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Direct Membrane Filtration of Domestic Wastewater: Implications for Coupling with Anaerobic

Membrane Bioreactor (DF-AnMBR) for Wastewater Resource Recovery

by

George H. Dick

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering Department of Civil and Environmental Engineering College of Engineering University of South Florida

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Keywords: Ultrafiltration, Modified Fouling Index, Membrane Fouling, Wastewater Treatment, Water Quality

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DEDICATION

To my family and friends, who have always supported and encouraged me through my educational efforts and through life.

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ABSTRACT

With the growing use of membranes in the water industry, different methods for using membranes to treat water is still occurring. Enhancing membrane performance is generally performed with extensive pretreatment methods before the feedwater is filtered by the membrane. With the utilization of direct membrane filtration (DF), no pretreatment is performed and the membrane is exposed to raw wastewater. While this may suggest that membrane performance and permeate quality would suffer in the process, DF testing with a 0.03 µm ultrafiltration PVDF membrane showed that relatively high membrane flux was sustained while producing a high quality effluent. Due to the rejection of the membrane, a highly concentrated fraction of the wastewater, which is significantly reduced in volume but high in solids and organic strength, is obtained and can be treated in other ways.

A process is proposed to treat municipal wastewater by coupling a DF system with an anaerobic membrane bioreactor (AnMBR). AnMBRs generally treat industrial strength wastewater, which is high in chemical oxygen demand (COD), and may struggle with domestic wastewater, which is generally considered low strength in terms of COD. By coupling the DF with an AnMBR, the DF-AnMBR can be used to treat the low strength domestic wastewater. The DF portion can handle the bulk of the liquid fraction, while the highly concentrated fraction of wastewater is treated by the AnMBR stage, thus improving the energy profile of the AnMBR and enhancing performance. A series of flow and mass balance equations for the combined DF-

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AnMBR was developed, and used to shed insight on design parameters relevant to this novel treatment process.

Since membrane fouling occurs gradually over weeks or months, it is difficult to systematically determine how processes changes may affect membrane performance. Hence, a method to rapidly determine the fouling propensity of wastewater was desired. The modified fouling index (MFI) was previously developed to test the fouling propensity of feedwater for seawater RO desalination, but has not been applied to membrane filtration of wastewater. The MFI method was adapted and used to test the fouling propensity of various treatment streams in the DF-AnMBR system, including raw domestic wastewater, concentrated domestic wastewater (20X by DF), and liquor from an active AnMBR. The effect of powdered activated carbon (PAC) on fouling propensity was also investigated. Raw wastewater had a fouling potential of about 25% of the AnMBR MFI, and with the utilization of PAC the fouling potential was further decreased to nearly 50% of the original fouling potential. The DF concentrated stream had a higher MFI value than liquor from the AnMBR, but presumably some of organics contributing to fouling would be degraded in the AnMBR. This study demonstrated that DF of raw wastewater is feasible, and the combined use of DF and AnMBR is highly promising.

CHAPTER 1: INTRODUCTION

1.1 Background

1.1.1 Conventional Wastewater Treatment

Conventional wastewater treatment is a well-defined practice with facilities designed to handle small flows of less than a million gallon per day (MGD) to extremely large flow of nearly 1.5 billion gallons per day. To achieve necessary wastewater treatment, these facilities often use many different processes, including physical, chemical, and biological processes (Metcalf and Eddy, 2014). Physical processes include the removal of constituents through screens, mixing, settling and filtration, whereas chemical treatment is the addition of chemicals to achieve a certain level of treatment, such as using chlorine to disinfection the water before discharge. Biological treatment is used primarily to remove biodegradable organics, colloidal material, and nutrients from the wastewater (Metcalf and Eddy, 2014). While this process works well for the liquid treatment process, the solids entering the facility and produced at the facility (through the use of polymers and biological treatment) creates additional challenges.

1.1.2 Solids Treatment

Solids at a wastewater treatment facility either enter the facility as fecal matter or are generated at the facility through biological, or through the addition of polymers. Solids treatment at conventional wastewater treatment plants can be achieved through various processes. To achieve a desired level of treatment, the facility has a variety of options to consider. Composting and digestion (either anaerobically or aerobically) are common practices within the wastewater industry. At these facilities, the final fate of solids (after proper treatment) is to be sent to a landfill for disposal or to be applied to land, depending on the region, the legal restrictions where the facility is located and/or common practice for the region (WEF, 2009).

1.1.3 Wastewater Treatment Alternative

While conventional wastewater treatment is effective, it is not without its limitations. These facilities are often dependent on high energy demand, trigger environmental impacts, and produce large quantities of residuals. Interest in improving the sustainability of domestic wastewater treatment has increased in recent years (Smith et al., 2012). Recently focus has shifted away from conventional treatment to developing technologies which aim to reduce the energy, materials, and footprint associated with conventional wastewater treatment. With the focus shifting to alternative wastewater treatment, membrane bioreactors (MBRs) have been proposed as a technology advancement that is needed to change the conventional treatment system.

According to Stephenson et al. (2000), the membrane bioreactor is able have high quality effluent within a small footprint. Within this small footprint, the MBRs utilize a bioreactor which houses microbial populations for biological degradation of waste and a membrane system which physically removes contaminants from wastewater. If the system acts as anaerobic membrane bioreactor (AnMBR), energy can be recovered from the system through the recovery of biogas (Prieto et al., 2013) thus offsetting the energy demand of operation. To date, AnMBRs are primarily used in industry to treat industrial wastewaters which have high chemical oxygen demand (COD). Whereas, domestic wastewater is generally considered low strength with COD

concentrations ranging from 250-800 mg/L (Metcalf and Eddy, 2014), presents challenges for the AnMBR. Figure 1.1 shows the generally layout of an AnMBR, where domestic wastewater is the feedwater and solids, energy, and water (permeate) are produced in the system.



Figure 1.1: Layout of a typical AnMBR

AnMBR have many advantages over their aerobic counterparts. Since the system acts anaerobically the energy demand is significantly less due to the due to the lack of aeration which generally accounts for large portion of the energy demand in biological treatment (Lateef et al., 2013). The generation of biogas can also be advantageous as the biogas can be used as energy source to offset the energy demands within the system. Additionally anaerobic microorganisms grow at a much slower rate due to their substrate utilization than aerobic microorganisms (Skouteris et al., 2012), thus leading to less sludge (solids) being produced and less wasting of solids. Lastly, AnMBRs give the possibility of nutrient recovery such as nitrogen which is generally vented into the atmosphere through nitrification and denitrification processes in aerobic MBRs (Stuckey, 2012)

While AnMBR are effective at treating high strength wastewater, the treatment of domestic wastewater which is generally considered low strength, presents challenges for the AnMBR. Domestic wastewater is a mixture of black water (fecal matter and flush water), yellow water (urine and flush water), and greywater (sinks, showers, and laundry). Due to mixing of these three sources and the dilution due to large volume of flush water this leads to lower kinetics for the anaerobic microorganism and a larger energy demand for heating. For anaerobic processes to be competitive over aerobic treatment, COD concentrations of 1500-2000 mg/L are needed (Metcalf and Eddy, 2003), making direct treatment of domestic wastewater in AnMBRs challenging.

To improve the AnMBR, source separation could be implemented. Source separation, would be the collecting the three sources of domestic wastewater in different methods allowing the wastewater to be smaller in volume and no longer mixed, thus a large portion of the wastewater does not have to be treated to as a fecal contaminated wastewater. However source separation would require large capital investment in infrastructure, as well as user acceptance and compliance, so domestic wastewater remains mixed and diluted. Since source separation is not easily attained, another method to concentrate the wastewater must be implanted.

Direct membrane filtration (DMF) or simply direct filtration (DF) of raw wastewater, which utilizes ultrafiltration (UF) membranes without prior pretreatment, is effective for removing particles and pathogens (Ravazzini et al., 2005). Able to obtain high membrane fluxes for wastewater (Lateef et al., 2013); DF can capture renewable energy embedded in organic

particulates which can be used in anaerobic digestion. Due to the rejection of the by the UF, the permeate quality is expected to be of high quality (Ravazzini et al., 2005). By utilizing DF as a pretreatment method to the AnMBR, the DF-AnMBR is produced. Ravazzini (2008) determined that the flux produced from a DF system is relatively high (over 100 L/m²/hr. (LMH)). Since AnMBR generally operates at a low flux (around 5 LMH), thus the DF-AnMBR could lead to better hydraulic performance of the system. Figure 1.2 depicts the general layout of the DF-AnMBR system, where the DF module is assumed to produce higher flux and the concentrate (rejected particles by the DF system) are delivered to the AnMBR for biological treatment. While the figure depicts the entire DF-AnMBR, only the system which is shown in the boxed area is the areas of focus for this research.



Figure 1.2: Layout of the DF-AnMBR. The dotted box indicates the focus of this research.

The main focus of this research is primary based in two overall goals, what is the expected effluent (permeate) quality of the DF system and can the concentrate reach high enough

concentrations of COD to the AnMBR to be effective. With the first overall goal, this research aims to determine whether the permeate from the DF system is of high quality and what is the rejection from COD and ways to enhance the removal of COD from the permeate though the use of additives such as powdered activated carbon (PAC). With the second overall goal in mind, the focus will shift to the concentration of COD and solids within feed reservoir that will be discharged to the AnMBR for biological treatment. Due to the concentration of these parameters, determining the expected influent and effluents at various sites in the DF-AnMBR must be determined as well as the expected fouling propensities.

1.2 Objectives

This work is to investigate the potential for utilizing a DF system and the implications of coupling with an AnMBR for the creation of the DF-AnMBR. This work will investigate permeate quality of domestic wastewater produced by a DF system as well as determine the concentration of COD and solids, which are rejected by the DF system. In addition the rejection of various parameters will be monitored and used to propose a model for the DF-AnMBR, which will determine various influents and effluents in the DF-AnMBR. Finally, the fouling potential of various feedwaters (domestic wastewater, DF concentrate, AnMBR reactor liquor, and wastewater with the additive PAC) will be determined to monitor how each feedwater interacts with the membrane and fouls the membrane.

1.3 Scope of Work

- Determine the effectiveness of a DF system for domestic wastewater treatment.
- Analyze the water quality of permeate generated through the DF process.

- Determine the concentration of COD, solids, and nutrients produced by the DF system.
- Propose a model for combining a DF and AnMBR.
- Develop a rapid assessment tool for determining fouling propensity of different wastewater streams.
- Analyze the fouling potential of domestic wastewater, DF concentrate, wastewater with PAC addition, and AnMBR sludge and show the reproducibility of this method.

CHAPTER 2: LITERATURE REVIEW

2.1 Membranes

Study of the membrane phenomena can be traced back to the eighteenth century philosopher scientists (Baker, 2004). While back in the nineteenth and early twentieth century membranes had no commercial propose, they were used within laboratories to develop physical/chemical theories (Baker, 2004). Today, membranes are designed to carry out physical or physicochemical separations. The role of the membrane is to serve as a selective barrier that will allow the passage of certain constituents and will retain other constituents found in the liquid (Metcalf and Eddy, 2014). With the advancement of membrane science, several different types of membranes have been developed. Depending on their particle size exclusion capabilities, membranes can be classified into four major categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (UF) and reverse osmosis (RO). These types of membranes have different pore sizes which depending on the type can even filter dissolved particles within the water. MF and UF membranes are considered low pressure membranes because these require less driving pressure compared to high-pressure membranes, NF and RO. The process for classifying membrane processes is determined in a number of different ways including membrane configuration, type of material used to manufacture the membrane, nature of the driving force, the separation mechanism, and the nominal size of the separation that is achieved (Metcalf and Eddy, 2014).

2.1.1 Membrane Configuration

Membrane configuration is the type of membrane within the membrane module. According to Metcalf and Eddy (2014), the term module is used in the membrane field to describe a complete unit comprised of the membrane element (or modules), the pressure support for the feed, permeate and concentrate structure as well as the overall support structure. There are three main configurations used in wastewater treatment including spiral wound, hollow fine fiber and tubular. While other configurations exist such as plate and frame and pleated cartridge filters, these configurations are primarily used for industrial purposes.

2.1.1.1 Spiral Wound Membranes

Spiral-wound membranes modules used primary used in nanofiltration and reverse osmosis water within desalination and water treatment. According to Karabelas (2013), for desalination using NF or RO membranes, the spiral wound membrane is the most important part of the desalination system. This type of membrane geometry is not widely used in the MF and UF due to inability to backwash the membrane and extensive pretreatment is required to allow the membrane not to clog and foul. (Li et al., 2014). Spiral wound membranes are comprised of several large size membrane sheets with a net-type spacer at the concentrate flow channel and a porous cloth/filler at the low press permeate side (Kostoglou and Karabelas, 2009). The membranes are then sealed on three sides with the open side attached to a perforated pipe lying in the center. After the membrane is attached to the perforated pipe, the flat sheet membranes and the feed spacer are rolled tightly around the perforated pipe into the shape of a circle. The term spiral wound membrane is derived from the flow within the module is in a spiral formation.

2.1.1.2 Hollow Fiber Membranes

Hollow fiber membranes, most commonly configured for MF and UF, commonly used for water treatment. Due to the membrane configuration and the geometry of the membranes the ability to backwashed is an advantage and does not required extensive pretreatment prior to utilization. (Li et al., 2008). One of the key benefits of hollow fiber membrane modules is the packing density, higher membrane surface areas within smaller module sizes. Packing densities as high as 40,000 m²/m³ are possible, and this is compared to 300 to 1000 m²/m³ for spiralwound modules and 130 to 300 m²/m³ for tubular modules (WEF, 2009). The way this high surface area ratio is achieved is through a bundle of hundreds to thousands of hollow fiber membranes, which are about the thickness of a human hair, placed within a pressure vessel.

Hollow fiber membranes treat the feed in two different methods based on direction of the permeate flow. The most common method is when the feedwater enters into the center or hollow part of the membrane and permeate is extracted to the outside of the membrane, in a process call inside-out flow (Metcalf and Eddy, 2014). In contrast, using the other method, pressurized feed is introduced to the outside of the membrane and permeate is collected inside the membrane, separating permeate from the unwanted constituents, in the outside-in flow. When the membrane module is immersed/ submerged, the outside-in process is used since the feed is contained outside the membrane.

2.1.1.3 Tubular Membranes

An extension of the hollow fiber membrane is the tubular membrane, but with a larger internal diameter and strictly inside-out flow (Li, et al., 2014). Within the pressure vessel of a tubular membrane configuration, one or a bundle of tubular membranes are used as the filtration

mechanism. A tubular membrane incorporates a porous wall tube with the membrane inside a support tube (WEF, 2009). Typically, these membrane modules are used when the feedwater has a high concentration of suspended solids or the feedwater has a potential to plug the membrane pores. The feedwater is pumped into the membrane tube, allowing permeate to filter through the membrane and collected on the outside of the tube. The rejected concentrate also called concentrate continues to flow through the center of the feed tube. The key benefit of tubular membrane is the ease of cleaning the membrane which is the process of using chemicals, backwashing procedures, or added material such as PAC, foamballs and spongeballs to clean the membrane surface (Metcalf and Eddy, 2014).

2.1.2 Membrane Materials

Membrane can be made of several different types of materials. Today, most membranes are made from a variety of inorganic materials and/or organic polymers developed for industrial processes. Organic polymers currently dominate the membrane market (Metcalf and Eddy, 2014). While many different organic materials are used, a large portion of the membrane market is devoted to polyvinylidene fluoride (PVDF) membranes (Metcalf and Eddy, 2014).

2.1.2.1 PVDF Membranes

PVDF membranes are used in all membrane sizes except for RO. This material is a semi crystalline polymer composed of the repeated unit of $(CH_2CF_2)_n$ (Kang and Cao, 2014). Due to the mechanical strength, thermal stability, lifespan and resistance to chemicals, PVDF membranes cover all aspects related to actual separation. While these membranes are not without their flaws, PVDF membranes are susceptible to two major problems: membrane fouling due to the feedwater characteristics, and wetting in membrane contactors. Fouling and wetting degrade

the performance and will reduce the membrane efficiency which can lead to higher operational cost or cause the system to fail. Recent research has focused on the hydrophilic and hydrophobic properties of PVDF membranes to improve the membrane performance (Kang and Cao, 2014).

PVDF membranes performance can be affected by the chemical composition and the physical morphology. Depending on the application, these properties can be adjusted to optimize the membrane performance. Membrane surface properties, structures, and mechanical properties can be optimized and are manipulated for certain membrane applications (Chen et al., 2013). While the topic of optimizing PVDF membranes is a highly popular research area, a large focus is based on material blending. Blended PVDF membranes is when the material used to manufacture the membrane are a combination of PVDF and another material such as polytetrafluoroethylene (PTFE) and polypropylene (PP) (Farrukh et al., 2013). The reason for blending materials is to enhance membrane performance by giving the membrane additional properties that are lacking in PVDF.

2.1.3 Driving Force of Membranes

Depending on the membrane process, membranes can be operated under two different ways to achieve the desired separation. Mostly commonly used in full scale facilities is the constant flux method. Due to membrane fouling, flux is reduced. To counteract this process to meet production demand, the transmembrane pressure (TMP) i.e., the pressure difference across the length of the membrane is increased. Due to the increase in pressure, feedwater is forced against the membrane, allowing the flux to remain relatively constant. Alternatively, the membrane can be operated under constant pressure. In this operating mode, when the membrane

begins to foul the membrane flux is decreased while allowing the pressure to remain constant. (Li et al., 2008).

2.1.4 Separation Mechanisms and Membrane Size

Membranes are able to separate particles smaller than the pore size within the respected size. MF membrane is considered macroporous, with minimum pore sizes generally greater than 50 nm. The nominal pore sizes are usually within the 0.07-2.00 μ m range. UF membranes are considered mesoporous, with minimal pore sizes between 2-50 nm and nominal pore sizes within the 0.008-0.200 μ m range. Due to the size of the pores, the removal mechanism is considered to be straining, physical size exclusion of particles with the feed (Metcalf and Eddy, 2014).

NF membranes also utilize straining to removal particles from the feed but unlike MF and UF membranes, NF also allow ionic species such as sodium and chloride to be removed from the feedwater through diffusion across the macromolecule pores which the membrane is composed of (Metcalf and Eddy, 2014). Physical separation in NF membrane is achieved through micropores which are generally less than 2 nm and reject particles between 1×10^{-3} to 1×10^{-2} µm.

Due to the very small pore sizes, which are typically less than 2 nm, and the dense layer within their polymer matrix, , RO membranes are considered effectively nonporous i.e., RO membranes do not sieve particles and rely solely on the diffusion of water across the dense layer, and the exclusion of the macromolecules from the produced permeate. RO membranes are generally able to reject particles smaller than 1×10^{-4} to 2×10^{-3} micrometers.

2.1.5 Pressurized Membrane Flow

In a membrane module, there are two modes of pressurized flow cross-flow and dead-end filtration. Cross-flow, also known as tangent flow, is where the feedwater is forced along the membrane surface causing a differential pressure within the module causing a portion of the feed to separate across the membrane creating permeate (Li et al.,2008). The feed that is rejected by the membrane, concentrate, is sent to a recirculated blending tank, to be blended with incoming feed, to be pumped back through the membrane module. Not all the concentrate is recirculated to the balancing tank, due to buildup of concentrate a portion of is bleed off to be treated through other processes (Metcalf and Eddy, 2014).

When a low solids concentration is present with the feed, dead-end filtration is a viable option. In dead-end filtration the feed is pumped into the membrane, in a similar fashion as cross flow, but the concentrate collection port is sealed forcing the feed to separate and flow through the membrane. This causes the solids within the feed to buildup on the membrane surface which leads to membrane fouling, decreased flux and increased TMP (Metcalf and Eddy, 2014).

2.1.6 Membrane Fouling

One of the major issues associated with membranes is membrane fouling. Fouling occurs due to a buildup of solids along the membrane surface which clogs pores (complete blocking) or in the form of a cake layer (cake filtration) causing flux to decline and/ or TMP to increase (Muthukumaran et al., 2013). Depending on the type of fouling that occurs determines whether membrane flux decreases, generally clogged pores increases the membrane resistance and cake formation decreases membrane flux (Muthukumaran et al., 2013). Fouling caused by pore

blocking is more severe than a cake layer but can be reduced by increasing the particle size of the feedwater (Soffer et al., 1998).

Many studies of membrane fouling often contradict each other as they report many different reasons for membrane fouling. According to Vanysacker et al. (2013) studies have reported that solutes are the main factor in fouling while others claim that suspended solids and another claims that colloidal material is the key issue. While the main reason for membrane fouling may still be debatable, the need for controlling fouling is necessary for a successful membrane system. Three main operating conditions including TMP, feedwater characteristics, and membrane characteristics are the driving factors which can reduce the fouling (Ravazzini et al., 2005)

2.1.7 Membrane Cleaning

Once a membrane has begun to foul, it can be cleaned using either physical or chemical processes to restore membrane performance. Seven key factors of membrane cleaning are defined by Shi et al. (2014) and include the following:

- Restoration of the initial flow without changing the membrane surface
- Keeping dislodged foulants in dispersion to prevent re-fouling
- Method must be compatible with both membrane and equipment
- Method must be compatible with water
- Possessing good buffering capacity and stability with time
- Promotes disinfection of wet surfaces

• Method must be easily available and cost effective.

Generally membrane cleaning is divided into two categories, physical and chemical cleaning.

2.1.7.1 Physical Cleaning

Physical cleaning is the process of physically removing foulants from the membrane surface through various practices. By changing the hydrodynamics within the membrane module through varies practices such as turbulence and temperature changes, foulants are forced off the membrane surface restoring membrane performance Shi et al. (2014). While three main physical cleaning include hydraulics, mechanical, and electrical, hydraulics and mechanical are among the more utilized methods. Hydraulic cleaning involves reversing the TMP essentially backwashing, forcing permeate in the reverse direction to wash away any easily removed particles. Additionally, hydraulic removal includes a relaxation on the membrane, lowering the feed pressure and the cross sectional velocity to allow particles to settle since they are no longer being pressed up against the membrane wall and removed when the cross sectional velocity is increased to operating conditions. Mechanical physical cleaning is the process of incorporating mechanical features such as air sparging and sponge balls to scrap the membrane wall. Air sparging is the continuous pumping of air through the feedwater to form a gas/liquid stream which in turn, limits particles from settling on the membrane surface while sponge balls are only acceptable in larger tubular membranes due to their size, which could potentially clog smaller membrane tubes (Shi et al., 2014)..

2.1.7.2 Chemical Cleaning

Chemical cleaning the process of removing foulants from the membrane surface by using chemicals to change the solution chemistry causing foulants to decompose rapidly or to be

electrostatically repulsed from the membrane is often used for severely fouled membranes and to prevent permanent fouling from occurring (Shi et al., 2014). Since not all foulants are able to be removed physically the degradation of these foulants though chemical is the only option to maintain membrane life. The cleaning can take place in situ or ex situ. In situ is performed by replacing the existing feedwater with a chemical solution and allowing the solution to be filtered through the membrane, whereas ex situ cleaning is the performed by removing the membrane and allowing it to soak within the chemical solution for a period of time (Shi et al., 2014). Depending on the type of fouling occurring different chemicals such as acids, oxidants and enzymes may be used within the chemical solution.

2.2 Direct Filtration

Conventionally, before a feedwater is processed by a membrane system it undergoes various steps of pretreatment before the feedwater is filtered by the membrane. These pretreatment processes remove larger particles which could potential increase membrane fouling consequently reducing flux and/or increasing TMP depending on the system. With global water demands rising, the need for non-conventional techniques for water and wastewater treatment is required (Ravazzini et al., 2005). DF, the process of filtering feedwater through a porous membrane with no pretreatment processes, can be the non-conventional approach to help bridge the gap in water and wastewater treatment.

2.2.1 DF Advantages

DF, a purely physical process does not rely on the pretreatment steps which could include chemical processes such as coagulation and flocculation, or biological process such aerobic treatment to treat water and wastewater. Due to the simplicity in design and maintenance there

are considerable less points of failure within the system that can occur compared to the conventional membrane filtration system (Ravazzini et al., 2005). Membrane systems in general, have an advantage over biological treatment, as biological treatment system are not as equipped to handle high variations in flow, where a membrane system, including DF, can be manage to account for various flows caused by seasonal changes (Ravazzini et al., 2005). Biological treatment also requires a long start-up time and is susceptible to toxicity and temperature variations which could affect the microbial populations. Since the DF system does not require the utilization of microbial populations these factors are not a major concern (Ravazzini A. M., 2008). Additionally because of the modularity of the DF system, plants can scaled, resized and adapted into a preexisting plant rapidly (Ravazzini et al., 2005).

The quality of permeate produced by DF is generally clear, free of solids and pathogens. The turbidity produced by a UF-DF system was able to achieve low turbidity and was reported by Ravizzini (2008) to be less than 1 NTU. Since the porous membrane is able to physical filter the feedwater, permeate produced from the DF system can be expected to have high removal of pathogens. van Nieuwenhuijzen et al. (2001) determined that DF creates a complete barrier of particles, allowing the particles to be collected within the concentrate without the use of chemicals. The membrane does not only concentrate particle but also pathogens which are not able to pass through the pores of the membrane allowing permeate to be pathogen free.

2.2.2 DF Disadvantages

Since the feedwater is no longer pretreated, strong flux decline occurs, which results in additional maintenance and operation cost. Fouling problems not only result in higher membrane maintenance but since the membrane is experiencing higher levels of particulates the membrane

life could be shorten considerably and thus resulting in a large capital investment for membrane replacement to be considered. According to Ravazzini (2008), permeate may not reach high aesthetic qualities compared to effluents treated through other processes. Since wastewater is transported to a treatment facility through a sewer system in an anoxic state, it is filtered through the membrane in this state and produces noxious odors when permeate is stored (Ravazzini A. M., 2008). Wastewater treatment facilities in the United States are additionally required to remove excess nitrogen and phosphorus in the wastewater and these nutrients are able to pass through the membrane pores (Ravazzini A. M., 2008), which could cause these facilities not to meet the discharge requirement in the area the facility is located. Heavy metals, similar to the nutrients, are able to pass through the membrane system and be present within permeate produced.

2.2.3 Solids in DF Systems

With colloidal matter being retained by the membrane system, DF is able to retain the suspended solids within the system. The suspended solids retained by a DF, a larger portion around 90%, are volatile which indicates that DF could be used with energy recovery systems such as anaerobic digesters for energy recovery at wastewater treatment facilities (Lateef et al., 2013). A large portion of the particulate matter are deposited on the membrane surface, cake filtration fouling, and also can be deposited along the feed tank walls making accountability for the solids difficult. (Lateef et al., 2013).

2.2.4 COD in DF Systems

The particulates in the DF contain COD as well as the soluble portion. Since the colloidal portion is retained by the membrane, only the soluble portion is can be passed through the

membrane which may be found in permeate. With a majority of the permeate having low COD concentrations (Ravazzini, 2005), concentrating of the feedwater can result in higher COD concentrations (Lateef et al., 2013). It has been observed by Lateef et al. (2013) that the sum of permeate and feedwater is not always accounted for. This can be explained by biodegradation within the feed tank even when the retention time is short (Lateef et al., 2013). Around 75% of the COD can be accounted for with 25% being loss to biodegradation (Lateef et al., 2013).

2.2.5 Potential Applications of DF

With the membrane process filtering the feedwater, separating the particles and the soluble fractions of wastewater, DF can be utilized in multiple stages of a conventional wastewater treatment facility. Given that permeate is able to produced pathogen free and low turbidity effluent DF could become the final polishing process before the effluent is discharge into the environment (Ravazzini et al., 2005). If DF is implanted in a wastewater treatment facility as the final polishing process, several other processes that are involved with aesthetics and tertiary treatment could be replaced such as sand and carbon filters.

The second potential application with a wastewater treatment facility would be used to concentrate the wastewater before other treatment. This application allows for the solids and non-soluble fraction of the wastewater to be treated separately from the soluble fraction. The concentrate would then be treated through the facilities' conventional process with a higher concentration rate but with a lower hydraulic loading rate (Ravazzini et al., 2005) while permeate produced from the DF process, depending on the quality produced, may have to be further treated to meet discharge standards. With this system, the question now becomes whether the DF module will be at the entrance to the wastewater treatment facility, acting as the grit removal and

primary clarifier or if the module will be placed after primary clarification to concentrate the wastewater before the biological processes.

2.2.6 Raw Sewage vs. Primary Clarification

The influent of a wastewater treatment depends on several factors that change not only from month to month but day to day. Seasonal behaviors of people as well as seasonal behavior of the weather can have a large impact on the concentrations entering a wastewater treatment facility (Mikola et al., 2011). In comparison the effluent produced through primary sedimentation has variation due to seasonal changes but the amount of variation is to a lesser degree than the influent (Mikola et al., 2011). Due to the settling of solids and the large volume associated with a primary clarifier, the primary clarifier could potentially act as an equalization basin to some extent, allowing for constant flow through the DF module. Due to these differences between a facilities' influent and a facilities' primary effluent, it can be expected that these two different feedwaters can have major differences in the performance of a DF system.

Since the facilities' influent is not treated before the filtration process, the influent has a higher particle distribution compared to the effluent (Ravazzini et al., 2005). This causes blocking of the membrane pores and fouling to occur at a higher rate than with the primary effluent. Also comparatively the facilities' influent contains higher concentrations of total nitrogen, total phosphorus, total solids, and total suspended solids (Ravazzini et al., 2005). The characteristics of the two different feedwaters have a different effect on the TMP and the flux through the membrane system. In an experiment performed over a short period of time by Ravazzini et al. (2005), it was determine that the flux produced in a DF system and using primary effluent as the feedwater was able to produce between 20 and 70 percent higher flux
productions compare when a facilities' influent was the feedwater source. The flux would decline at a much faster rate when exposed to the influent than the primary effluent resulting in the TMP to be higher in the influent sample tests at around 0.5 bar and the TMP in the primary effluent was around 0.3 bar for these tests (Ravazzini et al., 2005). Ravazzini et al. (2005) also determined that with the average fluxes of the DF system were very high and were 120 LMH for raw influent and 160 LMH for the primary effluent. While fouling did occur, the fouling was almost completely reversible and no signs of permanent fouling were observed making DF a largely possible (Ravazzini et al., 2005).

2.2.7 Improving DF Systems

Studies have investigated improving DF system through the addition of coagulants and air sparging. These methods for improving DF can be used to reduce fouling, resulting in lower TMP, lowering maintenance, and extending membrane life.

2.2.7.1 Coagulation

The addition of coagulate to improve the DF can be used to bulk solids allowing them to settle within the feed tank. Since these solids settle they are not exposed to the membrane surface, causing less buildup of particulates along the membrane surface reducing fouling. Diaz et al. (2012) investigated using Al^{3+} as the coagulate, allowing the particulate to settle before reaching the membrane surface reduced the turbidity of the permeate, and lowered the resistance caused by cake filtration.

2.2.7.2 Air Sparging

Utilizing air sparging within the membrane system can reduce membrane fouling by forcing air into the membrane can cause two phase filtration to overcome external fouling. (Psoch and Schiewer, 2006). By reducing the cake layer that is developed on the membrane surface, air sparging was able to increase permeability of virgin membranes with a DF system by 400% but it also was noticed that this effect is only viable on higher fouling potential feedwaters and air sparging has little effect on lower fouling potential feedwater (Psoch and Schiewer, 2006).

2.3 Anaerobic Membrane Bioreactors

As with conventional domestic wastewater treatment, a centralized facility is used to treat all wastewater generated within a certain area, unless local treatment i.e. septic tanks are utilized. A technology which has made decentralized wastewater reuse possible is the membrane bioreactor (MBR) which combines biological treatment with micro- or ultra- membrane filtration to generate high quality effluent suitable for reuse (Judd, 2010) AnMBRs have started to be viewed as an alternative to conventional treatment (Ozgun et al., 2013) and may be the idea need to divert from conventional treatment. AnMBRs couple a bioreactor which house anaerobic microorganisms to breakdown organic material found in domestic wastewater and membrane separation to effectively treat the wastewater. The utilization of membrane separation ensures the retention of biomass, solids, and pathogens within the bioreactor while water is able to be filtered through.

An AnMBR acts anaerobically, energy conversation is achieved since aeration is not provided and energy recovery is possible through the form of digester gas (biogas), produced by

the anaerobic microorganisms. According to Gao et al. (2013), stoichiometrically the AnMBR conserves energy through the reduction of aeration since to remove one gram of COD aerobically would require one gram of oxygen. However since the system acts anaerobically, the degradation of one gram of COD produces 0.35 L of methane, when biomass synthesis is ignored (Gao et al., 2013). In MBRs aeration accounts for over 76% of the energy demand (Wallis-Lage and Levesque, 2009) whereas with AnMBRs that energy demand is no longer needed, resulting in energy savings and closing the gap to net neutral energy demand. The AnMBR, in addition to energy savings, cost savings is usually associated with anaerobic treatment nutrient recovery (nitrogen and phosphorus) and lower sludge production (Wei et al., 2014) due to slower growth rate of the microorganisms (Ozgun et al., 2013).

2.3.1 Performance of AnMBR with Domestic Wastewater

AnMBR performance is very dependent upon the operating parameters in which the system is operating under. Many of the operating parameters many research facilities are focusing efforts on to improve the performance include the following: temperature, organic loading rate (OLR), hydraulic retention time (HRT), solids retention time (SRT), and the addition of adsorbents (Ozgun, 2013). With the given operating conditions, a desirable goal for the AnMBR should be maintaining suitable flux while maintaining minimal energy input (Prieto et al, 2013) should be a large focus when designing the AnMBR.

2.3.2 Temperature

Domestic wastewater, which can range in influent temperatures from 3 to 27 °C (Smith et al., 2012), heating of domestic wastewater is needed to effectively treat wastewater in an AnMBR. Heating of the reactor is performed in two main ways, heating the influent before

entering the bioreactor, or the heating of the bioreactor itself. In either case, a large volume of water needs to be heated to reach either mesophilic or thermophilic conditions.

The microorganisms within the AnMBR are highly dependent on the temperature. The biological processes are generally hindered at lower temperature thus resulting in lower COD removal and less energy recovery through biogas (Ozgun et al., 2013). Higher temperatures have been observed by Skouteris et al. (2012) to effectively remove COD concentration when compared to psychrophilic, around 20 °C. In addition to the effects on the metabolic rate, energy recovery through the utilization of biogas can be hindered if not operated within these ideal ranges due to biogas solubility. Finally temperature also plays a major role in the volumetric loading conditions. At higher temperatures, AnMBR are able to utilize the COD concentrations found within the wastewater, thus resulting in better energy recovery and treatment performance (Jeison et al., 2008)

2.3.3 Organic Loading Rate

AnMBR which are capable of dealing with high fluctuations in OLR, make perfect candidates for treating domestic wastewater (Ozgun et al., 2013). The OLR which can change drastically in domestic wastewater can still achieve high effluent quality in AnMBRs. Wen et al. (1999), varied the OLR between 0.5 and 12.5 kg COD/m³-day) was able to achieve high quality effluent, whereas compared to other anaerobic treatment technologies, perturbations. Additionally in a study by An et al. (2009), the effluent quality was not only high but relatively stable when dealing with fluctuations in the OLR and biogas was also increased at the high loading rates.

The issue with treating domestic wastewater with AnMBRs is that domestic wastewater is generally considered low strength with an average COD concentration of 500 mg/L (Metcalf and Eddy, 2014). AnMBRs are excellent at treating industrial wastewater, because industrial wastewater is considered high strength with much greater COD concentrations than domestic wastewater. Since the anaerobic microbial population grows at slow rate, low strength wastewater may not be effectively treated in the AnMBR because the required concentration of COD to be effective should be greater than 1500 mg/L (Metcalf and Eddy, 2014). According to Prieto et al. (2013), little information has been reported regarding the AnMBR treatment involving low organic strength domestic wastewater.

2.3.4 Hydraulic Retention Time

The hydraulic retention time is the average amount of time it takes for water molecules to pass through the system. A lower HRT means the microorganisms will have less time to be able to treat the waste within the feedwater. Since removal efficiency is reduced at lower temperatures, a higher HRT is needed to have the same treatment efficiency. The lowest HRT recorded for an AnMBR while maintaining COD removal efficiency over 90% was 2.3 hours (Yoo et al., 2013). On the other end of the spectrum HRT can be relatively large with values ranging up to 20+ days (Jeong et al., 2010).

The benefits of a lower HRT are desirable due to the reeducation in AnMBR size and overall footprint in operation (smith et al., 2012). Additionally according to Ho and Sung (2009) and Lew et al. (2009), higher HRT have little effect on the AnMBR permeate quality thus having a smaller footprint is desirable since performance is not increased by increasing the HRT. Due to this benefit, a smaller HRT and smaller reactor size can be beneficial especially when

considering an economical perspective as reactor size has an influence on capital cost and operation and maintenance (Ozgun et al., 2013).

2.3.5 Solids Retention Time

SRT is simply defined as the average retention time of solids within the bioreactor. Due to the membrane separation and recirculation of solids, the SRT is generally much larger than the HRT. The solids which are retained by the membranes are a combination of inert and biodegradable solids from the influent as well as biomass grown in the bioreactor from microbial community. According to van Lier et al. (2008), the SRT should be at least three times the doubling rate of the slowest growing microorganism in the bioreactor at the operating temperature.

As solids buildup within the bioreactor the effective volume of the bioreactor becomes smaller. To ensure enough volume is present to treat the wastewater, solids periodically have to be wasted and discharged. The fewer solids are wasted the higher the SRT is and can affect not only the performance of the biological treatment but also the membrane treatment. Saddoud et al., (2007) maintain an AnMBR with a SRT of 140 days and membrane fouling and a strong flux decline was observed. On the other hand studies by Herrera-Robledo et al. (2010) showed that SRT had little impact on the membrane performance. What is believed to be the cause of fouling in these AnMBRs that have high SRT is biofouling. Biofouling is caused by the ratio of proteins to carbohydrates with in the EPS and the soluble EPS also known as SMP, produce biomass which can easily attach to surface which is ideal for suspended biomass growth but can result to the biomass attaching to the membrane surface and causing an increase in the cake layer on the membrane surface which results in lower membrane filtration (Ozgun et al., 2013). As the

relationship between EPS, membrane fouling, and SRT is still not well understood in AnMBRs but controlling SRT is complicated by relationship with treatment performance (Smith et al., 2012). Due to the buildup of biofilm on the membrane, fouling may occur but the reduction of soluble COD may also be increased, thus resulting better treatment performance. Thus Smith et al. (2012) suggest that there is an appropriate limit for AnMBR SRT time to reduce membrane fouling but increase the treatment performance.

2.3.6 AnMBR with Adsorbents

The use adsorbents and other additives in AnMBR have become popularized for the increase in flux and reduction of membrane fouling. Additionally adsorbents can have a critical impact of the effluent quality generated by the AnMBR. The use of using PAC and granular activated carbon (GAC) was investigated by Hu and Stuckey (2007); the activated carbon was able to achieve better performances in terms of TMP and variation because the membranes were constantly scoured by the particles from the activated carbon. The enhancement was also better when PAC was used compared to GAC due to the higher surface area of PAC. However, adding excess amount of PAC observed to be detrimental to flux performance as the viscosity of the feedwater increased (Akram and Stuckey, 2008). In this study with a PAC concentration 1.67 g/L, flux was increased from 2 LMH to 9 LMH but when PAC concentrations were increased to 3.4 g/L the formation of a thin cake layer appears, viscosity increased and a decrease in the flux occurred. According to Ozgun et al. (2013), all studies utilizing PAC and other adsorbents in AnMBRs are performed on short term studies, thus the long term operation of a system still needs to access.

2.4 Modified Fouling Index

The Modified Fouling Index (MFI) is a reliable method to predict the fouling potential of feedwater with a membrane filtration system (Boerlage et al., 2003). Applications of the MFI can be used in the design stage to address pretreatment options for the feedwater and predict the performance of the pretreatment system before and during plant operations. The MFI is a relatively new method that is being used as a replacement for previous methods such as the Silt Density Index (SDI), which is the current industry standard used for predicting membrane fouling (Koo et al., 2013). In recent years, two different types of MFI test methods were developed: the MFI_{0.45}, which uses a 0.45 μ m microfiltration to measure membrane fouling based on cake filtration (Boerlage et al., 2002), and the MFI –UF, which is currently being developed to incorporate small colloidal particles in the MFI measurement using UF membranes (Boerlage et al., 2002).

In addition to the utilization of different type of membranes used in the MFI, the MFI has also seen a transformation in the parameters measured in the testing. In the early stages of the MFI, the tests were performed using constant pressure. As the membranes began to foul, the flux would decrease due to buildup of filtration resistance (Boerlage et al., 2003). Later on, the constant flux method was developed, which would force the membrane to maintain a constant flux causing the pressure to increase to force the same permeate through a fouled membrane. It was concluded by Boerlage et al. (2004), that the constant flux method provided a more accurate measurement to predict membrane fouling, as it established a linear relationship between membrane fouling and the rise in pressure. Additionally Koo et al. (2013) also states the linear relationship between membrane fouling and the increase in pressure is near perfect within a constant flux MFI system.

The MFI is based on the cake filtration theory which is where particles are retained on the membrane surface during filtration by a mechanism of surface deposition. (Boerlage et al., 1998). Many factors can contribute to potential membrane fouling within the MFI including pore size expressed as molecular weight cut-off (MWCO), but also particulate shape, and the interaction with the membrane surface (Boerlage et al., 2002).

2.4.1 MFI_{0.45}

The MFI_{0.45} utilizes a microfiltration membrane as the testing membrane within the system and was developed originally under constant pressure. When exposed to constant pressure, the MFI_{0.45} is dependent on the filtrate volume (V), time (t), the change in TMP (ΔP), feedwater viscosity (η), membrane resistance (R_m), the membrane surface area (A) and fouling index (I). Generally the results are represented in the $\frac{t}{v}$ vs. V equation shown below, equation 1, and form a three region plot which corresponds to (i) blocking filtration, (ii) cake filtration with or without clogging and a (iii) potential third region which cake clogging and/or cake compression (Boerlage et al., 2003). The first region is shown as a sharp increase in the plot, and represents the blocking filtration, which is where particles block the entry to the pores or inside pores of the membrane (Boerlage et al., 2004). This is generally followed by a slight linear slope where particles begin to deposit on the membrane surface, cake filtration, which may or may not be under compression depending on the reduction of the porosity of the cake (Boerlage et al., 2004). It was determined by Boerlage et al. (2003) that this region is highly dependent on the pressure within the MFI system, and at higher pressures it could increase the cake compressibility and must be corrected using a cake compressibility coefficient which is related to the specific resistance of the cake at the applied pressure within the system.

$$\frac{t}{V} = \frac{\eta R_m}{\Delta PA} + \frac{\eta I}{2\Delta PA^2} V \tag{1}$$

Some studies have shown that it is possible to measure the cake compression within the MFI_{0.45} system, which can occur due to fine particles within the feedwater (Boerlage et al., 2004). Shown as third region within the $\frac{t}{v}$ vs. V equation the buildup of the fines within the cake, the cake voids will become blocked, reducing the flux, and permeate produced, as well as increasing the TMP. This is commonly referred to as cake clogging. (Boerlage et al., 2004). The region is generally only a factor within the MFI_{0.45} and not within the MFI-UF system.

2.4.2 MFI-UF

The MFI-UF was developed to include smaller colloidal particles which were not previously measured in the SDI or the MFI_{0.45}. Developed using a 1300 Da with an average pore size estimated by scanning electron microscopy of 9 nm, the MFI-UF is able to demonstrate a linear relationship between the MFI-UF index and the cake filtration (Boerlage et al., 2003). Additionally the MFI-UF was developed to undergo both constant pressure as well as constant flux.

While the MFI-UF is able to retain smaller particles located in the feedwater, not all particles are retained by the membrane. An experiment conducted by Boerlage et al. (2003) showed that the membrane system was only able to retain 50% of the particles in the smallest channel size .05-.1µm. While the feedwater used in this experiment is used to determine the fouling potential within a RO system, which is primarily used to remove salts, the cake buildup on the membrane surface should be able to retain these salts. It was determined that not only does the retention of the particles within the MFI-UF depend upon particle size distribution but

also corresponds to the charge, flexibility of the membrane and shape of the particles (Pusch, 1982).

2.4.3 Constant Pressure Operation

When constant pressure is applied to the MFI-UF, the system responds similarly to the MFI_{0.45} but does not include the third region which represents the cake clogging. (Boerlage et al., 2002). When tested under constant pressure, the standard pressure of 2 bar is applied to the membrane system and the decrease in flux is measured over a period of time (Boerlage et al., 2003). Similar to the MFI_{0.45}, the MFI-UF is pressure dependent and an increase in pressure can lead to a higher compression of the cake, increasing the cake resistance and decreasing the flux faster (Boerlage et al., 2003).

2.4.4 Constant Flux Operation

Since previous research indicated that the $MFI_{0.45}$ could be operated under constant flux, it was determined that the MFI-UF could operate in a similar fashion even though the $MFI_{0.45}$ under constant flux was never adopted (Boerlage et al., 2004). Since most membranes systems, especially RO systems are operated under constant flux, the need to determine the fouling potential when flux is constant is crucial. Since flux is now considered constant, the dependent variable becomes pressure which is expected to rise with increasing fluxes.

2.4.4.1 Development of the Constant Flux MFI-UF

In the development of the MFI-UF under constant flux, two sources of feedwater were used: low fouling potential tap water and high fouling potential 10% diluted canal water (Boerlage et al., 2004). Within this test, the same fouling mechanisms were expected to occur: pore blockage and cake formation (Boerlage et al., 2004). In the two feedwaters, pore blockage and cake formation both occurred, with pore blockage having effect immediately after the test were started and cake formation occurring after some time. Once it was determined that the filtration mechanisms were the same within the constant flux and the constant pressure test, it was determined that constant flux was a viable option. Additionally the constant flux was able to establish the fouling potential in less time and with a higher degree of accuracy than under constant pressure (Boerlage et al.,2004).

2.4.4.2 Fouling Index under Constant Flux

The fouling index, I, was adapted from previous research by Boerlage et al. (2004) is represented empirically by equation 2, where I is the fouling index (1/m²), ΔP is TMP (Pa), J is flux (m³/m²s), η is water viscosity (Ns/m²), and t is time (s).

$$I = \frac{\Delta P - J\eta R_m}{J^2 \eta t} \tag{2}$$

Once the fouling index has been established, the MFI may be calculated using I. The MFI represents the fouling potential in reference to a standardized pressure of 2 bar and a test membrane which has an average pore size of 0.45 μ m. The correlation of the fouling index with MFI is represented by equation 3, from Boerlage et al., 2004.

$$MFI = \frac{\eta_{20} \circ_{C*I}}{2\Delta P_0 A_0^2}$$
(3)

where $\eta_{20^{0}C}$ is the viscosity of the incoming feedwater at 20°C (Ns/m²), ΔP is the reference pressure of 2 bar and A_o is the surface area of the reference MF membrane with an area of 13.8*10⁻⁴ m².

2.4.5 NF-MFI

Since the fouling potential and the MFI are dependent on the MWCO (Schippers et al., 1981), it was proposed by Khirani et al. (2006) that the MFI could be improved utilizing nanofiltration membranes and hence the NF-MFI was developed. With the MWCO as an important parameter to measure within the MFI, the distribution of natural organic matter which is present in the feedwater can have an effect of the fouling potential, a considerable fraction below 10,000 Da (Khirani et al., 2006). Due to the size of these particles an emphasis should be placed on these small particles making the utilization of a nanofiltration membrane considerable for the MFI. Khirani et al. (2006) found that while the MWCO of an NF membrane should retain a higher percentage of smaller colloidal particles and salts with the system This was not the case and generated similar results as the MFI-UF system. The main advantage of the NF-MFI compared to the MFI-UF was results were able to be generated in less time (generally 20% to 50% of the time) compared to that of the MFI-UF system (Khirani et al., 2006).

2.5 Summary

The utilization of DF for domestic wastewater has been shown to be able to remove large amount of COD and solids as well as pathogens (Ravazzini, 2008). While DF can be effective, the lack of pretreatment of the feedwater can result in higher fouling. The buildup of solids and cake layer along the membrane surface forms faster than that compared to pretreated wastewater. Additionally since solids are rejected by the membrane, the solids will need to be further treated by alternative methods.

The MFI can accurately predict the fouling potential of different feedwater before being treated by the membrane system. The quickest and most common method utilizes a UF

membrane and operates under constant flux (Boerlage, 2004). Under constant flux operations, the TMP becomes the independent variable and increases over time as the membrane begin to foul. Different particles makeup within the various feedwaters results in different fouling potential and thus a comparison between the fouling potential is established.

AnMBRs technology has been used for treating wastewater and excels at industrial wastewater. In domestic wastewater since the COD concentration is generally considered low strength at around 500 mg/L of COD (Metcalf and Eddy, 2014) may not provide sufficient energy for the anaerobic processes to take place. Anaerobic processes generally excel at higher COD concentrations, when greater than 1500 mg/L according to Metcalf and Eddy (2014). While the COD concentrations are low in domestic wastewater, the treatment efficiency is still high and is able to handle higher fluctuations of the OLR than other anaerobic processes (Ozgun, 2013).

CHAPTER 3: MATERIALS AND METHODS

3.1 Wastewater and AnMBR

Wastewater that would be utilized in the experiments was obtained at a local charter school, Learning Gate Community School (LGCS) in Lutz, FL. At LGCS, a research station known as Biorecycling and Bioenergy Research and Training Station (BBRATS) is established with a unique educational platform to help educate the younger generation to develop a better understanding for sustainability. The BBRATS facility houses four technologies including a food waste digester (FW digester), algae photobioreactor (APBR), a hydroponic/aquaponic system, and an AnMBR.

The AnMBR treats a portion of the wastewater generated by roughly 600 students and 50 staff members via the collection system that disposes wastewater into a septic tank. The system withdraws wastewater from the collection post grinder station to ensure the destruction of sanitary wipes and napkins, as well as any other large particles that may enter the system. The AnMBR is a 20.45 liter; two-stage AnMBR (Figure 3.1) designed to operate at ambient temperature for the treatment of domestic wastewater. Each phase of the sequence holds equal volume (10.23 liters). The first reactor operated as an upflow anaerobic sludge blanket (UASB) and the second as a completely stirred tank reactor (CSTR). Tubular PVDF membranes modules with a total membrane area of 0.0423 m² and average pore size of 0.03 μ m (X-Flow, Pentair) filtered the bioreactor contents from the second reactor and returned the concentrate to the bioreactor. Analysis of this reactors performance is included in another study by Bair et al.

(2015). Permeate from the AnMBR and effluent from FW digester provides the nutrient source for the hydroponic system as well as the APBR.



Figure 3.1: AnMBR established at LGCS for the treatment of domestic wastewater

Wastewater that was utilized in the experiments was withdrawn from the same location as the AnMBR, which is located at LGCS's BBRATS facility. Since the wastewater changes from day to day, sample of the wastewater must be characterized for each experiment. The AnMBR reactor samples utilized for this research were obtained from the CSTR portion of the AnMBR at this facility.

3.2 PAC

PAC was obtained from Multavita, (Hardwood, Food Grade) and was utilized in some the experiments for testing with the wastewater and had an average particle diameter of 0.16 mm. To determine particle size, 40 particles of PAC were observed under a 40X microscope (Reichart, Diastar) with a C-Chip (InCyto, DHC-NO1-5) grid pattern. The average particle size was determined by measuring the particles on the C-Chip with around 95% of the particles being within 0.05 mm of the average. The distribution of the particle diameter is shown in Figure 3.2. While the overall distribution ranges in size from 0.1 and 0.21 mm in diameter. It can be observed that a majority of the particles are between 0.15 and 0.18 mm in diameter.



Figure 3.2: PAC particle size distribution

3.3 Analytical Methods

Samples from the experiments were measured for some or all of the following parameters depending on each test; COD, total nitrogen (TN), ammonia, total phosphorus (TP), turbidity, total solids (TS), total volatile solids (VS), total suspended solids (TSS), and volatile suspended solids (VSS),pathogens via E. coli testing, color and yellowness. Samples were measured for total concentration (raw) and/or soluble fraction, which was obtained from the supernatant of a centrifuged sample (centrifuged at 3000 rpm for 15 minutes). Hence, soluble sample include both truly dissolved and unsettled colloidal matter.

3.3.1 Chemical Oxygen Demand

COD values were obtained using Hach HR plus digestion vials in Hach Method 8000 (Hach Company, Loveland, CO). Each COD test is able to measure concentration of COD from 20-1500 mg/L. Each test vial utilizes 2 mL of the sample and is heated in a Hach COD reactor for two hours at 150 °C. In certain samples, the expected COD values were higher than the maximum range and a dilution using deionized water was used to reach higher concentrations. The concentration of COD is determined using a spectrophotometer (Model DR/4000U, Hach Company, Loveland, CO).

3.3.2 Total Nitrogen

TN was measured using Hach Test'N Tube HR Persulfate Digestion Method, Hach method 10072 (Hach Company, Loveland, CO). This method allows for concentrations of TN to measure between 10 and 150 mg/L N utilizing 0.5 mL of the sample. Each vial is digested in a COD reactor at 104 °C for 30 minutes. Similar to COD, if samples were higher than the maximum range, dilutions of the sample using DI water were used until the concentration was within the appropriate range. The concentration of TN is determined using a spectrophotometer (Model DR/4000U, Hach Company, Loveland, CO).

3.3.3 Ammonia

Ammonia was determined using Hach HR Ammonia Nitrogen by the AmVERTM Salicylate Test'N Tube Method, Hach method 10031 (Hach Company, Loveland, CO). The respective range for this method is 0.4-50.0 mg/L NH₃-N. Only the soluble fraction of the samples was used in this test and many of the samples had to be diluted to ensure the concentration was within this concentration. The required sample size for this method is 0.1 mL.

3.3.4 Total Phosphorus

TP was measured utilizing Hach Total Phosphorus (phosphate) by the Molybdovanadte Test'N Tube Method, Hach method 10127 (Hach Company, Loveland, CO). This Hach method allows a concentration range of 1.0-100.0 mg/L PO₄. Each Test'N Tube utilizes 5.0 ml of sample and is digested for 30 minutes in a COD reactor at 150 $^{\circ}$ C for 30 minutes. Dilutions were obtained in similar fashions as the COD and TN.

3.3.5 Turbidity

Turbidity was measured using a Hach 2100P portable Turbidmeter (Hach Company, Loveland, CO). Concentrations of turbidity range from 0 to 1000 NTU and samples higher than this concentration were diluted with DI water until turbidity was within the appropriate range.

3.3.6 Solids

TS and VS were measured using EPA method 1684 and TSS and VSS were determined using EPA method 340.2. The filter used in the TSS and VSS samples was a Whatman Glass microfilter (Whatman 934/AH) with a diameter of 47 mm and pore size of 1.5 µm. According to both EPA methods a pre-weighed aluminum dish was measured, and a volume of sample is added to the dish. For TSS the aluminum dish is measured with the glass microfilter, and a sample is filtered using a vacuum pump to filter the liquid fraction through the filter. The aluminum dish with or without the filter is then placed in an oven at 104 °C . Dried samples are removed and allowed to cool in a desiccator and weighed again. Finally samples are ignited in a muffle furnace at 550 °C. The samples are removed after 15 minutes and placed in the desiccator to cool then weighed a third time. The difference between the sample after the oven and the preweighed dish is TS (unfiltered) and TSS (filtered), and the difference between the sample after

the oven and the sample after the muffle furnace is the VS (unfiltered) and VSS (filtered). The samples were corrected to mg/L by dividing the mass by the volume of the sample used. To determine total dissolved solids (TDS), or dissolved volatile solids (VDS), the difference between TS and TSS or the difference between VS and VSS determines TDS and VDS respectively.

3.3.7 Pathogens (E. coli)

Pathogens were measured using Hach Analytical Procedures, m-ColiBlue24 Broth Procedure for Membrane Filtration, Hach method 10029 approved for drinking water by U.S. EPA in 2000 (Hach Company, Loveland, CO). In this method 100 mL of sample are filtered through a 0.45 µm filter. The filter is then placed with on a sterilized pad and 0.2 mL of the m-ColiBlue24 Broth is poured onto the sterilized pad in a 50 mm petri dish. The filter is then placed on a sterilized pad and incubated at 35 °C for 24 hours. The petri dish is then removed and analyzed for color of red and blue blotches on the filter. The presence of a red and blue markers indicates total coliforms and the presence of blue indicate E. coli. This was performed at several dilutions as at higher concentration, the presence of E. coli colonies were too numerous measure and at lower dilutions, less colonies are present allowing for accurate determine of different colonies.

3.3.8 Color and Yellowness

Color was determined using a HACH spectrophotometer method 8025 (Model DR/4000U, Hach Company, Loveland, CO). A sample was adjusted to a pH of 7.6 using 1.0 N HCL and filtered through a 0.45 µm filter then the filter is rinsed with 50 ml of DI water. The

sample is placed in a cuvette was measured at a wavelength of 455 nm. Samples are displayed as unit of Pt.-Co where higher Pt.-Co indicates higher presence of color.

Yellowness was determined using a HACH spectrophotometer method 10104 (Model DR/4000U, Hach Company, Loveland, CO). A sample was placed in the cuvette and then analyzed at a starting wavelength of 780 nm. The spectrophotometer automatically adjusts wave length in 5 nm intervals until it reached 380 nm. Readings is displayed as the Yellowness Index (YI) where higher YI indicate higher presence of yellowness.

CHAPTER 4: DIRECT FILTRATION STUDY

4.1 Introduction

Since domestic wastewater is often dilute and has low organic loading strength, anaerobic processes may have reduced performance when treating this type of feedwater. By utilizing a DF system, the membrane within the DF module will be able to concentrate the wastewater by separating the liquid fraction from the colloidal fraction. Separating the liquid and the colloidal fraction, the organic colloids are returned to the feed reservoir, thus increasing the organic loading strength. By concentrating the wastewater, a lower volume of wastewater is now attained and the reactor size of the AnMBR can be reduced, since the system is no longer handling a large volume, thus reducing the overall footprint required by the reactor. The AnMBR will no longer be receiving 100% of the total volume but only a fraction of the total volume. This is represented by the concentration factor (CF), where the CF can be expressed as the equation (4). For example, if 10 L of wastewater is concentrated to 0.5 L, a CF of 20 is achieved, whereas if no concentrating of the wastewater occurs, V_{Inital} is equal to V_{Final}, thus resulting in a CF of 1. When volume is first treated by the DF system before being treated by the AnMBR, the concentrate volume is only a portion of the initial volume, thus resulting in a higher CF as more flow is diverted through the DF module and less overall volume is treated by the AnMBR.

$$CF = \frac{V_{Inital}}{V_{Final}} \tag{4}$$

The purpose of this DF study is to determine the performance of a DF system, how higher CFs will affect the DF system, and how well can the wastewater be concentrated. Additionally the DF system will aid in the determination of rejection by the membranes for the following parameters, COD, solids, TN, TP, ammonia, and turbidity. To test DF, a DF module was constructed to test these different parameters.

4.2 Experimental Setup for the DF Module

The DF module in the lab as shown in Figure 4.1 was constructed using tubular UF membrane (Pentair, X- flow Modules) made of polyvinylidene fluoride (PVDF). Each tubular membrane had an internal diameter of 5.2 mm and effective membrane length of 94 cm with an average pore size of 0.03 µm. Membrane modules consisting of three tubular membranes in parallel were constructed for the DF experiments resulting in the membrane module having a total effective membrane area of 460 cm^2 . A diaphragm pump (Propumps Microdiaphragm Pump) with max flow of 5 L/min was used as the feed pump and a peristaltic pump (Cole Parmer 7453-30) was used as the permeate pump with size 24 tubing (Masterflex). Flow rate utilized for the feed pump was approximately 3 L/min, allowing a cross sectional velocity of 0.9 m/s. Pressure transducers (Cole Palmer) connected inline to measure the pressure of the incoming feedwater, concentration, and permeate to measure pressures. The transducers were connected to a voltage input adapter (Onset) and data logger (HOBOware) for continuous data collection. A total of three pressure transducers were located at these locations in the DF module, feed line, concentrate line, and permeate line as shown in the schematic for the DF module in Figure 4.2. These transducers were calibrated periodically to ensure accurate representation of the pressure at these locations to determine the transmembrane pressure (TMP), described in Equation 5, where P, is pressure. Appendix A discusses the calibration process of the pressure transducers

and the calibration curves for the DF system. The flow rate, expressed in Equation 6, of permeate, Q_{p} , was determined by the volume of permeate, V_{p} , over time, Δt , and the flux, J, shown as Equation 7, was determined based on this flow rate and the area of the membrane, A_{m} .

$$TMP = \frac{P_{Feed} + P_{Concentrate}}{2} - P_{Permeate}$$
(5)

$$Q_p = \frac{V_p}{\Delta t} \tag{6}$$

$$J = \frac{Q_p}{A_m} \tag{7}$$



Figure 4.1: Direct filtration system in the lab



Figure 4.2: Schematic of the DF module

4.2.1 Membrane Cleaning

Prior to every DF test, backwashing of the membrane module and a chemical cleaning of the module were performed. Backwashing was performed by reversing the flow of the feed and permeate pumps for 10 minutes while maintaining a specific flux of 100 L/m²/hr.-bar (LMH/bar). After each backwashing period, a chemical cleaning ensued with a 150 ml/L concentration of sodium hypochlorite, that was performed for a total 5 minutes. After the sodium hypochlorite chemical cleaning a second backwash was performed to ensure the removal of sodium hypochlorite in the system and then finally a clean water test was performed to ensure a specific flux greater than 125 LMH/bar was obtained. If this limit of the flux was not obtained then a second cleaning was performed until the specific flux exceeded the lower limit.

4.3 DF Testing Phases

DF testing was conducted in two different phases, Phase I and Phase II. The first phase tested effluent quality such as nutrient concentrations. Determining how the membrane performed or the concentration of the wastewater was not performed during Phase I, as only permeate quality was the concern for this first test. A series of five tests will be done in Phase I, to determine permeate quality produced by the DF system. The DF system will be tested using wastewater with the addition of PAC. PAC concentrations will ranges from 0 to 2 g/L of PAC increasing in each test by 0.5 g/L of PAC. The addition of PAC will be used to adsorb the soluble portion of COD, thus resulting in higher retention of the COD and improving the permeate quality. Phase I will also be conducted using the same wastewater and cleaning of the membrane system will be performed between each test to ensure no cross contamination between each DF-Phase I testing.

The second phase of testing was more focused on membrane performance and concentration of the wastewater. In the second phase of testing, membrane flux and TMP were observed. Additionally, observations regarding the feed's concentration of solids and COD at various times during the DF testing were also noted. In Phase II, PAC was added to two of the six tests to the system to determine the effects on TMP, flux, and fouling in comparison to DF testing without PAC.

4.3.1 DF Testing, Phase I

Phase I DF tests were used to determine the permeate quality produced from a DF system. Nutrient concentrations and COD quality was only determined for the initial wastewater and permeate. At this phase of testing the concentration factor was not a main focus as the

quality of permeate was the main focus. For the Phase I DF testing, 2 L of wastewater with PAC concentration ranging from 0 to 2 g/L of PAC in were analyzed. The DF module was allowed to operate for 30 minutes until approximately half the initial volume remained and a well-mixed sample of permeate was taken for analysis of COD, TN, ammonia, turbidity, color, and yellowness. Membrane cleaning occurred between each test.

The wastewater for Phase I had an initial COD concentration of 440 mg/L with 145 mg/L that is soluble. Permeate generated by the DF system with no PAC was slightly less than the soluble concentration at 117 mg/L. While the soluble portion is slightly higher, indicating some of the soluble portion may still be rejected by the membrane thus resulting in a slight reduction. As the PAC increased the COD concentration in the permeate was able to attain a concentration of 52 mg/L with 2 g/L of PAC. The results COD concentrations at the various PAC concentrations are shown in Figure 4.3.



Figure 4.3: COD concentrations with various PAC concentrations from DF testing Phase I

Nitrogen and ammonia were also analyzed with from the same samples as the COD. PAC had little effect on the nitrogen and ammonia concentrations. Initial TN concentration was measured to be 116 mg/L with over 85% of the TN being soluble. Ammonia had an initial concentration of 104 mg/L, over 95% of which was soluble. Ammonia concentration remained stable as the PAC increased. TN in the permeate indicated that nitrogen passed through the membrane easier than water thus resulting in higher nitrogen concentrations in the permeate. TN in the permeate decreased as PAC concentrations in the feedwater increased. This may be caused by PAC diverting TN to the concentrate as well slight adsorption properties. TN and ammonia concentrations can be observed in Figure 4.4.



Figure 4.4: TN and ammonia concentrations with various PAC concentrations from DF testing Phase I

With PAC, a large increase in total and soluble TP in the permeate is observed. It can be observed in Figure 4.5, that a nearly linear increase occurs as PAC concentrations increase. The TP in the wastewater was about 30 mg/L, a third of which is soluble. Overall rejection from the DF test with no PAC was 73% for total TP and 20% for soluble TP. As the PAC increased the TP rejection became negligible for soluble as permeate had much higher concentration than the feed.



Figure 4.5: Phosphate concentrations with various PAC concentrations from DF testing Phase I

PAC, which is often treated with phosphoric acid to activate the carbon, may be leaching phosphates in the DF module. Since leaching was determined, a feasible option, PAC was later tested to be with deionized water and PAC at various concentrations to determine leaching capabilities. It was determined the PAC used in this testing leaches approximately 19 mg of TP per gram of PAC added. This observation can be seen in Figure 4.6.



Figure 4.6: Phosphate leaching from TP

The final permeate quality testing from Phase I DF testing was to determine the effect DF and PAC had on turbidity, color, and yellowness. DF and PAC had considerable effects on all three of these parameters with turbidity removal from both total and soluble turbidity removal over 99% for DF and all the PAC concentrations. Since the soluble portion is obtained from the supernatant of a centrifuged sample, the soluble turbidity is a representative of the colloidal turbidity and not necessarily being contributed from the dissolved particles. Total color was removed over 90% by the membrane only and soluble color was removed about 75%. There was a sudden spike in color presence in the permeate after the initial addition of PAC was added. However, color decreased as PAC increased thus resulting in higher overall reduction of color. Yellowness, which is primarily soluble, had low concentrations in the permeate through all five testing. The addition of PAC did not affect the yellowness of the permeate. Total yellowness

with the membrane only reached 4 YI and with various PAC concentrations of yellowness measuring between 5 and 7 YI. Figure 4.7 shows the concentration of these three parameters.



Figure 4.7: Turbidity, color, and yellowness for Phase I

After this Phase I DF testing of the permeate quality, it was determined the DF system was able to reject a large portion of COD and rejection was able to be increased with the addition of PAC. The aesthetic qualities of the permeate was low in turbidity and color, thus permeate quality may not need to be performed. From here, Phase II testing commenced where different parameters regarding membrane performance and the concentration were determined.

4.3.2 DF Testing, Phase II

Phase II studies were performed to determine the performance of the DF system membranes and the CF that could be obtained through the system through various parameters. A total of six small volume (less than 20L of feedwater) DF tests were performed. Test 1 was performed to determine the effectiveness of DF and determine if concentration and recovery of solids and COD was possible using UF membrane. The second test, Test 2, was used to determine the effects of filtering wastewater for a long period of time and how the system performed over a long period of time, including flux decline and TMP rise as well as how solids and COD became concentrated at various times, with samples taken every hour. For test 3 and 4, sub tests a and b were conducted consecutively with membrane cleaning in between. Test 3a, 3b, 4a, and 4b were used as a comparison with the utilization of PAC as compared to raw wastewater. Differences between the performance of the two tests without PAC, Test 3a and 3b, and the two tests with PAC, Test 4a and 4b, were used to determine the effectiveness of PAC in the DF module.

Table 4.1: Summary of each	DF test pe	erformed in	Phase II,	volume,	CF, runtime,	and PAC
concentration						

	Test 1	Test 2	Test 3a	Test 3b	Test 4a	Test 4b
Volume (Liters)	3	20	2	2	2	2
Final CF	6	9.1	40	40	40	40
System Runtime						
(hr.)	3.3	17	0.95	1.9	0.9	1.9
PAC						
Concentration						
(g/L)	0	0	0	0	1	1

4.4 Phase II, Test 1

4.4.1 TMP and Flux

To determine the effectiveness of DF, 3 L of wastewater was filtered through the DF system with concentrate returned to the feed tank. TMP and flux were measured continuously to determine the effects of wastewater and potential fouling that occurred in the system. Permeate

production was monitored every 15 minutes and TMP was monitored through pressure transducers connected to data loggers for continuous monitoring. Of the initial feedwater, only 500 ml of the initial 3 L remain, generating a concentration factor (CF) of 6. With no backwashing to reduce fouling, flux declined over 50% while TMP raised a total of 0.05 bar. To measure the effects of flux decline and TMP rise, specific flux (flux/TMP) is plotted in Figure 4.3. Even with the small increase in pressure, specific flux was determined to drop by nearly 60%.



Figure 4.8: TMP, flux, and specific flux data for Test 1 (3 L, DF test, no PAC)

4.4.2 Concentration of Solids and COD

With a CF of 6, it was theorized that suspended solids and COD from colloidal matter would also be concentrated by a factor of 6. Colloidal matter was retained along the surface of the feed tank wall shown in Figure 4.9. This caused an inaccurate balance of suspended solids and COD concentration. To limit the amount of material retained along the feed tank walls, the concentrate stream will be used to wash solids off the tank wall and be mixed into the feedwater in future tests. Total solids were concentrated to a factor of 1.6 and suspended solids were only increased by three times the orginal concentration. Samples of the feedwater were analyzed at the beginning and end of the Test 1 and shown in Figure 4.10.



Figure 4.9: Colloidal material attached to feed tank walls



Figure 4.10: Concentration of solids for Phase II, Test 1 (3 L, DF test, no PAC)

Due to flux decline, it can be suggested that colloidal material was retained along the membrane surface. If backwashing occurred, which was not performed during the DF experiments, a majority of the colloidal matter could be removed and returned to the feed tank. Soluble COD which may pass through the membrane can be found in the permeate. For this initial test, soluble COD was not measured but the total COD concentration present was monitored every 15 minutes.



Figure 4.11: COD concentrations for Phase II, Test 1 (3L, DF test, no PAC)

4.5 Phase II, Test 2

Due to colloidal matter becoming attached to the feed tank reservoir, modifications to the system were performed. The feed tank reservoir was replaced with an external tank that was mixed continuously with an overhead mixer and the concentrate piping was replaced with soft

tubing to be used to flush the solids off the feed tank walls. With this modification in place, Test 2 was performed with 20 L of wastewater to determine how the system performed over a longer period of time. Test 2 was performed until a volume of 500 ml remained. This would indicate a CF of 40, but due to the amount of sample removed (100 ml every hour, 1.7 L removed total), the CF is closer to 9.1.

4.5.1 COD for Phase II, Test 2

The COD concentration of Test 2 was performed on the initial feed at the beginning of the test, while concentrate and permeate samples were monitored every hour. Soluble COD was measured from supernatant portion of the centrifuge sample. Initial COD concentrations were on the lower spectrum for domestic wastewater with measurement slightly over 200 mg/L and 25% of the COD belonging to the soluble fraction. Final feed sample at a CF of 9.1 was determined to have a total COD over 2700 mg/L giving rise in concentration of 1250% while final soluble COD concentrations only increased by 600%. Permeate COD concentration remained relatively stable with COD concentration ranging between 120 and 190 mg/L. At the beginning of Test 2, the rejection of COD percentage was low, with only about 50% of total COD being retained by the membrane and higher COD concentrations found in the permeate than in the soluble fraction. At the end of Test 2 the COD was at 194 mg/L in the permeate, whereas the soluble fraction of the feed measured 310 mg/L. From this it was determined that the final rejection of COD is much higher than the initial with approximately 93% of the total COD being retained by the membrane and approximately 38% of the soluble fraction being retained by the membrane.


Figure 4.12: COD concentrations within the feed, concentrate, and permeate for Phase II, Test 2 (20L, DF test, no PAC)

4.5.2 Solids for Phase II, Test 2

For the solids testing, TS, VS, TSS, and VSS were monitored per hour. Initial total solids were determined to be around 750 mg/L with 120 mg/L being suspended solids. This indicates a high quantity of dissolved solids within the feedwater. Suspended solids were retained by the DF system and returned to the feed reservoir and increased by a factor of 11, whereas TS was only concentrated by 1.8, 95% of which were suspended. Due to utilization of UF membranes, dissolved solids are able to be pass through the membrane pores, and solids testing for Test 2 indicated the DF modules has low retention of the dissolved solids in the feedwater. VS and VSS were both concentrated to be about 300% of their initial concentrations. This increase in VS and VSS would be beneficial for solids treatment technologies such as anaerobic digestion, since the destruction of VS and VSS yield biogas which can be used for energy production.



Figure 4.13: Solids concentration profile for Phase II, Test 2 (20L wastewater DF test, no PAC)

4.5.3 Turbidity for Phase II, Test 2

Since UF membranes are able to produces permeate of high aesthetic quality, it was determined to measure the turbidity of permeate and the feedwater. A large portion of turbidity is caused by the colloidal fraction of wastewater, so permeate should be relatively clear. This is shown within Figure 4.14. The DF system was able to retain the particle and colloidal fraction so the turbidity is relatively high in the final concentration, whereas permeate still remains low around between 1 and 2 NTU. Since not all turbidity is caused by the particle fraction, soluble turbidity which is caused by the macromolecules and colloidal fraction were also measured to determine how well the membrane is able to reject these macromolecules. Greater than 99% and greater than 95% turbidity was removed from the final feed concentration and soluble fraction respectively.



Figure 4.14: Turbidity profile for Phase II, Test 2 (20L wastewater DF test, no PAC)

4.6 Phase II, Test 3a, 3b, 4a, and 4b

With Test 1 and Test 2 showing potential for the concentration of feedwater by the DF system with exceptional results in turbidity rejection by the DF system as well as large concentration of solids and COD, it was considered important to determine how concentrated that feedwater could become, as well as investigating ways to improve membrane flux and permeate quality. Two tests were conducted with wastewater with 2 L of initial feedwater. These tests were performed with samples of concentrate only being obtained at the end of the each to test, to ensure the highest CF possible, as compared to the sample analysis limiting the CF in Test 2. Test 3a and 3a were performed with raw wastewater, whereas Test 4a and 4b performed were mixed with 1g/L (2g total) of PAC. Each set of tests (two raw wastewater tests and two

with PAC addition) were performed in series, with no chemical cleaning or backwashing performed intermittently.

4.7 Test 3a and Test 3b (Wastewater Only)

With the initial focus of concentrating wastewater, a minimal CF of 40 was the end point and would divert 97.5% of the hydraulic loading through the DF system, whereas 2.5% of the flow would be diverted to other treatment methods (such as the AnMBR). With this CF in mind, 1950 ml of permeate must be generated through the DF system, leaving a high concentration of COD and solids within the feed tank. Chemical cleaning and physical backwashing were only performed prior to Test 3a. Since no backwashing or chemical cleaning was performed intermittently between each of the two tests, it would be expected for the second test to rise in TMP and drop in flux. Test 3a, the first wastewater-only test, was able to reach the required CF of 40 less than one hour, where test 3b, with flux decline, was performed for nearly two hours. While initial TMP varied between the two tests, TMP stabilized at around 0.87 bar for both tests. Additionally, flux from test 3a was initially very high with fluxes over 60 LMH but rapidly decreased due to fouling to around 28 LMH. Test 3b, was relatively stable with flux consistently producing 25 to 28 LMH. Figure 4.15 indicates the rapid decline of flux in Test 3a, and the stable TMP and flux of Test 3b. Due to the rapid decline in flux, which is caused by the fouling from particles within the feed, the effects that PAC have on the system will be tested in Test 4a and 4b. A comparison of these two groups of testing will aid in the determination if the addition of PAC will be effective in control fouling in the DF system or if other means of controlling fouling should be investigated.





4.8 Test 4a and Test 4b (Wastewater + 1g/L of PAC Addition)

Utilizing the size distribution of PAC and the potential application of improving membrane flux while reducing TMP 1g/L of PAC was added to the feed tank and continuously mixed. With the goal of improving flux and reducing fouling, it was also proposed that due to the adsorption properties of PAC, PAC could lower the COD concentrations found in the permeate generated. Test 4a and Test 4b were conducted in a same format as Test 3a and Test 3b. Chemical cleaning and backwashing were only performed prior to Test 4a to remove any foulants along the membrane surface from previous tests. A clean water flux test was also performed to ensure that the membrane was only experiencing fouling from the present feedwater.

As with test 3a, the first test with PAC addition (Test 4a) exhibited rapid flux decline from 68 LMH to 17 LMH. While the flux decline seemed drastic, this is caused by the low

feedwater remaining due to higher fluxes in the beginning stages, with only a 6 LMH drop in flux per 10 minutes, compared to 10-15 LMH per 10 minutes in Test 3a. TMP in this first PAC addition test was never stablized within the 55 minutes the test was performed.

The second PAC addition test (Test 4b), stablized with flux at 25 LMH and only deviated slightly between 20 to 28 LMH through the two hours the test was performed, until the last five minutes where little feedwater remained. Since low feedwater remained, the membranes were not able to separate the liquid fraction and the solids fraction as effectively, thus yielding lower flux performance. TMP in the second PAC addition test was able to stabilize within the first 30 minutes and remained relatively constant at 0.87 to 0.9 bar. Results from the two tests with PAC addition can be seen below in Figure 4.16.



Figure 4.16: TMP and flux for two DF tests with final CF of 40 (2L, DF test, 1g/L PAC)

4.9 Comparison of Wastewater Only and PAC Addition

4.9.1 COD

Due to adsorption properties of PAC and since PAC particle size is larger than average 0.03 µm pore size of the UF membranes, souble COD will be adsorbed by the PAC, thus reducing the COD concentrations in permeate, and increasing the concentration in the feed. Since wastewater properties change from day to day, different influent concentrations of COD existed for each DF test. Both tests performed with PAC had larger total initial concentrations of COD but lower soluble concentrations of COD than the wastewater only samples. While the soluble portion of COD may pass through the membrane pores, nonsoluble COD is likely to be retained by the membrane system. With the PAC addition in the DF module, soluble COD was able to be concentrated by a factor of 3 when the final and initial concentrations are compared whereas without PAC addition soluble COD was only concentrated by a factor of 2 when comparing the initial and the final concentrations. Final permeate samples were analyzed with PAC concentrations: both tests (Test 4a and 4b) were able to reject 90% of total COD, and have concentrations less than 100 mg/L, whereas when the wastewater without PAC was analyzed, total COD rejection was closer to 50% with permeate COD concentrations of 215 mg/L and 148 mg/L for Test 3a and 3b respectively. Below in Figures 4.17 and 4.18; the comparison of the four test COD concentrations are shown. In either case, with and without the addition of PAC, the final concentration of the feed was able to reach concentration above 2000 mg/L, which would allow for the AnMBR to treat the wastewater as if the wastewater was a high strenght industrail wastewater.



Figure 4.17: Comparison of COD concentrations in four DF tests (2 WW, 2 WW+PAC)



Figure 4.18: Comparison of COD removal in four DF tests (2 WW, 2 WW+PAC)

4.9.2 Solids

Since PAC, (2 g total) was added to two of the tests, it was necessary to determine how much solids were retained by the membrane system. By comparing the solids retention for each test, the solids rejected by the membrane system would be treated in the AnMBR. A buildup of

these solids in the AnMBR would increase wasting rates, thus they must be monitored within the DF-AnMBR.

Similar to COD, since the wastewater was obtained at different times, the initial solids were different for each test within the four test series. With the addition of PAC, the two test with PAC had an average higher TS and TSS of approximately 1g/L. Volatile solids (VS) of the wastewater, wastewater with PAC addition, and PAC only were also analyzed. PAC was determined to be 95% volatile with 99% being suspended, resulting in higher volatile solids and volatile suspended solids (VSS). By determining this, with PAC addition, the concentration of VS and VSS resulted in much higher total concentrations, and a total increase of 1300% and 2000% respectively. Whereas, the DF tests without PAC were only obtained an average increase of 1100% for VSS and a 500% for VS. Figures 4.19 and 4.20 depict different solids concentrations. While the concentrations of VS and VSS were much higher when PAC was added to the system, the VS and VSS is primarily PAC which would not be degraded by the anaerobic microorganisms in the AnMBR.



Figure 4.19: Comparison of TS and VS concentration in four DF tests (2 wastewater, 2 with PAC addition)



Figure 4.20: Volatile solids concentrations of four DF tests (2 wastewater, 2 with PAC addition)

4.9.3 Turbidity

Activated carbon (granular or powdered), is used in the polishing stages of many water treatment plants. PAC can reduce the turbidity, color, and odors associated with permeate that is generated by the DF system. Average turbidity of the DF system permeate was slightly below 1.8NTU, so a large rejection of the of turbidity is achieved and concentrated in the feed. As can be seen in Table 4.2 below, turbidity removal was slightly increased by the PAC, with average permeate of 1.2 NTU.

Turbidity				
Test number	Average	Std. Dev.		
Test 3a (wastewater)	1.87	0.19		
Test 4 (wastewater)	1.71	0.28		
Test 4a (wastewater with PAC)	1.08	0.12		
Test 4b (wastewater with PAC)	1.31	0.12		
Average wastewater permeate	1.79	0.24		
Average wastewater with PAC permeate	1.19	0.12		

Table 4.2: Turbidity of four DF tests (2 wastewater, 2 with PAC addition)

4.10 Pathogen Testing

Because the DF system is able to produce permeate that could be suitable for discharge and because of my concern for sanitation, pathogen removal and/or destruction must now be considered. Due to the membrane pore size of 0.03µm, pathogens including bacteria, viruses, and helminths, are considerably larger than the average pore size and should be retained in the concentrate to be treated in additional processes such as the AnMBR. To ensure this statement is valid, three additional DF tests were performed to measure pathogen retention within the system. Tests were performed with wastewater only, with 1 g/L PAC addition, and with 2 g/L PAC addition. The DF system retained pathogens within the system with a log removal greater than 6 (99.9999%) within all three tests. With wastewater only, pathogens concentrated by a factor of 40, where with PAC pathogens only increased by 10 times the original concentration. The PAC may adsorb the pathogens or force the pathogen to settle faster within the feed tank.

Since many anaerobic processes operate at high temperatures, either mesophilic (35 °C) or thermophilic (55 °C), and the concentrate will ideally be treated anaerobically, it was determined to heat the concentrate at various temperatures to ensure pathogen destruction was possible at these high concentration. Concentrate was heated for 25 minutes at 70 °C, 55 °C, or 40 °C, and then measured for the E. coli concentration. At the highest temperature, a log removal between 3 and 5 was achieved for all samples. At 55 °C and 40 °C, more colonies were present with only 97% and 95% of the original concentration being deactivated or destroyed due to the heating of the samples.

Sample	Explanation		
Fand	Sample of wastewater was taken before PAC was		
reeu	added at beginning of each test.		
Dermosta Start	Sample of the 1st ml of permeate produced was taken		
Termeate-Start	at start of each test.		
	Sample of permeate was taken at the end of each test.		
Permeate-Final	Container was well mixed to ensure proper		
	performance by the membrane and regrowth was not		
	an issue.		
Permeate-	Sample of permeate was disinfected using 3 mL/L of		
Disinfected	sodium hypochlorite and mixed for 25 minutes.		
Concentrate-Raw	Sample of concentrate was taken at the end of each		
	test.		
Concentrate 70 °C	Sample of concentrate was heated to 70°C for 25		
Concentrate-70 C	minutes.		
Concentrate-55 °C	Sample of concentrate was heated to 55°C for 25		
	minutes.		
	Sample of concentrate was heated to 40°C for 25		
Concentrate-40 °C	minutes.		

Table 4.3: Sample explanation for E. coli testing within the DF module.



Figure 4.21: E. coli colonies from the DF module within the feed, concentrate, and permeate. Numbers above bars indicate log removal with respect to feed.

4.11 Nutrients

The nutrients within the system, i.e. nitrogen, phosphorus, and ammonia, were also measured with and without PAC to determine the rejection and the concentration of each to determine appropriate design requirements for the future treatment in regards to discharge. Since AnMBR effluent can be used for water reuse purposes such as agricultural uses, the DF module permeate may be able to provide the nutrients for agricultural use.

4.11.1 Nitrogen

The nitrogen from the wastewater is 80% soluble and a large majority is able to pass through the membrane pores and will be found in permeate. Since some of the nitrogen is from the colloidal fraction the concentrate is only slightly increase when compared to the raw wastewater. With PAC addition of 1 g/L, PAC has little impact when of permeate and concentrate quality. Total and soluble nitrogen concentrations are shown in Figure 4.22.



Figure 4.22: TN concentration of the DF module, with and without PAC addition

In terms of wastewater only, the initial TP was slightly over 15 mg/L and was able to be concentrated over three times and reach a concentration slightly less than 40 mg/L. The permeate quality was able to reject about a third of the total TP with a final concentration around 11 mg/L.

With the addition of PAC, the rise in the TP concentration was drastic in the concentrate due to the concentration of TP within the PAC. This also lead to much higher concentrations of TP within the permeate with over 27 mg/L of TP present in the permeate. Since PAC is 100% rejected by the membrane, the rise in concentrate is very high due to the large concentration of PAC.



Figure 4.23: TP concentration within the DF module with and without PAC addition

4.11.3 Ammonia

Similar to TN, ammonia concentrations were not heavily affected by PAC and permeate within the wastewater is able to pass through the membrane pores and be found within permeate.

The concentrate of the DF module is only slightly increased with and without PAC. Additionally it seems that PAC has no adsorption qualities with ammonia and thus has no effect on the performance of the DF system.



Figure 4.24: Ammonia concentration of the DF module, with and without PAC addition

4.12 Conclusion

The results from the DF system met expected permeate qualities of DF set forth by Ravazzini (2008). The quality of the effluent which exceled in turbidity removal, below 2 NTU in permeate, as well as COD removal (approximately 100-200 mg/L in permeate). Due to the lack of backwashing during the performance testing of the DF membrane, TMP pressure rose to 0.9 bar, and flux decreased to 25 LMH. While flux production did decrease to such large extremes, which was expected due to the absence of backwashing, flux was still greater than traditional AnMBRs operations which may be less than 2 LMH depending on viscosity of the feedwater (Dereli et al., 2012). Concentration of the COD and the solids were not as high as expected due to solids and colloidal material adhering to the membrane surface. While concentration of these parameters was not as high as expected, suspended solids were not retained within the permeate, meaning all suspended solids were retained within the DF system. Additionally COD concentration was able to meet the required influent for concentrations of over 1500 mg/L set forth by Metcalf and Eddy (2003). As a result the concentrate is a prime candidate for anaerobic processes and the AnMBR.

CHAPTER 5: MODELING THE DF-AnMBR

5.1 Introduction

The AnMBR technology excels for the treatment of industrial wastewater due to the high COD concentrations. The AnMBR which is dependent on the influent concentration, which in field conditions can vary from day to day, may not be able to receive the required organic loading strength found in domestic wastewater. By coupling the DF system with an AnMBR, DF-AnMBR, the organic loading rate (OLR) can be increased to higher concentrations, which would be better suited for the anaerobic treatment. In addition to higher OLR, hydraulic performance can be improved due the higher flux potential in the DF system and energy conservation can be achieved by reducing the energy required to heat the digesters due to the reduced volume within the reactors. The purpose of this feasibility analysis section is to determine the potential of implementing the DF-AnMBR to treat domestic wastewater.



Figure 5.1: Mass balance diagram for the DF-AnMBR (A represents DF stage, B represents AnMBR stage, where B1 is the bioreactor and B2 is the membrane)

Parameter Superscripts		Subscripts			
Variable	Meaning	Variable	Meaning	Meaning Variable	
Q	Flow	А	Stage A, DF	f	Feed
С	Concentrate	В	Stage B, AnMBR	С	Concentrate
		B1	Bioreactor	р	Permeate
		B2	Membrane	w	Waste

Table 5.1: Variables, superscripts, and subscripts used in DF-AnMBR

5.2 Flow

The DF-AnMBR utilizing DF as the separation mechanism will be able to handle a large fraction of the hydraulic loading rate (HRT). The DF portion of the DF-AnMBR system will handle the liquid portion of the influent flow and the AnMBR will treat solids (colloidal and suspended particles). The flow of both systems will equate the total influent flow. The balance of flows is shown in the following equations.

System:
$$Q_{in} = Q_{out}$$
; $Q_{in} = Q_f^A$; $Q_{out} = Q_p^A + Q_p^{B2} + Q_w^{B1}$; $Q_f^A = Q_p^A + Q_p^{B2} + Q_w^{B1}$ (8)

$$A: Q_f^A = Q_p^A + Q_c^A \tag{9}$$

B1:
$$Q_C^A + Q_c^{B2} = Q_f^{B2} + Q_w^{B1}$$
 (10)

B2:
$$Q_f^{B2} = Q_p^{B2} + Q_c^{B2}$$
 (11)

5.2.1 Concentration Factor

The CF of the system was previously based on volume but in a continuous system is based on the flow rate diverted through the DF portion of the AnMBR. With higher CFs, less flow will be handled by the AnMBR but the OLR will be higher due to the concentration of COD and solids caused by the DF separation. Since the CF is defined as the amount of liquid from the DF system as compared to the total flow, it can be represented in the following empirical manner shown in equation 12.

$$CF = \frac{Q_f}{Q_c} = \frac{Q_c + Q_p}{Q_c} = 1 + \frac{Q_p^A}{Q_f^{B_1}}$$
(12)

In Figure 5.2, as the CF increases, the amount of flow handled by the DF increases at an equal amount that the flow handled by the AnMBR is decreased. So for example, 50% of the influent is directed to the AnMBR as a concentrated stream at CF=2, 20% at CF=5, 10% at CF=10, 5% at CF=20, 2% at CF=50, and so on. It can be seen that at higher CF, the increase in flow through the DF system in minimal thus showing that hydraulically there is a cutoff point at higher concentrate the remaining wolume.



Figure 5.2: Flow rate in various parts of the DF-AnMBR with different CF

5.2.2 HRT

In standard AnMBRs the HRT is related to the volume of the reactor and is inversely proportional to the flow rate of the system. When operated at a HRT of one day, the reactor size would need to be equivalent to the flow entering the system. Similarly for a HRT of 0.5 days, or 2 days the reactor volume needs to be half and double the flow respectively. For large volume flows, a choice needs to be made whether higher HRT are required, to minimize the land footprint.

Comparing with the operations of the DF-AnMBR, with higher CF more flow would be diverted through the DF system, resulting in less total flow in the An-MBR. Consequently this will result in one of three scenarios for the DF-AnMBR design. The first is having the same reactor size thus resulting in higher HRTs, and thus resulting in more contact time with the microbial population. In this case the HRT is increased at the same multiple as the designed CF. The second scenario is maintaining a constant HRT that the AnMBR would treat solely, thus resulting in smaller footprint. Similar to the first scenario the volume of the reactor size will decrease by the same factor of the CF. The final option is a combination of the previous scenarios. In this case the HRT is increase but the reactor volume is also impacted. This would allow for the largest form of variation and design freedom as each system could be operated under the criteria constraints for each area. Since the DF-AnMBR has this amount of flexibility, the HRT and the CF should be chosen accordingly to meet treatment requirements. Proper determination of membrane sizing and proper maintenance procedures should be addressed to ensure to sufficient permeate generation proper concentration of the initial feedwater.

5.3 Rejection

The particles and COD that are retained by the system will be treated by the AnMBR. To properly model the system, it is important incorporate a term for rejection, R. Rejection defined as factor of the concentration in permeates compared to the initial feedwater. Determining the amount of rejection for each parameter (COD, TS, TSS, VS, VSS, TN, TP and turbidity) can aid in the design of the DF-AnMBR and be able to determine influent and effluent qualities in each portion of the system. Once these parameters are established based on membrane rejection, proper management of the effluent can be determined based on local regulations. Empirically rejection can be shown as expressed in equation 13. In addition to rejection due to the membrane, the rejection is increased when PAC is added to the system. Due to the adsorptive nature of PAC, COD and turbidity are removed thus resulting in higher rejection than the membrane only thus resulting in an increasing factor, α . Since the rejection when PAC is added to the system is higher than the rejection without PAC addition, it can be represented empirically through Equation 14 and the empirical representation of α is in Equation 15.

$$R = 1 - \frac{c_p}{c_f} \tag{13}$$

$$\frac{R_{PAC+Membrane}}{R_{Membrane}} \ge 1 \tag{14}$$

$$\alpha R_{Membrane} = R_{PAC+Membrane} \tag{15}$$

5.4 OLR

The OLR to AnMBR system can be a critical factor which plays into the performance. If organic loading rates are low the system may perform properly as the microbial populations may not thrive due to improper nutrition. For this reason, AnMBR have primarily been used to treat high strength industrial wastewater which has high COD concentrations. Whereas domestic wastewater, generally considered low strength, due to the addition of flush water, which has much higher volumes and lower COD concentrations. With the DF-AnMBR the organic loading will be concentrated as the only soluble COD and dissolved solids are able to pass through the porous membranes. With the COD from suspended solids, and colloidal material will be retained by the DF model and the liquid fraction extracted. The rejection of particulate COD and TSS is expected to be high while rejection of soluble TDS is expected to be low.

5.5 Assumptions

For the basis of this model several assumptions needed to be made to accurately represent the OLR, HRT, COD concentrations, and concentration of solids with each portion of the DF-AnMBR system. Since dissolved solids are present in the concentrate the rejection of 0.05 will be used for dissolved solids due being retained by the cake layer formed on the membrane. Whereas, suspended solids are completely filtered by the membrane will result in a rejection ratio of 1. Soluble COD without PAC will have a rejection rate of 0.25 and with PAC 0.35, from Test 3a, 3b, 4a, and 4b averages. Particulate COD without Pac will be 0.9 and with PAC will be 0.95 also from Test 3a, 3b, 4a, and 4b. Turbidity for both PAC scenarios, (with and without PAC) will be 0.99 and 0.9 for total turbidity and soluble turbidity respectively from Test 3a, 3b, 4a, and 4b. PAC will be assumed to be dosed in the system at a concentration of 1 g/L, with 99% of the PAC being suspended and 90% being volatile. The rejection of TN will be 0.2 and the soluble rejection will be 0.05 since little soluble nitrogen is rejected and this is for both with and without PAC addition. Ammonia rejection is .05 as well. TP rejection factor is 0.5 and 0.3 for total and soluble for the membrane only. Since PAC leaches TP into wastewater the rejection factor is lower in this instance and will be 0.7 and for 0.9 and will have higher initial

concentrations than that of wastewater alone by increasing the original concentration by 60 mg of TP per gram of PAC added of for total and 20 mg per gram for soluble TP.

Since this model will be used a representative for domestic wastewater the influent concentrations will be that of domestic wastewater defined by Metcalf and Eddy (2014) shown in Table 5.2. It was also assumed that the soluble fraction of the COD will be 50% and the COD caused by particulate biodegradable COD will also be 50%. For nutrients, the soluble fraction of all nutrients (TN, ammonia, and TP) will be 0.5.

Feed Characterization				
Total Solids	755	mg TS/L		
Total Suspended Solids	195	mg TSS/L		
Total Dissolved Solids	560	mg TDS/L		
Volatile Solids	377	mg VS/L		
Volatile Suspended Solids	152	mg VSS/L		
Volatile Dissolved Solids	225	mg VDS/L		
Total COD	508	mg COD/L		
Soluble Biodegradable COD	254	mg COD/L		
Particulate Biodegradable COD	254	mg COD/L		
TN	40	mg/L-N		
Ammonia	25	mg/L-N		
ТР	7	mg/L-P		
Soluble fraction of nutrients	0.5	-		

Table 5.2: Typical influent concentrations for domestic wastewater (medium strength). Adapted from Metcalf and Eddy (2014)

5.6 Analysis

Since the membrane performance will change with various CFs it is important that each parameter is modeled according along various CF. Additionally, determining the permeate quality as well as the concentrate quality (AnMBR feedwater) is needed to determine effluent discharges and expected performance of the AnMBR system. The total COD within the system will become highly concentrated as the CF increases, with and without PAC addition. At a CF of greater than 5 for both situations, the concentration of COD exceeds the minimum strength of 1500 mg/L for anaerobic processes to excel (Metcalf and Eddy, 2014). At higher CFs, the concentration of COD becomes very high with concentrations greater than 6000 mg/L. Due to the low rejection rate of soluble COD, the concentration in minimal but permeate quality remains relatively stable through the concentrating process. The DF permeate and AnMBR feedwaters COD, with and without PAC addition, are shown in Figure 5.3



Figure 5.3: Expected COD concentrations of the DF-AnMBR ($R_{COD-Total}$, 0.9, $R_{COD-Soluble}$, 0.25, $\alpha_{COD-Total}$. 1.06, $\alpha_{Cod-Soluble}$, 1.4)

Solids within the DF-AnMBR will become highly concentrated within the concentrate; the majority of the solids will be suspended. With a large portion of PAC being suspended solids, the solids buildup with PAC addition is much higher with PAC than without. The dissolved solids remain relatively stable through the concentrating process due to the low rejection factor. VSS which are destroyed in anaerobic processes to yield biogas, will also be concentrated, while VDS will be present in permeate. PAC adds little VDS but will increase the amount of VSS significantly. In Figures 5.4 and 5.5 are show the concentration of solids within the system, without and with PAC addition respectively. As can be seen by comparing the figures with PAC TSS and VSS concentration can reach over five times the concentration of wastewater alone.



Figure 5.4: Expected solids in DF-AnMBR with no PAC addition (Rs_{uspended solids,} 1, R_{dissolved solid,} 0.05)



Figure 5.5: Expected solids in DF-AnMBR with 1g/L PAC addition ($\alpha_{suspended solids}$, 1, $\alpha_{dissolved solids}$, 1)

Initial turbidity is based on the average of the six Phase II DF tests that were performed since a standard turbidity was not established in literature for wastewater due to the large variation that can occur in turbidity. Since this model will base the initial turbidity will be 150 NTU and soluble turbidity is 10 NTU. Due to the high rejection factor, total turbidity is every high as the CF increases. Since soluble turbidity initial concentration is very low, the concentration is not very high in comparison to the total, even at a CF of 20, which yields a concentration of greater than eight times greater than the initial concentration. Permeate turbidity remains low, less than 6 NTU in the soluble portion and approximately 14 for total turbidity when a CF of 20 is reached.



Figure 5.6: Expected turbidity in the DF-AnMBR ($R_{Total Turbidity}$, 0.9, $R_{Soluble Turbidity}$, 0.99, α turbidity, 1)

Nitrogen and ammonia had little to no difference when compared with PAC, thusly it is considered that modeling TN and ammonia with PAC would not yield different results and thusly are not analyzed. The concentrations of TN within permeate and within the concentrate remains relatively stable with the final concentration being 125% the original concentration.

In terms of TP, since the PAC that was utilized leaches phosphorus due to the activation process of utilizing phosphoric acid to activate the carbon, different initial concentration will be used.as well as different rejection factors. TP is rapidly increased in both total and soluble fractions as the CF is increased.



Figure 5.7: Expected TN and ammonia concentrations in DF-AnMBR (R_{TN} , 0.2, $R_{Soluble TN}$, 0.05, $R_{Ammonia}$, 0.05)



Figure 5.8: Expected TP concentrations in DF-AnMBR (R_{TP} , 0.5, $R_{TP \text{ Soluble}}$, 0.3, α_{TP} , 1.2, α_{TP} soluble, 3.0)

5.7 Conclusion

Comparing the expected results to the data gathered from the DF tests indicate that there is some disconnect between what is expected and the actual performance of the system. Firstly, the initial concentrations differ than those from the experimental set. To represent proper influent that a conventional wastewater treatment facility experience standard medium strength wastewater was utilized from Metcalf and Eddy (2014). For the feedwater from the data analyses, wastewater was collected from a septic tank's grinding station. In this event, solids may have settled before being extracted for data analysis. Additionally, wastewater treatment facilities often receive influent from many sources including residential and commercial, which may affect the strength of the wastewater. Since the wastewater was extracted from school only urination, fecal material, and wash water are prevalent within the septic tank.

COD concentrations were much higher in the expected performance in terms of concentration than what is generated by the DF module. This could be for two main reasons, colloidal material retained on the membrane surface and biodegradation within the feed tank. Since the colloidal material is a large portion of the total COD concentration, 40 to 80 percent from the six experimental tests, by this material not being included in the data analysis can skew the result. Biodegradation of COD due to mixing within the system as well as aeration from the return of concentrate can lower the COD values as well. In a study of the recovery of organic material by Lateef et al. (2013) only 67% of the organic material was able to be recovered when backwashed and 70% when chemically backwashed with a NaOH and citric acid solution. Since backwashing was not performed intermittently the recovery of this high percent of COD was not attainable.

Solids were minimal in comparison as well. TSS was only concentrated by a factor of 10 in the DF experiments, and due to the total rejection of suspended material, in the expected performance a 20 times concentration was reached. Similar to the COD, this may be caused due to the colloidal material adhering to the membrane surface. PAC was able to aid in the recovery of solids with a total of 12.5 times the initial concentration being recovered, whereas the model predicts 20 since PAC is mostly suspended solids. VSS followed similar patterns when the comparison is made between the expected and actual performance.

In the case of turbidity, the DF experiment exceed the results of the model since turbidity was general less than 2 NTU and the model predicts a turbidity of 14 and 6 for total and soluble turbidity respectively. Soluble turbidity was much higher in the actual performance than the model and total turbidity was similar in total concentration. This may indicate the chosen rejection factor for soluble turbidity of 0.9 was too low and rejects more turbidity than previous assumed.

The nutrient performance of the model is much different than those of the actual performance. This can mostly be explained due to the fact that the vast difference between the modeled influent and the actual influent. Since the wastewater was derived from a school, it is expected that there is high levels of nitrogen and ammonia due to urine from the students and faculty. The higher levels of phosphorus can possible be explained thorough any cleaning agents that the school facility utilizes when and the less dilute concentrations from other sources such as inflow and infiltration.

One of the key differences between the experimental set and the expected performance was the lack of accountability for material adhering to the membrane surface. Membranes which

foul because of material adhering to the surface are often backwashed to remove a large portion of this material and it is often returned to the feed tank. In the cases of the DF experiment, backwashing was not performed during each experiment thus resulting in a buildup of foulants along the membrane surface. Backwashing was only performed after each test was completed and recovery of the material was not accounted for. Further investigation of the long term performance of a DF system with intermittent backwashing will develop more accurate representations of the DF concentrate and permeate quality. By backwashing intermittently the material believed to be adhered to the membrane surface will be returned to the feed tank and accounted for in the overall COD and solids concentration of the concentrate.

CHAPTER 6: FOULING POTENTIAL

6.1 Introduction to the Experiment

To preserve membrane function and membrane life the fouling potential of feedwater used within the DF-AnMBR must be analyzed. The MFI can standardize and rapidly determine the fouling potential of the feedwaters that would be seen by the DF-AnMBR. Since this new configuration of MBR is utilizing two different sets of membranes, one for DF and one for anaerobic bioreactor contents, the fouling rate of several feedwaters must be determined.

6.2 Experimental Setup for MFI System

The MFI was constructed using a Harvard Apparatus PHD Ultra Syringe pump utilizing 60 ml plastic syringes. Membrane holder with a membrane diameter of 47 mm (Pall) housed the membranes and had an effective membrane surface area of 9.6cm^2 . Two syringes were connected together to hold a total volume of 100 ml. The flow rate was selected to be 0.2 ml/min in each syringe, giving a total flow rate 0.4 ml/min and a flux of 25 LMH. The MFI system was constructed in a vertical orientation as shown in Figure 6.1, to ensure uniform flow in the system occurred. Pressure transducers (Cole Palmer) were connected to voltage input adapters (Onset) and connected to a data logger for continuous data collection. The MFI utilized four different membranes, 0.2 μ m (MF), 800 kDA (MF), 100 kDA (UF), and 50 kDA (UF), from Synder Filtration. The schematic for the MFI system shown in Figure 6.2 shows the location of the membrane, pressure transducers, and syringe pump.



Figure 6.1: Syringe pump setup for the Modified Fouling Index testing



Figure 6.2: Schematic of the MFI system

6.3 Membranes

A variety of membranes were chosen to accurately portray the MFI for these feedwaters. Since these membranes will be subject to domestic wastewater and anaerobic reactor contents, different pore sizes membranes were utilize spanning both MF and UF sizes. Ranging from pore size of 0.2 μ m to a MWCO of 50 kDA, these membranes should experience different fouling with more solids initially passing through the MF membranes compared to the UF membranes. The effective area of the membranes within the membrane holder was 9.6 cm².

Before the utilization of each membrane, the membrane was soaked in a 100% ethanol solution for 5 minutes to remove any preservative coating on the membrane surface from the manufacturer. After this initial soaking, the membrane would be rinsed with deionized (DI) water for 30 seconds to remove any chemicals remaining on the membrane surface. To ensure all preservative coating was removed, the membrane a clean water flux test was performed.

6.4 MFI Startup

Syringes were filled manually to approximately 55ml in each syringe and placed with the syringe pump. The membrane was placed within the membrane holder, closed, and the vent of them membrane holder was removed. The syringe pump would be then be operated using the manual injection button at a slow pace until the feedwater reached the vent to reduce the amount of time before the feedwater reached the membrane. The vent was then closed and the syringe pump was started at the select speed.

Additionally prior to each MFI test, a solids profile was for each of the feedwaters that would be utilized in the MFI system. As can be seen in Table 6.1, there is a vast differences in

solids content, both total and suspended, it would indicate different fouling mechanisms with all the feedwaters and fouling potential to be different in each circumstance.

Feedwaters	TS (mg/L)	VS (mg/L)	TSS (mg/L)	S (mg/L) VSS (mg/L)	
Domestic Wastewater	1060	370		355	195
Domestic Wastewater Concentrate					
(CF 20)	4115	3020	24	440	2010
Domestic Wastewater with PAC					
addition (1g PAC/L)	2195	1810	1(035	935
AnMBR Liquor	930	585		230	185

Table 6.1: Feedwaters solids concentrations for the MFI testing

6.5 MFI Shutdown

After the syringe pump injected the feedwater through the membrane, a sample of permeate would be collected. The membrane would be removed and then the syringe pump would be manually pressed to withdraw its contents. The syringes were removed and cleaned with DI water to ensure no cross contamination of particles from previous test effected the next test. Piping was flushed with DI water after each test to remove any particle disposition on the piping walls.

6.6 Flux

The MFI was operated under constant flux with pressure increasing with time as the membrane became fouled. Due to the results of the DF study, the constant flux of 25 LMH was chosen as this would be accurate representation of a long time average flux of the DF system. Operated at a flow rate of 0.2 ml per minute per syringe, the overall flow rate was 0.4 ml per minute. While increasing or decreasing the flow rate can change the overall fouling index of each

feedwater, a comparison of the four feedwaters at the same flux was the overall objective of this study. Additionally according to Boerlage et al. (2004) the MFI only varies slightly with increased flux.

6.7 Membrane Resistance

To determine initial resistance by each membrane, a clean water flux test was performed at various flow rates from 0.2 ml/min to .6 ml/min (Flux 12.5 LMH to 37.5LMH) and the resulting pressure was recorded. The initial membrane resistance is the slope of the *P vs Flux* * *Viscosity* curve and varied between the MF and UF membranes with membrane resistance measuring $2*10^{12}$ m⁻¹ and $5*10^{12}$ m⁻¹ respectfully. The resistance curves of the 50 kDA (UF membrane) and the 0.2 µm (MF membrane) are shown in Figures 6.3 and 6.4 respectively.



Figure 6.3: Membrane resistance curve of an UF membrane with a MWCO of 50 kDA


Figure 6.4: Membrane resistance curve of an UF membrane with a MWCO of 100 kDA



Figure 6.5: Membrane resistance curve of a MF membrane with a MWCO of 800 kDA



Figure 6.6: Membrane resistance curve of a MF membrane with average pore size of 0.2 μ m

6.8 Pressure Curves

Each feedwater was tested against each membrane to result in a total of 4 different pressure curves for each feedwater. Each test was operated until one of two scenarios was completed. The first scenario was a total of all 100 ml was filtered through the membrane, which only occurred for wastewater with the 0.2 μ m and for wastewater with PAC addition The second scenario which was more prevalent in the system, the pressure buildup with the system generally between 2.1 and 2.4 bar, became too overwhelming for the syringe pump and the pump would stall. For the purposes of standardization, the initial startup pressure is considered to be 0.3 bar and all pressures below this were not considered. For each feedwater and each membrane resulted in different pressure profiles and be seen in Figures 6.4 to 6.7.



Figure 6.7: Pressure curves for the feedwater, wastewater, with four different membranes



Figure 6.8: Pressure curves for the feedwater, concentrate, with four different membranes



Figure 6.9: Pressure curves for the feedwater, wastewater with PAC addition, with four different membranes



Figure 6.10: Pressure curves for the feedwater, AnMBR liquor with four different membranes

For each feedwater and each membrane the feedwater was tested on, the TMP would gradually rise until one of the two scenarios was met, except for the wastewater with PAC addition. The TMP profile of this feedwater resulted in various pressure drops and spikes within the system. This is believed to be caused by the scraping of the membrane surface while the pressure increases and forcing the cake formation of the membrane surface to shift resulting in the various pressure drops. As a result of these pressure drops the experiment was performed for much longer than any other feedwater at nearly double the time of the wastewater only feedwater and almost 10 times longer when compared to the wastewater concentrate and AnMBR reactor contents.

6.9 Fouling Index

From equation 2 the fouling index was plotted for each feedwater and membrane and shown in Figures 6.9 to 6.12. As can be seen in these figures the fouling index converges as time progresses to and a clear distinct of the fouling index generated may not from each membrane. Since it was determined that membrane would generate a similar fouling index an average of each of the four membranes will be used to determine the MFI. The fouling index valve at the representative pressure of 2 bar will be the representative as the MFI is adjusted to this pressure. For the two instances where 2 bar was not reached, the fouling index will be represented in the average as a projection of the fouling index indicated based on a linear trend was determined not to be an accurate representative of the four membranes it was determined that the 0.2 μ m did not give a clear representative compared to the other membranes, shown in Figure 6.15. While 0.2 μ m can help determine the fouling potential longer testing would be require, similar to results developed by Boerlage et al., (2002, 2004).

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Figure 6.11: Fouling index for wastewater tested on four different membranes



Figure 6.12: Fouling index for concentrate tested on four different membranes



Figure 6.13: Fouling index for wastewater with 1 g/L PAC addition tested on four different membranes







Figure 6.15: Fouling index of each feedwater on each membrane at 2 bar

6.9.1 Comparing Fouling Indexes

While the MFI is based on the standard pressure of 2 bar, comparing the indexes at different TMP on each membrane may yield trends that could indicate different potential for analyzing the fouling conditions. The fouling index was compared for all four feedwaters at the pressures of 0.5, 1.0, and 2.0 bar to notice if any trends were viable. From the observation of Figure 6.16, it was noticed that 1.0 bar and 2. 0 bar of pressure yielded similar fouling indexes on all four membranes, and 0.5 bar had vast differences in the fouling indexes. Since fouling index is dependent on time, since 0.5 bar occurred at different times this could account for the vast differences at 0.5 bar. By allowing the pressure and time to build past this pressure, the fouling index seems to stabilize over time.



Figure 6.16: Fouling index generated at pressures of 0.5, 1.0, and 2.0 bar for the four feedwaters on the four membranes

The second comparison is comparing the four feedwaters at the various pressures for each membrane on the same chart. Shown in Figure 6.17 this comparison allows for any trends that develop based on each membrane. By comparing each feedwater at various pressures on each membrane, any trend relating to the membrane performance for each membrane can be established. It can be shown in Figure 6.17, the fouling potential follows the same trend across the three pressures dour all the feedwaters. This is shown that at all the various pressures and on each membrane, concentrate has the highest fouling index, followed by the contents from an AnMBR, with wastewater and wastewater with PAC being much lower.



Figure 6.17: Comparison of the fouling index produced on each membrane by the feedwaters

6.10 Modified Fouling Index

Each feedwater produced different fouling index depending on the membrane on which it was applied. To standardize the process, the MFI is used to represent the fouling present on a reference membrane of average pore size 0.45 μ m. The average fouling index of the three membranes, shown in Table 6.2, was used in equation 3 to determine the MFI which is shown in Figure 6.18.

2		Concentrate		
Parameter	WW	(CF 20)	WW + PAC	AnMBR Liquor
Fouling Index				
$(1/m^2)$	5.6E+14	2.8E+15	3.2E+14	2.2E+15
Standard Deviation	3.4E+13	1.8E+14	7.0E+13	5.7E+13
Percent Deviation	6%	6%	22%	3%

Table 6.2: Average fouling index of each feedwater and the representative deviation



Figure 6.18: MFI for wastewater, concentrate, wastewater with PAC, and AnMBR contents

The MFI for each of the feedwaters is particularly high as when compared to previous research, (Boerlage et al., 2002, 2004; Khirani et al., 2005) the feedwater was pretreated seawater, and diluted seawater using MF, UF and NF membranes. Since seawater contains ions which may pass through the larger openings of these membranes, it may not clearly indicate a clear representation of the fouling potential and thus different methods to improve the MFI are being performed (Khirani et al., 2005). Additionally, seawater generally how low suspended solids and in one study by Wong et al. (2007) showed suspended solids concentrations between 5

and 30 mg/L, less than 10% of the suspended solids in the wastewater used in this study. Due to the high suspended solids being retained by the membrane, fouling is expected to be much higher due to the lack of pretreatment.

Domestic wastewater which has a relatively high fouling potential caused by the suspended solids, was higher than the wastewater with PAC addition. As a result of the PAC fouling was reduced nearly 60% even when applied in the dead end filtration method. This may be a result of several factors including the compressibility of PAC, cake filtration forming due to the PAC, the adsorption properties of the PAC with colloidal material, and/ or the increased settling caused by PAC within the MFI module. PAC generally used within crossflow filtration has shown result for reducing fouling and improving effluent quality in AnMBR (Do et al., 2009). Additionally in a study performed by Ivancev-Tumbas et al. (2008) the formation of a "PAC filter layer" became present which can result in the reduction of fouling in dead end filtration.

Comparing the concentrate of wastewater with the AnMBR reactor contents, the concentration has a MFI value 25% higher than the anaerobic reactor contents. This indicates that the concentration of wastewater will cause the membrane to foul faster than the AnMBR contents. Since the concentration of wastewater is the end product of the DF system thus varies CF are attained during the concentrating process and the fouling potential will gradually rise to this high extreme. Since domestic wastewater has a fouling potential of 25% of the AnMBR, this would indicate that a large portion of the fouling would only occur in the final stages of the DF system resulting in less overall fouling when compared to the AnMBR contents since it is assumed that the AnMBR solids content would remain relatively similar in steady state conditions.

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6.11 Reproducibility

While the MFI was consistent across three of the membranes, to ensure that the MFI module was able to generate consistent results a general reproducibility study was performed. The system will be test three times on the UF 100 kDA membrane with a variation of four different feedwaters. These feedwaters differ from those performed in the original MFI and will consist of domestic wastewater, the supernatant of domestic wastewater, domestic wastewater with 1 g/L of PAC, and the supernatant of domestic wastewater with 1g/L of PAC. To achieve the supernatant, PAC was added if applicable, and centrifuge at a rate of 1000 revolutions per minute for 10 minutes and extracted from the centrifuge vials.

With the goal of the reproducibility study to determine the effectiveness of generating constant results, a 10% or less standard deviation from the average was to chosen to be a representative as the cutoff point to whether the MFI module was able to provide consist results. With this in mind the four different feedwaters MFIs and the standard deviation is represented in Figure 6.19. Each of the MFI were able to achieve results with in the acceptable range of deviation and it should be noted the very low deviation in the soluble fraction of domestic wastewater and the soluble fraction of wastewater with PAC addition. The difference in the domestic wastewater may be due to because slight variations in the colloidal fractions of the feedwaters and the porosity of the membrane surfaces. The soluble fraction of domestic wastewater and wastewater with PAC, which is absent of colloidal material was able to achieve a high reproducibility factor.



Figure 6.19: MFI reproducibility study

6.12 Conclusion

The MFI which is a capable tool of predicting membrane fouling can be utilized for different design characteristics of the DFO-AnMBR. With domestic wastewater having lower fouling index compared to the contents of the bioreactor in the AnMBR, an increased life time and lower maintenance will be observed. Additionally the concentration of wastewater is slightly higher than the bioreactor contents, and since this is the final concentration of the DF module, the fouling potential is expected to rise as the wastewater becomes more concentrated. Thus resulting in less overall fouling potential compared to the AnMBR.

With the addition of PAC at a concentration of 1 g/L, the fouling potential is reduced by 25%, in dead end filtration. The pressure curves, that result in drastic spikes and declines in pressure may be due to the PAC layer shifting as pressure is increased. The compressibility and other factors may also be a contributor to this trend which was present on all four membranes.

The reproducibility of the MFI is high with deviation ranging from less than 1% to 9%. It was also noticed that during the reproducibility study that the soluble fraction is able to achieve lower fouling potential as well as more consistent results. This might be due to the colloidal makeup of the particles in the raw samples which can block pores and form cake layers differently.

CHAPTER 7: CONCLUSION

7.1 Conclusion

This work revealed the performance of a DF module at a variety of CFs and the quality of permeate generated through the module. The concentration of solids and COD was also measured with and without PAC addition and used to generate a model to determine the potential of coupling the DF with an AnMBR, creating a DF-AnMBR. The fouling potential of the DF-AnMBR was investigated with the construction of a MFI system. From these experiments and model, the major conclusions of this work are the following:

- The DF model is able to produce permeate low in COD, between 50 and 200 mg/L, even at higher CF.
- The suspended solids retained by the membrane are concentrated within the feed tank, except for solids retained on the membrane surface.
- The permeate of a DF system is mostly pathogen free, reducing the need for disinfection.
- Concentration of the feedwater (domestic wastewater) in the DF module is possible to generate higher strength wastewater at over 1500 mg/L of COD. Higher CFs were able to produce COD concentrations between 2000 and 2500 mg/L.
- PAC can be used to reduce membrane fouling and generate lower COD concentrations for the permeate.

- Permeate turbidity is consistently low with about an average of 1 NTU with and without PAC addition.
- Utilizing the model, high concentration of COD and solids will be present within the concentrate while permeate remains relatively stable, making the concentrate an ideal feedwater for the AnMBR.
- With PAC, the solids buildup in the concentrate is much higher, which could result in lower SRT or the need for a larger bioreactor to reduce solids buildup.
- Nutrients in the DF-AnMBR remain relatively stable in all phases of system, except for TP when the PAC is added to the system, due to phosphate leaching.
- The MFI system constructed produced highly reproducible results with the deviation of the MFI ranging from less than 1% in the soluble fraction to less than 10% when PAC was added
- Domestic wastewater fouling potential was improved with a PAC of dose of 1 g/L, in dead-end filtration, with a MFI value 60% with PAC than without PAC.
- Concentrate (CF of 20) and AnMBR liquor produced MFI values of 5 and 4 times higher than domestic wastewater, respectively.

7.2 Future Research

Future research should serve to show the performance of a DF-AnMBR. A pilot system of a DF-AnMBR should be tested for the treatment of domestic wastewater at various CFs. By utilizing different design CFs, various parameters of the DF-AnMBR can be established. The overall permeate production and flux can be determined from the coupling of the two systems. Since the DF module will handle a large burden of the liquid fraction, and the AnMBR will now receive higher solids concentrations, performance may be improved or hindered accordingly at larger SRTs. Ravazzini (2008) asserted that a upscale pilot system of a DF system using tubular membranes were needed to address energy consumption, economics, and maintenance for a DF system. Hence, while the operation of a DF pilot system would prove beneficial, by utilizing a DF-AnMBR system pilot scale, research about the DF performance, economics and maintenance can be acquired, while generating information about the combined system.

Since the DF performance is based on the CF, the MFI can be conducted at various CF to determine a CF which has a fouling potential that is in comparison to the AnMBR. By having comparable MFI from the domestic wastewater concentrate and the AnMBR, the maintenance and performance of both systems can be observed. Additionally, since the MFI was performed on AnMBR reactor contents that did not have PAC, the system could be tested with PAC being added to the DF module and observe how this now high concentration of solids affect the filtration of the membranes. Ozgun et al. (2013) noted that flux declination occurred at around 3.4 g/L, and since PAC is highly rejected by the membrane, the buildup of solids could prove more detrimental than beneficial reduce the performance of the AnMBR. Additionally the AnMBR reactor contents used in the experiment was treating domestic wastewater, but the coupling with the DF could result in higher fouling in the membranes connected to the reactor. Future research should observe how the fouling potential changes as the DF-AnMBR treats higher strength wastewaters and higher solids content.

Further research about water reuse in regards permeate from DF module would be beneficial for a life cycle assessment. AnMBR permeate and wastewater effluent has been used

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for several non-potable water uses such as irrigation, cooling system, and aquifer storage and recovery systems. If the DF system can meet the discharge requirements according to local, state and federal laws within a certain area, the DF permeate should be able to be utilized in a similar fashion. Depending on the discharge requirements, DF permeate may have to undergo post treatment or a polishing process before being discharge. Also DF permeate can be used as a source of nutrient recovery and be used for the creation of struvite or other nutrient recovery methods if further research is deem applicable.

Finally, energy consumption and generation from the DF-AnMBR should be researched. As a majority of energy in AnMBR is used for heating to allow for mesophilic or thermophilic conditions, in low strength wastewater it is very difficult to achieve net zero or net positive energy in AnMBR treating domestic wastewater. Since the main focus of the DF module is concentrating low strength domestic wastewater into higher strength wastewater, the benefits of energy recovery through the utilization of biogas can be optimized. Additionally since the DF module is essentially reducing the volume of water, the heating requirements for the AnMBR portion are now reduced heavily, thus resulting in better energy recovery. Depending upon the energy consumption of the DF module, the energy reduction minimal heating required due to the smaller volume, and the higher strength wastewater, the DF-AnMBR may be able to provide a positive energy sanitation system.

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APPENDICES

Appendix A: Calibrations

To effectively test the DF system and the MFI, the pressure transducers had to be calibrated. Since variations occur with time, the pressure transducers were calibrated regularly to ensure accurate measurements. To determine the pressure transducers, pressure was applied at various strengths ranging from -40 kPa to 60 kPa for the DF system and between -20 kPa and 100 kPa for the MFI and the respected voltage output was recorded. From this a trend line was developed to determine the pressure of the DF and MFI system.



Figure A1: DF module transducers





Appendix B: PAC Isotherms

While the permeate produced by the wastewater with PAC addition yielded lower COD concentration, PAC must be adsorbing COD, thus increasing the amount of rejection performed by the membrane. To determine the amount of adsorption possible with PAC addition, a PAC isotherm was conducted using domestic wastewater.

The first step is to determine the length of time that must be achieved to reach optimal absorption properties. A 1 g/L of PAC was added serveral vials of wastewater and soluble wastewater, to determine whether colliods affected to adsorptive capacity and various time constraints ranging from 0.5 hr to 48 hr were monitored. To ensure no interference from color bleeding in the COD reading, the samples were centrifgued at 1000 rpm for 10 minutes. After the time trial, it was determined that the colloidal and soluble COD removal was similar thus only the soluble portion will be tested in the next trial where the concentration changes. It was also determined that after 24 hours minimal changes in COD concentration were present thus, 24 hours will be used for the next trial.



Figure B1: PAC isotherm testing for COD removal with a 1 g/L PAC concentration at various times.

With the PAC testing determined to reach equilbrium in 24 hours, different PAC concentrations ranging from 0 g/L to 10 g/L of PAC were added to 20 ml of the soluble fraction of wastewater. A total of six vials were used and shaken for 24 before being centrifuged and tested for COD. COD removal was limited with a over 100 mg/L remaining with the vial even at the higher concentration of 10 g-PAC/L.



Figure B2: COD concentrations with various PAC concentration, Test 1

From this concentration table, linear, Langmuir, and Freundlich isoterms were conducted. Linear isotherms represent q vs C, where q is equal to the mass adsorbed per unit weight of the adospbent in mg/g and C is the COD concentration in mg/L. Langmuir isotherms represent the inverse of q vs. the inverse of C, and the Freundlich represent the log of q vs the log of C. From these different isotherms, the following figures C3 to C5 were created.



Figure B3: Linear isotherm attempt for COD removal from PAC, Test 1



Figure B4: Langmuir isotherm attempt for COD removal from PAC, Test 1



Figure B5: Freundlich isotherm attempt for COD removal from PAC, Test 1 While the Freundlich isotherm created a linear trend, the plot indicates that PAC has a negative adsoption capacity, as seen by a negative intercept along the axis that crosses the log of q. Thus resulting in a reproformance of the isotherms to try and analyze the PAC.

The second PAC isotherm testing utilized stronger wastewater at around 550 mg/L COD starting concentration. With this the adsorption capacity was conducted with PAC concentration ranging from 0 to 60 g/L to effectively adsoped the COD. In this case, a similar trend where less than 100 mg/L were not able to adsorbed by the PAC. A similarn trend in the isotherms were formed, where linear and Langmuir did not indicate clear isotherm values and Freundlich indicated that a negative adsoption capacity was present. This can be seen in figures C7 to C9.



Figure B6: COD concentrations with various PAC concentrations, Test 2



Figure B7: Linear isotherm attempt for COD removal from PAC, Test 2



Figure B8: Langmuir isotherm attempt for COD removal from PAC, Test 2



Figure B9: Freundlich isotherm attempt for COD removal from PAC, Test 2 Since much of the COD is not adsorb, there may be interference caused by the wastewater which is not allowing for the adorbance of COD by PAC. To ensure that the PAC, is

able to achieve proper adsorpation, a test with methtylene blue was conducted where 5 mg/L of methelyene blue were added to variious PAC concentration ranging from 0 to 5 g/L. From here the adsorpance capacity will be determine isotherms will be generated from this new test.

From the adsorbance test of methylene blue, almost all of the methylene blue was adsorb based on the adsorbance of the color on a 665 µm wavelength. The PAC produced an concentration plot shown in Figure B10. From this concentration curve, the linear isotherm and Freundlich isotherm were produced and shown in Figure B11 and C12. Since the Freundlich isotherm produced a ideal isotherm with a slope less than 1 and an intercept along the log y axis that is greater than 0,this is an acceptable isotherm. Thusly, there must be interference from the wastewater that is interfering with the adsorbance of COD by the PAC in the wastewater trial. Therefore COD may be adsorb by the PAC but there will still be a high level of COD that is remained since the PAC can not adsorb a large fraction of the COD. Since all wastewater is generated differently and have different characteristic and concentrations, PAC may be better suited for other wastewater and not for some.



Figure B10: Concentration of methylene blue with different PAC concentration



Figure B11: Linear isotherm for methylene blue adsorbance onto PAC



Figure B12: Freundlich isotherm for methylene blue adsorbance onto PAC

After determining that there is most likely interfence from the particles in wastewater that is not allowing the adsoption of COD by the PAC, PAC Test #1 was reanalyzed. In this second analysis, the unadsopable concentation of COD (approximately 104 mg/L of COD) will be removed from the initial concentration and the adsopable concentrations. From this method Figures B13 and B14 were produced.



Figure B13: Linear isotherm for COD absorbance by PAC with adjusted concentrations



Figure B14: Freundlich isotherm for COD absorbance by PAC with adjusted concentrations

From this observation, once the un-absorbable COD concentrations were removed, the isotherms were able to produce consistent curves. Both curves imply that higher dosage of PAC

may be able to remove additional COD which may pass through the membrane system. This would yield higher rejection by the membrane system with the addition of PAC. Since not all of the COD was able to adsorb by the PAC, there is a limit of increased performance from the addition of PAC.
ABOUT THE AUTHOR

George Dick is a graduate student in the Department of Civil and Environmental Engineering at the University of South Florida. As a Master of Science in Environmental Engineering, George focuses his academic interest in water/wastewater treatment as well as sustainable design. His research focuses on the water/energy nexus with interest in anaerobic membrane bioreactors and membrane filtration. George received his Bachelors of Science degree in Civil Engineering from the University of South Florida. While a student at the University of South Florida, George has served as president of the student chapter of the Florida Water Environment Association (FWEA) and marshal of Chi Epsilon, the civil engineering honor society. George is currently serving as the young professional chair of the west coast chapter of FWEA. George was also a member of the winning team for the 5th annual Cade Museum Prize for Innovation.