N-methyl-N-(trimethylsilyl)trifluoroacetamide solvent (MSTFA) (>98.5%, Sigma Aldrich) containing 1% chlorotrimethylsilane (TCMS) (>99.0%, Sigma Aldrich) in a 2 ml glass insert. The TCMS was added to the MSTFA solution to serve as a catalyst for the derivatization reaction, while a 25 µL aliquot of 18.8 ng/mL solution of 9-anthracene methanol (97%, Sigma Aldrich) was added to the glass insert as an internal standard. The insert containing the mixture was then placed into a sealed glass vial and vortexed for several seconds to ensure adequate mixing before being placed into an oven set to 80°C for one hour to allow the derivatization reaction to take place.

Following the derivatization step, a 1 μ L aliquot of each sample was passed through a 6890N gas chromatograph (Agilent) with a DB-17hT column (30m × 0.25 mm ID × 0.15 um film thickness). The mobile phase was transferred through the column by injecting helium carrier gas at a flow rate of 1.1 mL/s. The initial column temperature was set to 50°C, was increased to 300°C with an 8°C ramp. The column was then held at 300°C for 15 minutes, resulting in a total run time of 46.25 minutes. The integrated quadrupole mass-spectrometer analyzed each compound with a mass-to-charge (m/z) ratio of 50 to 800. Bruker Data Analysis 4.1 was used to analyze the GC-MS results with appropriate single-to-noise ratios being selected. Those peaks were subsequently analyzed using Automated Mass Spectral and Deconvolution Identification System (AMDIS) with mass-spectral data cross-referenced using a compound library. Matches were determined based on the R.MATCH probability values and visual comparisons for the characterized and library compounds, with R.MATCH values greater than 800 being considered good matches.

2.4 Results & Discussion

2.4.1 Comparison of NF membrane performance with real industrial wastewaters

The COD measurements of permeate samples and normalized permeate flux profiles over the two-hour filtration period for the four NF membranes with the three IWWs are presented in Figure 2.2. The filtration tests performed using Wastewater A and B resulted in high-quality permeate for all four NF membranes; the COD rejection for all eight combination of experimental conditions was greater than 85%. Notably, for Wastewater B there was no statistical difference between the COD values for the permeate samples obtained for each NF membrane based on overlapping standard deviation error values across replicate measurements. Overall, these results match those from previous studies of NF-based treatment of single-source IWW. For example, Lau, Ismail, and Fridaus were able to achieve similar levels of COD reduction with different NF membranes to treat car wash wastewater ²⁶. In addition, Galambos et al. reported a significant reduction in the COD of two wastewaters sourced from the food processing

industry using a commercial NF membrane (NF200) ²⁷. The filtration tests performed using Wastewater C and three NF membranes (TS80, NFS, NFX) yielded lower quality permeate samples with COD rejections ranging between $54 \pm 5\%$ for the NFS membrane and 75% +/- 1% for the TS80 membrane. The exact cause for these differences is not known, but our working hypothesis is that it is due to differences in the type of additives that are used during the manufacturing of the NF membranes. A simple comparison of the results for Wastewater B and C indicates that the wastewater composition is an important factor in the filtration performance. Previous studies with single-source wastewater have shown that COD rejection is only marginally impacted by variations in feed COD concentrations ²⁸ ²⁹. Interestingly, the COD rejection value for the NF90 membrane and Wastewater C was not significantly different than the corresponding value for Wastewater B. Thus, within the limitations of this study, the NF90 membrane was the most robust in terms of COD rejection.

The normalized permeate flux over the two-hour filtration period was also found to depend on the NF membrane and the wastewater source. For example, while there was no significant variation in the permeate flux profile of the NFX membrane during the tests with Wastewaters B and C, the permeate flux steadily decreased to 79 ± 4 % of its initial value after 120 minutes of exposure to Wastewater A. Conversely, the NF90 membrane had only a slight reduction in permeate flux (less than 10%) when exposed to Wastewaters A and C, but a steady decrease to 72 ± 4 % of the original flux following exposure to Wastewater B. The summary of results shown in Figure 2 suggests that both the COD rejection and permeate flux behavior of a NF membrane depend on its specific

interactions with the organic compounds present in the IWW. Our observations are supported by those of Hong and Elimelech who found a strong relationship between membrane permeate flux behavior and chemical composition of the wastewater ³⁰. Additionally, membrane surface charge during filtration significantly affects both removal and flux performance. For this study, the pH of all three wastewaters was ~7.0, while the isoelectric point for most NF membranes (the pH at which the surface charge on the membrane changes from being negatively to positively charged) is typically between 3.5 -4.5^{31} ³². Therefore, pore blocking due to organic fouling is most likely due to the attachment of organic molecules that exhibit a positive charge at a neutral pH ³³. As such, the membrane surface charge during the filtration of all three of these solutions was negatively charged. With this collective knowledge, it is apparent that the typical performance metrics that are provided by NF membrane manufacturers (namely water permeability and salt rejection) are wholly insufficient for the design of membrane-based treatment processes for IWW. Also, bulk measurements of the organic content of IWW such as COD are not well correlated with treatment efficacy. Thus, it is critically necessary to use sophisticated analytical tools to relate the composition of IWW and treatment efficacy.



Figure 2.2. Top Panel: The average feed (**■**) and permeate (**■**) COD (N = 2) for each of the four NF membranes and three IWW samples. Bottom Panel: The normalized permeate flux profiles for the four NF membranes between t_0 and t_{120} for each IWW sample; standard deviation error bars are shown for each permeate flux measurement (N = 5).

A comparison of the GC-MS chromatograms for the three IWW samples is shown in Figure A.1 (in the Supplemental Materials). It is apparent that there is good diversity with respect to composition and concentration for the three samples that were obtained from the one specialized treatment facility. For example, only Wastewater B contained a significant amount of dodecanol (peak with retention time ~11.8 min) and only Wastewater C contained a significant amount of benzoic acid (peak with retention time ~8.9 min).

As shown in Figure 2.3, the chemical compounds that were present in Wastewater A and could be identified based on mass spectra analysis were mostly organic acids, namely: 2-ethylhexanoic acid (5.2 min), ethandioc acid (5.7 min), nonanoic acid (7.0 min), decanoic acid (7.2 min), phosphonic acid (12.7 min), hexadecanoic acid (18.4 min), octadecanoic acid (20.5 min), and 1,2-benzenedicarboxylic acid (25.7 min). The GC-MS chromatograms for the corresponding permeate samples obtained with the four NF membranes were fairly similar to one another, but quite different from that for the feed sample. All the permeate samples contained no peaks with retention times between 9 and 18 minutes; unfortunately, due to limitations of the database, it was not possible to identify all of the compounds that were effectively rejected by the NF membranes. The chemical compounds that were present in the permeate samples (thus contributing to the respective COD values shown in Figure 2.2) mostly had retention times between either 5 and 9 minutes or 18 and 28 minutes; note that the one peak that appears at 22.9 minutes is the internal standard (9-anthracene methanol) that was added to all the samples during the derivatization step. The most obvious differences between the chromatograms of the permeate samples are seen in the sizes of the two peaks with retention times of 26.2 min and 27.3 min. Our results would suggest that the two compounds associated with those two peaks could be used in a new performance standard to compare the treatment efficacy of NF membranes for IWW applications.



Figure 2.3. GC-MS chromatograms for Wastewater A and the permeate samples from testing with four NF membranes. Peak intensities for retention times between 0 and 45 minutes, and compounds characterized via MS and their respective retention times are shown.

As shown in Figure 2.4, the chemical compounds identified by the GC-MS analysis of Wastewater B were fewer in number but higher in concentration to those found in Wastewater A; note that the y-axis scale of Figure 2.4 is much larger than that for Figure 2.3. It appears that most of the COD reading for Wastewater B is attributed to the presence of dodecanol (retention time ~11.8 min), a fatty acid which, as mentioned above, did not appear in an appreciable amount in either Wastewater A or C. The GC-MS chromatograms for the permeate samples from the NF membrane tests displayed far fewer and mostly smaller peaks than the feed sample. Also, while dodecanol was effectively rejected by all four NF membranes, there was a considerable amount of ethylene glycol butyl ether remaining in the permeate for all four NF membranes.



Figure 2.4 GC-MS chromatograms for Wastewater B and the permeate samples from testing with four NF membranes. Peak intensities for retention times between 0 and 45 minutes, and compounds characterized via MS and their respective retention times are shown.

As shown in Figure 2.5, the GC-MS analysis of Wastewater C identified many compounds at much lower concentrations than those shown in Figure 4 for Wastewater B. It is particularly interesting to make this comparison because these two samples had statistically identical COD values (2624 ± 144 and 2694 ± 83) and thus we can now better appreciate the large differences in COD rejection efficacy (for the same membrane) that were shown in Figure 2.2. The chemical compound with the largest peak intensity was benzoic acid (retention time ~8.9 min) which, as mentioned above, did not appear in an appreciable amount in either Wastewater A or B. The GC-MS chromatograms for the permeate samples show that all of the chemical compounds with retention times between 12 and 25 min were essentially completely rejected by all four NF membranes; this would include sebacic acid (17.3 min), hexadecanoic acid (18.4 min), and dodecanoic acid (19.5 min). However, the permeate samples were found to contain certain chemicals with lower retention times including ethylene glycol butyl ether in agreement with the results shown in Figure 2.4 for Wastewater B. This finding in particular suggests that the lower

overall COD rejection observed in Wastewater C was due to the presence of more lower molecular weight compounds that constitute the COD of 2694 ± 83 mg/L, as compared to wastewaters A and B. Unfortunately, we were not able to confidently identify the two chemical compounds with retention times just below and above 12 min that appeared in all of the permeate samples. Also, there were significant variations in the peak intensities for certain chemical compounds. For example, the order of peak intensity for nonanoic acid (retention time \sim 7.0 min) was NFS > NFX > NF90 ~ TS80. This observation would also suggest that nonanoic acid could be used in a new performance standard to compare the treatment efficacy of NF membranes for IWW applications. Interestingly, as shown in Figure 2.2, there was a similar ordering to the permeate COD values for Wastewater C. For this particular IWW sample, it is interesting to note that better removal of benzoic acid (MW = 122.12 g/mol) was observed when compared to nonanoic acid (158.23g/mol), particularly with the NFX and NFS membranes. These results are in good agreement with those from previous studies that reported no correlation between the rejection of chemical compounds and MWCO values ^{13, 14}.



Figure 2.5. GC-MS chromatograms for Wastewater C and the permeate samples from testing with four NF membranes. Peak intensities for retention times between 0 and 45 minutes, and compounds characterized via. MS and their respective retention times are shown.

2.4.2 Evaluation of nanofiltration membrane integrity and stability

Based on the experimental results presented in Figure 2.2, we felt it was judicious to monitor for any changes in the performance of the polymeric NF membranes following their exposure to the complex composition of chemicals in the IWW samples used in this study. A comparison of the pre-exposure and post-exposure measurements for hydraulic permeability, sodium chloride rejection, and magnesium chloride rejection are presented in Figure 2.6. The three columns of results correspond to the three IWW samples.

As shown in the top panels of Figure 2.6, there was some variability in the pre-exposure hydraulic permeability values for all four NF membranes; this is likely attributed to variations in the membrane pore structure across the large sheets (approximately 1 m²) that were procured from each manufacturer ³⁴. The most extreme variation was found for the TS80 membrane for which the one cut segment that was fit within the bench-scale crossflow SEPA cell had an initial hydraulic permeability of 7.5 \pm 2.2 LMH/bar (for filtration test with Wastewater A) while another cut segment had an

initial hydraulic permeability of 13.5 ± 1.4 LMH/bar (for filtration test with Wastewater C). Despite these variations we observed recurring trends in the relative changes in hydraulic permeability. For instance, the NF90 and TS80 membranes displayed the highest percentage decline in hydraulic permeability regardless of which IWW was used for the filtration test. These results are in good agreement with the declining permeate flux profiles shown in Figure 2.2. Conversely, the NFS and NFX membranes displayed no change in hydraulic permeability and for a few of the filtration tests, the hydraulic permeability was slightly higher in the post-exposure test. This trend of decreasing post-wastewater permeability that is observed for the NF90 and TS80 membranes is correlated well with the improved COD rejection that is also observed with these membranes. A denser and tighter pore structure on the NF90 and TS80 membranes allowed for improved rejection, but at the expense of greater membrane fouling.

As shown in the middle panels of Figure 2.6, there was negligible variation in the pre-exposure sodium chloride rejection across the different segments that were cut from the same membrane sheet. However, the variation between different NF membranes was quite significant. Notably, the order of NF membranes in terms of measured values of sodium chloride rejection (i.e. NF90 > TS80 > NFS > NFX) is in perfect agreement with the values reported in Table 2.1 by the respective manufacturers. It was much more difficult to identify trends in the post-exposure sodium chloride rejection values. For example, there was a significant decrease in rejection for the TS80 membrane following the filtration of Wastewaters A and C, but an increase was observed following filtration with Wastewater B. This outcome is likely due to swelling of the NF membrane upon

exposure to the particular chemical compounds in Wastewater B¹⁷. There was no significant change in sodium chloride rejection following exposure to the IWW samples for the NFS membrane. This observation in combination with the hydraulic permeability results outlined above indicates that the NFS membrane displayed the greatest performance 'stability' upon exposure to the IWW samples used in this study. Further studies using longer exposure times and IWW of different compositions should be conducted to confirm these results. As shown in the bottom panels of Figure 2.6, the preexposure magnesium sulfate rejection values of all four NF membranes were well below the manufacturers reported values of 99% and 99.5% (see Table 2.1). Again, we observed slight variations across the different segments that were cut from the same membrane sheet. Only for the NFX membrane did all three segments have magnesium sulfate rejection values less than 90%. In general, the relative changes in magnesium sulfate rejection following exposure to the IWW samples were well correlated with the sodium chloride rejection results. The one anomaly was for the TS80 membrane and Wastewater C.



Figure 2.6. Effect of wastewater filtration on permeability, sodium chloride rejection, and magnesium sulfate rejection. Top Panel: Measured permeability before (**■**) and after (**■**) exposure to the three wastewater samples. Permeability was determined by conducting an ANOVA analysis on clean water permeate flux measurements taken between 4.14 bar and 9.65 bar; the error bars correspond to a 95% confidence interval around the permeability. Middle Panel: Rejection of 2000 mg/L (w/v) sodium chloride before (**■**) and after (**■**) filtration. Standard deviation error bars are shown based on triplicate (N = 3) measurements of the feed and permeate samples. Bottom Panel: Rejection of 2000 mg/L (w/v) magnesium sulfate before (**■**) and after (**■**) filtration with the three W. Standard deviation error bars are shown based on triplicate (N = 3) measurements of the feed and permeate samples.

2.4.3 Comparison of nanofiltration performance with single component solutions

Based on the collection of results presented in Sections 3.1 and 3.2, it is readily apparent that the complex composition of IWW can significantly affect the filtration performance of NF membranes particularly with respect to COD rejection and permeate flux. The origin and complexity of the three IWW samples used in this study makes the work very practical, but also presents a challenge in identifying the specific interactions that may occur between individual chemical compounds and polymeric NF membranes. Thus, for the final part of this study we selected three chemicals to use in another set of filtration experiments: benzyl alcohol, 2-phenyl ethanol, and pentanoic acid; see Table 2.3 for the properties of the solutions prepared with each chemical. All three were found present in a multiple number of IWW samples from the same specialized treatment facility (see Figure A.3 in Supplemental Materials). Benzyl alcohol was selected for two reasons: first, it was found to be present in a majority of the IWW samples that were analyzed by GC-MS; second, it has been reported that benzyl alcohol can affect the filtration performance of polyamide-based reverse osmosis membranes ¹⁶. 2-phenyl ethanol was selected because it has a similar structure to benzyl alcohol but different polarity. Pentanoic acid (also known as valeric acid) was selected because it was one of the more commonly occurring acidic components in the IWW samples.

Figure 2.7. Measured feed parameters of each single component solution. Each solvent makes a different contribution to COD; thus, each solvent has a different mass concentration. Average values and standard deviation errors for each parameter are based on 16 measurements.

Solution	COD (mg/L)	Mass Concentration (mg/L)	рН	Conductivity (µS/cm)
Benzyl	1329 ± 60	530	6.9 ± 0.4	82 ± 62
Alcohol				
2-Phenyl	1278 ± 86	560	7.1 ± 0.3	15 ± 6
Ethanol				
Pentanoic	1330 ± 107	509	4.0 ± 0.1	105 ± 17
Acid				

Only the NF90 and NFX membranes were selected for this part of the study and since we were not limited by the available volume of wastewater, two runs were carried out on different segments from the same membrane sheet. As shown in Figure 2.7, there was a dramatic difference between the two NF membranes in terms of the rejection of each individual chemical compound. Indeed, the NFX membrane failed to reduce the COD of any solution to below 1000 mg/L, with the highest percentage removal found for the pentanoic acid solution ($15 \pm 2\%$). In contrast, at the same experimental conditions, the NF90 membrane had a percentage reduction approximately 4 times higher than the NFX membrane. The overall better rejection performance observed by the NF90 can be attributed to the tighter pore structure on the membrane, which allowed better removal of each of the three compounds as compared to the NFX membrane. The percentage rejection varied for the three chemicals with the highest rejection $(78 \pm 1\%)$ obtained for the 2-phenyl ethanol solution. These results complement the key findings from the GC-MS analyses presented in Section 3.2. Firstly, these results also reflect the membrane-tomembrane variation in the removal of specific compounds, such as the removal of

ethylene glycol butyl ether in Wastewaters B and C. Secondly, different levels of rejection for certain compounds were observed across all membranes, the clearest example of which being the rejection differences between ethylene glycol butyl ether and dodecanol. The preferential removal of 2-phenyl ethanol over benzyl alcohol confirms that variability in the removal of individual compounds is due to specific interactions between the compound and the membrane. It has been shown that hydrogen bonding effects determine the rejection of phenol by polymeric membranes ³⁵. Also, it has been shown that the filtration of phenolic compounds resulted in higher rejections for NF90 over other NF membranes ³⁶. Studies have shown that pH is also an important factor in determining rejection, as acidic solutes have a higher affinity to the membrane surface and therefore low rejections, as observed in our results. When the pH of the solution is lower than the pKa of the acid, the cationic behavior of the acid leads to low rejections ³⁷. This specifically affects the rejection of pentanoic acid, as the reported pKa of pentanoic acid is 4.81. This is lower than the pH of the solution that was tested. Once again, the NF90's superior rejection can be attributed to its tighter MWCO, which would lead to higher rejection via sieving. Nonetheless, the literature suggests that higher rejections could have been attained for both membranes by adjusting the pH of the solution.

The permeate flux profiles for both NF membranes (see Figure A.4) showed a slight difference in that the NFX membrane exhibited a small, but significant increase in permeate flux over the course of the 2 hour filtration test; the greatest effect (10% increase) was observed for the pentanoic acid solution. Given that the3re was no statistical change in permeate flux during filtration of tap water (results not shown), it is

believed that this effect is due to specific chemical-membrane interactions. Previous studies have reported on the phenomena of 'solvent activation' of reverse osmosis membranes during the filtration of solutions containing benzyl alcohol ¹⁶ and dimethylformamide ¹⁸ through a combination of pore opening and swelling mechanisms. Previous studies on this topic have shown that exposing a polyamide membrane to an "activating solvent" such as dimethylformamide or benzyl alcohol will produce a "healing effect" that increases the membrane's permeance without adversely affecting its rejection properties. The proposed theory suggests that this effect is induced via two separate mechanisms. Firstly, dissolution of small polyamide fragments that block the pores of the membrane result in an increase in water permeance. Secondly, an increase in rejection properties is observed due to swelling-induced compaction effects.

Our results suggest that the action of certain chemicals in the IWW samples can induce a similar 'activation' effect with the NFX membrane. Previous studies on the nanofiltration of water-alcohol and water-acid binary mixtures have made observations like those made in this study. For example, Geens et al. found that, in the filtration of water-alcohol mixtures using hydrophilic membranes, the less polar compound has a significant influence on the permeability of the more polar compound, causing it to increase when the polarity difference between the two is large enough ³⁸. Importantly, solvent activation effects have been shown to not affect the salt rejection properties of reverse osmosis membranes. Our results from sodium chloride and magnesium sulfate rejections tests (see Figure A.5) are consistent with the literature results.



Figure 2.8. Average COD rejection observed for NF90 (\blacksquare) and NFX (\blacksquare) observed for three single-component solutions with approximate COD concentrations of ~1333 mg-O₂/L. The average rejection was calculated for two separate filtration experiments for each membrane and solution, with duplicate measurements taken for the feed and permeate samples. Standard deviation error bars are shown for each calculated rejection.

2.5 Conclusions

Four commercially available NF membranes (NF90 [Dupont], TS80 [Microdyn-Nadir], NFX [Synder], and NFS [Synder]) were used to filter three samples of multisourced IWW to evaluate their COD-reduction ability. The three IWW samples varied in both concentration (as measured through COD) and composition (as analyzed through GC-MS). COD reduction was dependent on which membrane was used (the NF90 and TS80 membranes consistently produced a permeate with lower COD concentrations than the NFX and NFS membranes) and the wastewater being filtered (greater COD reduction was achieved in the filtrations with Wastewaters A and B). GC-MS analysis of the feed and permeate samples showed variability in the concentration of each compound present in the IWW samples, as well as in the levels that were removed by filtration. For example, Wastewater B contained high concentrations of dodecanol and ethylene glycol butyl ether; while all four membranes completely removed dodecanol during filtration, ethylene glycol butyl ether rejection varied depending on the membrane that was used. Furthermore, changes in magnitude and direction (observed increase or decrease) in membrane permeability, monovalent (sodium chloride) and divalent (magnesium sulfate) salt rejection after filtration, as well as the flux behavior during filtration, varied based on the wastewater that was filtered. For instance, the permeate flux of the NFX membrane declined during filtration with Wastewater A, but remained relatively stable during filtration with Wastewaters B and C. Conversely, the permeate flux of the NF90 membrane declined during filtration with Wastewater B, yet remained stable during filtration with Wastewaters A and C.

To further investigate this finding, three compounds—benzyl alcohol, 2-phenyl ethanol, and pentatonic acid—were selected based on their recurrence in the characterized wastewater. Solutions with COD concentrations of ~1333 mg/L were prepared and filtered using the NF90 and NFX membranes. The NF90 membrane consistently produced a permeate with a lower COD concentration than the NFX membrane. The permeate flux behavior of the membranes during these tests demonstrated that exposure to these solvents induces an increase in permeate flux during filtration. Previous studies on "solvent activation" have shown that solvents are able to remove pore-blocking fragments on the membrane's surface, thereby increasing water permeance. This suggests

that solvents in IWW strongly influence the transport properties of compounds in the wastewater, and it confirms the results of the GC-MS analysis. Ultimately, the application of this technology for the treatment of multi-sourced IWW can yield varying results interms of rejection and permeate flux behavior, depending on the composition of the wastewater being filtered.

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Chapter 3

Development of a crossflow nanofiltration process for polishing of wastewater by-product from biogas production processes

Chapter 3 Development of a crossflow nanofiltration process for polishing of wastewater by-product from biogas production processes

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3.1 Abstract

The growing adoption of biogas production from source-separated organics has resulted in a need for advanced treatment processes for the resulting liquid waste byproducts. While previous studies have demonstrated the potential of using nanofiltration (NF) membranes to polish the outlet stream of a membrane bioreactor (MBR) in municipal wastewater applications, there is little known about the performance of such membranes to treat the more complicated streams that result from the processing of source separated organics. In this study, crossflow filtration experiments with three flatsheet NF membranes (NFS, NFX, NF90) were run on two batches of MBR permeate (identified as Batch A and Batch B) that were sourced four months apart from a biogas production facility. For each batch, there was a remarkable difference in performance of the three NF membranes with a clear trade-off between permeate quality and recovery. For example, the NF90 membrane gave the best permeate quality but the lowest recovery. Interestingly, the NFS permeate COD for Batch B was approximately 60% lower than that for Batch A; it is believed that this was due to differences in the amount of ammonia in the two batches. This work bridges a technical gap in the water-energy nexus by demonstrating the viability of using NF technology to polish liquid waste streams from biogas production processes, while highlighting their susceptibility to variable feed conditions caused by upstream process deviations.

3.2 Introduction

The production of methane-rich biogas from source separated organics (SSOs) in an anaerobic digestion (AD) facility is an emerging clean-tech solution to divert organic waste away from landfills^{1,2}. There are currently nearly 300 AD facilities throughout Canada, which collectively produce approximately 6 million gigajoules of energy each year. Notably, only nine of these facilities are equipped to process SSOs, despite a 50% increase in biogas facilities between 2011 and 2020³. The on-site treatment of waste, in particular the spent feedstock known as digestate, is a challenge for many facilities. Typically, facilities will 'dewater' the digestate into the respective solid and liquid fractions using process equipment such as screw presses and centrifuges⁴⁻⁶. The solid fraction is disposed via land-based applications (e.g., as fertilizer) in landfills or sometimes incinerated⁷. The liquid fraction (comprising up to 90% of the total mass of digestate) is either hauled away to a separate treatment facility or is treated on-site⁶. Over the past 30 years, membrane bioreactors (MBRs) have become a well-established water treatment technology that require minimal footprint while achieving water quality effluent that is free of pathogenic microorganisms. The vast majority of MBR facilities in operation treat municipal wastewater, however MBR technology is seeing rapid adoption in industrial treatment applications such as for wastewaters sourced from tanneries, pulp and paper production, textile dyeing, pharmaceutical production, and landfill leachate^{8,9}. The application of MBRs have also been extended to treating liquid fractions of anaerobic digestate, namely sourced from farm manure^{10,11}. In these particular MBR feed streams, the high concentrations of salts, natural organic matter (NOM), and nutrients demands the use of advanced 'polishing' treatment processes to achieve the increasingly stringent constraints on water quality discharge¹². For example, the Wastewater Systems Effluent Regulations in Canada established national standards for deleterious substances that are known to have environmental impacts (e.g. un-ionized ammonia has a discharge limit of 1.25 mg/L)¹³.

Nanofiltration (NF) membranes were developed as low-pressure alternatives to reverse osmosis membranes for water softening applications, however they have since been adopted for a wide array of challenging applications such as the treatment of 'high-strength' industrial wastewater that contain high contaminant concentrations ^{14–17}. Previous studies have shown that a combined MBR-NF process results in a better quality effluent than just an MBR for treating feeds from landfill leachate^{18–20}, dairy production ²¹, pharmaceutical production ²² and municipal wastewater facilities^{23,24}. These studies have shown that the addition of NF polishing greatly improves the quality of the process effluent, especially for reducing COD and NOM concentrations, however there are two shortcomings that remain unaddressed for applying a similar treatment process for treating MBR effluents from digestate sourced from municipal organic waste. First, the performance of NF membranes is source dependent as contaminant transport and removal is highly dependent on specific solute-membrane interactions^{25,26}. Therefore, two

wastewaters with similar bulk properties but different feed compositions may have completely different treatment efficacies, and studies using real MBR permeates sourced from an SSO processing facility are required to truly assess the treatment performance¹⁷. Second, studies using feeds with high NOM concentrations reported significant NF permeate flux declines due to membrane fouling. This outcome is undesirable as it results in higher operational costs due to the need for frequent cleaning cycles. As such, a fouling mitigation technique may be required to make an MBR-NF process more viable.

The present work aims to bridge these concepts by investigating a hybrid coagulation- NF process for polishing MBR permeate sourced from the liquid fraction of dewatered AD. The addition of an inorganic coagulant is an effective, low-cost method of removing NOM foulants prior to membrane filtration that has been shown to improve membrane productivity $(flux)^{27-31}$. To understand the true performance of NF in this application, three commercially available membranes were evaluated with two batches of MBR permeate with complex compositions that were sourced from a generation facility that produces biogas via anaerobic digestion of municipal SSO waste- we felt it was crucial to assess the treatment performance using actual MBR permeates rather than proxy solutions to avoid making inferences based on simple chemical mixtures³². Our study is divided into four areas of investigation: (1) characterization of the MBR permeate through bulk measurement techniques (i.e., COD) and more complex analytical techniques (i.e., LC-OCD); (2) high-throughput screening of a commercial coagulant in order to identify an operating point that maximizes NOM removal while maintaining a negative zeta-potential; (3) filtration experiments to assess membrane performance based on COD removal (permeate quality) and permeate recovery (membrane productivity), and (4) understand the influence of varying upstream feed properties on treatment efficacy by comparing the filtration performance of two batches.

3.3 Materials & Methods

3.3.1 MBR permeate sampling and characterization

Two batches of MBR permeate were sampled from a local SSO processing facility. Here, shipments of municipal SSO waste are pre-processed to remove non-organic material (mainly plastic bags), and fed into an anerobic digestor to produce biogas. Following digestion, the 'spent' digestate is dewatered using a centrifuge, and the liquid fraction is treated using an MBR, at which point samples of the MBR permeate can be taken. Both batches of MBR permeate were sampled four months apart and characterized in terms of the following:

COD was measured using a Hach 8000 HR COD Kit (Digestion Method) following the method provided by the supplier.

- Zeta-potential was measured using a Zetasizer Nano ZA instrument (Malvern Analytical).
- pH and conductivity were measured using an HI5522 pH/conductivity meter.
- Total organic carbon, ion (sodium, potassium, magnesium & calcium), and nutrient (chloride, sulphates, ammonia, nitrites, and nitrates) concentrations were measured by AGAT Laboratories (Oakville, Ontario, Canada).
- Liquid chromatography organic carbon detection (LC-OCD) analysis was conducted at the University of Waterloo's Water Institute.

A comparison of the quality parameters of Batch A (165 L that was sampled in March 2021) and Batch B (60 L that was sampled in July 2021) is given in Table 3.1. The average measurements and standard deviation errors are presented for those parameters that were measured by our team; all parameters were measured in duplicate for each bucket in which the samples were received (11 buckets for Batch A, and 4 buckets for Batch B). Most of the parameters were quite similar between the two batches, however there were a few exceptions. Most notably the concentration of ammonia in Batch A was nearly 300 times higher than that in Batch B.

Parameter	MBR permeate, Batch A (March 2021)	MBR permeate, Batch B (July 2021)
Chemical Oxygen Demand (mg/L)	666 ± 142	654 ± 17
pH	7.7 ± 0.1	8.3 ± 0.03
Conductivity (µS/cm)	19.6 ± 0.4	20.9 ± 0.2
Zeta-Potential (mV)	-15.6 ± 3.7	-17.5 ± 2.8
Total Organic Carbon (mg/L) *	208	225
Sodium (mg/L) *	2770	4390
Potassium (mg/L) *	1310	1460
Magnesium (mg/L) *	74.5	42
Calcium (mg/L) *	95.9	47
Chloride (mg/L) *	1570	1520
Sulphates (mg/L) *	114	112
Ammonia (mg/L) *	134	0.48
Nitrites (mg/L) *	59.4	34
Nitrates (mg/L) *	1640	1770

Table 3.1. Measured parameters of two batches of MBR permeate. All parameters denoted with an asterisk (*) were measured by AGAT laboratories.

3.3.2 High-throughput and jar testing protocol

An inorganic alum-based coagulant (PAX-18, 9.05% Al) was obtained from Kemira Water Solutions and used to pretreat the Batch A of MBR permeate in advance of the membrane filtration tests. An aluminum based coagulant was selected because the optimal coagulation pH (7.5 – 8.0) is similar to the pH of the MBR permeate^{33,34}. The effect of coagulant dosage was studied using a multi-point magnetic stirrer and eight lab beakers of sufficient size to accommodate 80 mL of MBR permeate and coagulant concentrations ranging from 40 to 120 mg-Al³⁺/L; each beaker was mixed for 3 minutes at 300 rpm then the beaker contents were allowed to settle for 30 minutes. Previous work has shown that this small-scale high-throughput (HT) screening of coagulants provides good scalability³⁵. The effect of pH adjustment to 7.6 using 0.1M HCl and NaOH (VWR, 98%+) was also studied.

A PB-700 Jar Tester (Phipps & Bird) was used repeatedly to produce 60 L of coagulated MBR permeate as follows. Each jar was filled with 2 L of MBR permeate, dosed with the desired amount of PAX-18, and then mixed for 3 minutes at 300 rpm. The mixture was then allowed to settle for 30 minutes, after which the supernatant was filtered using a 1-micron bag filter to remove any unsettled flocs. The composition of the coagulated MBR permeate was determined using the same battery of tests described above for the as-received batches of MBR permeate, including compositional analysis and LC-OCD analysis.

3.3.3 Membrane filtration system

Rectangular coupons (140 cm²) of three flat-sheet polyamide NF membranes (NFS [Synder], NFX [Synder], and NF90 [Dupont]) were cut from a large sheet in order to fit in the SEPA crossflow filtration cell used in this study. The coupons were wetted in deionized (DI) water prior to filtration and refrigerated when not in use.

The surface charge properties of the three membranes were determined using the streaming potential method of a SurPASS 3 electrokinetic analyzer (Anton Paar) as follows. A pair of rectangular membrane samples (2 cm x 1 cm) were cut and then attached onto the adjustable gap cell of the SurPASS 3. The distance between the two rectangular samples was set to 100 (\pm 10) micrometers. The NFS and NFX membranes were soaked in DI water for 12 hours prior to testing, while the NF90 membrane was soaked in a 25% isopropyl alcohol solution for 1 hour before testing. The zeta-potential measurements were performed using an electrolyte solution of 1 mM KCl, which was adjusted from pH 2 to 10 using 0.05 M HCl and 0.05 M NaOH solutions. After each zeta-potential measurement, the system was rinsed twice with the electrolyte solution.

A schematic of the bench-scale crossflow filtration system used in this study is shown in Figure 3.1; additional details are provided in Figure A.1. The fluid from the feed tank (T01) is pressurized using a positive displacement pump (P01) and fed directly into the SEPA cell membrane housing (M01) at a constant flow rate of 6.6 L/min. The transmembrane pressure (TMP) is calculated using equation 1, where P_F , P_C and P_P are the feed, concentrate and permeate pressures respectively.

$$P_{TMP} = \frac{P_F + P_C}{2} - P_P \tag{3.1}$$

The TMP is controlled through a precision needle valve (V04) and is manipulated to control the backpressure of M01. The concentrate stream is recycled back to the feed tank, and the permeate stream is continuously withdrawn from the system through valve V05. A temperature controller in the feed tank ensured that the fluid temperature stayed in the range of 20°C; a Type-K thermocouple gave a precise measurement of the actual fluid temperature.



Figure 3.1. Schematic of the bench-scale crossflow filtration system used to evaluate NF membrane performance. A full process & instrumentation diagram is available in Figure A.2.

Each membrane coupon was first compacted under a TMP of 6.9 bar and flowrate of 6.6 L/min for 30-minutes with regular tap water. Following the compaction step, the water permeability $L_P(\frac{L}{m^2h \cdot bar})$ was determined from an ANOVA regression analysis of average permeate flux, J ($\frac{L}{m^2h}$) versus TMP (ranging from 4.1 to 9.6 bar) via Equation 3.2, where v (L) is the dispensed permeate volume, t (h) is the time required to dispense the volume, A (m²) is the surface area of the membrane, P_{TMP} (bar) is the transmembrane pressure, $\eta_T \left(\frac{N \cdot s}{m^2}\right)$ is the dynamic viscosity of water at the fluid temperature and $\eta_{20^{\circ}C} \left(\frac{N \cdot s}{m^2}\right)$ is the dynamic viscosity of water at 20°C.

$$L_p\left(\frac{L}{m^2h\cdot bar}\right) = \frac{J}{P_{TMP}} = \frac{\left(\frac{v}{t\cdot A} \times \frac{\mu_T}{\mu_{20}\circ_C}\right)}{P_{TMP}}$$
(3.2)

Permeate flux was calculated from timed measurements to collect 1 mL of permeate, with five measurements taken at each TMP. A sodium chloride (NaCl) rejection test was also conducted on each membrane coupon as follows: a 5-L NaCl solution at a concentration of 2000 ppm was prepared in deionized water and the system was run with complete permeate recirculation for 30 minutes at 6.9 bar, after which three 10 mL samples of the feed and permeate were collected. The electrical conductivity was measured using a HI 5522 pH/conductivity meter (Hanna Instruments), and rejection was calculated via Equation 3.3,

$$R_{NaCl}(\%) = \frac{EC_F - EC_P}{EC_F} \times 100\%$$
(3.3)

where $\text{EC}_{\text{F}}\left(\frac{\text{mS}}{\text{cm}}\right)$ and $\text{EC}_{\text{P}}\left(\frac{\text{mS}}{\text{cm}}\right)$ are the average electrical conductivities of the feed and permeate samples, respectively. The average permeabilities (and the 95% confidence interval around the regression line) and average salt rejection (and standard deviation error) for the three nanofiltration membranes used in this study are presented in Table 3.2; the corresponding values for each individual membrane coupon used in this study is listed in Table B.1 in the Supplemental Material.
Table 3.2. Properties of the commercial nanofiltration membranes used in this study. The molecular weight cut-off (MWCO) values are those reported by the membrane manufacturer whereas all other values were measured. The water permeability and sodium chloride rejection values are the average and standard deviation error measured across a minimum of six coupons. Zeta potential values are the average and standard deviation measured for three membrane coupons, with each membrane coupon having two zeta-potential measurements taken at each pH value (a total of 6 measurements per membrane). The full zeta potential versus pH profiles are shown in Figure B.1 in the Supplemental Material.

Membrane	Manufacturer	MWCO	Water	NaCl Rejection	Zeta-
ID		(Da)	Permeability	(%)	Potential (pH
			(LMH/bar)		7.6) (mV)
NF90	Dupont	200-400	10.1 ± 0.9	89 ± 11	-23 ± 1
NFS	Synder	100-250	7.4 ± 1.1	44 ± 18	-33 ± 1
NFX	Synder	150-300	3.7 ± 1.1	37 ± 6	-25 ± 2

Filtration tests with MBR permeate (or coagulated MBR permeate) were conducted at a constant TMP of 6.9 bar and constant feed flow rate of 6.6 L/min. Each experimental conditions (e.g. membrane type, feed solution) was tested in duplicate (referred to as Replicate 1 and Replicate 2) in order to confirm the reproducibility of the results. Within an experiment, the permeate was collected in a container located on top of a load-cell that recorded the cumulative mass at one-minute time intervals. The cumulative mass data was converted to temperature-corrected flux by conducting a numerical differentiation on the mass and time data sets obtained from each experiment. Permeate recovery for each filtration experiment was calculated via Equation 3.4, where $V_{\text{final},p}$ (L) is the total permeate volume at the end of the filtration period.

Permeate Recovery (%) =
$$\frac{V_{\text{final},p}}{5L} \times 100\%$$
 (3.4)

The constant-pressure filtration experiments were conducted until 8-hours had elapsed or 80% permeate recovery had been reached. Two feed and permeate samples were collected at every 20% increment of permeate recovery, as well as at the end of the 8-hour filtration period. The COD of the feed and permeate samples were measured using the method described in section 2.1, and percentage removal of COD was calculated via Equation 3.5, where $C_F\left(\frac{mg}{L}\right)$ and $C_P\left(\frac{mg}{L}\right)$ are the feed and permeate concentrations, respectively. NFS and NF90 permeate samples collected from the filtration of both batches were sent for compositional analysis. Additionally, NFS and NF90 samples collected from the filtration of Batch A were sent for LC-OCD analysis.

$$R_{COD}(\%) = \frac{C_{F} - C_{P}}{C_{F}} \times 100$$
(3.5)

3.4 Results & Discussion

3.4.1 Determination of coagulation operating point via high-throughput screening tests

A comparison of the treatment results obtained with Batch A MBR permeate is shown in Figure 3.2; the measured COD and zeta-potential of the supernatant are shown at different coagulant dosages without pH adjustment (left panel) and with pH adjustment (right panel). As expected, the zeta-potential steadily increased as the coagulant dosage increased. It has been previously shown in the membrane literature that neutralization or reversal of the colloidal NOM charge can result in increased cake formation due the loss of charge repulsion between the negatively charged membrane surface (see Table 3.2) and cake-forming foulants^{36–38}, and thus our objective was to determine the coagulant dosage that maximized NOM removal while maintaining a negative solution zeta-potential. It

was found that charge neutralization occurred between dosages of 80 mg-Al³⁺/L and 85 mg-Al³⁺/L in the absence of pH adjustment. In a similar manner, the COD of the supernatant steadily decreased until charge neutralization was attained, at which point it plateaued around 370 mg/L. As reported in a previous study with a polyaluminum chloride coagulant, this suggests that charge neutralization is the dominant form of coagulant³⁹. A visual comparison of the effect of increasing coagulant dosage is shown in Figure B.2 in the Supplemental Material. As shown in Figure B.3 in the Supplemental Material, it was found that the pH of the supernatant decreased from 7.6 to around 4 with the addition of coagulant; it is believed that this is due to the consumption of alkalinity brought about by aluminum hydroxide formation⁴⁰. Interestingly, a negative zeta-potential was observed for each coagulant dosage after the supernatant pH had been adjusted to ~7.6. This is most likely due to deprotonation of colloidal matter as the solution pH is increased, thereby leading to a lower zeta-potential⁴¹. Once again, the measured COD steadily decreased up to a coagulant dosage of 90 mg-Al³⁺/L, after which point it remained relatively stable at around ~370 mg/L.



Figure 3.2. Comparison of COD concentration and zeta-potential values for the supernatant obtained after dosing Batch A MBR permeate with PAX-18 coagulant. The left panel shows measurements without adjustments to the supernatant pH, and the panel on the right shows measurements with the pH adjusted to ~7.6. Standard deviation error bars are shown for duplicate measurements.

Coagulation tests performed with the six-cell jar tester were required to produce the large volume of coagulated MBR permeate that was required for conducting crossflow filtration experiments. At the dosage of 90 mg-Al³⁺/L, the supernatant produced in the jar test had a slightly higher zeta-potential (-10.3 \pm 0.1 mV) than the corresponding samples from the beaker tests (-4.7 \pm 2.0 mV). The average COD of the 60 L of coagulated MBR permeate was 354 \pm 16 mg/L which was approximately half of the corresponding value for the as-received sample (see Table 3.1). In order to gain further insight into the coagulated samples were analyzed using liquid chromatography-organic carbon detection (LC-OCD); this semi-quantitative analytical method resolves compounds based on their molecular weight and hydrophobicity into five groups: biopolymers, humic substances, building blocks (decomposed humic substances), low molecular weight (LMW) acids, and LMW neutrals⁴². An overlay of the LC-OCD chromatograms for the MBR permeate and coagulated MBR permeate is shown in Figure 3.3. Peak integration was used to estimate the concentrations of biopolymers and humic substances in both the coagulated and as received MBR permeate and showed approximate removals of 80% and 90% respectively. The peaks of smaller building blocks, LMW acids and LMW neutrals were too low in concentration to accurately integrate, however Figure 3.3 shows that these fractions were nearly unremoved by coagulated MBR permeate was 84 mg/L, and the poor removal of the smaller NOM fractions can be assumed to the primary contributors to the measured TOC. Thus, any NOM fouling observed while filtering the coagulated MBR permeate can be attributed to these unremoved fractions.



Figure 3.3. Overlay of LC-OCD chromatograms for the as-received Batch A MBR permeate, coagulated Batch A MBR permeate, and permeate sample obtained from filtration of Batch A with NF90 membrane.

3.4.2 Effect of pretreatment conditions on filtration performance

As shown in Figure 3.4, the filtration performance was first compared in terms of the permeate flux profiles obtained for DI water (included in our study as a control), the as-received MBR permeate, and the coagulated MBR permeate (obtained from six-cell jar tests). The continuous flux profile for each test condition was obtained via a numerical differentiation of the mass versus time data, which was obtained through load-cell measurements. Two replicate filtration experiments (using separate membrane coupons) were conducted for each membrane and feed condition, thus a total of 18 independent filtration experiments are presented in Figure 3.4. In terms of the filtration of DI water, the flux remained quite stable throughout the filtration experiments conducted with all three membranes demonstrated negligible fouling. Interestingly, the NFS membrane gave a DI water flux (~41 LMH) nearly double that of the NFX membrane (~20 LMH), despite both membranes having similar rated MWCOs (see Table 3.1). Yet, it was found that the NF90 membrane demonstrated the highest DI water flux (~50 LMH), which has been reported in the literature as being due to the hydrophilic nature of the NF90 due to the presence of carboxylic acid and amine functional groups that facilitate water transfer via hydrogen bonding interactions^{43,44}.

The NFS and NFX membranes both showed similar initial wastewater and DI water fluxes, however flux decline due to membrane fouling was observed with the NFS membrane, whereas a relatively flat profile was observed with the NFX membrane. In contrast to this, despite having the highest DI water flux, the NF90 membrane had the lowest wastewater flux. Additionally, the flux of the NF90 membrane decreased from ~12 LMH to ~8 LMH during wastewater filtration. This discrepancy between the initial "clean" and "wastewater" fluxes was also observed by Dolar et al.⁴⁵ who reported a 53% decline in flux when changing from the filtration of DI-water to landfill leachate. While it has been reported that the NF90 membrane has a tight pore structure⁴⁶, several factors such as the polymeric structure, the hydrophobicity and the membrane surface charge could have contributed to the dramatic differences in flux values that was observed.

It was found that pretreating the MBR permeate with coagulant did not improve the flux performance of any of the three nanofiltration membranes. Previous studies have shown examples of coagulation-NF hybrid processes where coagulation had minimal to

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no impact on fouling mitigation ^{47,48}, ⁴⁶. Liang et al. suggests that a higher residual Al³⁺ concentration leads to an increase in osmotic pressure on the permeate side which in turn reduces the concentration differential that drives permeation; the aluminum concentration in the coagulated MBR increased from 0.2 mg/L to 1.5 mg/L, which suggests that this phenomena is a likely cause for the lack of improvement seen in the flux performance⁴⁹. Targeted NOM removal via coagulation failed to improve on the permeate flux and recovery, which can be explained via two possible mechanisms: first, there was insufficient coagulant dosing to remove smaller NOM fractions (building blocks, LMW acids and LMW neutrals), that still enabled NOM fouling; second, residual amounts of Al³⁺ build up on the permeate recovery values for the twelve filtration experiments shown in the bottom three panels of Figure 3.4 are given in Table 3.3. For all three nanofiltration membranes, there was no appreciable improvement to permeate recovery following coagulation of the MBR permeate.



Figure 3.4. Permeate flux profiles for the crossflow filtration of DI water (top three panels) and coagulated or as received MBR permeate (bottom three panels) using three NF membranes: NFS (left panels), NFX (middle panels), NF90 (right panels). Replicates of each condition are shown with red, unfilled markers.

Table 3.3. Percentage of the original 5-L feed recovered through permeate using NFS,
NFX, and NF90 membranes after either 8 hours of filtration or attaining 80% recovery.
Asterix (*) denote trials that were completed in less than 8 hours.

	MBR permeat	e recovery (%)	Coagulated MBR permeate recovery (%)		
Membrane	Replicate 1	Replicate 2	Replicate 1	Replicate 2	
NFS	80.9*	71.8	79.0	78.9	
NFX	53.2	50.3	43.6	39.0	
NF90	23.4	21.9	23.7	19.3	

Due to the crossflow configuration of the system used in our study and given that the filtration experiments were conducted with the permeate stream continuously withdrawn from the system (i.e. permeate was collected in container located on top of a load-cell), the properties of the feed solution changed during each filtration test. As an example, the results we obtained for the filtration of the as-received MBR permeate (Batch A) using the NFS membrane are shown in Figure 3.5. The four points for each filtration test correspond to samples of the feed and permeate that were taken when permeate recoveries of 20%, 40%, and 60% were achieved and another set of samples taken at the of the 8-hour filtration experiment. While the feed COD increased steadily to a concentration nearly four times the initial COD of 666 mg/L, the permeate COD remained constant. As a result of this, the COD rejection (calculated using Equation 5) increased with permeate recovery. This trend was also observed with the NFX and NF90 membranes under both feed conditions (see Figure B.4 in the Supplemental Material). This result highlights the robust nature of NF membranes.



Figure 3.5. Comparison of feed and permeate COD concentrations (top panel) and corresponding percent COD rejection (bottom panel) during 8-hour filtration experiment of the as received MBR permeate (Batch A) with the NFS membrane (same experiment presented in the bottom left panel of Figure 3.4). Standard deviation error bars are shown based on duplicate feed and permeate COD measurements taken at each sampled recovery.

Since vastly different permeate recoveries were obtained with each membrane, removal performance was compared based on the COD measured at the end of the filtration experiment (i.e., the highest obtained recovery after 8-hours, or at 80% recovery). Figure 3.6 shows the feed and permeate COD measurements obtained for the filtrations of coagulated and as received MBR permeate using each membrane. Similar to the flux results, no improvements in removal were observed following the coagulation of the MBR permeate, despite the initial feed COD was significantly lower. The NF90 membrane produced the highest quality permeate, while the COD measurements obtained for the NFS and NFX membranes were comparable and nearly double that of the NF90 membrane. Once again, targeted NOM removal did not improve permeate quality or the permeate recovery rates of the three membranes. Referring back to Figure 3.2, it can be seen that the LC-OCD chromatogram for the NF90 permeate shows the near perfect removal of all organic fractions. This trend was observed for the permeates obtained from all membranes under both feed conditions, which suggests that some inorganic species are not being removed by the membrane and are contributing to the observed permeate COD. These results are in good agreement with those reported by Chang et al. ⁴⁶ that the removal of COD obtained with a nanofiltration process was unaffected by the addition of an aluminum-based coagulant. The superior COD removal observed with the NF90 membrane may be attributed to it's tight pore structure, which is widely reported in the literature¹⁷. The enhanced removal ascertained by the tight pore structure is however accompanied by a lower flux and greater fouling potential. Additionally, charge effects may also explain the high rejection observed with the NF90 membrane⁵⁰, however as presented in Table 3.2, there is no significant difference in membrane surface charge between the NFX and NF90 membranes, yet the NF90 membrane produced a permeate with a much lower COD.



Figure 3.6. Comparison of feed (samples taken before filtration) and permeate (samples taken at 20% increments of recovery) COD measurements taken following the filtration of coagulated and as received MBR permeate using three NF membranes. Measurements were taken from the same filtration experiments presented in the bottom panels of Figure 3.4. Average measurement and standard deviation error bars are based on duplicate measurements of feed COD, and multiple measurements of permeate COD, where the number of samples taken depended on the permeate recovery of the filtration experiments (two samples taken at 20% increments of recovery and two final samples taken after 8 hours of filtration).

3.4.3 Effect of feed properties on filtration performance

The filtration performance of the NF90 and NFS membranes was also determined for the second batch of MBR permeate (i.e. Batch B); the NFX membrane was excluded from these tests, as filtration results using Batch A indicated that it offered neither the high recovery rates of the NFS membrane, nor the high permeate quality produced by the NF90 membrane. Additionally, the MBR permeate from Batch B was used as received since we determined that pretreating with the coagulant had no effect on filtration performance.

Figure 3.7 compares Batches A and B with respect to the flux (panel a) and COD removal (panel b) observed during filtration with the NFS and NF90 membranes. The NF90 membrane produced very similar flux profiles during the filtration of both batches. Specifically, very low fluxes (compared to the clean water flux) were observed, including similar flux declines over the 8-hour filtration window. This resulted in very similar permeate recoveries obtained for both batches. Interestingly, a marginally lower flux was observed for the NFS membrane when it was used to filter Batch B, with recovery rates of <70% being recorded across both replicates. Regardless, the NFS membrane displayed superior overall wastewater flux performance compared to the NF90 membrane for both batches. The most striking observation pertains to COD removal, where the NF90 membrane produced high quality (<100 mg/L) permeate for both batches, however the NFS membrane produced a much higher quality of permeate during the filtration of Batch B ($95 \pm 14 \text{ mg/L}$) than it did for the filtration of Batch A ($234 \pm 14 \text{ mg/L}$).



Figure 3.7. (a) Flux performance and (b) COD removal between Batch A and Batch B following filtration with the NFS and NF90 membranes (two replicate filtrations). Results for both batches were obtained via the filtration of as received MBR-permeate (without coagulant dosing). Error bars on COD measurements represent duplicate (N = 2) measurements of feed COD, and multiple measurements of permeate COD, where the number of samples taken depended on the permeate recovery of the filtration experiments (two samples taken at 20% increments of recovery and two final samples taken after 8 hours of filtration).

Results in Figure 3.7 are presented in alternative format in Figure 3.8 to explicitly show the trade-off in filtration performance. Here, the percentage of permeate recovered by each membrane and each batch, to the permeate COD concentration. This graphical approach was originally developed by Robeson to visualize the trade of between

selectivity and permeability of polymeric membranes used for gas separation⁵¹; it has since been used to visualize the trade- off in performance parameters in other areas of membrane research such as the advancement of desalination membranes, the development of electrically conductive membranes, and the development of metalorganic frameworks⁵²⁻⁵⁴. To our knowledge, this is the first time this analysis has been extended to wastewater byproducts from biogas production, and for analyzing the performance of membranes when filtering wastewaters with varying feed properties. The plot area is divided into four quadrants, with the lower-right quadrant (i.e., recovery greater than 50%, permeate COD less than 180 mg/L) representing the "high quality, high recovery" operating region. A permeate COD of 180 mg/L was chosen as an analogue for typical sewer discharge limits. Notably, for filtrations with Batch A, a trade-off was observed between permeate recovery and the permeate COD concentration. As a result, none of the membranes operated in the "high quality, high recovery" region. Conversely, filtering Batch B with the NFS membrane operated in the "high quality, high recovery" operating region, despite Batch B having very similar bulk properties to Batch A. This analysis highlighted how different membranes behave differently when filtering a single source of wastewater. However, this analysis also showed that the treatment efficacy of a single membrane can be impacted by variations to the incoming membrane feed.



Figure 3.8. Comparison of permeate quality (in terms of COD) and permeate quantity (in terms of percent recovery) for the crossflow filtration tests that were conducted with three nanofiltration membranes and two batches of wastewater. The average permeate recovery and standard deviation error bars were based on the percentage permeate recovery obtained from two (N = 2) independent filtration experiments. The average permeate across two independent filtration, where each run had several COD measurements based on the permeate recovery of the filtration experiments (two samples taken at 20% increments of recovery and two final samples taken after 8 hours of filtration).

In all cases, NF enabled the removal of more than 90% of TOC from the permeate (as observed in LC-OCD results presented in Figure 3.3), which implies that the variation in the permeate COD observed between both batches was derived from a non-organic fraction. In order to further investigate this batch-to-batch variation, feed samples from both batches and permeate samples obtained from both membranes were sent to AGAT Laboratories for a compositional analysis, which provided measurements of select nutrients, metals, and ions. As shown in Figure 3.9, the rejection of the various species (values given in Table B.2 in the Supplemental Material) was compared to the Stokes radius to account for both solute size and hydration shell effects. The Stokes radius for each solute was calculated assuming an infinite dilution using the Stokes-Einstein equation (Equation 3.6),

$$R(nm) = \frac{k_B T}{6\pi\eta D}$$
(3.6)

where $k_B \left(\frac{kg \cdot m^2}{s^2 \cdot K}\right)$ is the Boltzmann constant, T (K) is the solution temperature, $\eta \left(\frac{N \cdot s}{m^2}\right)$ is the solution dynamic viscosity and D $\left(\frac{m^2}{s}\right)$ is the diffusion coefficient (obtained from the CRC Handbook of Chemistry & Physics⁵⁵). As shown in Figure 3.9, the rejection of solutes by both the NF90 and NFS membranes was well correlated with their respective Stokes radius values. We found that solute molecular weight was a poor predictor of rejection (see Figure B.6 in the Supplemental Material), which has been previously reported in the literature²⁵. The solutes with the largest Stokes radius (e.g., magnesium) had the highest rejection values. Additionally, for those solutes with similar Stokes radii (e.g., potassium and chloride), the highest rejection values were found for negatively charge solutes. This observation agrees with the membrane zeta-potential measurements presented in Table 3.2 and Figure B.2. For each solute, greater rejections were observed with the NF90 membrane as compared to the NFS membrane, and thus indicates why the NF90 membrane was consistently able to produce a permeate with a lower COD concentration. As shown in Figure B.6 in the Supplemental Material, the same trends

were observed in the filtration experiments conducted with Batch B. The relationship between Stokes radius and rejection has been previously reported in the literature, however those comparisons were based on experiments done with single-component solutions or simple multi-component mixtures ^{56,57}. The results from this study show that the relationship between Stokes radius and solute rejection can be extended to complex industrial wastewater mixtures. In particular, the removal of individual components observed by various membranes can be compared to it's hydrated size, and components within the wastewater that passed through the membrane and negatively impacted permeate quality can be readily identified. The significant source of difference between the two batches was the concentration of ammonia, which was significantly higher in Batch A (134 mg/L) than Batch B (0.48 mg/L) due to incomplete nitrification in the MBR. Figure 3.9 shows that ammonia was virtual unremoved by the NFS membrane and exhibited very low removal with the NF90 membrane. Although it is well-known that standard COD measuring kits that use dichromate oxidizers do not oxidize ammonia, it can form an interference when present in conjunction with high concentration of chloride⁵⁸. The oxidation of chloride ions into chlorine significantly affects the accurate measurement of COD, but the addition of mercuric sulfate can mask chloride interference by forming mercuric chloride complexes that cannot be oxidized. However, in the presence of high concentrations of nitrogenous compounds, the oxidation of chloride to chlorine occurs through the formation of chloroamine intermediates, even in the presence of mercuric sulfate⁵⁹. Thus, the high permeate COD in the samples from Batch A were likely due to the high concentrations of ammonia and chlorides in these samples. Furthermore, nitrites also have a profound impact on COD, which has a theoretical oxygen demand of $1.1 \text{ mg-O}_2/\text{L}$ per 1 mg/L of NO_2^{60} . The higher COD concentrations in the permeate produced by the NF90 membrane filtrations of Batch A were likely due to the relatively better performance with respect to chloride removal offered by the NF90 membrane, as observed in Figure 3.9.



Figure 3.9. Comparison of rejection of the various wastewater solutes (in Batch A) and the Stokes Radius of the solute, obtained from crossflow filtration experiments with the NF90 and NFS membranes.

3.5 Conclusions

This research assessed the ability of three commercially available flat-sheet NF membranes to "polish" the permeate stream from a MBR that treats the liquid fraction of dewatered anaerobic digestate, a by-product from the conversion of municipal source-separated organics into biogas. Batch A was subject to coagulation pretreatment, whereas

Batch B was filtered without pretreatment. Intrinsic differences between the three NF membranes evaluated and the composition of Batch A resulted in a trade-off observed between the volume of permeate recovered and the permeate COD concentration. More permeable membranes (NFS & NFX) demonstrated a higher permeate recovery, however often at the sacrifice of permeate quality. To improve membrane performance, 90 mg-Al³⁺/L (determined through high-throughput screening) of an aluminum based coagulant was dosed to reduce the NOM concentration. Despite reducing the COD concentration by nearly 50%, pre-coagulation failed to improve permeate quality or recovery. This was hypothesized to be due to the failure of the coagulant to remove smaller NOM fractions (building blocks, LMW acids & LMW neutrals) and a build-up of residual alum that decreases the osmotic pressure needed to drive filtration. Filtration of Batch B (sampled 4 months after Batch A), showed a significant improvement in COD removal when filtered with the NFS membrane (Batch A: $95 \pm 14 \text{ mg/L}$ vs. Batch B: $234 \pm 8 \text{ mg/L}$), without sacrificing the high permeate recovery. Analysis of the permeate indicated high concentrations of both chlorides and nitrogenous compounds (namely, ammonia and nitrite). The interference caused by the oxidation of chloride into chlorine is usually masked by the addition of mercuric sulfate in standard COD kits. However, this approach is ineffective in the presence of high levels of ammonia, as the oxidation of chloride occurs through the formation of chloroamine intermediates. Comparing individual solute rejection to the solvated size of the solute (determined via calculation of Stokes' radius) determine that the NF90 was able to produce a better overall permeate quality due to it's superior removal of chloride ions. Ultimately, this work shows that, under the right conditions, the NFS membrane is a good candidate for polishing liquid waste streams resulting from biogas production. Furthermore, Batch A's high ammonia concentration was due to incomplete denitrification occurring upstream of the MBR permeate, which highlights the susceptibility of NF-based PTPs to deviations in up-stream processes. Thus, a comprehensive sensitivity analysis is required to understand the operating window of these membranes.

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Chapter 4

High-throughput screening to evaluate optimum coagulation conditions via colloidal stability analysis

Chapter 4 High-throughput screening to evaluate optimum coagulation conditions via colloidal stability analysis

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Published work at the journal *Chemosphere*. Reprinted with permission. Copyright© Elsevier 2023 https://doi.org/10.1016/j.chemosphere.2023.139798

4.1 Abstract

Current methods of optimizing the coagulant dosage in wastewater treatment processes typically rely on the use of labor- and material-intensive jar testers, which are inadequate when coagulation processes require frequent adjustments due to variations in properties of the incoming feed. Analytical centrifuges (ACs) employ an integrated optics system that simultaneously monitors the position of the boundary between two separating phases in multiple samples of fairly low volumes ($\sim 2 \text{ mL}$) – thus it was expected that ACs would be ideally suited to study the stability and settling kinetics of coagulation treatment processes. In this study, wastewater samples from a biogas generation facility (known as centrate) were collected in February 2022 (Batch A) and July 2022 (Batch B). A comprehensive screening of the treatment performance for Batch B was conducted at three pHs (5, 6, and 7) and nine concentrations of ferric chloride (0-500 mg-Fe3+/L) – it was found that the front-tracking profiles measured by the integrated optics system could be used to identify the minimal coagulation conditions needed to transition from slow to rapid settling. While the settling velocity was found to be well correlated with the instability index, a dimensionless number between 0 and 1 (where values closer to 1

indicate better separation), it was determined that the percentage of COD removal from the centrate samples increased up to an instability index of approximately 0.5 and then plateaued. Finally, it was found that the front-tracking profiles could be used to estimate the volume of sludge produced at various coagulation conditions. Thus, the results from this study establish ACs as an important screening tool for rapid evaluation of treatment performance while consuming minimal material and time – in this study, a total of 132 screening experiments were conducted using approximately ~11 L of centrate and ~6 hours of operator time.

4.2 Introduction

Colloidal natural organic matter (NOM) is a significant source of contamination in several wastewater sources¹. Typically between 1 nm and 1 μ m in size, colloidal NOM remains stable in wastewater systems via electrostatic repulsive forces that prevent it from coalescing into larger aggregates that would otherwise settle into a separated phase.^{2,3} Since aquatic NOM possesses a negative surface charge over a wide range of pHs, positively charged coagulants (such as ferric chloride) are generally used in treatment processes to destabilize and aggregate colloids into settleable flocs that can sediment out of the wastewater.⁴ Thus, coagulant dosages must be carefully determined to ensure that the added amount is sufficient to destabilize the colloids and maximize treatment. Treatment facilities typically employ conventional jar testing to optimize coagulant dosages, as this method effectively simulates common coagulation processes via a simple parallel stirring apparatus containing between four and six 1-2L jars.⁵ Though the use of jar testing is widespread, it can also be both time- and material-intensive, as

comprehensive screenings of multiple conditions (e.g., pH, coagulant concentration, coagulant type) requiring several liters of wastewater and a high number of operator hours.^{5,6} Additionally, jar testing assesses separation performance by measuring the removal of specific analytes and requires the use of external zeta-potential analyzers to obtain information about colloid stability.⁷ For facilities that experience seasonal variations, rapid and scaled-down screening techniques are needed to respond quickly to variations in feed properties.⁸

Recent research efforts have aimed to address these challenges. For example, prior studies have addressed the large volume requirements of jar testing by screening coagulants in micro-well plates,^{6,9,10} microfluidic devices,^{11,12} and ultra-scaled-down mixing vessels that emulate jar testers,^{13,14}, combined with measurement techniques that require low sample volumes such as optical density measurements,¹⁵ and various imaging techniques.¹⁶ Despite enabling the successful screening of coagulants using only milliliters of wastewater, these techniques remain time intensive, as sedimentation must still be conducted under gravitational conditions. Furthermore, these approaches often require external analysis techniques, such as confocal imaging¹⁶ or capillary suction time measurements,¹⁰ and, in the case of microfluidic devices, it is necessary to fabricate a new device when evaluating a new condition. At present, Abarca et al.'s work is the only attempt to determine colloid stability by calculating the critical coagulant concentration using a 96-well plate assay; however, this technique is still time-consuming, as it is conducted under gravitational conditions.⁹ Studies have also attempted to reduce screening times by coupling techniques such as capillary suction time and focused beam reflectance measurements,¹⁷ or by developing novel spinning disc devices to assess colloid stability.¹⁸ Unfortunately, both of the aforementioned techniques are limited, as they only allow the evaluation of one condition at a time. Thus, there is a need for a screening tool that can rapidly assess the separation performance of coagulants while using a low volume of wastewater.

Analytical centrifugation is a technique wherein centrifugation is combined with optical density measurements to study the sedimentation kinetics and stability¹⁹ of a multiphase suspension.²⁰ In analytical centrifugation, the position of a phase boundary is identified by measuring the transmission of light along the length of a sample and tracking the phase boundary's movement under accelerated conditions.²¹ Analytical centrifuges (AC) are applied to rapidly assess the stability and shelf life of formulations under accelerated conditions in a variety of industries, including the pharmaceutical,²² food and beverage,²³ and personal care product²⁴ industries. Previous studies have used ACs for environmental applications, specifically for evaluating the performance of coagulants and flocculants with various colloidal materials (e.g., clay^{21,25}, titanium dioxide ²⁶, calcium carbonate ²⁷, and quartz ²⁸) suspended in water. Though these studies demonstrate the utility of ACs, results obtained with these ideal solutions do not adequately reflect the separation performance that is expected with complex wastewater samples. To the best of our knowledge, there is only one study that has demonstrated the usefulness of ACs for a treatment application. Sobisch & Lerche used an AC to measure the compaction of anaerobic digester sludge after treatment with polymer flocculants, however, no measures of colloidal stability or water quality parameters were made in that study²⁹.

In the present work, we demonstrate the extreme usefulness of ACs to perform rapid and high-throughput screening of coagulants to optimize the treatment of centrate, which is the liquid fraction obtained following the dewatering of anaerobic digestate. Firstly, the solution conditions (i.e. pH and coagulant dosage) were optimized for a single batch of centrate that was sampled in July of 2022 by leveraging readily available measurements of stability and settling kinetics. Secondly, centrate experiences significant seasonal variability and coagulation processes need to be adapted to responded to changes in influent properties, either by readjusting the coagulant dosage or by using a different coagulant entirely. We show how stability measurements inherent to ACs can be utilized to quickly compare coagulants and readjust dosages. This was achieved by using two batches of centrate, which have different compositional properties and were sampled in February (winter) and July (summer) of 2022. Finally, we demonstrate how transmission profiles provided by the AC can be used to identify the positions of phase boundaries, which in turn can be used to estimate the volume of sludge that is produced after coagulation and adapt downstream sludge handling processes in response to dosage adjustments.

4.3 Materials & Methods

4.3.1 Anaerobic digester centrate sampling & characterization

Wastewater samples were collected from a biogas generation facility in North America, where municipal organic waste is anaerobically digested to produce biogas and

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the spent digestate (typically between 70-80% liquid) is dewatered via a centrifuge. The liquid fraction coming off the centrifuge, referred to as centrate, is a source of high-strength industrial wastewater. Six batches of wastewater were collected in February, April, June, July, August, and December of 2022, with the batches collected in February (Batch A) and July (Batch B) being used directly in this work. Table 4.1 lists the values for 18 water quality parameters measured for Batches A and B, as well as the average values measured across the six sampled batches. The chemical oxygen demand (COD) was measured using a Hach 8000 HR COD kit in accordance with the manufacturer's instructions, and the zeta-potential was measured using a Zetasizer ZA Nano instrument (Malvern Analytical). All other measurements were performed by AGAT Laboratories (Oakville, Canada).

Catgory	Parameter	Units	Average	Batch A (Feb- 2022)	Batch B (Jul-2022)
	Chemical Oxygen Demand (COD)	mg/L	6388	4788	5883
	Total Organic Carbon (TOC)	mg/L	1023	780	874
	True Colour	TCU	6367	2110	6990
Bulk Properties	Turbidity	NTU	1009	664	689
L	Total Dissolved Solids (TDS)	mg/L	9288	7080	8940
	Zeta-Potential ¹	mV	-	-15.4	-17.1
	pН	~	8.30	8.51	8.29
	Electrical Conductivity	µS/cm	21882	19000	21400
	Ammonia	mg/L	2268	1920	2220
Nutriants	Sulphates	Mg/L	113	42.5	309
Induitents	Chloride	mg/L	1585	1510	1730
	Total Phosphorous	mg/L	42.1	21.3	33.4
Metals	Total Calcium	mg/L	98.6	48.1	97.0
	Total Magnesium	mg/L	70.3	43.6	48.6
	Total Potassium	mg/L	1317	1080	1020
	Total Sodium	mg/L	1918	1360	1230
	Total Aluminum	mg/L	2.9	0.408	0.515
	Total Iron	mg/L	17.2	6.32	9.69

Table 4.1. Measured water quality parameters of centrate from a biogas generation facility in North America. Parameters denoted with an asterix (*) were measured by AGAT laboratories.

¹Zeta-potential was measured only for the two batches used in this study.

The amount and type of solid organic feedstock entering the process upstream influences the composition of the centrate and drives the considerable seasonal variability in the measured water quality parameters. To demonstrate the inter-batch variability, the
time variations for six select parameters are shown in Figure 4.1, with the measurements for Batches A and B highlighted in red and blue, respectively.



Figure 4.1. Time-variations of COD, TDS, chloride, total phosphorus, total sodium, and total iron across batches of centrate sampled in February, April, June, July, August, and December of 2022. The two batches selected for analysis in this study, Batch A (February 2022) and Batch B (July 2022), are highlighted in each panel.

4.3.2 Coagulation experiments

Liquid ferric chloride (FeCl₃, 13.1% Fe³⁺) and polyaluminum chloride (PACl, 9.05% Al³⁺) coagulants were obtained from Kemira Water Solutions. The as-received centrate was portioned into ~1L aliquots in beakers, and the pH of each aliquot was adjusted using either HCl (36%) or NaOH (5M). For pH adjustment, the centrate was placed on a stir plate and mixed at 100 rpm, with HCl or NaOH being slowly added dropwise until the pH was reduced from ~8.5 to either 5, 6, or 7 (Hanna Instruments, HI5522). The pH-corrected centrate was then distributed into eight 80-mL beakers containing a 25×8 mm stir bar and then placed on a multi-point stir plate. The coagulant was then pipetted into each beaker at a concentration of 50 to 500 mg-ion/L and mixed for 3 minutes at 300 rpm to induce coagulation. After mixing, a 1.6 mL aliquot of the two-phase mixture was transferred to a specialized polycarbonate vial containing an optical window (see Figure 4.2) for analysis using an AC.

4.3.3 Analytical centrifuge screening

A LUMiFuge (Lum, GmbH) AC was used to study the settling kinetics and separation performance of the coagulants. The LUMiFuge used in this work contained a charge-coupled device (CCD) camera, which tracked the position of the phase boundary in the two-phase mixture by measuring the transmission of near infrared (NIR) light at discretized radial positions along the length of the optical window on the vial. The LUMiFuge analysis involved centrifuging the eight vials containing the two-phase mixtures obtained via the coagulation experiments (described in Section 4.2.2) at 2000 rpm (483 g) for 5 minutes and recording the transmission profiles at 1s intervals. 2000

rpm was selected as the rotation speed, as it was the maximum speed at which it was possible to resolve the settling kinetics of rapidly settling samples (i.e., high coagulant dosages) at the highest selectable resolution (i.e., 1s). These parameters allowed a maximum of 300 profiles to be recorded, resulting in a 5-minute centrifugation time. Additionally, the LUMiFuge allows for temperature control and an ambient set-point temperature set-point of 25°C was maintained for all experiments.

The transmission profiles obtained from each sample contained the percentage transmission of NIR along the length of the vial at 1s time intervals. The position of the phase boundary was visually observed as the position at which a large drop in transmission was observed; this position could be measured for a single percentage transmission. For all the samples in this study, the phase boundary position was determined as occurring at 30% transmission, as this value was a typical midpoint between the transmission of the liquid and solid phases that was observed. By extension, front-tracking profiles were generated by plotting the position of the solid-liquid phase boundary versus time.

The stability of the two-phase mixture was quantified via the LUMiFuge software using an "instability index" metric, which is a dimensionless number between 0 and 1 (stable mixtures showing poor separation have a value closer to $zero^{30}$). The instability index was calculated as the ratio of transmissions (T) measured at a time interval (i) to their radial positions along the sample vial (j), as shown in Equation 1. For further detail, please see Equation C.1 in the Supplemental Information. In this chapter, the final instability index value (i = 300 s) is reported.

Instability Index =
$$\frac{\Delta T_i}{\Delta T_{max}} = \frac{\sum_{j=r_{min}}^{r_{max}} T_{i,j}^{diff}}{(\overline{T}_{end} - \overline{T}_1)(j_{r_{max}} - j_{r_{min}})}$$
 (4.1)

A schematic of the coagulant screening workflow that is described in sections 4.2.1 - 4.2.3 is shown in Figure C.1 of the Supplemental Information.

4.3.4 Sludge volume

The volume of sludge produced was estimated by assuming that the sludge layer is a compacted disk with a radius equal to the inner diameter of the LUMiFuge vial (10.5 mm). The height of the cake was determined based on the transmission profiles as the distance between the phase boundary's position on the last profile (300^{th} profile at t = 5 min.) and the end of the vial. The cake volume was then calculated as the volume of a cylinder using the vial radius and the sludge height. The sludge volumes reported in Section 4.3.3 were normalized by dividing by the initial centrate volume placed into the LUMiFuge vial (1.6 mL).

4.4 Results & Discussion

4.4.1 Optimizing coagulation performance for a single batch of centrate

Figure 4.2 shows representative transmission profile data obtained from the LUMiFuge analysis. A representative transmission profile is shown in Panel A, and was obtained via AC analysis of Batch B centrate that was first adjusted to a pH of 5, and then treated with 250 mg-Fe³⁺/L. For each transmission profile, an analysis window is set between the meniscus (radial position of the air-liquid phase boundary) and the last phase boundary (radial position of the solid-liquid phase boundary). The solid-liquid phase

boundary is denoted by the sharp decrease in transmission, and shifts rightwards as floc settling occurs, this phase boundary moves to higher radial positions along the vial (rightward shift). As described in section 4.2.3, each transmission profile contains transmission measurements taken at 1 second intervals, and the color of each profile transitions from red to green between the first and last profile.

Panel B shows the effect of two different coagulant dosages on the subsequent transmission profiles. Here, raw centrate from Batch B (left-most image in Figure 4.2) was pH adjusted to 5 and treated with a low (50 mg-Fe³⁺/L) and high (300 mg-Fe³⁺/L) doses of ferric chloride (see Section 4.2.2), followed by processing on the LUMiFuge using the method described in Section 4.2.3. The resulting transmission profiles and instability index values are shown along with images of the vials after the 5-minute centrifugation period. Panel B highlights three important facets that are crucial to interpreting the data presented in later sections. Firstly, high-coagulant dosages were characterized by larger differences in light transmission between the two phases compared to lower dosages. The position of the phase boundary is best observed in the transmission profile obtained for the 300 mg-Fe³⁺/L dosage, where a clear drop in transmission from 80 to 5% can be observed. In contrast, a much smaller difference in transmission between the two phases was observed for the 50 mg-Fe³⁺/L dosage. The relationship between NIR transmission and instability index is shown in Equation 4.1. Simply put, the equation calculates instability index as the ratio of the total change in transmission (known as clarification) across the analysis window at a given time $(\sum_{i=r_{min}}^{r_{max}} T_{i,i}^{diff})$, to the maximum possible clarification $((\overline{T}_{end} - \overline{T}_1)(j_{r_{max}} - j_{r_{min}}))$ by assuming that the maximum *attainable* transmission of the supernatant phase is the difference between the transmission of pure water (\overline{T}_{end}) and the average transmission at the first time point (\overline{T}_1). ³⁰ The higher coagulant dosage generates greater colloidal instability and clarifies the supernatant phase more than a lower dosage, and thus providing a higher instability index value. The images of the vials after coagulation supports these observations, as the supernatant phase is significantly clearer after treatment with a higher dosage.

Secondly, as floc settling occurs, the phase boundary moves to higher radial positions along the vial (right-ward shift); once again, this movement is best observed in the case of the higher coagulant dosage. Front-tracking profiles are generated by plotting the position of this moving boundary measured at a set transmission of 30% at 1s intervals. Finally, due to the larger difference in transmission observed between the two phases, higher coagulant dosages yielded higher instability index values (see Eq.1). Although the instability index quantifies the instability of a mixture, it was used as a pseudo metric for colloidal stability in this study.

The reproducibility of the LUMiFuge data was assessed by conducting coagulation experiments at three adjusted initial centrate pHs (5, 6 and 7) and two coagulant dosages (50 and 300 mg-Fe³⁺/L) in triplicate. The front-tracking profiles and instability index values (see Figure C.2 of the Supplemental Information) indicated the good reproducibility of the obtained measurements and provided confidence in the use of these metrics as coagulant screening tools.



Figure 4.2. (A) An example of an annotated transmission profile showing the position of the meniscus, the last phase boundary, the analysis window, and direction of phase boundary movement with time. This transmission profile was taken after coagulating a sample of centrate from Batch B with 250 mg-Fe³⁺/L and initial pH of 5. (B) (Left) LUMiFuge vial (10 mL, polycarbonate) containing centrate from Batch B next to a Canadian quarter for reference. (Right) Transmission profiles obtained following the coagulation of Batch B centrate (adjusted pH of 5) with 50 mg-Fe³⁺/L and 300 mg-Fe³⁺/L of ferric chloride, and centrifugation at 2000 rpm for 5 minutes and transmission profile recording every 1s. Images of the vials following coagulation and centrifugation are shown beside their respective transmission profile.

The same process was used to assess the separation performance of ferric chloride under various solution conditions. Figure 4.3 shows the front-tracking profiles (top) and instability index values (bottom) obtained following the coagulation of Batch B centrate at three pHs (5, 6, and 7) and ten coagulant dosages $(0 - 500 \text{ mg-Fe}^{3+}/\text{L})$. The raw transmission profiles used to generate this data are presented in Figures C.3-C.5 in the Supplemental Information. Standard error bars for conditions tested in triplicate (described above) are shown for the instability index data in the bottom panels. The trends observed in the data demonstrate that ACs are suitable for use in screening coagulant conditions. Firstly, for a given pH, it was possible to identify the concentration of Fe³⁺/L required to achieve rapid settling. For example, the front-tracking profiles obtained at a pH of 5 revealed that rapid settling occurred when the concentration of Fe³⁺ was increased from 100 to 150 mg-Fe³⁺/L. These results showed good agreement with the obtained instability index values, which increased from 0.204 to 0.672. The instability index increased to 0.831 at a dosage of 200 mg-Fe³⁺/L and remained relatively unchanged for higher concentrations. This data implies that, at a pH of 5, a coagulant dosage between 150 and 200 mg-Fe³⁺/L should be chosen, as higher doses will not achieve further colloid instability or higher settling. These trends were also observed for the higher pHs that were tested.

The results presented in Figure 4.3 also illustrate the effect of pH on both the front-tracking profiles and instability index. As can be seen, rapid settling and higher instability index values were achieved at the lower pH values; for example, at a coagulant concentration of 200 mg-Fe³⁺/L, rapid settling was observed at a pH of 5, whereas almost

no settling was observed at pHs of 6 and 7. This result was mirrored in the instability index values, which were 0.831 at a pH of 5, and 0.258 and 0.120 at pHs of 6 and 7, respectively. The effect of pH on ferric chloride coagulating agents is well-understood. In particular, it is well-known that Fe³⁺ rapidly hydrolyzes when added to aqueous solutions, with higher proportions of positively charged hydrolysis products (i.e., Fe(OH)₂⁺, FeOH²⁺) being observed at lower pHs. As such, lower coagulant concentrations are needed to neutralize negatively charged colloids.^{31,32}



Figure 4.3. Front-tracking profiles (top panels) and instability index values (bottom panels) obtained following the coagulation of Batch B centrate with ferric chloride at concentrations ranging between 0 and 500 mg-Fe³⁺/L. The three columns show data collected from three adjusted initial centrate pHs (left to right: pH 5, 6, and 7).

The 30 independent screening experiments presented in Figure 4.3 took approximately 85 minutes with the AC, which is much faster than the estimated 370 minutes (assuming 1 hour of gravitational settling^{33,34}) it would take with a standard sixcell jar tester. Additionally, only 2.4L of centrate was required for screening with the AC, which is much lower than the 60L that would be require with the jar tester. Moreover, the time estimate for jar testing does not include the additional time required to assess separation performance via external water quality tests (e.g., turbidity removal, COD removal). A comparison of the estimated time required to screen coagulants with the LUMiFuge and a standard jar tester is shown in Table C.1. These results convincingly demonstrate that ACs can be used to rapidly optimize a coagulation process, while requiring low material consumption and time commitment. While our study demonstrated the utility of ACs for coagulation optimization using centrate, we see an opportunity to apply this method to other high strength industrial wastewaters, such as from the dairy (COD: 1500 - 5200 mg/L) or pulp and paper industry $(1000 - 15000 \text{ mg/L})^{35}$, or in municipal wastewaters, such as raw influents ³⁶ or primary effluents ³⁷, where coagulation induces a change in optical density of the wastewater.

4.4.2 Coagulant selection and dosing in response to feed variation

Beyond screening the separation performance of a single coagulant within a batch of wastewater, data provided by ACs can be used to rapidly compare coagulants and batches of wastewater with different compositional properties. This is demonstrated in Figure 4.4, which shows the impact of feed properties (left) and coagulant type (right) on the instability index. The left panel compares the instability index values obtained following the use of ferric chloride to coagulate Batch A (February) and Batch B (July) at an adjusted pH of 6. As can be seen, the instability index was higher for Batch A compared to Batch B at each concentration between 50 and 300 mg-Fe³⁺/L. Both batches reached a maximum instability index of ~0.83, which was achieved with ferric chloride at a dosage of 250 mg-Fe³⁺/L for Batch A and 400 mg-Fe³⁺/L for Batch B. These differences can be explained by the compositional differences between both batches (see Table 4.1). For example, the higher COD, TOC, and TDS content in Batch B suggests higher NOM loading; thus, Batch B requires a higher coagulant dose to achieve charge neutralization.^{38,39} This finding is supported by the higher zeta potential measured in Batch B (-17.1 mV vs. -15.4 mV for Batch A)⁴⁰.

The right panel compares the instability index values obtained following the coagulation of Batch A with either ferric chloride or polyaluminum chloride. For these comparisons, the instability index measurements were made at the same mg-ion/L concentrations for both coagulants. As with the results in the left panel, a maximal instability index of ~0.83 was achieved for both coagulants, however, this was achieved at a lower concentration with ferric chloride, likely due to differences in the equilibrium concentration of positively charged hydrolysis observed at the adjusted centrate pH of 6.^{32,41} Figure C.6 in the Supplemental Information shows the instability index vs. coagulation concentration curves for both coagulants at adjusted pHs of 5, 6, and 7. While similar trends to those previously described can be seen across the range of tested pHs, higher instability occurs at lower concentrations when the centrate pH is adjusted to a lower value, which aligns with the results observed in Figure 4.3.^{32,41} Figure 4.4 shows

how ACs can be used to make rapid adjustments to coagulation processes. Once again, coagulant screening was much faster (~60 minutes vs. 220 minutes) and require less material (1.44L vs. 36L) when using an AC compared to a jar tester (see Table C.1).



Figure 4.4. Comparing the effects of coagulant concentration on the instability indices for two coagulants (FeCl₃ and PACl) and two batches of centrate sampled in February 2022 (Batch A) and July 2022 (Batch B) with a starting pH of 6.

Thus far, separation performance has been assessed based on instability index. However, it is important to understand how the instability index, which is intrinsic to ACs, correlates to traditional separation performance metrics. Following centrifugation, the COD of the supernatant fraction in the LUMiFuge vial was measured. The COD removal was calculated as the percentage decrease in comparison to the condition without the addition of coagulant. Figure 4.5 illustrates the relationship between COD removal and the instability index observed in 35 coagulation experiments conducted at a pH of 6 and using ferric chloride and polyaluminum chloride at concentrations ranging between 0 - 500 mg-ion/L. The results indicate that COD removal increases at higher instability index values, but plateaus at values beyond ~0.4 - 0.5. This trend approximately aligns with the inflection point of the instability index vs. coagulant concentration curves shown in Figure 4.4. These results establish instability index values as a suitable metric for guiding the selection of coagulant dosages, as the data presented in Figures 4.4 and 4.5 indicate that operators should strive for dosages around the inflection point of the instability index vs. coagulant dosage curves. This correlation can be observed across the pH range that was studied (5 – 7) and is presented in Figure C.7 in the Supplemental Information.



Figure 4.5. Relationship between Instability index and COD removal for FeCl₃ and PACl and two batches of centrate sampled in Feb-2022 (Batch A) and Jul-2022 (Batch B) at an initial adjusted pH of 6.

4.4.3 Estimating sludge production rate

Estimating the amount of sludge produced by coagulation is critical to developing waste disposal processes and strategies. In facilities with coagulation processes, the supernatant fraction is either discharged or undergoes further downstream treatment, while the solid sludge is dewatered as much as possible and then shipped off for external disposal. As solid waste disposal can be extremely costly, facilities may look to optimize their coagulant dosing by minimizing the amount of sludge produced. The transmission profiles obtained from ACs can be used to assess the amount of sludge produced by measuring the height of the solid phase and using it to determine the volume (as outlined in Section 4.2.4). The top panel of Figure 4.6 shows the last transmission profile (t = 300s) obtained following the coagulation of Batch B with 100, 300, and 500 mg-Fe³⁺/L at an adjusted pH of 6. The position of the solid liquid phase boundary is highlighted for each profile. As can be seen, the phase boundary shifts to lower radial positions along the length of the vial as the coagulant concentration increases, thus indicating a larger cake height.

This technique can be extended to the full range of evaluated coagulant concentrations. The bottom panel of Figure 4.6 shows how the solid volume (normalized by the initial concentration of coagulated centrate placed into the LUMiFuge vial) varies with the coagulant dosage. Standard error bars are also shown for conditions evaluated in triplicate (50 and 300 mg-Fe³⁺/L). The amount of sludge produced increases alongside the coagulant concentration but appears to plateau at concentrations greater than 400 mg-Fe³⁺/L. Notably, sludge production appeared to plateau at approximately same

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concentration as in the instability index experiments. This trend can be extended to the range of pHs evaluated in this study and is illustrated in Figure C.8 in the Supplemental Information. As discussed in Section 4.3.2, operating at a concentration around the inflection point of the instability index vs. coagulant concentration curve provides the best trade off between coagulant dosage and COD removal. Based on the results shown in Figure 4.4, this concentration is around 250 mg-Fe³⁺/L for Batch B, which, according to the data presented in the bottom panel of Figure 4.6, the use of this concentration should yield 0.09 mm³ of sludge per 1 mL of centrate treated. The inflection point for Batch A occurs at around 200 mg-Fe³⁺/L, which would be expected to result in the production of lower volumes of sludge. This data can be used to rapidly adjust downstream sludge handling processes in response to varying feed properties and coagulant dosages.



Figure 4.6. (Top) The final transmission profile (t = 300s) obtained with coagulant dosages of 100, 300, and 500 mg-Fe³⁺/L, with the position of the solid-liquid phase boundary of each profile highlighted. (Bottom) The calculated sludge volume based on the final phase boundary position and the corresponding instability index. The data presented in this figure was collected using Batch B with an initial adjusted pH of 6.

4.5 Conclusions

The results of this study demonstrate that an AC can be used to rapidly screen coagulants with very low material consumption. The ability of ACs to measure transmissions over the length of a sample enables unique measurements of settling kinetics and sample stability, which are ideal for assessing the separation performance of coagulants. To demonstrate this application, two batches of centrate were sampled from a biogas generation facility in February (Batch A) and July (Batch B) of 2022. The centrate was sourced from dewatered anaerobic digestate and exhibited significant variability in its composition depending on the upstream organic waste that entered the process. Thus, such facilities need a tool that allows coagulant dosages to be rapidly optimized in response to feed variability. Batch B was subjected to a comprehensive screening study wherein the separation performance of ferric chloride was assessed at all possible combinations of three adjusted pHs (5, 6 and 7) and 10 coagulant concentrations (0 - 500)mg-Fe³⁺/L). The obtained front-tracking profiles enabled the identification of the minimum coagulant dose required to achieve rapid settling at a given pH, and these results were further supported by a sharp increase in the instability index. The data obtained via the AC were then used to compare the performance of two coagulants within a single batch of centrate, and the performance of a single coagulant for two batches of centrate with different compositional properties. The resultant instability index vs. coagulant concentration curve was used to rapidly compare coagulants and assess how the feed properties impacted their performance. Furthermore, the findings showed that COD removal is positively correlated with the instability index up to a value of ~ 0.5 , after which plateauing occurs. This trend corresponds to the inflection point of the instability index vs. coagulant concentration curve and may represent an operating point that can be used in coagulation processes. Finally, transmission profiles were used to determine the volume of sludge that was produced, with results indicating that sludge production increases alongside the coagulant dosage. Estimating sludge volume using ACs is useful for making rapid adjustments to sludge-handling processes when sludge production changes in response to alterations in the coagulant dosage. Overall, 132 individual screening experiments were conducted in this work, which required approximately 10.6L of centrate and 6 hours of operator time. Ultimately, the results presented herein demonstrate that the proposed approach can be used to rapidly screen coagulants while enabling minimal material consumption. An unexplored benefit of the LUMiFuge is the ability to conduct coagulant screening experiments at different temperatures. This can be used to simulate coagulation processes to emulate seasonal temperature fluctuations that treatment facilities experience and is a direct extension to this study.

4.6 References

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Chapter 5

Leveraging colloidal stability measurements to optimize the treatment of anaerobic digester centrate

Chapter 5 Leveraging colloidal stability measurements to optimize the treatment of anaerobic digester centrate

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In preparation for submission to the Journal of Environmental Chemical Engineering.

5.1 Abstract

Coagulation-Flocculation (CF) processes are commonly used to remove natural organic matter from wastewater streams prior to downstream membrane processes. When paired with membranes, CF processes needs to be appropriately calibrated to ensure coagulants are not over- or under-dosed. This is often done through colloidal stability measurements via a zeta-potential analyzer; however, these measurements are affected by the salinity of the solution. Zeta-potential is challenging to use as a metric for optimizing coagulant doses when the salt concentration of the incoming feed is either too high, or the concentration varies with time, which is common problem for many industrial wastewaters. In this study, an analytical centrifuge is used to rapidly and efficiently estimate the colloid stability of a CF process that is treating a real industrial wastewater containing a high organic loading (TOC = 1791 mg/L) and salt concentration (conductivity = $23,600 \text{ }\mu\text{S/cm}$). Based on this optimization, ferric chloride doses of 50, 250 (identified as the critical coagulant concentration), and 500 mg-Fe³⁺/L were selected to represent a range of treatment levels. Additionally, measurements of settling velocity were used to select 200 mg/L as an appropriate dose of an anionic polyacrylamide flocculant. Wastewater pretreated at these conditions were filtered using a commercially available nanofiltration membrane in a crossflow filtration cell. The average membrane flux increased from 11.4 ± 1.8 LMH without any pretreatment, to 16.1 ± 2.5 , 17.6 ± 1.7 and 21.7 ± 3.5 LMH for the low, intermediate, and high conditions. Despite having the highest average flux, a significant flux decline was observed at the high condition, which was attributed to excess iron pooling in the supernatant at doses above the critical coagulant concentration. Finally, the permeate TOC tended to increase with increasing coagulant dose, and thus the intermediate condition was determined to provide the best trade-off between flux improvement and NOM removal amongst the four conditions tested.

5.2 Introduction

Coagulation-flocculation (CF) and membrane processes have been widely paired together to treat variety of water^{1–3} and wastewater^{4–6}. In these studies, CF processes are used to pretreat the water by removing suspended colloidal material that would otherwise foul the membrane surface. Natural organic matter (NOM) is a colloidal contaminant that encompasses a broad class of naturally occurring organic compounds, that range in size between 1 nm – 1 μ m⁷. Unlike nutrients, salts and metals, NOM is much larger than the membrane pores of ultrafiltration (UF) and nanofiltration (NF), and completely fouls the membrane surface by forming a less-permeable cake layer⁸. NOM remain stable through electrostatic repulsive forces that prevent colloids from coalescing into settleable aggregates⁹.

Colloid stability is typically measured through zeta-potential, which is the surface charge on a colloid that is suspended in a liquid medium¹⁰. NOM in wastewater

predominantly negative zeta-potential over a wide range of pHs¹¹. CF processes remove NOM by first destabilizing the colloids through the addition of a positively charged coagulant (a hydrolyzing metal such as Al^{3+} or $Fe^{3+})^{12}$, and then the addition of a negatively charged polymer flocculant to form large flocs that settle out of the wastewater, leaving a supernatant with less colloidal material that would foul membrane surfaces. Measurements of zeta-potential are useful in identifying the coagulant dose needed to achieve charge neutralization ($\zeta = 0$ mV) or whether the coagulant has been under or overdosed. Previous studies have shown the importance of monitoring zetapotential in hybrid CF-membrane processes. For example, previous studies by Ang et al.^{13,14} and Schrader et al.¹⁵ have shown that maintaining a negative zeta-potential allows electrostatic repulsion between colloids and the surface of negatively charged polymeric membranes to minimize fouling. Additionally, numerous studies have shown that coagulant overdosing leads to additional fouling from suspended metal hydrolysates that become foulants themselves¹⁶⁻¹⁸. Thus zeta-potential is a critical process parameter that should be monitored in hybrid CF-membrane processes.

Zeta-potential is indirectly measured by measuring the movement of solutes under an applied electrical field (electrophoretic mobility), and it is affected by factors such as concentration of colloids and the pH and ionic strength of the dispersing solution¹⁰. Zetapotential measurements become challenging to accurately determine in high ionic strength solutions due to Debye screening, a phenomenon where the measured zetapotential is reduced due to a shielding effect that is caused by the presence of excess counter ions^{19,20}. The distance over which charge screening occurs is a function of the ion concentration, composition, and valency of ions present²¹. Thus, using zeta-potential as a CF control parameter for wastewaters that contain a high salt and colloidal matter concentrations, such as pharmaceutical wastewater^{22,23}, landfill leachates^{24,25}, dewatered digestates²⁶, and textiles wastewater²⁷, is not recommended, with one source citing 1000 μ S/cm being the highest allowable conductivity²⁸.

Analytical centrifuges (ACs) use an integrated optics system to measure the separation kinetics and solution stability of multiphase mixtures under accelerated conditions, and they are primarily used to study the stability of formulated mixtures. In our previous work, we introduced the use of ACs as a high-throughput screening tool that can be used to optimize coagulation processes through rapid approximations of colloid stability using an integrated "instability index" measurement²⁹. The instability index uses a ratio of transmissions between the two separating phases to assess solution stability, and this was shown to be well correlated with coagulant concentration. As this technique is optical and does not rely on measurements of ion mobility, there is an opportunity to use ACs to optimize coagulation pretreatment processes based on colloidal stability for wastewaters that contain high concentrations of salt and colloidal matter. In this study, we build on previous studies on the effect of colloid stability on membrane filtration using zeta-potential measurements by evaluating membrane performance at various instability index values for a real wastewater containing a high NOM concentration and ionic strength.

5.3 Materials & Methods

5.3.1 Wastewater sampling and characterization

The wastewater used in this study was sampled in August of 2022 from a biogas generation facility operating in North America, and is the liquid fraction of spent digestate that forms after a centrifugation dewatering process, which is known as centrate. The centrate contains a high organic loading (total organic carbon = 1791 mg/L) and salinity (conductivity = 23,600 μ S/cm), and thus is an ideal real wastewater system for this study. A more detailed table of measurements provided in Table D.1.

Several techniques were used to characterize the untreated and treated centrate throughout the study. This includes:

- Total organic carbon (TOC) measurements using a Shimadzu TOC analyzer
- Chemical oxygen demand (COD) measurements using Hach 8000 HR COD kit by following the manufacturers instructions
- Conductivity and pH were measurements using a bench top HI5522 pH/conductivity meter
- Iron concentrations measurements using a Varian Vista Pro Inductively Coupled
 Plasma Optical Emission Spectroscopy (ICP–OES) instrument

5.3.2 Coagulation and flocculation experiments

Coagulation and flocculation experiments were first conducted at an 80 mL scale to rapidly identify doses for investigation, and then at a 2 L scale at to produce enough pretreated centrate for membrane filtration. The as-received centrate was first acidified to a pH of 5 using 36% hydrochloric acid. To induce coagulation, ferric chloride (Kemira Water Solutions, 13.1% Al³⁺) was dosed at concentrations ranging between 0 – 500 mg-Fe³⁺/L and mixed for three minutes at 300 rpm using a magnetic stirrer. If the centrate was also being flocculated, the pH of the solution was increased to between 7 – 7.5 using 5M NaOH while slowly being mixed at 50 rpm. A high molecular weight anionic polyacrylamide flocculant (Superfloc A-150, Kemira Water Solutions) was added at concentrations ranging between 0 – 200 mg/L (w/v) and mixed for 3 minutes. If experiments were being conducted at the 2 L scale, flocs were allowed to settle under gravitational conditions for 1 hour, after which the supernatant phase was extracted using a pipette pump and stored refrigerated for filtration.

5.3.3 Analytical centrifuge screening

A LUMiFuge (Lum, GmbH) AC was used to rapidly evaluate the separation performance of both coagulants and flocculants. A detailed description of how separation performance is assessed via analytical centrifugation can be found in Chapter 4²⁹. In summary, 1.6 mL of the two-phase formed after coagulation or both coagulation and flocculation was transferred to a specialized polycarbonate vial. Up to eight vials were centrifuged for 5 minutes at 2000 rpm and profiles of near-infrared light transmission (T) versus radial vial position (j) were recorded at 1 second interval (i). Instability index values and floc settling profiles were generated by applying data transformations to the transmission profile data. Instability index values are calculated from Equation 5.1, which simply put, is a ratio of transmissions between the treated and untreated phases, where values closer to 1 suggest greater colloid instability.

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Instability Index =
$$\frac{\Delta T_i}{\Delta T_{max}} = \frac{\sum_{j=r_{min}}^{r_{max}} T_{i,j}^{diff}}{(\overline{T}_{end} - \overline{T}_1)(j_{r_{max}} - j_{r_{min}})}$$
 (5.1)

The floc settling velocity was determined by transforming the transmission data into phase boundary position vs. time graphs (known as settling profiles). These graphs were developed by plotting the radial position of the phase boundary in which ~15% transmission was observed, for each time point. A 15% transmission was observed as a typical midpoint in ΔT_i values observed at low concentrations, and allowed the movement of the phase boundary to be measured. The slope of the linear portion of the settling profiles were used to determine the settling profiles. An annotated graphic showing how this was done is shown in Figure D.3.

5.3.4 Membrane nanofiltration

A high-pressure crossflow filtration apparatus was utilized to study the membrane performance at various levels of CF pretreatment. A schematic of the system is shown in Figure 5.1. In summary, liquid is loaded into either tanks T01 or T02, with valve V01 being used to select which tank liquid is drawn from. The liquid is pressurized using a positive displacement pump and passed into a cross flow filtration cell (SEPA, Sterlitech) containing a flat-sheet membrane with an active filtration area of 140 cm². The transmembrane pressure (TMP) is set by controlling the opening of a needle valve on the retentate line (V06). The retentate is passed back into the feed tank, and the permeate is collected in a vessel that is positioned on three load cells that record the cumulative mass over time.

The NFS membrane supplied by Synder Filtration was selected as previous studies have demonstrated both a high selectivity and flux when filtering liquid streams contain high organics loadings with the membrane³⁰. Filtration experiments were conducted at a constant TMP of 100 psi, and crossflow rate of 1.6 L/min. Filtration experiments were eight hours, with DI water being filtered in the first and last hour from tank T01, and centrate being filtered for the intermediate six hours from tank T02. Separate vessels were used to collect the filtered centrate and filtered DI water. The flux was measured by performing a numerical differentiation on the mass vs. time data collected on the load cells. Additionally, the separation performance of the membrane was quantified by measuring the removal of TOC after pretreatment and after filtration.



Figure 5.1. Process & instrumentation diagram of the high-pressure membrane filtration system used to evaluate filtration performance of commercial nanofiltration membranes.

5.4 Results & Discussion

5.4.1 Evaluation of colloidal stability in coagulation and flocculation processes

The effect of varying only the coagulant concentration on instability index is shown in Figure 5.2. Coagulation experiments were performed in triplicate with 80 mL of centrate that was first acidified to a pH of 5, and instability index measurements were made immediately after three minutes of mixing at 300 rpm. Panel A shows the instability index (left axis) and percentage removal of COD (right axis) at ferric chloride concentrations ranging between $0 - 500 \text{ mg-Fe}^{3+}/\text{L}$. Based on the sigmoidal shape, the change in instability index with concentration is non-linear, with a slow increase observed between $0 - 150 \text{ mg-Fe}^{3+}/\text{L}$, a rapid increase between $150 - 400 \text{ mg-Fe}^{3+}/\text{L}$ and a plateauing at concentrations above 400 mg-Fe³⁺/L. The plateauing of observed at 400 mg-Fe³⁺/L suggests that charge neutralization occurs at this concentration and is supported by the lack of increase in COD removal observed at a higher coagulant concentration.

Representative transmission profiles obtained from one of the triplicate coagulation experiments performed at doses of 50, 250 and 500 mg-Fe³⁺/L, along with an image of the AC vial after centrifugation is shown in Panel A. Each transmission profile contains 300 measurements of NIR transmission along the length of the AC vial taken each second, and changes from red to blue between the first and last profile. The boundary between the liquid dominant and solid dominant phase is denoted by a sharp decrease in transmission at a given radial position and shift rightwards with time as floc settling occurs. As expected, the difference in transmission between the two phases increases as doses increases, thereby yielding a higher instability index. Transmission

profiles for each replicate at each concentration is shown in Figure D.2, and shows that the difference in transmission (ΔT_i) between the two phases increases at a similar manner to the instability index, with a noticeable ΔT_i occurring at concentrations above 200 mg-Fe³⁺/L.



Figure 5.2. (A) Instability index (left) and COD removal (right) measured at ferric chloride doses ranging between $0 - 500 \text{ mg-Fe}^{3+}/\text{L}$. Error bars are shown on each data point to indicate the standard error observed across three independent coagulation experiments. (B) Transmission profiles obtained after coagulating centrate (at an initial pH of 5) with three concentrations of ferric chloride (50, 250 and 500 mg-Fe^{3+}/L) and centrifugation at 2000-rpm for 5 minutes, with a transmission profile being recorded at 1s intervals. An image of the LUMiFuge vial taken after centrifugation is shown beside each transmission profile.

Coagulant doses of 50, 250 and 500 mg-Fe³⁺/L were selected for experiments moving forward to represent a range of treatment levels, and henceforth will be referred to as 'low', 'intermediate' and 'high' concentrations respectively. The 50 mg-Fe³⁺/L concentration was selected as an underdosing concentration where membrane fouling due to NOM would dominate, whereas the 500 mg-Fe³⁺/L was selected as an overdosing

concentration where it was expected that fouling due to excess iron would dominate. The 250 mg-Fe³⁺/L was selected since as it lies right on the inflection point of the instability index vs. coagulant concentration curve, which suggests that this concentration is likely the critical coagulant concentration $(CCC)^{31,32}$. The critical coagulation concentration is commonly defined as the minimum coagulant concentration required to induce coagulation. Based on the transmission profiles presented in Figure D.2, an appreciable chance in ΔT_i occurs between 200 – 250 mg-Fe³⁺/L, suggesting that the CCC likely occurs between those two points. This is further supported by the COD measurements, which shows a very marginal change to the COD removal at concentrations above 250 mg-Fe³⁺/L. It was hypothesized that 250 mg-Fe³⁺/L would provide the optimal trade-off between NOM removal and coagulant doses, in which fouling from NOM and excess iron would be minimized. The high-throughput nature of ACs allowed eight instability measurements (and the CCC) to be determined in approximately 10 minutes per replicate.

Flocculation is a critical for ensuring that floc settling occurs quickly and that smaller flocs that may remain suspended are effectively removed from the supernatant³³. The effect of adding an anionic polyacrylamide flocculant was evaluated at three concentrations (0, 100 and 200 mg/L) for each coagulant dose. Figure 5.3 shows the effect of the flocculant doses on instability index (3A) and settling velocity (3B) for each of the coagulant doses. By leveraging the front-tracking capabilities of the AC, the slope of the linear portion of radial position of the phase boundary vs. time was used to estimate settling velocity, and an example of how this was determined is shown in Figure D.3. The flocculant had almost no impact on the instability index, however, did increase the floc

settling velocity, particularly for the intermediate and high coagulant doses. For example, increasing the flocculant dose from 100 to 200 mg/L resulted in the settling velocity increasing from 3.24 to 4.81 cm/s for the intermediate coagulant dose, and from 4.05 to 6.11 cm/s for the high coagulant dose. This result was expected as the action of flocculant is to bridge existing pin flocs into larger settleable flocs, and not to destabilize colloids³³. From these findings, 200 mg/L of flocculant was added to aid floc settling and to ensure smaller suspended flocs were removed prior to membrane filtration.


Figure 5.3. (A) Instability index and (B) floc settling velocity (in cm/s) measured after coagulation with ferric chloride at the three previously identified concentrations, and flocculation with either 0, 100 and 200 mg/L of an anionic polyacrylamide flocculant. Error bars indicating the standard error across triplicate coagulation and flocculation experiments are shown.

Batches of centrate were treated with either the low, intermediate or high coagulant dose, and 200 mg/L of flocculant in 2 L beakers. Each condition was repeated six times to generate sufficient volumes (~10 L) of CF treated centrate prior to filtration. Samples of the two-phase mixture were taken after both coagulation and flocculation, and

the instability index was measured to ensure that results at the 2 L scale conformed with results obtained at the 80 mL scale. These results are presented in Table D.2 and show good agreement between both scales for each condition tested with some variability observed at the intermediate dose.

5.4.2 Membrane flux and fouling analysis

The CF treated centrate was filtered using a commercially available flat sheet nanofiltration membranes (NFS, Synder) in a high-pressure crossflow filtration cell ($A_M = 140 \text{ cm}^2$). The filtration experiments lasted eight hours, with DI water being filtered during the first and last hour, with centrate filtered for six hours in between at a constant pressure of 100 psi. Figure 5.4(A) shows the membrane flux measured while filtering both DI water, and centrate across all levels of CF pretreatment, and an image of the membrane surface after the entire 8-hour filtration window for a single replicate is shown in Figure 5.4(B). Images of the membrane surfaces following filtration from both replicates is shown in Figure D.4.



Figure 5.4 (A) Permeate flux obtained following filtrations of (from left to right) as received centrate, and centrate pretreated with 50, 250 and 500 mg-Fe³⁺/L of ferric chloride and 200 mg/L of flocculant using commercial NFS (synder) membranes across two replicates. Filtration experiments lasted eight-hours, with DI water being filtered during the first and last hour, and centrate pretreated at various conditions being filtered for the six hours in between. (B) Images of the membrane surface of one replicate that was taken after the 8-hour filtration is shown below each filtration profile.

Table 5.1 shows the average flux measurements across two replicates for each stage of the filtration cycle. The average DI water flux before centrate filtration across all eight membranes was 35.9 ± 2.9 LMH, and a dramatic drop in flux was observed immediately after switching to centrate filtration across all conditions. The average flux across both replicates for the no CF control was 11.4 ± 1.8 LMH bar, which is a 68.7% decrease from the average DI water flux. The centrate flux varied with the level of CF pretreatment, however a general trend of the average flux increasing with coagulant dose was observed. The flux increased from 11.4 ± 1.8 with no pretreatment, to 16.1 ± 2.5 at the low dose condition and 17.6 ± 1.7 LMH at the intermediate dose condition. Additionally, the average DI water flux after centrate filtration was not statistically

different from the average DI water flux measured before filtration, which indicates that fouling is reversible at these conditions. With reference to the classical Hermia models, the dominant mechanism is likely some combination of intermediate and complete pore blocking where NOM foulants occlude the membrane pores³⁴. Images of the membrane surfaces at these three conditions show that a dense cake layer was not formed, and this is likely due to shear forces preventing the accumulation of foulants on top of each other through weak hydrophobic interactions³⁵.

An average flux of 21.7 ± 3.5 LMH was measured at the high condition, however unlike the previous conditions, flux declines of 43% (replicate 1) and 26% (replicate 2) were observed between the highest measured flux and the end of the centrate filtration cycle. The flux decline suggests that a cake layer builds over the initial fouling layer, which gradually becomes thicker as filtration occurs, resulting in a steady decline in flux³⁴. Additionally, the average DI water flux after centrate filtration was 31.4% lower than before centrate filtration, suggesting that the form of fouling is partially irreversible. It was suspected that this is due to fouling from excess hydrolyzed iron products that remained in the supernatant after coagulation. Figure 5.2(A) shows that for coagulant doses above the CCC, marginal improvements in COD removal were observed with addition of more coagulant. Thus, the additional coagulant contributes minimally to charge destabilization, and pools within the supernatant³⁶.

Table 5.1. Average flux measurements during filtration of CF pretreated centrate across four treatment levels, and the pre- and post-DI water filtrations. Average and standard deviations for each flux were calculated based on measurements taken every minute during each filtration cycle, across two replicates for each condition.

	Average DI water	Average wastewater	Average DI water
	flux before Centrate	flux (LMH)	flux after centrate filtration (LMH)
No CF Control	36.4 + 1.3	11.4 + 1.8	36.7 + 4.7
Low Condition	32.6 ± 2.9	16.1 ± 2.5	29.3 ± 6.4
Intermediate Condition	33.4 ± 3.6	17.6 ± 1.7	31.9 ± 3.6
High Condition	41.1 ± 3.3	21.7 ± 3.5	28.8 ± 1.8

To verify this hypothesis, the concentration of iron within the supernatant was measured directly from AC vials following coagulant screening presented in Figure 2. Figure 5 shows the measured instability index (left) and the concentration of iron measured via ICP-OES (right) for nine different coagulant doses. It is important to note that the as received centrate had an initial iron concentration of 52.2 mg/L. The supernatant iron concentration gradually increases with coagulant dose up until the CCC, however, increases rapidly at concentrations higher than the CCC. This confirms that coagulant dosing beyond the CCC results in the excess coagulant pooling within the supernatant, and the fouling behaviour observed is due to the presence of excess hydrolyzed iron products.

At a neutral pH, the dominant form of ferric is $Fe(OH)_2^+$, and the surface zetapotential of the NFS membrane is ~-20 mV^{30,37}. Images of the membrane surfaces presented in Figure 5.4(B) show that a significant orange discoloration is observed on the membrane at the high condition, suggesting that the formed caked layer contains a high amounts of hydrolyzed iron products that have adsorbed onto the membrane surface. As these images were taken after the second DI water filtration, this cake layer was able to resist surface shearing with clean water and explains why a lack of flux recovery was observed compared to previous conditions. The excess iron contributes to a charge reversal that allows $Fe(OH)_2^+$ -NOM complexes to easily adhere onto the membrane surface through electrostatic interactions. The cake layer that forms on the surface of the membrane is likely held together via stronger electrostatic interactions between iron and the NOM, that are better able to resist shearing from crossflow and accumulate as a cake on the membrane surface^{34,38}.



Figure 5.5. Instability index (left) and the supernatant iron concentration (right) measured directly from the LUMiFuge vials using ICP-OES for coagulant doses ranging between 0 $-500 \text{ mg-Fe}^{3+}/\text{L}$. Error bars are shown on each data point to indicate the standard error observed across three independent coagulation experiments.

5.4.3 NOM removal performance of CF and nanofiltration process

In addition to the effect on membrane flux, the effect on organics removal was also investigated through measurements of TOC. Figure 5.6 shows the measured TOC after CF treatment, and NF for the three doses coagulant doses and the no pretreatment control. When considering just the CF process, the average TOC dropped 60.6% between the low and intermediate conditions, from 1691 ± 93 mg/L to 666 ± 42 mg/L. However, at the high condition, the TOC only dropped marginally to 520 ± 20 mg/L. These results compliment the COD removal results collected during coagulant screening that is presented in Figure 5.2 and is likely due to the coagulant contributing less to NOM colloidal destabilization beyond the CCC. Images of samples of centrate taken after each stage of treatment for each condition tested is shown in Figure D.5.

Following membrane filtration that the permeate TOC was reduced by over 90% across all trials when compared to the original feed TOC of 1791 mg/L. The lowest TOC was measured at the no CF pretreatment condition at 51 \pm 11 mg/L, and marginally increased to 76 \pm 7 and 79 \pm 3 mg/L for the low and intermediate dose. At the highest dose, the permeate COD was 136 \pm 2 mg/L, more that double the no coagulant condition. Similar results have been presented in previous studies³⁹ and is likely due to charge reversal effects that allow Fe-NOM complexes to more easily transport through the negatively charged membrane⁴⁰. These results suggest the existence of an interesting trade off between the gain in membrane productivity and the loss in permeate quality that exists when a centrate is pretreated via a CF process. When considering both the membrane flux results and the TOC removal results, the best operating condition for the

combined process is at the inflection point of the instability index vs. coagulant concentration curve, or the CCC. The AC used in this study allowed for the CCC to be rapidly determined (<10 minutes) and proves to be a valuable tool when optimizing CF pretreatment processes.



Figure 5.6. TOC measurements taken of samples after CF at the 2L scale, and after membrane filtration for the four coagulant concentrations evaluated. Standard deviation error bars are shown for three triplicate measurements of TOC for each sample

5.5 Conclusions

In this study, an AC is used to preselect conditions for a CF treatment process through measurements of colloidal stability and floc settling velocity, and study the effects of different levels of pretreatment on a downstream NF process. A sample of real anaerobic digester centrate was sampled from a biogas generation facility. A relation between colloidal stability and coagulant dosing was first established by measuring the "Instability Index" of the wastewater system after being coagulated with ferric chloride at concentrations between $0 - 500 \text{ mg-Fe}^{3+}/\text{L}$. Combined with measurements of COD, the CCC was identified as being around 250 mg-Fe³⁺/L, and was selected for experiments moving forward, along with a low dose (50 mg-Fe³⁺/L) and high dose (500 mg-Fe³⁺/L).

The front tracking capabilities of the AC were also used to select a flocculant dose of 200 mg/L based on settling velocity. The low, intermediate, and high coagulant doses, along with 200 mg/L of flocculant, were then used to pretreat the centrate at a 2 L scale to produce sufficient volumes of CF treated centrate for filtration with a commercially available nanofiltration membrane in a crossflow filtration cell. The results showed a dramatic decrease in flux when filtering centrate compared to DI water, however, the flux generally increased with instability. At concentrations above the CCC, a steady flux decline was observed, and was attributed to excess iron that accumulates in the supernatant, and this was confirmed with measurements of the iron concentration in the treated supernatant. Measurements of TOC removal after both CF and NF showed that the TOC tended to increase with coagulant dose, and the operating point around the CCC provides the best trade-off between flux improvement and TOC removal. ACs have demonstrated that they can be used to optimize CF pretreatment processes through measurements of NIR in lieu of traditional zeta-potential measurements that are affected by the ionic strength of a solution.

5.6 References

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Chapter 6

High-throughput and miniaturized screening pipeline for optimizing two stage coagulation-membrane filtration processes

Chapter 6 High-throughput and miniaturized screening pipeline for optimizing two stage coagulation-membrane filtration processes

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In preparation for submission to Environmental Science & Technology

6.1 Abstract

Two stage coagulation and filtration processes are widely used in combination to treat various wastewaters, however, identifying the optimal coagulation pretreatment conditions is critical for optimizing the downstream membrane process. In this study, we present an integrated high-throughput and miniaturized screening (HTMS) pipeline that combines analytical centrifugation (AC) with filter plate technology to rapidly and efficiently screen coagulation-filtration processes in unison. Elements of automation (via a liquid handling system) were used to perform coagulant dosing and liquid transfer tasks, and spectroscopy measurements were utilized to rapidly assess process system performance. The HTMS pipeline enabled a total of 648 coagulation-filtration experiments to be conducted over the course of four days, in which six coagulants were screened at all combinations of four wastewater pHs and nine dosing concentrations in triplicate. The separation performance during coagulation was assessed using the AC via an instability index measurement, which quantifies the degree to which the wastewater has been clarified via a ratio of light transmission measurements between the treated supernatant phases and settling floc. When the instability index is determined for an array of concentrations, the critical coagulant concentration (CCC) can be rapidly identified. The CCC shifts depending on the solution conditions, however, an instability index of ~0.2 was measured at the CCC across all coagulation experiments. The supernatant fraction from each coagulation experiment was filtered in 96-well filter plates containing 30K Omega ultrafiltration membranes, and the permeated volume and permeate quality were determined by measuring absorbances at 977 nm and 272 nm respectively. Interestingly, the permeated volume tended to increase only at concentrations above the CCC, while the absorbance at 272 nm decreased up until the CCC and then plateaued at ~0.4 above the CCC. When correlating the volume permeated to the absorbance at 272 nm, the best performing pretreatment condition occurred when the wastewater was acidified to a pH of six and alum sulfate was dosed at a concentration of 400 mg-Al³⁺/L, which resulted in an 83% decrease in 272 nm absorbance and 282% increase in the permeated volume.

6.2 Introduction

Upstream coagulation processes are frequently paired with downstream membrane processes when treating wastewaters containing a high concentration of colloidal matter that would foul a membrane surface^{1–3}. The size of colloidal matter ranges anywhere between 1 nm to 100 μ m in size⁴, and can be much larger than the typical pore size found in many commercial UF (1 – 100 nm)⁵ and NF membranes (0.5 – 1.5 nm)⁶. For wastewaters containing high concentrations of colloidal matter, such as wastewaters produced from the textile production⁷, landfill leachates⁸ and pulp and paper mills⁹, direct filtration leads to either pore plugging or cake layer formation depending on the size of the colloid⁴. Natural organic matter (NOM) is a common source of colloidal fouling that is found in many wastewaters, and remain stable through negative electrostatic repulsive forces that prevent aggregation into settleable flocs¹⁰. Coagulation via a hydrolyzing metal (such as Fe³⁺) can effectively neutralize these charges and promote floc formation. However, when paired with membrane processes, careful monitoring of the upstream coagulation process is needed to ensure good operation of the downstream process. Firstly, the coagulant dosing concentration needs to be controlled to prevent underdosing (suboptimal NOM removal) or overdosing (source of metal fouling and colloid restabilization)¹. This can be challenging for facilities that experience influent variability and require the coagulant dose to be frequently readjusted, such as those treating high-strength industrial wastewaters^{11,12}. Secondly, changes made to the solution conditions of the wastewater to optimize the coagulation process, such as changing the wastewater pH or the amount of coagulant added, can also affect the efficacy of the downstream membrane process^{1,13}. Thus, when developing and optimizing integrated coagulation-filtration processes, a holistic approach that considers both processes in unison is needed.

Process screening involves replicating industrial processes at a smaller scale such that rapid testing can be carried out to optimize operating conditions or choose between process alternatives. The current standard for screening both coagulation and filtration process involve large and laborious bench scale equipment that requires several liters of wastewater and several hours of operator time to effectively screen processes. Coagulants are often screened with jar testers, which emulate industrial coagulation processes with four to six 1-2 L jars and an integrated paddle stirrer¹⁴. Similarly, membrane technologies are screened using bench scale (1 - 10L) membrane systems that similarly require large volumes of wastewater and have a low throughput as only one membrane can be screened

at a time. Several studies exist in which the supernatant fraction from jar tester has been filtered via a bench scale membrane system to evaluate the improvements in membrane performance^{15–18}. However, due to the laborious nature and material intensity of both processes, the scope of these studies only includes a few combinations of conditions tested, and optimization of these processes often occurs independently (i.e., the coagulation process is independently optimized before the filtration process).

Influenced by advancements made in the biomanufacturing^{19,20} and material discovery²¹ space, screening technologies are moving towards technologies that are miniaturized and high throughput (HT) such that several combinations of process variables and alternatives can be evaluated in a short period of time with a low material requirement. Though not as mature as technologies that exist for biological and material synthesis applications, high-throughput screenings exist for both coagulation and filtration process. Previous studies have introduced the use of microwell assays^{22,23}, microfluidic devices²⁴, scaled down mixing vessels²⁵, imaging methods²⁶ and spinning disc devices²⁷ as HT and miniaturized screening alternatives to jar testing. Moreover, our previously published work established analytical centrifugation as a viable highthroughput and miniaturized (HTMS) tool that rapidly evaluates the separation performance of coagulants through light-based pseudo-measurements of colloidal stability²⁸. Similarly for membrane process development, technologies such as filter plates^{29,30}, parallelized systems^{31–33}, miniaturized testing cells^{34,35} and vial-based techniques³⁶ have been proposed to facilitate HTMS. However, to our knowledge, studies have yet to combine these technologies to screen integrated coagulation-filtration processes.

Inspired by recent work related to combinatorial screening pipelines that combine multiple screening technologies^{37–39}, this work aims to develop a HTMS platform that combines coagulation and membrane screening technologies to facilitate HT process development and optimization of integrated coagulation-filtration processes. This work builds upon our previous work with ACs as a HTMS tool for coagulant screening⁴⁰, by filtering the supernatant fraction with commercially available filter plate technology. Filter plates were selected as the volume requirements from AC screening (~1.6 mL/sample) closely matches the well volumes of filter plates (~0.35 ml/well). Though filter plates are primarily used for bioseparations applications (namely DNA and protein separation), limited studies have used this technology for HT process development (HTPD)²⁹, and to evaluate membrane surface modifications to minimize NOM fouling⁴¹. To the authors knowledge, filter plate technology has yet to be used as part of a screening pipeline in the development and optimization of wastewater treatment processes. Additionally, the screening pipeline presented in this study aims to incorporate current trends in HTPD by incorporating elements of automation, and by replacing traditional water quality characterization techniques with rapid absorption-based analytical techniques¹⁹. The HTMS pipeline presented in this study enabled 648 individual coagulation-filtration experiments to be conducted over the course of four working days, where a total of six coagulants were screened at four pHs and nine concentrations in triplicate.

6.3 Materials & Methods

6.3.1 Wastewater sampling and characterization

The industrial wastewater used in this study was sampled from a biogas generation facility in North America. At this facility, municipal source separated organics are trucked in and fed into an anerobic digestor to produce biogas. The spent digestate is then separated via a centrifuge, and the liquid fraction coming off the centrifuge forms a high strength industrial wastewater with a high NOM loading known as anaerobic digester centrate. The centrate sample was collected in April 2023 the TOC, chemical oxygen demand (COD), conductivity and pH of the as-received centrate were measured and summarized in Table 6.1.

Table 6.1. Measurements of four water quality parameters of the as received centrate, along with details of the instrument that was used to perform each measurement. Measurements are shown as the average and standard deviation across three triplicate measurements of each parameter.

Measurement	Average ± Standard Deviation	Instrument
pH	9.1 ± 0.04	Hanna HI 5522
Conductivity (mS/cm)	14.8 ± 0.43	pH/Conductivity Meter
Total Organic Carbon (mg/L)	1524 ± 193	Shimadzu TOC Analyzer
Chemical Oxygen Demand (mg/L)	4810 ± 431	Hach 8000 HR COD Kit

6.3.2 HTS of coagulants

6.3.2.1 Automated coagulant screening platform

Six commercially available coagulants that were supplied by two companies were used at a concentration of 2.5% in this study: ferric sulfate and alum sulfate supplied by Sigma Aldrich, and ferric chloride, polyaluminum chloride, sodium aluminate and aluminum chlorohydrate supplied by Kemira Water Solutions. All coagulants were appropriately diluted to make a 2.5% w/v solution on a per ion basis. An epMotion 5070

(Eppendorf) liquid handling system (LHS) was used to automate coagulant dosing and liquid transfer tasks between plates and AC vials. To complement the use of a LHS, coagulation experiments were conducted in standard polystyrene 24-well plates. The as received centrate was first acidified to a desired pH with concentrated sulfuring acid (95%, VWR), and then 2 mL was transferred into each well of the 24-well plate, along with a 25 x 8mm magnetic stir bar. Following acidification, coagulants were dosed at eight concentrations ranging between 25 - 400 mg/L into eight wells of the 24-well plate. The plates were then removed from the LHS and the coagulant-wastewater mixtures in each well were mixed on a tumble stirrer for three minutes at 300 rpm (see Figure E.1). The plate was then placed back into the LHS and 1.6 mL of the two-phase solution was transferred to polycarbonate AC vial. Each solution was pipette mixed with the LHS prior to transferring the solution to the vial to ensure a representative mixture of both phases were transferred to the AC vials. This process was repeated twice more for the remaining two sets of 8-wells to obtain triplicate measurements at each condition. The no coagulant controls at each pH were conducted independently to this screening.

6.3.2.2 Colloidal stability assessment via analytical centrifugation

A LUMiFuge (LUM GmbH) AC was used to rapidly assess the separation performance of eight coagulated wastewater mixtures simultaneously. A detailed outline of the screening procedure and explanation of how ACs can be used to screen coagulation processes is available through our previous publication⁴⁰. In short, ACs rapidly assess solution stability by measuring the transmission of NIR along the length of sample containing a multiphase mixture. A dip in the percent transmission is observed at the radial position of the phase boundary, and by tracking the position of the phase boundary over time under accelerated conditions, the separation kinetics can be rapidly determined. For coagulated wastewater systems, the phase boundary is the boundary between the supernatant layer and the settling floc later. A metric of solution stability provided by the AC, known as the instability index, allows for various coagulants, wastewaters, and solution conditions to be easily compared. Essentially, the instability index is a ratio of transmission between the treated supernatant fraction and the untreated solids fraction, with values closer to 1 indicating better separation. The LHS played a pivotal role in ensuring the uniform mixing of coagulant-treated samples before their transfer from the 24-well plate to AC vials. Sets of eight samples were centrifuged at 2000 rpm for 5 minutes and the instability index at each condition was measured via the SEPview software that was provided with the AC.

6.3.3 HTS of integrated coagulation-filtration process

6.3.3.1 Filter plate experiments

AcroPrep 96-well filter plates (Pall Life Science) fitted with 30K polyethersulfone Omega membranes were used in this study to filter coagulation pretreated centrate samples. It was determined that prewetting the membranes with 30% isopropyl alcohol (IPA) was needed to improve permeate recovery (see Figure E.2). To facilitate this, 300 μ L of 30% IPA was transferred into each well of the 96-well filter plate. A standard polystyrene receiver plate was placed under each filter plate and sealed using lab tape. The joined filter plate and receiver plate were then centrifuged at 1500 *g* for 45 minutes. The LHS was then used to transfer 300 uL of supernatant directly from the AC vials into wells with the filter plate. A new receiver plate was then fit under the filter plate, and similarly centrifuged at 1500 g for 45 minutes. The collected permeate within the receiver plates were analyzed using a Spark M10 microplate reader (Tecan) to determine permeate recovery and quality.

6.3.3.2 Permeate volume recovery

Previous studies have shown good correlation between the absorbance at 977 nm and the volume of liquid within a well⁴². A calibration curve was first created by measuring the absorbance at 977 nm for wells within a 96-well plate containing the permeate of a 30K Omega membrane that filtered the as received centrate, at volumes ranging between 0 and 350 μ L (see Figure E.3). Following filtration, the absorbance at 977 nm of wells within the receiver plate were then measured, and the calibration curve was used to determine the permeated volume.

6.3.3.3 Quality performance assessment via Abs_{272nm} measurements

Permeate quality was assessed via measurements of absorbance at 272 nm. Samples needed to be diluted 10-fold for the absorbances to be measurable at this wavelength. The LHS was used to transfer 10 μ L of permeate from each well of the receiver plate, and 90 μ L of DI water into a well within a UV-transparent 384-well plate. Each well was thoroughly pipette mixed by the LHS to ensure that each diluted sample was homogenous. A schematic of the entire screening workflow is presented in Figure 6.1.



Figure 6.1. A schematic representation of the coagulation-filtration screening pipeline. The coagulant screening is shown in the top panel, and the subsequent membrane screening is shown in the bottom panel.

6.4 Results & Discussion

6.4.1 Assessments of coagulant performance via high-throughput measurements of

colloidal stability

The separation performance of a coagulant at a given concentration and pH was assessed by measuring the instability index via an AC. Figure 6.2(A) shows a comprehensive screening of six commercial coagulants at all combinations of nine concentrations (0 – 400 mg/L) and four initial pHs (5 -8) conducted in triplicate. The instability index values allow practitioners to rapidly compare the performance of

coagulants and identify the solution conditions needed to maximize treatment efficacy. For most coagulants, effective separation only occurs when the centrate is acidified to <7, and this is best observed in Figure 6.2(B) which shows the maximum instability index achieved by each coagulant at each pH. This is expected when coagulating with hydrolyzing metals, as the proportion of positively charged hydrolysis products increases as the pH is lowered. However, the rapid screening quantifies the degree to which lowering the pH improves the effectiveness of the coagulation process. Sodium aluminate and aluminum chlorohydrate remained ineffective regardless of pH and coagulant concentration as the instability index fails to appreciably increase with coagulant dose. Increases instability index with coagulant concentration were observed with polyaluminum chloride and aluminum sulfate, with pH 6 generating higher instability index values. The ferric based coagulants generated the highest instability index values, with a pH 5 favouring high instability index values compared to pH 6. The HTS results shown in Figure 6.2 includes 648 individual measurements of instability index (6 coagulants \times 9 concentrations \times 4 pHs \times 3 replicates). The combination of low volumes (2 mL), low measurement time (5 minutes/8 samples) and task parallelization through automation allowed the entire screening to be completed within two days with less than 1.3L of centrate.

In our previous work, we describe how ACs allow the critical coagulation concentration (CCC) to be rapidly identified. The CCC is the minimum coagulant dose required to induce coagulation, and is influenced by factors such as pH, NOM concentration and ionic strength. The instability index vs. coagulant concentration curves

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demonstrates a characteristic sigmoidal shape, where a slow increase in instability index is follow by a rapid increase, and the concentration at which this transition occurs at is the CCC. Based on the definition of the CCC provided, an instability index of ~ 0.2 is measured at the CCC, and shifts to lower or higher values based on the pH of the solution and the coagulant that is used.



Figure 6.2. (A) Relationship between coagulant concentration and instability index shown for concentrations between 0 - 400 mg/L, and centrate pHs ranging between 5 - 8. (B) The maximum instability index achieved at each pH for each of the six coagulants screened. The average measurement and standard error were determined through independent coagulation experiments conducted in triplicate.

6.4.2 HTS of combined coagulation-filtration processes

As described in section 2.3.1, 300 μ L of coagulant pretreated centrate was filtered using a 30K Omega PES ultrafiltration membrane contained within a 96-well filter plate. The permeate was analyzed via two absorbance-based techniques to determine the relationship between the level of pretreatment achieved during the coagulation process, to the volume of permeate recovered and the quality the permeate achieved by the filtration process.

6.4.1.1 Permeate Volume Recovery

The volume permeated during filtration was determined through absorbance measurements at 977 nm. Figure 6.3 shows the relationship between instability index and permeate volume recovery for each pH and coagulant. The observed trends align well with previously described trends between the instability index and coagulant concentration. For example, the permeated volume remains relatively unchanged when the centrate is pretreated with either sodium aluminate or aluminum chlorohydrate, as floc formation and separation was not induced with these coagulants. When the centrate was pretreated with either ferric sulfate, polyaluminum chloride or ferric chloride, a proportionate increase in permeate volume are observed with instability index. Interestingly, increases in permeate volume only occur at instability index values above ~0.2, which aligns with the observed CCC for this wastewater. Similarly, these increases occur when the centrate is acidified to a pH < 7. A vastly different trend was observed with aluminum sulfate, where a rapid increase in volume is observed up until the CCC, followed by a plateauing in the permeated volume.

The variations in both the shape and gain of these correlations show that commercial coagulants have vastly different impacts on improving the throughput of downstream membrane processes. Moreover, these results highlight the interplay between the CCC and improvements to membrane productivity. For industrial wastewaters that experience variations in feed parameters that affect the CCC (i.e. salinity, NOM loading, pH etc.), ACs prove to be a valuable HTMS tool that allows rapid identification of this concentration.



Figure 6.3. Average permeate volume recovered following membrane filtration versus the average measured instability index measuring during coagulation pretreatment for the six coagulants and grouped by the centrate's acidified pHs. Horizontal and vertical error bars represent the standard error across three independent pairs of coagulation and filtration experiments.

6.4.1.2 Removal of Abs_{272m},

To complement the absorbance technique that was used to benchmark membrane productivity, a similar technique was needed to quantify the improvements to water quality that was achieved after both treatment stages. UV absorbance at 254 nm is a widely used measurement that is used to monitor the concentration of NOM (usually measured via TOC or DOC) since many chromophores containing conjugated double bonds (such as aromatics, phenols, carboxylic acids) absorb light in the UV range ($\lambda <$ 400nm)^{43,44}. The ideal UV wavelength to use varies depending on the composition of the wastewater and can be assessed through absorbance scans at a of the wastewater at a range of wavelengths. Moreover, the addition of chemical coagulants can be a source of interference for UV measurements. For example, it is well established that ferric ions can affect UV254 measurements due to strong absorbances between 200 – 330 nm^{45,46}.

Figure 6.4 shows absorbance scans between 250 - 500 nm performed on the as received centrate (A) and the six coagulants (B) at a 10x dilution. Scans were conducted at dilutions ranging between 8 – 100x for both the centrate and coagulants, and this is presented in Figure E.4. A minimum dilution of 8x was required to get readable measurements that were in range of the microplate reader. For the centrate, an absorbance at 272 nm was found to provide a good resolution between the various dilutions that were measured. The inset within panel A shows a very linear trend between the TOC and the absorbance at 272 nm. As expected, the two ferric coagulants showed high absorbances between 250 – 400 nm. Above 400nm, the absorbance decreases to below that of the centrate, however, the resolution between concentration at high wavelengths becomes too

low distinguish between concentrations. Interestingly, the sodium aluminate also demonstrated a high absorbance across the same wavelengths, and is likely due to the presence of Al₂O₃, which absorbs light in the UV spectrum due to its crystalline structure⁴⁷. Moving forward, a wavelength of 272 nm was used to analyze the removal of NOM, and samples that have been treated with either ferric chloride, ferric sulfate or sodium aluminate were eliminated from this analysis due to interference.



Figure 6.4. Absorbance scans at wavelengths between 250 - 500 nm measured for the (A) centrate and (B) the six coagulants at a 10x dilution. All absorbance measurements were measured in triplicate.

The absorbance at 272 nm was measured for each sample after being diluted 1:10. Figure 6.5 shows the relationship between absorbance at 272 nm and the instability index measured via the AC, for the coagulation step (panel A), and the combined coagulation and filtration step (panel B). A very linear downward trending correlation is observed in panel A. This result is expected as the absorbance is expected to decrease as more colloids are destabilized and removed from the centrate. Once again, a large data cluster is observed at instability index values <0.2, and significant decreases in absorbance are observed after the CCC is achieved. This is only observed for the alum sulfate and poly aluminum chloride where coagulation is achieved. The best-case treatment saw the absorbance decreasing from ~1.7 to ~0.7, a more than two-fold decrease in the absorbance.

When paired with the filtration process, the measured absorbance drops to below 0.75 under all instability index values. Similarly, a cluster of data is observed at instability index values below the CCC and spans absorbance values between 0.5 and 0.75. Beyond the CCC, the values plateau at an absorbance ~0.38 for all instability index values above the CCC. This result highlights an important interplay between the permeate quality and the critical coagulant concentration for integrated processes. The permeate quality is mostly dictated by the membrane, however, if pretreated below the CCC, the final permeate quality is influenced by coagulation process as well. Once again, this result highlights the importance of identifying the CCC when integrating coagulation-filtration processes. For facilities where the CCC of the incoming feed changes due to variations in

salt and NOM loadings, being able to rapidly re-establish the CCC and readjust coagulant doses can have a significant impact on the final permeate quality.



Figure 6.5. The relationship between the absorbance at 272nm (1:10 dilution) and the measured instability index of AC supernatant samples after only coagulation (A) and after both coagulation and membrane filtration (B). Horizontal and vertical error bars represent the standard error across three independent pairs of coagulation and filtration experiments.

6.4.3 Trade-off analysis to identify optimal operating conditions

The relationship between permeate quality and membrane throughput has been widely studied, most notably to identify the trade-off these two variables when comparing membrane materials. The most notable example if this is the seminal study by Lloyd Robeson, where the trade-off between O₂ selectivity and permeability was determined for various gas membranes separating N₂ and O₂, and an upper boundary was established⁴⁸. This has been extended to several other fields such as electrically conductive⁴⁹ and desalination⁵⁰ membranes. In these studies, the relationship between quality and throughput have been studied for a variety of different membranes. Here, we utilize the

HTMS platform to study the relationship between these two variables for a single membrane and wastewater source under various levels of pretreatment, and to our knowledge this is the first time such a correlation has been made with a large data set.

In Figure 6.6, the permeate quality and membrane productivity are compared by plotting the average absorbance at 272 nm against the average permeate volume recovery. The size of each data point is proportional to the average instability index measured by the AC. The Figure shows a very interesting trend, where improvements to permeate quality happen before improvements to permeate quality, and the inflection point of this curve appears aligns with the CCC. Mechanistically, this finding suggests that the removal performance of the membrane was only affected when the centrate was pretreated at concentrations lower than the CCC, whereas improvements to the permeability of the membrane improves proportionally at concentrations higher than the CCC. Thus, coagulating at the CCC removes some critical compound that has a significant impact on both the quality and productivity of the membrane.

The best-case treatment occurred when the centrate was pretreated with 400 mg- Al^{3+}/L of alum sulfate with the centrate acidified to a pH of 6. The combined process reduced the absorbance from 2.20 to 0.38, and the permeate volume recovery increased from 71.5 to 273.7 µL. An artificial lower bound line was included such that all available data points are encompassed within it. This line separates the "attainable" from the "unattainable" region of this two-stage process. The pretreatment process was able to significantly improve the permeate recovery of the membrane process, however, there is still an opportunity to lower the absorbance at 272 nm (i.e. reduce the organics loading).

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This is likely a limitation of the 30K Omega membrane, and a downward shift may only be attainable by using a tighter membrane with a smaller molecular weight cut-off.



Figure 6.6. Correlation plot to establish the relationship between the average absorbance at 272 nm of permeate samples (metric of permeate quality), and the average total permeated volume (metric of membrane throughput). The size of each data point is proportional to the average instability index measured via the AC during the coagulation pretreatment step. The no coagulant controls at each pH are highlighted as black hollow data points. A red dashed 'lower bound line' separates the attainable and unattainable regions of the combined coagulation-filtration process.
6.5 Conclusions

Integrated coagulation-filtration wastewater treatment processes are widely paired together to improve the performance of filtration stage. However, optimizing the membrane process often requires careful tuning of the upstream coagulation, where factors such as the coagulant used, the dosing concentration and the pH all affect the efficacy both the upstream coagulation and downstream membrane stages. In this study, a HTMS pipeline is introduced that combines HTMS tools for coagulation (analytical centrifugation) and membrane filtration (filter plates) to screen these integrated processes in unison. Overall, 648 individual pairs of coagulation-filtration experiments were conducted over the course of four standard working days (eight hours/day), which includes six coagulants that were screened at all combinations of four pHs and nine dosing concentrations conducted in triplicate, while only consuming 1.3 L of centrate. The large volume of data collected provided great insight into the relationship between the level of pretreatment achieved during the coagulation process, to the performance of the downstream membrane process. Firstly, the coagulant screening process unveiled which coagulants were able to induce coagulation, and the solution conditions (i.e. pH and coagulant dosing) that were required to achieve effective separation with those coagulants. The instability index parameter provided via the AC enabled rapid determination of the CCC. The exact concentration shifts depending on the solution conditions, however, an instability index of ~0.2 was observed at the CCC. Identifying the location of the CCC is critically important for understanding the performance of the downstream membrane process. For all coagulants except alum sulfate, improvements to

the volume of permeate recovered only occurred at instability index values above the CCC. Conversely, the removal of NOM (measured via absorbance at 272 nm) was only affected the final permeate quality when the level of pretreatment is below the CCC and remained fairly stable at concentrations above the CCC. A correlation analysis between the permeate quality and membrane throughput confirmed this, and showed that at doses above the CCC, membrane throughput can be improved. This finding is particularly important that coagulating below the CCC might not only result in membrane fouling, but also result in poor permeate quality that results in discharge criteria not being met. However, the final quality of the permeate is dictated by the characteristics of the membrane. The HTMS platform can be used both efficiently screen several process variables and alternatives when developing these integrated processes, and to optimize pre-existing processes that need to frequently readjust their dosages due to feed variations. This work demonstrated a HTMS screening platform with a single filter plate, a direct extension of this study would be incorporate different filter plates containing a variety of membranes type and cut sizes.

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Chapter 7

Conclusions and future work

Chapter 7 Conclusions and Future Work

7.1 Conclusions

Treating "tough-to-treat" industrial wastewaters remains the next frontier for commercial membrane technology. Wastewaters generated by industrial processes contain high contaminant loadings, and the composition of the wastewater can vary significantly with time. Available studies have shown success in treating industrial wastewaters with commercial membrane technology, however, fouling due to the high contaminant concentrations, and variable treatment efficacy due to variable feed properties remains a significant challenge when adopting these technologies into "tough-to-treat" applications. On-going research efforts lie in trying to develop novel materials with advantages properties for treating these challenging wastewaters, however, the translation of these technologies into commercial membranes remains extremely low. There is a need for research to overcome these challenges at the process level, where membranes are integrated into a treatment train that adapts to the properties of the wastewater that is being treated. This thesis aims to advance the adoption of membrane technology into industrial wastewater treatment applications through an integrated systems approach. The first two chapters of this thesis studies the effects of treating high-strength industrial wastewaters with time varying feed properties using commercial nanofiltration membranes by using advanced analytical techniques to resolve the contaminant removal at the single-component level, while the latter three chapters outlines the development of a high-throughput and miniaturized screening tool that aids in the development and optimization of integrated coagulation-filtration processes.

Prior to developing membrane-based solutions for treating industrial wastewaters, a mechanistic understanding of the effects of varying feed properties was needed. Chapters 2 and 3 explore the effects of variable feed properties when treating wastewaters from two distinct industrial wastewater treatment models by applying state-of-the-art analytical techniques, most notably GC - MS and LC - OCD. Chapter 2 explores the effect of treating industrial wastewater that was sourced from a dedicated facility that collects, blends and treats industrial wastewaters from various industrial facilities. The treatment efficacy was evaluated by filtering three batches of multi-sourced wastewater with four commercially available NF membranes: the NFS (Synder Filtration), NFX (Synder Filtration), NF90 (Dow Filmtec) and TS80 (Microdyn Nadir). Despite having similar bulk properties (COD: Batch A = 1212 mg/L, Batch B = 2624 mg/L, Batch C = 2694 mg/L), the wastewaters were shown to have very different compositions when analyzed via GC-MS. Most notably, filtering Batch B resulted in a significantly higher COD removal (>85% for all membranes) compared to Batch C (between 54 - 75%) despite having similar feed COD values. The GC-MS analysis revealed that Batch B contained a high concentration of a large compound (retention time > 12 min.) that were easily removed by the membrane, where as Batch C had lower concentrations of several different compounds, and smaller compounds (retention time < 12 min.) showed poor removal. Similarly, chapter 3 explores the treatment of a wastewater that is generated from a single industrial process (biogas generation) that varies depending on the composition of the incoming solid feed. In this study, the wastewater is sourced from permeate of an MBR that is treating the liquid fraction of anaerobic digestate. Unlike the previous treatment model, the variation in the wastewater comes from upstream process variations, particularly, the operation of the MBR and the solid feed entering the anaerobic digestors. Once again, both batches had similar bulk COD measurements (Batch A COD = 666 mg/L, Batch B COD = 654 mg/L), however, when treated with the NFS and NF90 membranes, the treatment efficacy was both wastewater and membrane dependent. Resolving the composition of the wastewater with LC-OCD showed that the membranes were able to entirely remove the organic fraction of the wastewater. Lower treatment efficacies were observed when the concentration of both ammonia and chlorides were higher, which affects the COD measurements due to the formation of chloroamine intermediates that gets oxidized in the presence of dichromate oxidizing agents. A higher COD removal was achieved with the NF90 membrane as compared to the NFS membrane, primarily due to the superior removal of ammonia and chloride. These chapters highlight how both industrial wastewater treatment models can be extremely challenging for commercial membranes, and smart processes that account for feed variability are needed.

To over-come challenges with feed variability, membrane processes need to be integrated into adaptive systems that can be finely tuned to account for variations in feed properties. In chapters 4 to 6, a high-throughput screening platform for an integrated twostage coagulation-filtration process that is treating the liquid fraction of anaerobic digestate is introduced. Chapter 4 introduces analytical centrifugation as an alternative high-throughput screening tool for designing and optimizing coagulation processes. Analytical centrifugation uses an integrated optics system to rapidly assess the stability of

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a multiphase solution. The optics system simultaneously measures the transmission of NIR light along the length of eight sample vials containing ~1.6 mL of a multiphase solution solution. A drastic change in transmission is observed at the boundary between two phases, and by measuring the change in radial position over time, the separation kinetics can be resolved. This technology is primarily used to measure the stability of formulated solutions, however, in chapter 4, we extend this to approximate colloidal stability for coagulated systems. In particular, a metric known as the "Instability Index" is calculated via a ratio of transmissions between the two phases, and can be used to gauge the level of treatment achieved following coagulation. This metric was used to rapidly optimize a coagulation process under a variety of solution conditions (pH, coagulant concentration), to compare coagulants and study the effects of feed variability. Measuring the instability index at various coagulant concentrations displays a characteristic sigmoidal shape, and the location of the inflection point was identified as the critical coagulant concentration (CCC), which shifts to higher and lower concentrations depending on the solution properties (particularly the pH and ionic strength of the wastewater). The rapid screening time (<5 mins. /8 samples) and low material requirement (80 mL/condition tested) enabled 132 screening experiments to be conducted with 11 L of wastewater and 6 hours of operator time. This technology is particularly useful when optimizing coagulation processes for highly saline industrial wastewaters, as traditional zeta-potential measurements are inaccurate when the ionic strength of the wastewater is high (>1000 μ S/cm) and variable. In chapter 5, instability index measurements were used to select three concentrations of ferric chloride: a low concentration (50 mg-Fe³⁺/L), and intermediate concentration at the CCC (250 mg- Fe^{3+}/L) and a high coagulant dose (500 mg-Fe³⁺/L). Additionally, the front-tracking feature of the AC was used to select 200 mg/L as a dosing concentration for an anionic polyacrylamide based on improvements made to settling velocity. When filtering wastewater pretreated at the three coagulant doses and the flocculant dose, it was evident that the intermediate concentration provided the best trade-off between flux improvement and organics removal (measured via total organic carbon measurements). At the highest dose, fouling via iron hydrolysates was observed which fouled the membrane surface and resulted in flux loss. This chapter showed the importance of being able to control the coagulant dose when it is being used as a membrane pretreatment process, as the coagulant itself can become a foulant. The AC provides a valuable tool rapidly identify the CCC and adjust coagulant pretreatment processes prior to filtration processes. A significant short coming of this chapter was that traditional jar testing was needed to generate enough pretreated wastewater that at conditions identified by the AC, in order to evaluate membrane performance using a traditional benchtop membrane system. In chapter 6, a miniaturized high-throughput screening pipeline was developed by integrating the AC with filter plate technology. Filter plates are similar to regular microplates, however, contain a membrane filter at the bottom of a well that can filter an array of solutions. In this study, coagulation experiments were scaled down to 2 mL, and performed within 24 well plates and analyzed using the AC. Following this, 300 μ L of the supernatant fraction of a coagulated wastewater sample was directly transferred from the AC vial and into the well of a 96-well AcroPrep filter plate containing a 30K Omega UF membrane and filtered. A liquid handling system was used to automate and expedite the liquid transfer and coagulant dosing tasks. Spectroscopy-based techniques were used to benchmark membrane performance based on removal (absorbance at 272 nm) and permeated volume (absorbance at 977 nm), which was related back to the level of pretreatment via the instability index measurements. In all, 648 combinations of coagulation-filtration experiments were performed in which the performance of six coagulants were compared at all combinations of nine coagulant dosages and four pHs in triplicate, all in four standard working days.

7.2 Recommendations for future work

7.2.1 Identifying fouling mechanisms using HTMS platform

The integrated HTMS platform presented in chapter 6 was able to generate a large volume of data in relatively short period of time. The correlation plot presented in Figure 6.6 benchmarks the performance of the filtration process under a variety of pretreatment conditions by plotting the absorbance at 272 nm (metric for permeate quality) against the permeated volume (metric of membrane productivity). As mentioned in section 6.4.3, the reduction in the absorbance at 272 nm occurs until the CCC, after which point increasing the coagulant concentration results in a proportional increase in the volume permeate. An extension of this project would be to identify the dominant fouling mechanisms at different sections of the correlation plot with the goal of identifying the transition regions where the dominant fouling mechanism changes. This exercise would be critically useful for the membrane field and processes operators since identifying the mechanism of fouling is important in applying cleaning strategies that target the type of fouling on the

membrane. For example, if the pretreatment is insufficient and NOM cakes on the membrane surfaces, a simple backflushing or high pH cleaning agents (e.g. NaOH at a pH of 11 - 12) would be sufficient to remove the loosely bound organic foulants¹. However, if the coagulant is overdosed and excess metallic salt binds scales the membrane surface, chelating agents such as citric acid or ethylenediaminetetraacetic acid (EDTA) would be needed to chemically cleave bonds between metals and the membrane surface¹.

The first method involves resolving the fouling mechanism using the filter plate directly. Identifying the dominant fouling mechanism typically requires the dynamic flux (flux vs. time) to be measured, however, this is extremely challenging with current filter plate technology. Few studies that have looked at developing anti-fouling coatings for membranes have introduced a "Fouling Index" calculation (Eq. 7.1), where R_{fouled} is the hydraulic resistance of the membrane and R is the hydraulic resistance of the fouled membrane^{2–5}.

$$\Re = \frac{(R_{Fouled} - R)_{modified}}{(R_{Fouled} - R)_{control}}$$
(Eq. 7.1)

The numerator and denominator are the difference in hydraulic resistance between the virgin and fouled membranes for the modified (numerator) and unmodified (denominator) membranes. Here, the hydraulic resistance is the reciprocal of the membrane permeability. In this application however, the numerator would be the difference in resistance obtained for a given pretreatment condition, and the denominator would be the no pretreatment control. Lower values of fouling index indicate lower fouling. Even though this method takes advantage of the current technology in the HTMS platform, very limited information is provided about the mechanism of fouling. For example, few studies have used the fouling index calculation to indicate that the value of \Re is proportional to the amount of cake fouling, and lower values can be attributed to pore blocking.

Another method would be to use techniques external to the HTMS that enable the fouling mechanism to be resolved by measuring the dynamic flux. To achieve this, the pretreated wastewater would have to be filtered either under pressure or under a vacuum, and the flux would have to be measured at regular time intervals over a set time or set filtration volume. Hermia's pore blocking model (Eq. 7.2) is a mechanistic model that allows the mechanism of fouling to be easily determined. Here *t* denotes filtration time and *V* represents filtration volume, and *k* and *n* are constants that depend on the fouling mechanism. The value of *n* can take on four different values: n = 2 for describes complete pore-blockage, n = 1.5 describes internal pore blockage, n = 1 describes intermediate pore blockage and n = 0 describes cake formation.

$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV}\right)^n \tag{Eq. 7.2}$$

The linearized form of this equation is show in Table 7.1 for each fouling mechanism. Here, each model is fit onto the experimental flux versus volume data, and the value of k is selected that minimizes the root mean square error (RMSE) between the experimental data and the model values. The model with the largest k value is the dominant fouling mechanism⁶.

Blocking Model	Equation	Equation Number	
Complete Blocking	$J = J_0 - K_b V$	(Eq. 7.3)	
Standard Blocking	$J = J_0 \left(1 - \frac{K_s}{2} V \right)^2$	(Eq. 7.4)	
Intermediate Blocking	$J = J_0 e^{-K_i} V$	(Eq. 7.5)	
Cake Filtration	$J = \frac{J_0}{J_0 K_c V + 1}$	(Eq. 7.6)	

Table 7.1. Linearized form of Hermia's blocking models for the four fouling mechanisms.

Since the HTMS does not support the measurement of dynamic flux, a significant downside to this method is the need to use an external screening technology that is capable of measuring dynamic flux. Certain technologies, such as the highly miniaturized filtration cell presented by O'Neal⁷ and Jensen, or the high-throughput stirred cell device presented by LaRue et al.⁸, require a very low feed volume, and can be used to directly filter the supernatant from the AC vials. Other screening tools such as bench-scale filtration apparatus or the parallelized system Vandezande et al.⁹ require a higher filtration volume, and the conditions used in AC testing would have to be reproduced with larger equipment.

7.2.2 Membrane cleaning study using HTMS platform

Similar to using the HTMS platform for identifying fouling mechanisms, the HTMS can also be used to rapidly compare and optimize membrane cleaning solutions

and strategies. Such an exercise is critical to ensuring the long-term stability and performance of the membrane. Membrane cleaning can be achieved through both chemical and physical cleanings, and both strategies can be studied using the HTMS screening platform. The fouling index calculation presented in Equation 7.1 can be used to compare relative resistances of fouled and cleaned membranes. For this application, the numerator of Equation 7.1 would include the resistance of the cleaned membrane, and the denominator would include the resistance of the membrane without cleaning. The most effective cleaning method would be the one that yields the lowest fouling index value after cleaning.

Physical cleaning removes reversible foulants by dislodging the cake or gel layer, and this is achieved by either backwashing (used in hollow fiber and tubular membranes) ¹⁰ and surface shearing (used in spiral wound membranes)¹¹ with clean water. Neither of these methods can be replicated in filter plates, however, surface shearing with clean water can be achieved through the use of small stir bars that can fit into wells within a microplate, as demonstrated by Kazemi et al¹². These cylindrical stir bars rotate tangentially to the to the membrane surface and generate a shear force that will dislodge foulants on the membrane surface. Several variables dictate cleaning efficacy, such as the duration of the cleaning cycle, the shear rate (controlled by the rotational speed of the stir bar) and the temperature of the water, which can be easily optimized using the HTMS platform.

Secondly, chemical cleanings are widely used to remove membrane surface foulants through a dissolution mechanism, and the type of cleaning agent, either acidic, caustic, or enzymatic, needs to be selected based on the type of fouling on the membrane surface. For wells that contain significant NOM fouling (when the coagulant is dosed below the CCC), NaOH at a pH of 11-12 aids in the dissolution of phenolic groups and carboxylic acids, while NaOCl aids in the dissolution of carboxyl, aldehydes and biofoulants such as large proteins^{1,13}. For instances where the coagulant may have been overdosed, acids such as HCl and H₂SO₄ are used to remove surface precipitates via dissolution, and chelating agents such as citric acid or ethylenediaminetetraacetic acid (EDTA) are used to chemically cleave bonds between metals and the organic membrane surface¹. Similarly, enzymatic cleaners such as those that are protease-based, are very effective for targeting biofouling, however, these cleaning agents are highly sensitive to pH and temperature¹⁴. The temperature and concentration of these chemicals affect their efficacy; higher temperatures and concentrations are often preferred as it improves solubility, however, exposing these harsh acids and bases to the membrane can negatively affect its performance. Thus, there is an opportunity to use the HTMS platform to select the best cleaning agents and optimize their operation.

7.2.3 Development of high-throughput platform with changeable membranes

In chapter 6, 648 combinations of coagulation-filtration experiments were performed. One limitation of this work was that all 648 experiments were performed at various coagulation conditions (pHs, dosing concentrations, coagulant type etc.), with only one membrane type. Screening different membranes would require a different filter plate to be purchased, however, the availability of filter plates is very limited. For example, Agilent sells a variety of filter plates containing membranes with options 12 different pore sizes, seven different membrane materials, and four well numbers (24, 48, 96 and 384) and 10 well volumes. However, not all combinations of pore sizes, materials and well numbers exist, and purchasers often have to make trade-offs when selecting filter plates. Similarly, the AcroPrep filter plate line manufactured by Pall Life Science sells a similar catalogue to the Agilent line with filter plates containing the Omega, Supor or Mustang membranes, but the customizability options are very limited. Furthermore, commercial filter plate technologies is almost always limited to membranes designed for bioseparations applications. Thus, finding filter plates with NF or RO membranes, or with polyamide backbones, is virtually impossible.

The HTMS platform would be significantly improved by incorporating a method to screen various membranes within a plate. Another goal of this project would be the development of a customizable filter plate that allows the practitioner to customize the membrane coupon that goes into each well, thus exponentially increasing the combinations of pretreatment conditions and membrane types that are being screened. Few attempts in the literature have been made to customizable filter plates. Both Jackson et al.¹⁵ and Kong et al¹⁶. designed and fabricated similar filter plates that allowed filtration of 8 membranes simultaneously. In Jackson et al.'s design, membrane coupons with an effective filtration area of 0.79 cm² are placed into an insert with a 40.5 mm height and 14 mm diameter, and then placed into one of eight slots within a housing that has the standard dimensions of a microwell plate. Similar, Kong et al.'s design was insert based,

however, with a smaller active filtration area of 0.28 cm^2 . There is an opportunity to build on this work by replicating standard 96-well filter plates, however, with inserts that allow any membrane filter disk to be inserted into the well.



Figure 7.1. Schematic of the 8-well filter plate design with interchangable membranes that was designed by Jackson et al¹⁵. The membrane coupons are placed into the bottom of an insert (a), which is then placed into one of the eight slots in the housing (b), which was fabricated to be the same size as a standard 96-well filter plate.

Advancements made to 3D printing technology has seen it's widespread adoption in laboratory settings, particularly in the fabrication of microfluidic devices¹⁷. These devices have become increasing more affordable and have capabilities of printing with chemical resistance materials such as polypropylene¹⁸. As such, a future step for this project would be to design and fabricate a 3D printed filter-plate with interchangeable membrane capabilities. Not only would this directly improve the scope of screening that would be possible through the HTMS, but also be useful in all facets of membrane research, such as HT materials development, evaluating new coatings and membrane process development.

7.2.4 Development of self-driving laboratory platform for integrated high-throughput screening

The HTMS platform presented in chapter 6 is semi-autonomous; some tasks are automated by a robotic LHS to perform liquid handling and reagent dosing tasks. However, human intervention is still needed for several tasks, such as plate centrifugation, and changing the AC vials. The next frontier for high-throughput screening technologies is their integration into fully automated platforms known as self-driving laboratories (SDLs). Self driving laboratories integrate robotics, automation and machine learning (ML) to autonomously perform experimentation without the need for human intervention¹⁹. Self-driving labs have becoming increasingly prevalent in the materials development²⁰. In these studies, robotic platforms are used to conduct experiments, and ML algorithms are used to parse through the large volumes of data and select optimal materials or conditions based on a set criterion.

Two elements are required to pivot the semi-autonomous work presented in chapter 6, into an SDL. Firstly, an external robotic arm is needed to perform the current set of experiments that are performed by human intervention. Burger et al. utilized a KUKA robotic arm that was mounted on a KUKA Mobile Platform to autonomously perform 688 experiments with a ten-variable experiment space over the course of eight days to identify the optimal catalyst for hydrogen production from water²¹. Here, the robot was placed into a dedicated room containing all necessary equipment to perform the experiments, such as sonicators, liquid reagents and a GC instrument, and programmed to sequentially move through each piece of equipment in order to perform the experiments.

Other studies have also demonstrated successful applications of free roaming robots to perform high-throughput experimentation in life-sciences applications^{22–24}. In this work, a free roaming robot such as the KUKA robotic arm would be used to perform the following tasks such as capping and moving AC vials between the LHS and the AC and moving filter plates between the LHS and the plate centrifuge.

Secondly, a ML or optimization algorithm is required to parse through the large volume of data and identify the next set of experiments to conduct until some optimal is reached. For the work presented in chapter 6, ML inputs would include coagulant type, concentration, solution pH, and membrane type. Other unexplored variables that could be incorporated include the coagulant mixing conditions (time and speed), and the centrifugal force that was applied to the filter plates to induce filtration. The outputs of this model the three primary measured variables: absorbance at 272 nm, the permeated volume (via absorbance at 977 nm) and the instability index measurements. The experimental data collected in chapter six can be used as the basis for an initial training set for a ML learning algorithm, such as ANNs, Fuzzy Logic or Genetic Programs, that can be then used to create a black box model that predicts filtration performance based on the pretreatment conditions 25 . These algorithms can be coupled with optimization techniques, such as Particle Swarm Optimization or Genetic Algorithms, to perform multi-objective optimizations that identifies a subset of pretreatment conditions that would provide the optimal filtration, which would then be inputs to subsequent rounds of high-throughput experimentation²⁵.

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7.3 References

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Appendix A: Supplemental Material for Chapter 2

Figure A.1. Chromatograms obtain via gas chromatograph analysis of the as-received wastewaters A, B and C prior to membrane treatment. Peak intensities are shown for retention times between 3.7 and 30 minutes.



Figure A.2. A complete process and instrumentation diagram of the high-pressure membrane testing system that was used to evaluate membrane performance.



Figure A.3. Frequency of compounds identified by via. GC-MS by over 29 samples of multi-sourced industrial wastewater from a single client. This library of compounds was used to select three compounds to test single component solution testing.



Figure A.4. Normalized flux behavior for the NF90 (\bullet) and NFX (\bullet) membranes over 2-hour filtration of single component solutions. Standard deviation error bars are shown for each flux measurement (N = 5).



Figure A.5. Rejection of 2000 mg/L solution of sodium chloride (left) and magnesium sulfate (right) obtained by NF90 (top) and NFX (bottom) membranes before and after 120-minute exposure to individual component solutions that were prepared to have a COD of 1333 mg-O₂/L. Standard deviation error bars are show for each rejection measurement (N = 3).



Appendix B: Supplemental Material for Chapter 3

Figure B.1. Membrane surface zeta-potential vs. pH for all three membranes ranging from pH values of 2 to 10. Zeta-potential measurements were made by decreasing from pH values of 6 to 2, and then increasing from pH values of 7 to 10. This was repeated three times on different coupons for each membrane.







Figure B.3. Measured pH of supernatant after coagulation of Batch A with PAX-18 for concentrations ranging between 40 mg-Al³⁺/L to 120 mg-Al³⁺/L.



Figure B.4. Comparison of the measured (as received) feed and permeate COD samples taken at various fractions of permeate recovery over the 8-hour filtration experiment. Results are shown for two independent replicates of the NFX and NF90 membranes. Standard deviation error bars are shown for duplicate COD measurements from each sample.



Figure B.5. Comparison of solute rejection observed in batches A & B to (a) the Stokes radius of the solute and (b) the molecular weight of the solute.

Table B.1. Measured permeability and salt rejection for each membrane coupon used for all filtration trials. The measured permeability is presented with the 95% confidence interval around the regression line, and the average salt rejection is presented with the standard deviation error (n = 3).

			Permeability (LMH/bar)		Salt Rejection (%)	
Batch	Membrane	Coagulated/	Replicate 1	Replicate 2	Replicate 1	Replicate
		Uncoagulated				2
А	NFS	Uncoagulated	8.7 ± 0.8	9.1 ± 1.4	44.0 ± 0.9	48.3 ± 1.7
А	NFS	Coagulated	7.6 ± 0.6	7.5 ± 0.4	40.3 ± 2.1	45.1 ± 6.9
А	NFX	Uncoagulated	5.2 ± 1.3	5.0 ± 0.9	46.8 ± 2.8	39.7 ± 1.0
А	NFX	Coagulated	3.4 ± 0.3	3.1 ± 0.5	33.8 ± 1.2	36.7 ± 1.1
А	NF90	Uncoagulated	10.0 ± 0.7	11.8 ± 0.7	86.6 ± 1.3	89.5 ± 1.5
А	NF90	Coagulated	10.8 ± 0.8	9.0 ± 1.0	89.4 ± 2.9	87.7 ± 4.4
В	NFS	Uncoagulated	6.6 ± 0.7	6.4 ± 0.9	44.7 ± 0.5	44.2 ± 1.8
В	NF90	Uncoagulated	9.0 ± 1.6	9.9 ± 2.6	90.7 ± 2.0	90.7 ± 2.5
DI Water	NFS	Uncoagulated	6.4 ± 0.6	6.9 ± 0.9	42.0 ± 0.9	43.6 ± 1.5
DI Water	NFX	Uncoagulated	3.3 ± 0.4	2.7 ± 0.3	34.0 ± 0.9	37.3 ± 0.7
DI Water	NF90	Uncoagulated	11.2 ± 1.1	9.4 ± 0.5	91.1 ± 2.2	88.5 ± 0.7

Table B.2. Comparison of permeate quality following filtrations of Batches A and B using the NF90 and NFS membranes. Parameters denoted with an asterisk (*) were measured by AGAT Laboratories.

	NF90		NFS	
Parameter	Batch A	Batch B	Batch A	Batch B
Chemical Oxygen Demand (mg/L)	71 ± 14	63 ± 14	234 ± 8	95 ± 14
Total Organic Carbon (mg/L)*	2.5	5.3	3.8	7.1
Sodium (mg/L)*	901	961	2180	2880
Potassium (mg/L)*	578	404	1020	939
Magnesium (mg/L)*	1.99	< 0.68	12.1	9.4
Calcium (mg/L)*	2.74	1.64	39.9	18.6
Chloride (mg/L)*	267	151	1330	1130
Ammonia (mg/L)*	128	0.12	180	0.11
Nitrites (mg/L)*	14.7	8.50	41.5	27.8
Nitrates (mg/L)*	779	632	1420	1650



Appendix C: Supplemental Material for Chapter 4

Figure C.1. Workflow diagram outlining the process of high throughput coagulant screening using the LUMiFuge. Buckets of centrate are sampled directly at the biogas generation facility, and when needed, ~1L aliquots are taken and adjusted to the desired pH. From here, 80 -mL aliquots are placed into smaller 80-mL beakers and placed on a 8 point magnetic stirrer. Varying amounts of coagulant is dosed into each beaker and mixed for 3-minutes at 300 rpm, after which a 1.6 mL aliquot of the now two-phase mixture is placed into a LUMiFuge vial. After 8 vials are collected, the samples are placed into the LUMiFuge and centrifuged at 2000 rpm for 5 minutes. A computer containing the SEPView software reports the transmission profile across the LUMiFuge vial and the instability index every second. After centrifugation, the COD of the supernatant fraction is measured.

Equation C.1: Instability Index Equation

Equation C.1 is used by the LUMView software to determine the instability index value for a sample(Detloff et al., 2013). In numerator of equation one, $T_{i,j}^{diff}$ is the difference between the transmission obtained at t = 1 (T₁) and t = i (T_i), at a radial position of r = j. In the denominator, the difference in mean transmission for a cell containing only water and the first transmission profile ($T_{end} - T_1$) is multiplied by the difference between last and first position increment ($j_{rmax} - j_{rmin}$). The latter is selected by the user, with j_{rmin} being chosen at the meniscus and j_{rmax} being chosen the last recorded phase boundary position. All instability index values reported in this thesis are measured at the last time interval (i = 300s)

Instability Index =
$$\frac{\Delta T_i}{\Delta T_{max}} = \frac{\sum_{j=r_{min}}^{r_{max}} T_{i,j}^{diff}}{(\overline{T}_{end} - \overline{T}_1)(j_{r_{max}} - j_{r_{min}})}$$
 (C.1)


Figure C.2. Triplicate coagulation experiments were carried out at a low (50 mg-Fe³⁺/L) and high (300 mg-Fe³⁺) ferric chloride concentrations and at solution pHs of 5, 6, and 7 to demonstrate the reproducibility and precision of the LUMiFuge. Settling kinetics as shown by the position of the solid-liquid phase boundary at 20% transmission is shown in the top panels, while the instability index is shown in the middle set of panels, and the calculated sludge volume is presented in the bottom set of panels.



Figure C.3. Transmission profiles obtained after coagulating Batch B with various concentrations of ferric chloride at an initial pH of 5. The selected meniscus point is shown on each transmission profile, and was used to normalize the front tracking positions.



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Figure C.4. Transmission profiles obtained after coagulating Batch B with various concentrations of ferric chloride at an initial pH of 6. The selected meniscus point is shown on each transmission profile, and was used to normalize the front tracking positions.



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Figure C.5. Transmission profiles obtained after coagulating Batch B with various concentrations of ferric chloride at an initial pH of 7. The selected meniscus point is shown on each transmission profile, and was used to normalize the front tracking positions.



Figure C.6. Comparing the effect of coagulant concentration on instability index for two coagulants (FeCl₃ and PACl) and two batches of centrate sampled in February 2022 (Batch A) and July 2022 (Batch B) for initial centrate pHs of 5 (left), 6 (centre) and 7 right.



Figure C.7. The correlation between instability index and COD removal shown for Batch A and Batch B. The data presented for both batches is the accumulation of COD and instability measurements taken following coagulation at initial centrate pH's of 5, 6 and 7, and using two coagulants, ferric chloride and polyaluminum chloride.



Figure C.8. Sludge volume (normalized by initial centrate volume) measured following the coagulation of Batch B with ferric chloride concentrations ranging between 50 - 500 mg-Fe³⁺/L and initial centrate pHs of 5, 6 and 7.

Table C.1. Estimated coagulant screening time using LUMiFuge and Jar Tester

The Table below provides a time estimate to conduct screening experiments with the LUMiFuge and a jar tester. The following assumptions were made in the estimation:

- The time estimate for jar testing was based off a standard six-cell jar tester (e.g. Phipps & Bird PB-900)
- The time estimate for jar testing does not include time required for additional water quality testing to assess coagulant separation performance (i.e. COD removal, turbidity removal).
- One minute of additional time was added to the 3 minutes of coagulant mixing time to account for a time offset between coagulant dosages.
- The time estimate does not include the time required to start up the LUMiFuge and for the temperature to reach the set-point (~10 minutes).

- For time estimates provided in the thesis, if the number of tests exceeded the testing capacity of the instrument, the number of runs was rounded up (e.g. testing 10 samples with the LUMiFuge would require two full runs).
- A wide variety of gravitational settling times were reported in the literature (15 mins. 2 hrs.), however, 1 hour was selected as a representative time for this estimation^{2,3}.

Table C.1. Estimated time to conduct eight coagulant screening experiments with the LUMiFuge and six with the Jar Tester.

Step in Process	LUMiFuge – 8 Samples	Jar Tester – 6	
		Samples	
pH Adjustment	5 mins.	5 mins.	
Pouring samples into vessel	5 mins.	5 mins.	
Coagulant Dosing and mixing*	4 mins.	4 mins.	
Transfer to LUMiFuge Vials and loading	2 mins.	-	
LUMIFuge			
LUMiFuge Run Time	5 mins.	-	
Gravitational Settling	-	60 mins.	
Total	21 mins.	74 mins.	

Supplementary References

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Appendix D: Supplemental Material for Chapter 5

Table D.1. Measured water quality parameters of the centrate. Parameters denoted with an asterix (*) were measured by AGAT laboratories.

Catgory	Parameter	Units	Value
	Chemical Oxygen Demand	mg/L	6388
Bulk Properties	Total Organic Carbon	mg/L	1791
	True Colour*	TCU	6000
	Turbidity*	NTU	249
	Total Dissolved Solids*	mg/L	10,600
	pH*	~	8.3
	Electrical Conductivity*	μS/cm	23600
Nutrients	Ammonia*	mg/L	2900
	Sulphates*	mg/L	309
	Chloride*	mg/L	1810
	Total Phosphorous*	mg/L	74.4
Metals	Total Calcium*	mg/L	201
	Total Magnesium*	mg/L	83.2
	Total Potassium*	mg/L	1730
	Total Sodium*	mg/L	2410
	Total Aluminum*	mg/L	8.5
	Total Iron*	mg/L	52.2



Figure D.1. A schematic showing the experimental procedure for selecting the coagulant and flocculant dosages, as well as the scale-up and membrane filtration and the selected conditions.



Figure D.2. Transmission profiles obtained from the coagulation of pH adjusted centrate with ferric chloride doses ranging between 0 - 500 mg-Fe 3+/L. Each coagulant concentration was evaluated in triplicate.



Figure D.3. An example of how front tracking profiles were generated from transmission profile data to measure the settling velocity. Data in both sets of panels were taken following coagulation with 500 mg-Fe³⁺/L, however the top panel has no flocculant, whereas the bottom panel was dosed with 200 mg/L of flocculant. The position (mm) vs. time (s) graphs were developed by plotting the radial position of the front in which a ~15% transmission was observed at each time point. The blue points indicate the linear portion of the front tracking profiles, which is the maximum number of points in which a fitted regression model maintains a R² of over 0.95. The settling velocity was determined from the slope of the linear regression model.

	Low Condition		Intermediate Condition		High Condition	
	80 mL	2 L	80 mL	2 L	80 mL	2 L
Instability After Coagulation	0.05 ± 0.001	0.02 ± 0.001	0.40 ± 0.01	0.58 ± 0.05	$\begin{array}{c} 0.78 \pm \\ 0.01 \end{array}$	0.82 ± 0.01
Instability After Coagulation & Flocculation	0.14 ± 0.003	0.03 ± 0.01	0.49 ± 0.02	0.59 ± 0.03	0.83 ± 0.02	0.81 ± 0.02

Table D.2. Comparison of instability index values measured after coagulation and after coagulation and flocculation for experiments conducted at the 80 mL scale and 2 L scales, at each pretreatment condition.

Table D.3. Average flux measurements during filtration of wastewater at each pretreatment condition, along with DI water flux measured before and after wastewater filtration.

	Average DI water flux before wastewater (LMH)		Average wastewater flux (LMH)		Average DI water flux after wastewater (LMH)	
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2
No CF control	34.5 ± 1.1	38.3 ± 1.5	10.9 ± 1.5	11.8 ± 1.5	34.2 ± 5.8	39.2 ± 3.2
Low Condition	33.1 ± 3.5	32.1 ± 2.0	15.6 ± 2.6	16.7 ± 1.3	28.9 ± 3.8	29.6 ± 8.2
Intermediate Condition	32.8 ± 3.4	34.0 ± 3.7	17.2 ± 1.3	17.9 ± 1.5	32.9 ± 4.7	30.8 ± 1.7
High Condition	38.9 ± 4.1	43.3 ± 2.4	18.9 ± 3.5	24.5 ± 2.3	25.0 ± 2.4	32.7 ± 1.0



Figure D.4. Images of membrane surfaces after filtration experiments at each pretreatment condition. Each filtration cycle consisted of six hours of wastewater filtration, and one hour of DI water filtration before and after wastewater filtration. Images shown were taken after the second DI water filtration.



Figure D.5. Images of samples taken before treatment, after CF pretreatment and after membrane filtration at each pretreatment condition. TOC measurements are shown under each sample vial.



Appendix E: Supplemental Material for Chapter 6

Figure E.1. Schematic of the stir bar tracking results. (A) Using the Tracker software, a unique digital marker is placed at the tip of each stir bar and for each frame of the recorded video. The numbered icons represent the locations of each stir bar for the first 20 frames (corresponding to two-thirds of a second) of the recorded video. (B) Typical data for linear displacement versus time (\blacklozenge) and Microsoft Excel's smoothed line interpolation (—) for a single stir bar at a 'power level' of 40. Note that a displacement of x represents a distance relative to arbitrarily set axes in the Tracker software. The rotational speed is calculated from the period of the smoothed line interpolation. (C) Average rotational speed across the 24 well microplate versus the tumble stirrer 'power level'. The dashed line represents the linear 'line of best fit' ($R^2 = 0.997$).



Figure E.2. Average volume of permeate recovered following the filtration of as received centrate with membranes that were prewetted by prefiltering either with 30% isopropyl alcohol, de-ionized water or no prefiltration. Filtrations were carried out in triplicate within wells of a 96-well AcroPrep filter plate containing 30K Omega ultrafiltration membranes. Data is presented as the average across the three filtrations, along with error bars representing the standard error.



Figure E.3. Calibration curve between well volume and absorbance at 977nm. The calibration was created with permeate obtained following the filtration of as received centrate with a 30K Omega membrane in a 96-well filter plate. Horizontal error shows the standard error across three independent measurements.



Figure E.4 Absorbance scans conducted between wavelengths of 250 - 500 nm for (A) the as received centrate, and (B) the six coagulants at dilutions ranging between 8 - 100x. Absorbance scans at each dilution were conducted in triplicate, and the calculated average at each wavelength is shown in the figure.