BIOLOGICAL NITRIFICATION WITHIN THE FOULING LAYER OF CROSS-FLOW MICRO-FILTRATION

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With the fouling layer being established in most membrane filtration applications, a study of the possible benefits of the fouling layer was researched. This investigation was aimed at the determination of a viable nitrifying biofilm within the fouling layer of membrane filtration which could oxidize ammonia. The membrane used was a 0.2 μ m ceramic tubular membrane used in cross-flow operation. Nitrifying organisms were inoculated into a bench top filtration apparatus to oxidize ammonia and the corresponding rates of ammonia oxidation were determined in two different operating modes. A "filtering mode" included the process of membrane filtration by enabling filtration and "a non-filtering mode" established the ammonia oxidation rate occurring in the apparatus without the process of filtration.

The comparison of the two modes showed a significant increase in the oxidation rate of the filtering mode. The ammonia oxidation rates seen in the six experimental runs corresponding to the surface of the membrane were: 0.94, 2.38, 3.81, 3.14, 6.24, and 9.30 (mg/l-hr-m2) compared to the internal surface of the bench top apparatus which were: 0.12, 0.12, 0.12, 0.11, 0.20, and 0.29 (mg/l-hr-m2) respective to each run. The differences in ammonia oxidation rate suggests that not only will viable nitrifying organisms grow within the fouling layer of a membrane they will grow at rate approximately 20 times faster than that seen occurring on the internal surface of the bench top apparatus.

Also discussed in the research is the ammonia oxidation rate as a function of cross-flow velocity and trans-membrane pressure. Varying the cross-flow velocity and trans-membrane pressure suggested that the organisms on the membrane surface may actually be undergoing nitrification from the influent end of the membrane to effluent end of the membrane.

DESCRIPTORS

Alkalinity	Cross Flow Micro Filtration
Ammonia Oxidation	Fouling Layer
Biofilm	Nitrification
Cell Yield	Nitrosomonas
Ceramic Membrane	

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1.0 INTRODUCTION

Membrane filtration is growing in acceptability as a water and wastewater treatment process. Much attention has been given to the operational parameters concerning the process. Flux rates and factors that limit flux rates are focal points for research and development. Flux rates are limited by a fouling layer which accumulates on a membrane surface during the membrane treatment process. Current thinking is that this fouling layer is thought of as a negative aspect, as it minimizes the potential flux of the membrane.

This research differs from most of the current research in that it examines a potential beneficial aspect of the fouling layer of wastewater membrane filtration. During active research in the area of membrane filtration at the University of Pittsburgh unexpected experimental results suggested that the fouling layer may have attributed some biological nitrification during the processing of dilute wastewater. If the fouling layer contained viable active organisms it may have acted like a small biofilm treatment apparatus. It then became the goal of this research to determine if the fouling layer could be considered as a thin biofilm serving to treat soluble pollutants.

In this research ammonia was used as the substrate for the yet to be determined biofilm. Nitrifying organisms were inoculated into a membrane filtration apparatus and the corresponding rates of ammonia oxidation were measured in two operating modes. The two operating modes were a "Filtering mode" and "Non Filtering mode". The filtering mode established the rate of ammonia oxidation with the aid of the membrane filtration process. The Non-Filtering Mode established the rate of ammonia oxidation of the membrane apparatus without the aid of the membrane filtration process.

1

2.0 LITERATURE REVIEW

2.1 MEMBRANE MICROFILTRATION

There are many basic concepts that have to be developed to understand the engineering aspects of membrane technology for water and wastewater. A basic overview will be presented along with the different operating process and essential engineering parameters.

A membrane process separates particles from a wastewater. The wastewater, referred to as the feed, is driven through the membrane by an applied force. The feed that is able to pass through the membrane is referred to as the permeate. While the driving force for separation can be pressure, concentration, electrical potential, or thermal force, for practical purposes the common driving force, and the one used within this research, is an applied pressure force. This is schematically shown in Figure 1 (Bendick 2003).



Figure 1: Basic Membrane Separation

The basic separation mechanism is the same for all membrane processes. There are four recognized classes of membrane processes categorized by the size or molecular weight of the particles that are able to pass through the membrane. The four classifications of membrane processes are: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Table 1 lists the sizes, the typical operating pressures, and the specific types of particles that are rejected for each membrane classification.

Membrane	Size	Operating	Rejected
Classification	Range	Pressure	Particles
Migrafiltration	0.01 1.000	0.5 2 hor	Bacteria, Silts, Cysts,
Microintration	$0.01 - 1 \mu m$	0.3 - 2 bal	Spores
			Proteins, Viruses,
Ultrafiltration	1 nm – 100 nm	1 – 5 bar	Endotoxins,
			Pyrogens
Nanofiltration	200 – 1,000 MWCO	3 – 15 bar	Sugars, Pesticides
Reverse Osmosis	< 200 MWCO	10 – 60 bar	Salts
Source: Cardew and Le, 1998			
Note: MWCO = Molecular Weight Cut Off; 1 bar = 14.7 psi			

Table 1: Membrane Classifications

In microfiltration processes, the rejection of particles is controlled by several mechanisms: the pore size of the membrane, the particles that that accumulate on the membrane surface, and the particles that accumulate within the membrane pore structure. The particles that accumulate on the membrane surface and within the membrane are known as the fouling layer. Combining the fouling layer and the membrane allows four general mechanisms to retain particles (Figure 2, Bendick, 2003). The mechanisms are: Surface Sieving, Surface Collection, Surface Cake Collection and Internal Pore Adsorption. Surface sieving rejects particles by the size of the membrane pores. Surface collection rejects particles by the membrane surface charge.

Surface cake collection allows for particles to be rejected by the particles that accumulate on the membrane surface. Internal pore adsorption allows for particles to adhere to the inside of the membrane pores.



Figure 2: Filtration Mechanisms

The microfiltration process is classified by the membrane material and by the membrane configuration. The ceramic membranes used within this study are a special class of microporous membranes that have the ability to withstand variations in temperature and pressure, as well as an increased durability

Membrane apparatus are available in a variety of engineered configurations. The four basic types of membrane configurations are: dead-end, spiral wound, cross-flow, and hollow fiber. The configuration used in this research is cross-flow. The different configurations have been developed to account for flux, process flexibility, and ease of maintenance and operation. In cross flow microfiltration the feed flows parallel to the membrane surface scraping particles away from the surface and reducing the impact of the fouling layer.

2.1.1 Flux

The flux is defined as the flow of filtering water per unit surface area of the membrane. The filtering flux determines the required membrane surface area for a design flow rate. The filtering flux is defined as follows:

$$J = \frac{Q_p}{A_s} \tag{1}$$

Where: $J = flux (L/hr-m^2)$ $Q_p = filtering flow rate (L/hr)$ $A_s = membrane surface area available for filtration (m²)$

During cross-flow microfiltration the filtering flux is initially very high followed by a rapid decrease and then a gradual decrease towards a constant flux rate (Figure 3). The constant flux rate is referred to as the steady state flux rate.



Figure 3: Steady State Flux

2.1.2 Cross Flow Velocity

The cross flow velocity is the rate at which the feed water tangentially flows along the membrane surface and is calculated as follows:

$$V = \frac{Q_{b}}{A_{c}}$$
(2)

Where:

V = cross flow velocity (m/s)

 Q_b = bulk flow rate of the raw water within the tube (m³/s)

 $A_c = cross sectional area of the channel (m²)$

The cross flow velocity is a very influential design parameter for cross-flow microfiltration apparatus. Typically, the cross-flow action is used minimize the fouling layer of the membrane by sweeping away particulates from the membrane surface. Another important phenomenon though, considering the cross-flow velocity action, is the resistance to mass transfer. A general equation for mass transfer can be seen in equation 3.

$$N = K_L * (C_L - C_S)$$
(3)

Where:

N = Flux of constituent

 C_L = Concentration in liquid

 $C_S = Concentration of substratum$

 K_L = Mass transfer coefficient

The mass transfer coefficient is of special importance as it is determined by the operating conditions of the apparatus. The value of the coefficient is a function of many variables shown in equation 4. Specifically, the variable of V shows that the mass transfer will be affected by the cross-flow velocity.

$$K_{L} = f(V, \eta, \rho, D)$$
(4)

Where:

V = Velocity $\rho = Density$

 η = Molecular diffusivity of the fluid

D = Characteristic dimension of the system

2.1.3 Trans-membrane Pressure

The trans-membrane pressure is the driving force for membrane filtration. The transmembrane pressure is the difference in pressure from the inlet side of the membrane to the outlet side of a membrane shown in Figure 5.



Figure 4: Trans-membrane pressure

It is calculated as follows:

$$\Delta P = \frac{P_i + P_o}{P_p} \tag{5}$$

Where:

 ΔP = trans-membrane pressure (bar)

 P_i = inlet pressure (bar)

P_o= outlet pressure (bar)

 P_p = filtering pressure (bar)

2.1.4 Backpulse

Low filtering flux rates are the result of a build up of particles on the membrane surface and within the membrane [Shondi, 2001]. In attempt to maintain a high flux rate in engineered apparatus a backpulse technique has been incorporated into the membrane process. Backpulsing is the redirection of water flow from the filtering side of the membrane to the feed side of the membrane. The water flow is reversed by supplying a greater pressure on the filtering side of the membrane. The flow of solution is redirected and breaks up the fouling layer carrying particles away from the membrane surface (Figure 5, Bendick, 2003). A typical backpulse is performed once a minute for about 0.5 seconds.



Figure 5: Filtration during Ordinary and Backpulse Operation

2.1.5 Fouling Layer

The accumulation of particles on the membrane surface and within the membrane pores is referred to as the fouling layer. The fouling layer is a broad term used to describe the various mechanisms of flux decline. The flux decline caused by the fouling layer is a significant factor that does not allow for the wide spread implementation of membrane filtration.

2.2 BIOFILMS

A biofilm consists of a collection of cells attached to a surface. Biofilms are created when microorganisms accumulate on surface in which water containing nutrients and minerals within a non-sterile water source flows.

Biofilms can be considered a detriment in many applications because they grow and cause fouling. Biofilms can be considered positive though, when they are used as treatment process. The most common positive uses of biofilms are Trickling Filters and Rotating Biological Contactors (RBCs) which are described further in Section 2.2.2.

2.2.1 Biofilm Formation

For a biofilm to be useful as a treatment process, it must first attach to a surface. The progression of biofilm formation is the net result of various processes identified by: adsorption,

desorption, attachment, detachment, and growth (Hjortso, 1995). The following paragraphs will describe each process in brief.

The first step in the development of a biofilm is the adsorption of a cell to a solid surface. Adsorption is defined as the accumulation of cells from the bulk liquid directly to the substratum. One of the most important factors to the adsorption of cells to the substratum is the shear stress of the apparatus. The shear stress of the system can be emphasized by its sticking efficiency expressed in Equation 6 (Escher, 1990).

Sticking Efficiency = Number of cells adsorbed to the substratum / Number (6) of cells transported to the substratum

From Equation 6, if the flow is increased in the system the number on cells transported to the substratum should also increase. Because of the shear stress from increased flow, the sticking efficiency is actually reduced. More cells are transported to the substratum but less are adsorbed. The adsorption of cells is also affected by the properties of the substratum such as the material and roughness (Hjortso, 1995).

Attachment is the second process in the progression of a viable biofilm. Attachment is defined as cells from the bulk liquid sticking to an existing biofilm. Attachment of cells could play an important role in the displacement of one cell species by another (Hjortso, 1995).

Along with the attachment of cells is the detachment of some cells from a biofilm. Cells and cellular material detach from a biofilm in the following ways: erosion, sloughing, human intervention, predator grazing and abrasion (Bryers, 1987). Detachment is one of the least understood processes affecting biofilm accumulation and is probably the most important process limiting both the rate and the extent of biofilm accumulation (Hjortso, 1995).

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Growth is the next process in the progression of biofilm formation. Growth is defined as an increase in microbial cell numbers of microbial mass as a result of cell replication. Under the proper environmental conditions, i.e., temperature, concentration of electron donor / acceptor, pH, etc., cell replication will occur due to the degradation of the substrate. Growth occurs in two basic phases: exponential growth and substrate-limited growth. Exponential growth occurs where the substrate is abundant and maximum growth of the biofilm can occur. Substrate limited growth occurs were the substrate concentration is below that which is required for maximum growth. In many biofilm applications, the substrate concentration is below what is required for growth.

2.2.2 Biofilm Treatment Process

Biofilms are typically seen when a polluted water source is passed over a solid substratum. Biofilms can be seen naturally on rocks and pebbles in almost any stream and provide a measure of natural biotreatment of the water in the stream. This natural treatment in streams is mimicked in many treatment process used today. Today's biofilm treatment processes are primarily trickling filters and rotating biological contactors (RBC). The pollutant for removal in most RBCs and trickling filters is soluble, typically containing organic compounds and ammonia.

Depending on the substrate which is treated, a general population of organisms forms to make the biofilm. In treatment apparatus where the primary pollutant is organic, the population of bacteria is primarily heterotrophic. These organisms work well to treat the pollutant of organic compounds, but do not oxidize ammonia. In situations were trickling filters and RBCs are used to treat ammonia a population of chemotropic organisms will develop. These chemotropic organisms will be described in detail below.

2.3 NITRIFICATION AND NITRIFYING BACTERIA

Nitrifying bacteria consists of chemoautotrophic organisms. Chemoautotrophic organisms use inorganic carbon as their carbon source and derive their energy needs by oxidizing inorganic compounds. In the case of nitrifying bacteria the inorganic compound that is oxidized is ammonia which is ultimately oxidized to nitrate. Nitrifying bacteria primarily consist of the Nitrosomonas and Nitobacter genera.

2.3.1 Nitrification

The ultimate oxidation of ammonium to nitrate is broken up into two stages: ammonia is first oxidized to nitrite and second nitrite is oxidized to nitrate. The first stage of nitrification is the oxidation of ammonia to nitrite. This is best studied in the genus Nitrosomonas and is shown in Equation 7.

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + H_2O + NO_2^-$$
 (7)

The second stage of the nitrification process is the oxidation of nitrite to nitrate carried out by members of the Nitrobacter and Nitrospira genera. The reaction is catalyzed by the enzyme Nitrite Dehydrogenase and is shown in Equation 8.

$$NO_2^- + 0.5 O_2 \rightarrow NO_3^- \tag{8}$$

Adding Equation 7 and 8 together gives the overall oxidation of Ammonia as shown in Equation 9.

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$
 (9)

From Equation 9 it is also seen that there is an oxygen demand during the nitrification process of 4.57 mg O2 / mg $NH_4 - N$.

In oxidizing ammonium to nitrate, nitrifying bacteria generate energy. Nitrifying organisms use this energy to assimilate carbon. The carbon requirements for nitrifying organisms are satisfied by assimilating carbon dioxide, bicarbonate, or carbonate. The equation that governs carbon assimilation for Nitosomonas and Nitrobacter is given by Equations 10 and 11.

$$NH_4^+ + 1.5O_2 + 2HCO_3 \rightarrow NO_2^- + 2H_2CO_3 + H_2O$$
 (10)

$$NO_2^- + 0.5 O_2 \rightarrow NO_3^- \tag{11}$$

The overall carbon assimilation during the nitrification process is shown in Equation 12.

$$NH_4^+ + 2O_2 + 2HCO_3 \rightarrow NO_3^- + 2H_2CO_3 + H_2O$$
 (12)

As can be seen in Equation 12, theoretically 7.14 mg of alkalinity as $CaCO_3$ is used per mg $NH_3 - N$ removed. Experimental results of alkalinity as $CaCO_3$ used per mg $NH_3 - N$ are given in Table 2 (U.S. EPA, 1975).

Ratio (mg Alkalinity / mg NH ₃ -N)		
Medium	mg Alkalinity / mg NH ₃ -N	Reference
Suspended	6.4	Mulbarger, 1971
Suspended	6	Horstkoffe, 1974
Suspended	7.1	Newton, 1973
Attached	6.5	Gasser, 1974
Attached	6.3 -7.4	Osborn, 1965
Attached	7.3	Haug, 1971

 Table 2: Ratio (mg Alkalinity / mg NH₃-N)

During the nitrification process, the theoretical mass of cells grown per NH₃-N used can be estimated by Equations 13, 14 and 15 with Equation 15 being the overall synthesis of both nitrifying bacteria (U.S. EPA, 1975).

$$55 \text{ NH}_4^+ + 76 \text{ O}_2 + 109 \text{ HCO}_3^- \rightarrow \text{C}_5\text{H}_7\text{NO}_2 + 54 \text{ NO}_2^- + 57\text{H}_2\text{O} + 104 \text{ H}_2\text{CO}_3$$
(13)

$$400 \text{ NO}_2^{-} + \text{NH}_4^{+} + 4 \text{ H}_2\text{CO}_3 + \text{HCO}_3^{-} + 76 \text{ O}_2 \rightarrow \text{C}_5\text{H}_7\text{NO}_2 + 57\text{H}_2\text{O} + \text{NO}_3^{-}$$
(14)

$$NH_4^+ + 1.83 O_2 + 1.98 HCO_3^- \rightarrow 0.021C_5H_7NO_2 + 1.041H_2O + 0.98 NO_3^- + 1.88 H_2CO_3$$
(15)

In these equations cell, yields for Nitrosomonas and Nitrobacter bacteria are 0.15 and 0.02 (mg cells / mg NH₃-N), respectively. Thus, the overall theoretical cell yield for both reactions is 0.17 (mg cells / mg NH₃-N). Listed in Table 3 are some of the experimental cell yield values which are very similar to theoretical value of 0.17.

Experimental Cell Yield Values (mg cells / mg NH ₃ -N)		
Value (mg cells / mg NH ₃ -N)	Reference	
0.15	U.S. EPA, 1975	
0.22	Beccari, 1979 Benefield, 1980	
0.13	Rozich, 1980	
0.17	Bidstrup, 1988	

Table 3: Experimental Cell Yield Values

2.3.2 Suitable Conditions

Nitrifying bacteria typically require a specific range of environmental parameters to strive in an environment. The environmental parameters include: ammonia / nitrate concentration, dissolved oxygen concentration, pH, alkalinity, temperature, C/N ratio, and the presence of toxic chemicals.

The ammonia / nitrate concentration is the source of energy for nitrifying organisms. Organisms oxidize the ammonia and use the energy to assimilate carbon and collect the minerals essential for growth. The concentration of ammonia / nitrate is used to determine the rate at which nitrifiers grow and is modeled by Monod Kinetics described further in Section 2.3.3.

Another essential parameter to nitrifying bacteria is the dissolved oxygen concentration. Oxygen is used as the electron acceptor for the nitrifying bacteria. During the process of nitrification 4.57 mg O_2 / mg NH₃-N is used as described in Section 2.3.1. Variations in the D.O. concentration can be accounted for by the Monod equation also. The half saturation constant for the D.O. has been reported to fall within a range of 0.3 to 1.3 mg/l (Charely et al, 1980). Therefore, the D.O. should be kept at a high and consistent concentration to allow for consistent nitrification rates.

The pH value is also a very important parameter of concern. As nitrification is taking place, protons are liberated as shown in Equation 4 which may lower the pH of the supporting environment. If the pH is lowered to approximately 6.0 or lower nitrification ceases (Painter, 1970). The optimum pH range lies between 7.5 and 8.5 (Barns and Bliss, 1983).

Alkalinity is an essential parameter concerning nitrification, as it is a pH buffer and the inorganic carbon source for nitrifying bacteria. As shown in equation 7 nitrification uses alkalinity as CaCO₃ in a ratio of 7.14 mg/ mg of $NH_3 - N$ oxidized (U.S. EPA, 1975). Therefore, there has to be enough alkalinity in the supporting environment to balance the acidity produced by nitrification and enough alkalinity to provide the inorganic carbon necessary for microbial growth.

Temperature is another very important environmental parameter concerning the growth of nitrifiers. The optimal temperature range for nitrification has usually been reported to be in the range of 28 - 36 degrees C (Hailling-Sorensen and Sorgensen, 1993), with an overall range of 4 - 50 degrees C (Barnes and Bliss, 1983).

Another environmental parameter of concern is the C/N ratio. Nitrifiers perform best when the C/N ratio is low. Nitrifiers will only perform well in a low C/N ratio since their growth rate is lower than heterotrophs. The specific growth rate of nitrifiers is typically in the range of (0.006 - 0.035 h-1) where heterotrophs are typically in the range of (0.18 - 0.38 hr-1) (Grady and Linn, 1980). Therefore, there must be a high concentration of ammonia-N and a low concentration of organic carbon for the nitrifying bacteria to compete well.

Finally, as in all microbiological apparatus, nitrifiers are subject to product and substrate inhibition as well as heavy metals and toxic organics. Substrate inhibition for Nitrosomonas bacteria is very high, where concentrations as high as 65 mg/l did not inhibit the growth of Nitrosomonas (Wiesmann, 1994). Since, typical domestic sewage has a NH₃-N concentration much lower than 65 mg/l, substrate inhibition is not typically a factor. The most toxic compounds inhibiting nitrifiers are: cyanide, thiourea, phenol, anilines, and heavy metals especially silver, mercury, nickel, chromium, copper, and zinc.

2.3.3 Kinetics

The environmental parameters discussed in Section 2.2 play a very important role in the kinetics of nitrifier's growth. In the nitrification process the growth of Nitrobacter is faster than that of Nitrosomonas. Thus, the rate limiting step in nitrification is the conversion of ammonia to nitrite by Nitrosomonas. The growth rate of Nitrosomonas can be represented by Figure 6.



Limiting food concentration S, (mg/l)

Figure 6: Monod Growth Rate Constant as a Function of Limiting Food Concentration

Figure 6 shows the conceptual growth rate of Nitrosomonas bacteria modeled by the Monod Equation. The Monod equation is shown by equation 16.

$$U = U_{max} [NH_4] / (K_s + [NH_4])$$
(16)

Where:

U = specific growth rate (day^{-1}) U _{max} = maximum specific growth rate (day^{-1}) [NH₄] = ammonia concentration K_s = half saturation constant

Using a first order equation and the Monod Equation for the kinetic constant, the growth rate of nitrifiers can be represented by Equation 17.

$$dX / dt = U_{max} [NH_4] X / (K_s + [NH_4])$$
(17)

Where:

X = Organisms (mg) dX = Change in Organisms dt = Change in time

Equation 17 is used where the limiting substrate concentration is minimal. From figure 7 it can also be determined that after a certain concentration, the growth rate of nitrifiers should reach steady state. In situations where the limiting substrate concentration is in excess compared to the half saturation coefficient, the Monod equation essentially converges to a maximum rate constant and the reaction rate of the nitrifying organisms can be considered zero-order. The half saturation coefficient for ammonia is variable but a common accepted value is 1.0 mg/l (Grady, 1999) The concentration where the growth rate approaches zero order kinetics is approximately 2.5 mg/l (Kiff, 1972). Equation 18 shows a zero order representation of the growth rate of Nitrifying organisms.

$$dX / dt = -U$$
 (18)

The growth rate of organisms can also be related to the rate of food utilization by the cell yield value. Equation 19 is used to relate the ammonia oxidation rate to the growth rate of organisms. The theoretical cell yield value is 0.17 mg/mg as described in section 2.3.

$$dX / dt = - dS / dt * Y$$
(19)

Where:

Y = (mg of cells grown / mg of NH₃-N oxidized) S = Substrate Concentration (mg/l) Once the growth rate is converted to the ammonia oxidation rate, the specific rate of food utilization considering a pseudo-zero order reaction can be modeled by Equation 20 (Eckenfelder, 1970).

$$-1/X * dS / dt = k$$
 (20)

Where:

 $k = kinetic constant (days^{-1})$

For attached growth systems, the average cell mass can be related to the surface area (As) by equation 21 (Eckenfelder, 1970).

$$X \sim A_s$$
 (21)

Where:

 $A_s = Surface Area (m^2)$

By assuming the active microbial mass is proportional to the specific surface of the substratum the specific rate of food utilization can be represented by Equation 22. Equation 22 is dependent on the specific surface of the substratum, thus any characteristic change in substratum considerable alters the effluent substrate concentration.

$$S_o - S_e = -ktA_s \tag{22}$$

Where:

 $S_e = Effluent Substrate Conc. (mg/l)$ $S_o = Original Substrate Conc. (mg/l)$

2.4 NITRIFYING FILMS ON CONDUITS

It is seen from previous research (Camper, 1996, Emde, 1992, LeChevallier, 1987) that biofilms are present in municipal drinking water systems. Biofilms that occur in distribution systems are subject to the same type of shear stresses of cross-flow velocity as that of membrane filtration. The shear stresses seen in distribution systems are typically lower than applications of cross-flow membrane filtration, were a high cross-flow velocity in a distribution apparatus is around (1.3 m/s) (AWWARF, 1990). A high cross flow velocity in membrane filtration applications, specifically considering this research, is around 8 m/s ranging from 2 m/s to 8 m/s. Assuming the operating parameters of water distribution apparatus are similar to that of membrane filtration it is feasible that biofilms will occur during membrane filtration processes.

3.0 MATERIAL AND METHODS

3.1 BENCH TOP MEMBRANE FILTRATION APPARATUS

Laboratory testing was performed using a cross flow filtration bench top apparatus. Figure 7 shows the basic experimental setup of the bench top apparatus which consists of a ³/₄ HP centrifugal pump, a 16 quart feed tank, a in-line flow meter, a ceramic test module, a temperature gauge, an automatic backpulse device, six process control ball valves, and three pressure gauges to monitor the inlet, outlet and filtering pressure. The bench top apparatus is comprised primarily of stainless steel with an estimated internal surface area of 2000 cm². The internal surface area was estimated by measuring the length and diameter of conduit in the bench top apparatus.


Figure 7: Bench Scale Experimental Setup of Cross Flow Microfiltration Apparatus

The membrane used is a Membralox \mathbb{R} T1-70 alpha alumina membrane with a mean pore size of 0.2 *u*m. The tubular membrane is 250 mm in length, 7 mm in diameter and has 55 cm² of available surface area. The membrane is capable of withstanding a pressure limit of 115 psi, a temperature limit of 225°C and a pH range of 0-14.

The filtration apparatus also includes a backpulse unit which uses 80-120 psi of oil-free, dried, filtered nitrogen gas. The backpulse has two controls: one control sets the frequency of backpulse, while the other control sets the duration of the backpulse.

3.1.1 Operation

All experiments were run using the bench top apparatus as described in section 3.1. In all experiments the bench top apparatus was run in cross-flow mode at an average temperature of 27° C, with range of 26° to 29° C. The bench top apparatus was always operated so that the retentate was sent back to the feed tank. The bench top apparatus was also always operated so that the permeate, if collected in a designated experiment, was sent back to the feed tank.

3.1.2 Modes of Operation

To determine the ammonia oxidizing ability due to growth on the membrane, the bench top apparatus was operated in either a "filtering mode" or a "non-filtering mode". The filtering mode established the rate of ammonia oxidation with the aid of membrane filtration process. The Non-Filtering Mode established the rate of ammonia oxidation of the membrane apparatus without the aid of the membrane filtration process.

3.1.3 Filtering Mode

In the "filtering mode" of operation, the solution within the bench top apparatus was filtered by the membrane. Permeate was collected and sent back to the feed tank. Operation in the filtering mode uses a driving force across the membrane surface to enable filtration. To enable operation in filtering mode valve E in Figure 7 was left in the open position. Opening valve E enabled the solution to be filtered through the membrane and the process of membrane filtration to occur.

3.1.4 Non-Filtering Mode

In the "non-filtering" mode of operation, filtering by the membrane was disabled. The non-filtering mode was needed to establish the degrading ability of organisms attached to the internal surfaces (~1500 cm2) of the bench top apparatus without the added effect of the process of membrane filtration. Operation in the non filtering mode was established by the closing of permeate valve E on Figure 7. The non-filtering mode did not enable the solution to be filtered through the membrane. Thus, the actual process of membrane filtration did not occur.

3.1.5 Back Pulse

During operation in permeate mode the back pulsing device was also used. A back pulse was used to allow for extended experimental runs and to lessen the effects of fouling on the membrane. The operational conditions of the back pulse were: a backpulse duration of 0.5 seconds, a back pulse frequency of 1 pulse every 120 seconds, at a backpulse pressure of 100 psi. A compressed nitrogen cylinder was used as the pressure source.

3.2 SUBSTRATES, SAMPLING, AND SAMPLE ANALYSIS

3.2.1 Artificial additions

At the start of each experimental run, deionized water, ammonia, Na₂CO₃, and trace nutrients were added to the feed tank of the bench top apparatus. During the course of an

experimental run, the volume of the feed tank would slowly decrease. The decrease in volume is in large part due to sampling throughout the course of the run, and to a lesser degree, due to evaporation of the feed solution to the atmosphere. Prior to the start of each experimental run approximately 3 liters of deionized water was added to the apparatus along with ammonia, Na₂CO₃, and trace nutrients. Trace nutrients were added in solution form and were a comprised of a magnesium sulfate solution, ferric chloride solution, calcium chloride solution, and a phosphate buffer made according to Standard Methods (Standard Method 5210). Approximately 10 ml of each trace nutrient solution was added at the start of each experimental run.

Depending on the operational parameters and rate at which organisms were oxidizing ammonia, a desired amount of ammonia and alkalinity was added to get the feed solution to the concentrations as needed. For the duration of an experimental run it was necessary to produce several artificial concentration spikes of ammonia and alkalinity. Typically, in any experimental run, the ammonia concentration and alkalinity concentration was spiked two to four times. Concentration spikes were achieved by preparing a solution of ammonia and alkalinity, adjusting the pH to approximately 7.4 ranging from 7.1 to 7.8. The prepared concentrations of ammonia as N, and Alkalinity as CaCO₃ ranged from 100-300 mg/l and 800-1800 mg/l, respectively. The prepared solutions of Ammonia and alkalinity were then added to the feed tank several times during an experimental run. The concentration of ammonia as N, and Alkalinity as CaCO₃ in the feed tank ranged from 10-30 mg/l and 80-180 mg/l, respectively.

3.2.2 Sampling

To monitor the conditions of the apparatus, samples were taken over the course of each experimental run. Experimental runs lasted anywhere from 3 to 15 days containing 2 to 4 concentration spikes per experimental run. During the oxidation of a typical concentration spike, approximately 4 to10, 300 ml samples were taken from the bench top apparatus at various times, depending on the start of the test and rate at which apparatus was operating. All samples were taken by opening the valve D of the feed sampling line as seen in Figure 8. Approximately 300 ml was taken per sample which represented the overall concentration of the solution in the bench top apparatus at the given time of sampling. The samples were then taken and analyzed for ammonia concentration, alkalinity, and pH.

3.2.3 Sample Analysis

Samples were analyzed for ammonia (Standard Method 4500-NH₃ D), alkalinity (Standard Method 4500-H B), and pH (Standard Method 2320). Testing equipment for ammonia analysis was an ammonia selective electrode model by Fisher, and a Fisher Accumet model 50 pH/Ion/Conductivity Meter. Calibration of the ammonia probe was done by measuring standard solutions of NH₃Cl of 1, 5, 10, 100 (mg/l) and plotting a standard curve. Alkalinity and pH were also both analyzed with a Fisher Accumet model 50 pH/Ion/Conductivity Meter. A glass combination pH probe was used for both pH and Alkalinity measurements.

3.3 EXPERIMENTAL PROTOCOL

The purpose of this section is to describe the experimental procedures used. A series of tests were performed on the bench top unit in order to determine the ability of the biofouling layer of the membrane to degrade ammonia. Section 3.3.1 describes the physical chemical ammonia loss in the apparatus. Section 3.3.2 describes the inoculation of nitrifying organisms in the bench top apparatus. Section 3.3.3 describes the varied operational parameters used in the bench top apparatus in order to isolate any phenomena along the membrane surface.

3.3.1 Physical – Chemical Ammonia Loss

The bench top apparatus was operated with no membrane and without inoculation to determine the physical – chemical loss ammonia in the apparatus. This experiment is used to show that the majority of ammonia oxidation with inoculation and a membrane in the system is by biological means.

3.3.2 Inoculation

The membrane apparatus was inoculated with organisms from 12 liters of secondary effluent obtained from the secondary clarifier of Alcosan (Allegheny County Sanitary Authority). The secondary effluent was artificially spiked with NH₄Cl and Na₂CO₃ to give favoring conditions for nitrifier growth. The artificially spiked secondary effluent was run for approximately 10 days while, monitoring the oxidation of ammonia and alkalinity consumption.

The ammonia and alkalinity concentration was repeatedly spiked three times in the bench top apparatus during inoculation to establish a viable population of nitrifying organisms throughout the apparatus.

3.3.3 Methodology of Testing

After a slurry of nitrifying organisms were established in the tank, the bench top membrane apparatus was used for a series of tests to determine the membranes ability to degrade ammonia. The same experiments were run in the "filtering mode" and the "non- filtering mode" to isolate nitrifying activity in the biofouling layer of the membrane. Experiments run in the filtering mode were to establish the rate at which ammonia was oxidized by organisms in the bench top apparatus plus organisms accumulating on the surface of the membrane. Experiments run in the non- filtering mode were to establish the oxidation rate of ammonia in the bench top apparatus only, without the aid of a trans-membrane pressure applied to membrane.

The operating parameters of the bench top apparatus that were varied were transmembrane pressure and cross-flow velocity. Trans-membrane pressure was varied in three experiments and run in both filtering mode and non-filtering mode for a total of 6 experimental runs. The terminology of trans-membrane pressure is still used in the non-filtering mode even though there is no pressure differential occurring within the membrane (since the filtrated valve is closed) to give an equal comparison to the filtering mode. Trans-membrane pressure was initially set at 10 psi and changed to 20 psi and finally to 30 psi in three experimental runs in both modes of operation. Cross-flow velocity was varied in a similar fashion with three experiments and run in both filtering mode and non-filtering mode for a total of 6 experimental runs. Cross-flow velocity was initially set at 8.1 ft/s and changed to 16.1 ft/s and finally to 24.2 ft/s in three experimental runs in both modes of operation.

Oxidation rates in the two different modes were then compared. A discussion of the Influence of trans-membrane pressure and cross-flow velocity is given. Finally, a discussion of the oxidation rate per surface area of membrane and bench top apparatus is given.

4.0 RESULTS AND DISCUSSION

This section will discuss the results of four experimental steps. The experimental steps were used to determine if the process of membrane filtration can support a biofilm that may oxidize ammonia simultaneously. The section describes the results of the research in a progressive format. The experiments described include: physical – chemical ammonia loss, initial inoculation, results of ammonia oxidation in filtration mode and non-filtering mode, comparison and discussion of the two operation modes, and finally a comparison of the growth rates on the internal surface area of the bench top apparatus and the internal surface area of the membrane.

4.1 PHYSICAL – CHEMICAL AMMONIA LOSS IN BENCH TOP SYSTEM

As described in Section 3.2, the bench top apparatus was operated with no membrane and without inoculation of nitrifying organisms. This procedure was used to determine the physicalchemical loss of ammonia in the system. Figure 8 shows the results of this procedure. The experiment was run for approximately 170 hrs and the average ammonia loss per hour was found

to be (.027 mg /l –hr).



Figure 8 Physical – Chemical Ammonia Loss in Bench Top System

4.2 INOCULATION OF NITRIFYING ORGANISMS

As described in section 3.2.3, the bench top apparatus was inoculated with nitrifying organisms. The procedure created a slurry of nitrifying organisms. The experiment was run for approximately 10 days. The ammonia and alkalinity concentrations were spiked three times in the bench top apparatus during inoculation to establish a viable population of nitrifying organisms. The inoculation of organisms in the apparatus is shown by Figures 9 and 10. Figures 9 and 10 show three successive spikes of ammonia and alkalinity concentrations, respectively. In each of the three spikes, ammonia and alkalinity concentrations are consumed by organisms in the apparatus to minimal concentrations. From the first to the third spike, it can be seen that the slope of the three degradation lines are increasing. The increasing slopes suggested that the nitrifier population was accumulating and was zero order; likely in the log growth phase of growth. The nitrification rate appears to be reaching approximately steady state by the third inoculation based on the convergence of slope rates from the first to the third inoculation.



Figure 9: Inoculation of Nitrifying Organisms



Figure 10: Alkalinity Analysis during Accumulation of Nitrifying Organisms

4.3 FILTERING MODE

Rates of ammonia oxidation and alkalinity consumption were monitored in five experimental runs. Experimental runs lasted from approximately 100 hrs to 300 hrs. Each experimental run was run in filtering mode where the driving force across the membrane surface was enabled and filtration occurred, as described in section 3.1.2. In each run, the bench top

membrane apparatus was already inoculated with organisms and spiked with ammonia, alkalinity, and trace nutrients, as described in section 3.2.4.

4.3.1 Ammonia Analysis

Figure 11 shows the ammonia concentration in the bench top apparatus for the first experimental run as a function of time. Four successive concentration spikes were made over the course of the experimental run and their corresponding changes in concentration are shown in Figure 11. Each set of data points relative to the four spikes in the apparatus can be analyzed by the slope of their respective trend lines. The linear slope of the four trend lines indicates that the oxidation rate of ammonia follows a zero order reaction rate. A zero order reaction can be expected as the substrate concentrations in this research typically are over the minimal value of 2.5 mg/l (Kiff, 1972). The slope of the trend lines then represents the kinetic value constant of a zero order reaction given in equation 15 of Section 2.3.

The first data set and spike in the apparatus gives an oxidation rate of ammonia at approximately 0.35 (mg/l-hr). The second, third, and fourth spikes in the apparatus give a oxidation rate of ammonia at 0.33, 0.32, and 0.31 (mg/l-hr), respectively. These rates where then averaged to give 0.33 (mg/l-hr) as shown in Table 4.

The procedure used to get the average oxidation rate of ammonia in the bench top apparatus for the first experimental run was then repeated for the four additional experimental runs. In the four additional experimental runs, the pressure and the cross-flow velocity was changed to analyze the change in the oxidation rate of ammonia. The cross-flow velocity, transmembrane pressure, and resulting ammonia reduction rates of the four additional runs are given in Tables 4 and 5. The average rates are then plotted in comparison to the non-filtering mode

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rates in Section 4.5 and 4.6. Figures similar to Figure 11 used to get the resulting ammonia reduction rates for each of the experimental runs are given in Appendix B.



Figure 11: Ammonia Analysis of Filtering Mode at 8.1 ft/s and 10 PSI

Filtering Mode @ 1.5 GPM					
		NH ₃ Oxic	lation Rate	e (mg/l-hr)	
Pressure (psi)	1 st Run	1 st 2 nd 3 rd Run Run Run			Average
10	0.35	0.33	0.32	0.31	0.33
20	0.40	0.38	0.37		0.38
30	0.43	0.51	0.51	0.43	0.47

Table 4: Ammonia Oxidation Rates of Filtering Mode varying Trans-membrane Pressure

 Table 5: Ammonia Oxidation Rates of Filtering Mode varying Cross-flow Velocity

Filtering Mode @ 20 PSI					
		NH3 Oxid	lation Rate	(mg/l-hr)	
Cross Flow velocity	$1^{\text{st}} \qquad 2^{\text{nd}} \qquad 3^{\text{rd}} \qquad 4^{\text{th}}$ Run Run Run A				
(ft/s)	Run	Run	Run	Run	Average
(ft/s)	Run	Run	Run	Run	Average
(ft/s) 8.1	Run 0.40	Run 0.38	Run 0.37	Run	Average 0.38
(ft/s) 8.1 16.2	Run 0.40 0.83	Run 0.38 0.98	Run 0.37 0.79	Run	Average 0.38 0.87

4.3.2 Alkalinity Analysis

Figure 12 shows the alkalinity concentration in the bench top apparatus as a function of time. The rates of alkalinity consumption were analyzed for each of the six experimental runs in the same fashion as described for the rates of ammonia oxidation. These rates and averages are shown in Tables 6 and 7. Figures similar to Figure 12 for each experimental run are given in Appendix C.



Figure 12: Alkalinity Analysis of Filtering Mode at 8.1 ft/s and 10 PSI

Table 6: Alkalinity Reduction Rates of Filtering Mode varying Trans-membrane Pressure

Filtering Mode @ 8.1 ft/s					
	All	kalinity	Reducti	ion Rate	e (mg/l-hr)
Pressure (psi)	1st2nd3rd4thRunRunRunRunAverage				Average
10	2.80	2.30	2.20	2.16	2.37
20	2.72	1.96	2.72		2.47
30	4.04	2.50	3.26		3.27

Filtering Mode @ 20 psi					
	Alka	linity Red	luction Re	ate (mg/l-hr)	
Cross Flow velocity (ft/s)	1 st Run	2 nd Run	3 rd Run	Average	
8.1	2.72	1.96	2.72	2.47	
16.2	5.36	6.34	6.34	6.01	
24.2	9.42	8.74	7.54	8.57	

 Table 7: Alkalinity Reduction Rates of Filtering Mode varying Cross-flow Velocity

4.3.3 Comparison of Ammonia and Alkalinity reductions in Filtering Mode

Tables 8 and 9 show the mg CaCO₃ consumed per mg NH₄-N oxidized for the experimental runs varying the trans-membrane pressure and cross-flow velocity, respectively. The ratio is given to show the correlation of ammonia oxidation to alkalinity consumption for further support of the biological activity in the apparatus. Values shown range from 6.43 to 7.79 mg CaCO₃ consumed per mg NH₄-N oxidized, which is close to the values reported in Table 2 and the theoretical value of 7.1.

	Filtering Mode @ 8.1 ft/s			
Pressure (psi)	Oxidation Rate of Ammonia (mg/l-hr)	Alkalinity Reduction Rate (mg/l- hr)	Ratio: mg CaCO ₃ consumed per mg NH ₃ -N oxidized	
10	0.33	2.37	7.25	
20	0.38	2.47	6.43	
30	0.47	3.27	6.95	

 Table 8: Ratio of Alkalinity / Ammonia Filtering Mode at 8.1 ft/s

	Filtering Mode @ 20 psi			
Cross Flow velocity (ft/s)	Oxidation Rate of Ammonia (mg/l-hr)	Alkalinity Reduction Rate (mg/l- hr)	CaCO ₃ consumed per mg NH ₃ -N oxidized	
8.1	0.38	2.47	6.49	
16.2	0.87	6.01	6.91	
24.2	1.10	8.57	7.79	

 Table 9: Ratio of Alkalinity / Ammonia Filtering Mode at 20 psi

4.4 NON- FILTERING MODE

Rates of ammonia oxidation and alkalinity consumption were monitored in six experimental runs in the same fashion as described in Section 4.2. These experimental runs were operated in non- filtering mode as described in Section 3.1.3, rather than in filtering mode used in section 4.2.

4.4.1 Ammonia Analysis

Figure 13 shows the ammonia concentration in the bench top apparatus for the first experimental run as a function of time. Each set of data points relative to the four spikes in the apparatus can be analyzed by the slope of their respective trend lines as in Section 4.4. The slope of the four trend lines indicates that the oxidation rate of ammonia follows a zero order reaction

rate as in Section 4.2. The slope value listed in the figures corresponds to the kinetic value constant of zero order reaction as in Section 4.3. The rates and averages of the experimental run along with four addition runs are then shown in Tables 10 and 11, much like in Section 4.3.



Figure 13: Ammonia Analysis of Non-Filtering Mode at 8.1 ft/s and 10 PSI

Non-Filtering Mode @ 8.1 (ft/s)				
		Oxidation	Rate (mg/l-hr)	
Pressure (psi)	1 st slope	Average		
10	0.26	0.24	0.26	0.25
20	0.34	0.25	0.31	0.30
30	0.25	0.24	0.23	0.24

Table 10: Ammonia Oxidation Rates of Non-Filtering Mode varying Trans-membrane Pressure

Table 11: Ammonia Oxidation Rates of Non-Filtering Mode varying Cross-flow Velocity

	Non-Filtering Mode @ 20 PSI				
		Oxidation .	Rate (mg/l-hr	•)	
Cross Flow velocity (ft/s)	1 st slope	2 nd slope	3 rd slope	Average	
8.1	0.34	0.28	0.32	0.31	
16.2	0.33	0.32		0.32	
24.2	0.58	0.72	0.77	0.69	

4.4.2 Alkalinity Analysis

Figure 14 shows the alkalinity concentration in the bench top apparatus as a function of time. The rates of alkalinity consumption were analyzed for each of the six experimental runs in the same fashion as described for the rates ammonia oxidation. The rates and averages are

shown in Tables 12 and 13. Figures similar to Figure 14 for each experimental run are given in Appendix C.



Figure 14: Alkalinity Analysis of Non-Filtering Mode at 8.1 ft/s and 10 PSI

 Table 12: Alkalinity Reduction Rates of Non-Filtering Mode varying Trans-membrane Pressure

Non-Filtering Mode @ 8.1 ft/s					
	Alkali	nity Redu	ction Rate	e (mg/l-hr)	
Pressure (psi)	1 st 2 nd 3 rd Average				
10	1.86	1.64	1.72	1.74	
20	2.00	2.20	1.80	2.00	
30	1.96	1.94	2.12	2.01	

Non-Filtering Mode @ 20 PSI				
	Alka	linity Rea	luction Rate	e (mg/l-hr)
Cross Flow velocity (ft/s)	1 st	2 nd	3 rd	Average
8.1	2.00	2.20	1.80	2.00
16.2	3.60	3.28		3.44
24.2	5.02	6.02	7.18	6.07

Table 13: Alkalinity Reduction Rates of Non-Filtering Mode varying Cross-flow Velocity

4.3.3 Comparison of Ammonia and Alkalinity reductions in Non-Filtering Mode

Tables 14 and 15 show the mg CaCO₃ consumed per mg NH₃-N oxidized for the experimental runs varying the trans-membrane pressure and cross flow velocity, respectively. The ratio is given to show the correlation of ammonia oxidation to alkalinity consumption for further support of the biological activity in the apparatus. Values shown range from 6.4 to 10.6 mg CaCO₃ consumed per mg NH₃-N oxidized which is higher than the values reported in table 2 and the theoretical value of 7.1. The range would be much closer to the theoretical and experimental values if the experimental run of 16.2 ft/s at 20 psi is not included (6.4 - 8.8 mg/l). It will be shown more clearly in Section 4.5.2 Figure 15 that the data point of 16.2 ft/s at 20 psi is more likely an outlier as it not necessarily consistent with the rest of the data.

	Non-Filtering Mode @ 8.1 ft/s				
Pressure (psi)	Oxidation Rate of Ammonia (mg/l-hr)	Alkalinity Reduction Rate (mg/l- hr)	mg CaCO ₃ consumed per mg NH ₄ -N oxidized		
10	0.25	1.74	6.86		
20	0.30	2.00	6.75		
30	0.24	2.01	8.37		

Table 14: Ratio of Alkalinity / Ammonia Non-Filtering Mode at 8.1 ft/s

Table 15: Ratio of Alkalinity / Ammonia Non-Filtering Mode at 20 psi

	Non-Filtering Mode @ 20 psi				
Cross Flow velocity (ft/s)	Oxidation Rate of Ammonia (mg/l-hr)	Alkalinity Reduction Rate (mg/l- hr)	mg CaCO ₃ consumed per mg NH ₄ -N oxidized		
8.1	0.31	2.00	6.45		
16.2	0.32	3.44	10.63		
24.2	0.69	6.07	8.80		

4.5 ANALYSIS OF FILTERING MODE VS. NON- FILTERING MODE

4.5.1 Ammonia Oxidation varying the Pressure

Figure 15 shows the oxidation and consumption rates of ammonia and alkalinity respectively in both modes of operation. Alkalinity consumption rates were measured to show the similar tendencies in alkalinity consumption compared with ammonia oxidation. Ammonia

data is only discussed as the primary difference between ammonia and alkalinity data is the ratio (mg CaCO₃ consumed per mg NH₃-N oxidized) discussed in Sections 4.3.3 and 4.4.3. The ratio can be observed in the two different axis of Figure 15. Oxidation rates of ammonia are plotted against 3 different trans-membrane pressures; 10, 20 and 30 psi. Each data point represents the average oxidation rates of the experimental runs, as described in Sections 4.3 and 4.4. Each data point is plotted with error bars to signify how the oxidation rates in the 3 to 4 degradation slopes in an experimental run differed.



Figure 15: Comparison of the Ammonia Oxidation Rate and the Alkalinity Consumption Rate between the Filtering Mode and the Non-Filtering Mode varying the Transmembrane Pressure

It is evident from Figure 15 that the ammonia oxidation rate in the filtering mode is higher than that of the non-filtering mode. The increase in oxidation rate from the non-filtering mode to the filtering mode, suggests there are organisms within the fouling layer of the membrane, and that they are increasing the overall oxidation rate of the system. As explained in Section 3.1.2, the only difference between the two modes is the actual filtering of membrane in the filtering mode. The actual oxidation of ammonia is suggested to happen in two different ways:

- Actual filtering of feed through the membrane and proposed biofilm (oxidation in the perpendicular direction).
- 2. Oxidation of the feed where the trans-membrane pressure induces the proposed biofilm which metabolizes ammonia from the influent side of the membrane to the effluent side of the membrane (oxidation in the parallel direction).

The actual increase in oxidation rate from the non-filtering mode to filtering mode is suggested to be a combination of the two processes. Discussed below in further detail is the analysis of the process of oxidation in the parallel direction and the process of oxidation in the perpendicular direction.

In Figure 15 the ammonia oxidation rate in the filtering mode is linearly increasing with increased trans-membrane pressure while the ammonia oxidation rate in the non-filtering mode is staying approximately constant with increased trans-membrane pressure. The increasing ammonia oxidation rate in the filtering mode compared to the approximately constant ammonia oxidation rate in the non-filtering mode suggests that only trans-membrane pressure is influential in the filtering mode of operation. Since the only difference between the two modes of operation

was the actual filtering of membrane in the filtering mode, the membrane is solely responsible for the increased oxidation rates with increased trans-membrane pressure.

The operational parameter of permeate flux rate was taken during the experimental runs in the filtering mode to further understand the phenomena occurring on the membrane surface. The steady state flux rates were found for each experimental run and used for analysis. The estimated average steady state flux rates were found to be 100, 60, and 60 (l/hr-m2) corresponding to the runs at 10, 20, and 30 psi, respectively (values of flux corresponding to time into each run are listed in Appendix A in the filtering modes). If these steady state values were increasing with increased trans-membrane pressure, the increase of ammonia oxidation rate from the non-filtering mode to filtering mode could be explained by the increased oxidation in the perpendicular direction which is shown graphically in Figure 16. However, since these steady state flux values are not increasing with trans-membrane pressure, the only explanation for increased oxidation rates with increased trans-membrane pressure is the operational parameter of trans-membrane pressure itself.



Perpendicular Direction C_e

Figure 16: Oxidation Perpendicular Direction

It is suggested that the phenomena of increased oxidation rates with increased transmembrane pressure can be related to the sticking efficiency of the membrane surface (Equation 6, Section 2.2.1). In a high sheer environment, as in cross-flow micro-filtration, increasing the trans-membrane pressure would essentially increase the sticking efficiency of the membrane. As the trans-membrane pressure is increased, essentially more filtering force is seen at the membrane surface. It is suggested that this increase in filtering force then holds more organisms along the sidewalls of the membrane which allows for higher ammonia oxidation rates with increased trans-membrane pressures in the filtering mode.

Ammonia oxidation however, in the perpendicular direction is also evident from Figure 15. Considering the steady state flux rates once again, it suggested that the variation of the ammonia oxidation rate data points from the trend line values are attributed to the differences in flux rates in each of the runs. Because more or less permeate was collected, more or less flow through the membrane was occurring. For example, if increased flow through the membrane occurred, the biofilm within the fouling layer of the membrane would slightly oxidize the ammonia in the system at a faster rate. This is possible since the bench top apparatus was always operated where the permeate was recycled back to the feed tank. Consequently, the variations in data points from their respective trend line values were found to be correlated by the following: the higher the observed steady state flux of the experimental run, the higher the ammonia oxidation rate of the experimental run, and vice versa. These phenomena can be observed in all three data points where:

 The data point corresponding to 10 psi is significantly higher than its corresponding trend line value because of a high (100 l/hr-m2) steady state flux rate.

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- 2. The data point corresponding to 20 psi is lower than its corresponding trend line value because of a low (60 l/hr-m2) steady state flux rate.
- 3. The data point corresponding to 30 psi is higher but should be lower than its corresponding trend line value because of a low (60 l/hr-m2) steady state flux rate. The data point corresponding to 30 psi would be lower than the trend line value if a new trend line was drawn according to the revised values at 10 & 20 psi.

Observation of steady state flux rates on the ammonia oxidation rate of the system suggests that oxidation in the perpendicular direction is occurring.

4.5.2 Ammonia Oxidation varying the Cross-flow Velocity

Figure 17 shows the oxidation and consumption rates of ammonia and alkalinity respectively in both modes of operation compared to the cross–flow velocity. Alkalinity consumption rates were measured to show the similar tendencies in alkalinity consumption compared with ammonia oxidation. Ammonia data is only discussed as the primary difference between ammonia and alkalinity data is the ratio (mg CaCO₃ consumed per mg NH₃-N oxidized) discussed in Sections 4.3.3 and 4.4.3 which can be observed in the two different axis of Figure 17. Each data point represents the average ammonia oxidation rates of the experimental runs as described in Sections 4.3 and 4.4. Each data point is also plotted with error bars to signify how the oxidation rates in the 3 to 4 degradation slopes in an experimental run differed.



Figure 17: Comparison of the Ammonia Oxidation Rate and the Alkalinity Consumption Rate between the Filtering Mode and the Non-Filtering Mode varying the Cross Flow Velocity

It is evident in Figure 17 that the ammonia oxidation rate in the filtering mode is higher than that of the non- filtering mode. Similar to Section 4.5.1, the suggested reasoning behind the increase in ammonia oxidation rate for Figure 17 from the filtering mode to the non-filtering mode is the combination of the two ammonia oxidation directions (oxidation in the parallel direction & oxidation in the perpendicular direction). The difference in modes suggests that organisms are again accumulating on the membrane surface and increasing the overall oxidation of ammonia in the apparatus. It is also evident in Figure 17 that the oxidation rates in the filtering mode and the nonfiltering mode are both greatly influenced by the cross-flow velocity. This can be explained by an increasing activity of the nitrifying organisms in the entire apparatus by increasing the crossflow velocity and thereby reducing resistances to mass transfer as explained in Section 2.1.2. It is suggested that the increase in oxidation rates while increasing the cross-flow velocity is primarily due to the oxidation in the parallel direction. Oxidation in the parallel direction is shown graphically in Figure 18. Oxidation in the parallel direction is based on the increasing oxidation rate with increasing cross-flow velocity in the non-filtering mode. In the non-filtering mode only cross-flow velocity is changed while all other operating parameters are constant. Consequently, the only basis for increased oxidation rates while increasing cross-flow velocity is oxidation in the parallel direction as there is no perpendicular flow occurring through the membrane.



Figure 18: Ammonia oxidation in the parallel direction

Although the oxidation rates in both modes are increasing with increasing cross flow velocity, the ammonia oxidation rate in the filtering mode seems to be increasing slightly more than the ammonia oxidation rate in the non- filtering mode. The faster increasing oxidation rate of filtering mode compared to the non-filtering mode suggests that the activity of the organisms

in the filtering mode are increased compared to those in the non-filtering mode while increasing the cross-flow velocity.

The faster oxidation rates from the non-filtering mode to filtering mode are most likely because of the difference in cross-flow velocities at the membrane surface and internal conduits of the bench top apparatus. The cross-flow velocity is directly related to the diameter of the tubular membrane and piping of the bench top apparatus used within these experiments, which are: 7 mm and 20 mm, respectively. Where the cross-flow velocity at the membrane surface would be 8.1 ft/s, the cross-flow velocity within the piping of the system would only be about 1 ft/s. Therefore, as the cross-flow velocity was changed from 8.1 to 16.2 to 24.2 ft/s within the tubular membrane, the cross-flow velocity within the piping of the bench top apparatus was only changed from 1 to 2 to 3 ft/s. According to the laws of mass transfer, the small change in velocity in the piping system could have increased the ammonia oxidation rate by a certain factor while the higher changes in cross-flow velocity seen in tubular membrane could have increased the ammonia oxidation by a much a higher factor. When the change in oxidation rate of the system is compared in the non-filtering mode and filtering mode as a function of cross-flow velocity, the change would be very small since the surface area of the membrane is very small compared to the surface area of the system. In conclusion, it is suggested that the increasing oxidation rate of the filtering mode is related to the higher activity of organisms in the filtering mode. More specifically, the increase in activity while increasing cross-flow velocity is more profound on the membrane in the filtering mode of operation.

Ammonia oxidation in the perpendicular direction is also evident in Figure 17. The operational parameter of permeate flux rate was also taken during the experimental runs in Figure 17 in the filtering mode to further understand the phenomena occurring on the membrane

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surface, similar to Section 4.5.1. The steady state flux rates were found for each experimental run varying the cross-flow velocity. The estimated average steady state flux rates were found to be 60, 130, and 110 (l/hr-m2) corresponding to the runs at 8.1, 16.2, and 24.2 psi, respectively (values of flux corresponding to time into each run are listed in Appendix A in the filtering modes). The relatively same steady flux rates are suggested to be affecting the oxidation rates seen by the system as in Section 4.5.1. The variations in data points from their respective trend line values were found to be correlated in the same fashion as in Section 4.5.1. The higher the observed steady state flux of the experimental run, the higher the ammonia oxidation rate of the experimental run, and vice versa. These phenomena can be observed in all three data points where:

- The data point corresponding to 8.1 ft/s is significantly lower than its corresponding trend line value because of a low (60 l/hr-m2) steady state flux rate.
- The data point corresponding to 16.2 ft/s is significantly higher than its corresponding trend line value because of a high (130 l/hr-m2) steady state flux rate.
- 3. The data point corresponding to 24.2 ft/s is lower but should be higher than its corresponding trend line value because of a higher (110 l/hr-m2) steady state flux rate. The data point corresponding 24.2 ft/s would be higher than the trend line value if a new trend line was drawn according to the revised values at 8.1 & 16.2 ft/s.

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The observation of steady state flux rate on the ammonia oxidation rate of the system suggests that oxidation in the perpendicular direction is also occurring, similar to Section 4.5.1 when in the filtering mode.
4.6 AMMONIA OXIDATION CONSIDERING THE UNIT SURFACE AREA

Assuming the oxidation of ammonia within the apparatus was converted primarily by fixed film organisms, a comparison between the ammonia oxidation rate on the bench top apparatus internal surfaces and the membrane internal surface can be made. Table 18 lists the ammonia oxidation rates determined in each experimental run and the ammonia oxidation rates correlating to the unit surface area. The ammonia oxidation rate per unit surface area was based on the surface areas listed in Section 3.1, where the membrane surface area was 55 cm² and the estimated bench top apparatus surface area was 2196 cm². The trend line ammonia oxidation values described in Section 4.5.1 and 4.5.2 were also used to determine the ammonia oxidation rate per unit surface area was estimated based on the type and amount of surface area where organisms could grow. The ammonia oxidation rates due to the internal surfaces of the bench top apparatus alone are considered to be the ammonia oxidation rates shown in the non-filtering mode. The ammonia oxidation rates from the non-filtering mode.

		Oxidation Rate (mg/l-hr) (mg/l-hr-m2)					Percent increase from
Pressure (psi)	Cross- Flow Velocity	Filtering	Non- Filtering	Difference	Surface of Membrane Filtration apparatus	Surface of Membrane	membrane filtration surface to membrane surface (%)
10	8.1	0.32	0.27	0.05	0.12	0.94	763
20	8.1	0.39	0.26	0.13	0.12	2.38	1984
30	8.1	0.47	0.26	0.21	0.12	3.81	3271
20	8.1	0.42	0.25	0.17	0.11	3.14	2753
20	16.2	0.78	0.44	0.34	0.20	6.24	3107
20	24.2	1.14	0.63	0.51	0.29	9.30	3246

Table 16: Ammonia oxidation rates considering type of surface area and amount

From Table 18 it is clear that the ammonia oxidation rates of the organisms on the membrane surface are much higher than that observed on the internal surface of the bench top unit. As described earlier in Section 4.5, it is suggested that the difference is due to viable organisms within the fouling layer. Also suggested in Section 4.5 is ammonia oxidation in two directions, which causes the accumulation of organisms on the membrane surface.

4.6.1 Ammonia Oxidation rates varying cross-flow velocity based on unit surface area

The ammonia oxidation rate at the membrane surface was 3.14, 6.24, and 9.30 (mg/l-hr-m²), whereas the internal surface of the bench top apparatus was 0.11, 0.20, and 0.29 (mg/l-hr-m²) at the operational parameters 8.1, 16.2, and 24.2 (psi), respectively. These significant

differences in ammonia oxidation rates, further support, that the nitrifying organisms are actively oxidizing ammonia in the apparatus.

In table 16, the slight percent increase shown in oxidation rate from the bench top apparatus internal surface to the membrane internal surface varying cross-flow velocity, is suggested to be due to the mass transfer differences as described in Section 4.5.2. The difference in oxidation rates in the two surfaces as a function of the cross-flow velocity can be seen graphically in Figure 19.



Figure 19: Ammonia Oxidation Rate on Membrane Surface varying Cross Flow Velocity

4.6.2 Ammonia Oxidation rates varying trans-membrane pressure based on unit surface area

Based on the unit surface area, the ammonia oxidation rate as a function of transmembrane pressure was 0.94, 2.38, 3.81 (mg/l-hr-m²) at the membrane surface, whereas the internal surface of the bench top apparatus was 0.12, 0.12, 0.12 (mg/l-hr-m²) at the operational parameters 10, 20, 30 (psi), respectively. These significant differences in ammonia oxidation rates, also shown in Section 4.6.1, further support, that the nitrifying organisms are actively oxidizing ammonia in the apparatus.

As shown in Table 18, the percent increase from the bench top apparatus internal surface to the membrane internal surface varying the trans-membrane was 763, 1984, 3271 % at 10, 20, and 30 psi, respectively. The average steady state flux rate measured at each of the transmembrane pressures was essentially the same, at 100, 60, and 60 (l/hr-m2) at 10, 20, and 30 psi, respectively. As can be seen from the similar steady state flux rates, the percent increase in oxidation rate from the bench top apparatus internal surface to the membrane internal surface can only be attributed to the increase in trans-membrane pressure, as described earlier in Section 4.5.1. Thus, the influence of trans-membrane pressure to the ammonia oxidation rate on the membrane surface is also further supported

The difference in oxidation rates from the internal surface of the membrane filtration apparatus to the internal membrane surface as a function of the trans-membrane pressure can be seen graphically in Figure 20.

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Figure 20: Ammonia oxidation rate on Membrane Surface

5.0 SUMMARY AND CONCLUSIONS

This investigation was aimed at the determination of the existence and capability of a viable nitrifying biofilm within the fouling layer of a ceramic membrane micro-filter. The membrane used was a $0.2 \ \mu m$ ceramic tubular membrane used in cross-flow operation. Nitrifying organisms were inoculated into a bench top filtration apparatus to oxidize ammonia and the corresponding rates of ammonia oxidation were measured in two different operating modes.

A bench top apparatus was operated in two modes, a "Filtering Mode" and a "Non-Filtering Mode", to isolate any ammonia oxidation occurring on the membrane surface. The filtering mode established the rate of ammonia oxidation with the aid of membrane filtration process. The non-filtering mode established the rate of ammonia oxidation of the membrane apparatus without the aid of the membrane filtration process. Ammonia oxidation rates were determined in six different experimental runs in the non-filtering mode and the filtering mode. The comparison of the two modes showed a significant increase in the oxidation rate of the filtering mode over the non-filtering mode.

The ammonia oxidation rates corresponding to filtering mode and non-filtering mode can be seen in the following table.

	Ammonia Oxidation Rate (mg/l-hr)							
Operating Parameters	8.1 ft/s 10 PSI	8.1 ft/s 20 PSI	8.1 ft/s 30 PSI	8.1 ft/s 20 PSI	16.2 ft/s 20 PSI	24.2 ft/s 20 PSI		
Filtering Mode	0.32	0.39	0 47	0.42	0.78	1 14		
	0.02	0.00	0111	0112	0110			
Non-Filtering Mode	0.27	0.26	0.26	0.25	0.44	0.63		

 Table 17 Ammonia Oxidation Rates for each mode

The differences in ammonia oxidation rate suggest that viable nitrifying organisms will undergo nitrification within the fouling layer of a cross-flow micro-filtration.

Ammonia oxidation rates were also considered based on unit surface area. The unit surface area rates were determined by the internal membrane surface area and the internal bench top apparatus surface area. The ammonia oxidation rates due to the internal surfaces of the bench top apparatus alone are considered to be the ammonia oxidation rates shown in the non-filtering mode. The ammonia oxidation rates due to the internal membrane surfaces are considered to be the difference in ammonia oxidation rates from the non-filtering mode to filtering mode. The ammonia oxidation rates corresponding to the surface of the membrane and the bench top apparatus surface can be seen in the following table.

	Ammonia Oxidation Rate (mg/l-hr-m ²)									
Operating Parameters	8.1 ft/s 10 PSI	8.1 ft/s 20 PSI	8.1 ft/s 30 PSI	8.1 ft/s 20 PSI	16.2 ft/s 20 PSI	24.2 ft/s 20 PSI				
Membrane Surface	0.94	2.38	3.81	3.14	6.24	9.3				
Bench Top Apparatus Surface	0.12	0.12	0.12	0.11	0.2	0.29				

 Table 18 Ammonia Oxidation Rates pertaining to each surface

The differences in ammonia oxidation rate suggests that not only will viable nitrifying organisms undergo nitrification within the fouling layer of a cross-flow micro-filtration membrane, they will undergo nitrification at rate approximately 20 times faster than that seen occurring on the internal surface of the bench top apparatus.

Alkalinity consumption was also measured in two operating modes to show the biological nature of the system. The average ratio of mg of Alkalinity as CaCO₃ consumed per mg of NH₃-N was found to be 7.6 which is close to the theoretical value of 7.14.

The influence of the operational parameters of cross flow velocity and trans-membrane pressure was also determined in the research. The ammonia oxidation rate as a function of cross-flow velocity was 3.14, 6.24, and 9.30 (mg/l-hr-m²) at the membrane surface, whereas the internal surface of the bench top apparatus was 0.11, 0.20, and 0.29 (mg/l-hr-m²) at the operational parameters 8.1, 16.2, and 24.2 (psi), respectively. Both modes of operation showed that the increase in cross-flow velocity increased the ammonia oxidation rate of the system. This suggested that the activity of the organisms was increased by means of reducing resistances to mass transfer. This also suggested that ammonia oxidation in the "parallel direction" on the membrane surface was possible. Oxidation in the "parallel direction" can be thought of as a situation were organisms are oxidizing ammonia is from the influent end of the membrane to the effluent end of the membrane. The opposite of oxidation in the "parallel direction" can be thought be oxidation in the "perpendicular direction" can be thought of as a situation were the organisms are oxidizing ammonia as it passes through the

biofilm and pores of the membrane to become the permeate. In this situation, ammonia oxidation is from the retentate to the permeate.

The ammonia oxidation rate as a function of trans-membrane pressure was also determined at the membrane surface. The ammonia oxidation rates at the membrane surface were 0.94, 2.38, 3.81 (mg/l-hr-m²), whereas the internal surface of the bench top apparatus was 0.12, 0.12, 0.12 (mg/l-hr-m²) at the operational parameters 10, 20, 30 (psi), respectively. Consequently, the percent increase from the bench top apparatus internal surface to the membrane internal surface varying the trans-membrane pressure from 10, 20, and 30 psi was 763, 1984, 3271 %, respectively. The percent increase varying the trans-membrane and the reduced resistances to mass transfer at the membrane surface. The increased sticking efficiency allows for more organisms per unit surface area and the reduced resistances to mass transfer seen at the membrane surface allow for high conversion rates.

The influence in permeate flux rates, oxidation in the "perpendicular direction", were also determined in the research. As the steady state permeate flux rate was varied in each experimental run the corresponding ammonia oxidation rate seemed to be related. It is then also suggested, that oxidation in the "perpendicular direction" was occurring.

Finally, it is suggested that the increase in ammonia oxidation rate from the filtering mode to the non-filtering mode is the combination of two ammonia oxidation directions. The two directions being: oxidation in the "perpendicular direction", and oxidation in the "parallel direction". Oxidation in the "parallel direction" offers a new concept of possible biological treatment using cross-flow micro-filtration. With an increased number of organisms per unit surface area and very reduced resistances to mass transfer, the possibility of a very fast treatment

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system could be possible. In this new concept of treatment using cross-flow micro-filtration, the retentate and would actually be the treatment objective rather than the permeate.

6.0 RECOMMENDATIONS FOR FUTURE RESEARCH

In this research it has been found that nitrifying bacteria will undergo nitrification within the fouling layer of a cross-flow micro filtration system. From this research the ammonia oxidation by bacteria can happen in two ways.

- 1) The organisms are oxidizing ammonia as it passes through the biofilm and pores of the membrane to become the permeate (Oxidation in the perpendicular direction).
- 2) The organisms are oxidizing ammonia as it passes parallel to the biofilm of the membrane and the oxidation of ammonia is from the influent end of the membrane to the effluent end of the membrane (Oxidation in the parallel direction).

Within these two options lies a major difference. If the nitrifying bacteria are oxidizing the ammonia in the perpendicular direction, the treatment of the solution will only be minimal since the solution is passed though the pores relatively quickly, and the permeate would be essentially the same concentration as the retentate. If the nitrifying bacteria are treating the ammonia in the parallel direction it may be applicable for large membrane treatment systems. In large membrane treatment systems there are many linear feet of membrane resulting in large surface area for membrane filtration. If the nitrifying bacteria along the sidewalls of the membranes in the membrane filtration system act to oxidize ammonia in the parallel direction, the concentration of ammonia by the last stage could possibly be very much reduced. Since ammonia is soluble, it should start at the membrane filtration system at a certain concentration and should end the membrane filtration apparatus at that same concentration. But, if the organisms along the sidewalls of the membrane system are oxidizing ammonia in the parallel direction throughout the many stages of a large membrane filtration system it is very possible that the ammonia concentration in the latter stages of the membrane filtration plant will be significantly reduced.

Suggestions for research:

- Determine the portion of ammonia oxidized in the parallel direction versus perpendicular direction.
- Determine if the oxidation in the parallel direction could be of beneficial use to large membrane filtration plants.
- 3) Determine the possibility of using cross-flow micro-filtration with an active biofilm as a novel biological treatment technology. Novel in the sense that treatment is of the retentate rather than the permeate because of treatment in the parallel direction.
 - a. Use any kind of substrate degradable by organisms who would attach to the side walls of a cross-flow membrane filtration unit.
 - b. Measure that actual rate at which organisms treat the substrate.
 - c. The rate should be very high::
 - i. Because of extremely reduced resistances to mass transfer.
 - Because of increased sticking efficiency (corresponding to the effect of trans-membrane pressure) on the membrane surface which allows for a greater number of organisms per unit surface area.

APPENDIX A Data Tables

Date	2/26/2003										
Exporimont	Ammonia A	nolvois durin		ion of Nitrify	ing Organian						
Experiment											
Notes	Mixed liquor is from Secondary Effluent										
Sample	Sample time	Time in Filtration apparatus (hr)	SE (-mv)	Ammonia as N (mg/l)	Alkalinity as CaCO ₃ (mg/l)	рН					
	2:30 pm										
S.E.	2/26	0.5	92	3.41	55	6.7					
	3:30 pm	1.5			105	= 2					
S.E.	2/26	1.5	52.5	16.70	135	7.3					
SE	12:00	22	57 1	10.00	105	77					
5.E.	6:00 pm		57.1	13.88	105	1.1					
SE	2/27	28	53.4	16 10	105	77					
0.11.	11:00	20	00.1	10.10	100	,.,					
S.E.	am 2/28	45	62	11.39	97.5	7.7					
	5:00 pm										
S.E.	3/1	75	73.2	7.26	96	7.3					
	3:00 pm		100.1								
S.E.	3/2	97	100.1	2.46	81	7.4					
SE	11:00	117	101 1	0.00	61.5	75					
5.E.	1:00 pm	11/	101.1	0.09	01.5	1.5					
S.E.	3/3	119	63.1	10.90	79.5	7.5					
	9:00 pm										
S.E.	3/3	127	68.8	8.67	75	7.3					
	11:00										
S.E.	am 3/4	141	77.1	6.21	61.5	7.1					
	3:00 pm	1.45	5 0 (60	- 1					
S.E.	3/4	145	/8.6	5.84	60	7.1					
SE	11:00 am $3/5$	165	128.6	0.70	27 5	60					
J.L.	1.00 nm	103	120.0	0.78	57.5	0.9					
S.E.	3/5	167	50.7	17.95	100.5	7.5					
	9:30 pm										
S.E.	3/5	175.5	53.8	15.85	97.5	7.4					

 Table A-19:
 Ammonia Analysis during Accumulation of Nitrifying Organisms

S.E.	12:00 pm 3/6	190	57.4	13.71	84	7.2
	8:30 pm					
S.E.	3/6	198.5	63.8	10.60	70.5	7.2
	10:30					
S.E.	am 3/7	212.5	74.5	6.89	55.5	7
	11:30					
S.E.	pm 3/7	237.5	109.7	1.67	88	7.1
	2:30 pm					
S.E.	3/8	240.5	138.7	0.52	78	7.2
	5:00 pm					
S.E.	3/9	267	157.1	0.25	72	7.8

 Table A-19: (continued)

Date	3/10/2003									
Experiment	Ammonia Ar	alysis of Ber	nch top s	system sample	s with 0.2 men	nbrane				
NT. 4		() (2.0)								
Note:	IVIIXed liquor from 2/26 was used and Spiked with NH4 and NaCO3									
Sample	Sample time	Time in Filtration system (hr)	(-mv)	Ammonia as N (mg/l)	Alkalinity (mg/l) as CaCO3	рН	Permeate Flux (l/hr-m ²)			
S.E.	2;00 pm 3/10	0.5	54.2	15.69	159	7.4	845.45			
S.E.	8;00 p m 3/10	6.5	57.8	13.56	126	7.2	327.27			
S.E.	12;00 pm 3/11	22.5	72.4	7.51	93	6.9	163.64			
S.E.	10;30 pm 3/11	33	92.7	3.30	135	7.1	152.73			
S.E.	11;30 am 3/12	46	176.3	0.11	108	7.1	147.27			
S.E.	3;00 pm 3/12	49.5	50	18.60	135	7				
S.E.	10;00 pm 3/12	56.5	54.8	15.31	126	7				
S.E.	11;30 am 3/13	70	62.2	11.35	99	6.9	130.91			
S.E.	11;00 pm 3/13	81.5	77.5	6.11	180	7.1				
S.E.	11;00 am 3/14	93.5	96	2.89	147	7.1	114.55			
S.E.	10;00 pm 3/14	104.5	151.3	0.31	150	7	114.55			
S.E.	1;00 pm 3/15	119.5	162	0.20	150	7.3	87.27			
S.E.	9;30 pm 3/16	151.5	53.2	16.34	189	7.5	109.09			
S.E.	11;30 am 3/17	165.5	62.1	11.40	150	7.1	103.64			
S.E.	8;00 pm 3/17	174	69.3	8.52	135	7	98.18			
S.E.	8;30 am 3/18	186.5	84.1	4.68	111	6.9	81.82			
S.E.	11;00 pm 3/18	201	141.7	0.46	180	7.3				

Table A-20: Filtering Mode 8.1 ft/s @ 10 psi

	_		-	<u>.</u>		-	
S.E.	12;30 pm 3/19	214.5	165.8	0.17	174	7.8	
S.E.	2;30 pm 3/19	217.5	45	22.77	210	7.4	
S.E.	11;00 pm 3/19	226	49.7	18.82	216	7.2	
S.E.	1;00 pm 3/20	240	52.7	16.67	195	7.2	76.36
S.E.	12;00 am 3/21	251	59.1	12.87	168	7.2	81.82
S.E.	12;00 pm 3/21	263	67.2	9.27	138	7.1	70.91
S.E.	12;30 pm 3/22	287.5	112.4	1.49	87	6.9	76.36
S.E.	6;00 pm 3/23	317	155.2	0.26	84	7.4	

Table A-20: (continued)

Date	4/16/2003										
Experiment	Filtering Mo	Filtering Mode 8.1 ft/s @ 20 PSI									
Note:	Mixed liquor from 4/2/03 was used Spiked with NH4 and NaCO3										
Sample	Sample time	Time in Filtration system (hr)	SE (-mv)	Ammonia as N (mg/l)	Alkalinity as CaCO3 (mg/l)	рН	Permeate Flux (l/hr- m ²)				
S.E.	8;00 pm 4/16	0.5	43.2	20.05	150	7.2	250.91				
S.E.	12;00 pm 4/17	16.5	55.6	12.20	105	6.9	87.27				
S.E.	9;00 pm 4/17	25.5	62.4	9.29	81	6.8	76.36				
S.E.	10.30 am 4/18	39	82.4	4.17	45	6.5	70.91				
S.E.	8;00 pm 4/18	48.5	148.2	0.30	180	7.1	60.00				
S.E.	10.30 am 4/19	63	177.1	0.09	159	7.6	65.45				
S.E.	11;30 am 4/19	64	45	18.65	210	7.6	65.45				
S.E.	6;00 pm 4/19	70.5	48.7	16.08	207	7.3	60.00				
S.E.	2;00 pm 4/20	88.5	62.8	9.15	180	7.1	60.00				
S.E.	8;00 pm 4/20	94.5	70.1	6.83	159	7.1	60.00				
S.E.	10;00 am 4/21	110.5	112.1	1.27	123	7	54.55				
S.E.	7;00 pm 4/21	119.5	164.4	0.16	0		60.00				
S.E.	1;30 pm 4/22	138	54.6	12.70	183	7.2	98.18				
S.E.	8;00 pm 4/22	144.5	61.5	9.64	153	7.1	84.55				
S.E.	1;00 pm 4/23	161.5	86.8	3.50	114	7	62.73				
S.E.	8;00 pm4/23	168.5	112.4	1.26	96	6.9	60.00				

Table A-21: Filtering Mode 8.1 ft/s @ 20 psi

Date	4/24/2003										
Experiment	Filtering Mode 1.5 GPM 30 PSI										
Note:	Mixed liquor from 4/16/03 was used Spiked with NH4 and NaCO3										
Sample	Sample time	Time in Filtrati on syste m (hr)	(-mv)	Ammonia as N(mg/l)	Alkalinity as CaCO3 (mg/l	рН	Permeate Flux (I/hr-m ²)				
SE	2;30 pm 4/24	0.5	46	17.92	207	7.1	100.91				
SE	9;30 pm 4/24	7.5	51	14.67	177	7.1	68.18				
SE	11;00 am 4/25	21	62.9	9.11	156	7	62.73				
SE	8;00 pm 4/25	30	77.6	5.06	129	7	60.00				
SE	12;00 pm 4/26	46	186.3	0.07	84	6.8	60.00				
SE	5;30 pm 4/26	51.5	197	0.04	78	6.9	60.00				
SE	2;30 pm 4/27	72.5	47.6	16.81	165	7.2	60.00				
SE	11;30 pm 4/27	81.5	55.3	12.35	111	7	60.00				
SE	11;00 am 4/28	93	70	6.86	81	6.8	60.00				
SE	7;30 pm 4/28	101.5	106	1.62	165	7	60.00				
SE	12;00 pm 4/29	106	191.1	0.05	150	7.2	60.00				
SE	2;00 pm 4/29	108	45.2	18.50	195	7.4	60.00				
SE	7;30 pm 4/29	113.5	48.7	16.08	171	7.2	60.00				
SE	11;30 am 4/30	129.5	65.5	8.21	123	7	60.00				
SE	9;00 pm 4/30	139	94.3	2.59	75	6.7	57.27				

Table A-22: Filtering Mode 8.1 ft/s @ 30 psi

SE	10;30 am 5/1	152.5	159.3	0.19	54	6.7	54.55
SE	4;00 pm 5/1	158	50.7	14.85	156	7	54.55
SE	8;30 pm 5/1	162.5	52.7	13.70	150	7.1	54.55
SE	1;00 pm 5/2	179	67.5	7.58	90	6.8	54.55
SE	1;00 am 5/3	191	131.2	0.59	105	6.9	54.55
SE	2;00 pm 5/3	204	172.7	0.11	105	7.2	54.55

Table A-22: (continued)

Date	5/5/2003										
Experiment	Filtering M	lode 16 2 ft/s	s @ 20 ps	si							
Note:	Mixed liquor from 4/24/03 was used Spiked with NH4 and NaCO3										
Sample	Sample time	Time in Filtration system (hr)	SE (-mv)	Ammonia as N (mg/l)	Alkalinity as CaCO3 (mg/l)	рН	Permeate Flux (I/hr-m ²)				
SE	2;30 pm 5/5	0.5	50.5	14.97	198	7.3	627.27				
SE	7;00 pm 5/5	5	60.1	10.19	159	7.1	169.09				
SE	12;30 pm 5/6	22.5	190.1	0.06	75	6.9	152.73				
SE	2;30 pm 5/6	24.5	46.1	17.85	165	7.1					
SE	9;00 pm 5/6	31	56.4	11.82	123	7					
SE	3;00 am 5/7	37	67.5	7.58	93	6.9					
SE	12;00 pm 5/7	45	129.7	0.63	33	6.3	141.82				
SE	5;30 pm 5/7	50.5	32.1	31.26	228	7.1	141.82				
SE	11;00 pm 5/7	56	37.2	25.49	195	7.2					
SE	12;00 pm 5/8	69	54.4	12.80	114	7					
SE	7;00 pm 5/8	76	72.8	6.13	66	6.8	133.64				
SE	12;00 pm 5/9	93	195.9	0.04	135	7.4					
SE	1;30 pm 5/9	94.5	41.4	21.54	225	7.3	141.82				
SE	8;00 pm 5/9	101	44.7	18.88	194	7.2	136.36				
SE	1;30 am 5/10	106.5	55	12.50	144	7					
SE	1;30 pm 5/10	118.5	87.9	3.35	75	6.7	136.36				
SE	3;00 am 5/11	132	156	0.22	54	6.7	136.36				

Table A-23: Filtering Mode 16.1 ft/s @ 20 psi

Date	5/12/2003										
Experiment	Ammonia Analysis of Bench top system samples with 0.2 membrane installed and pressure to 20 psi Q= 24.2 (ft/s)										
Note:	Mixed liquor from 5/12/03 was used Spiked with NH4 and NaCO3										
Sample	Sample time	Time in Filtration system (hr)	SE (-mv)	Ammonia as N (mg/l)	Alkalinity as CaCO3 (mg/l)	рН	Permeate Flux (I/hr-m ²)				
SE	3;00 pm 5/12	0.5	40	22.78	204	7.1	114.55				
SE	7;00 pm 5/12	4.5	42.6	20.53	171	7	120.00				
SE	11;30 am 5/13	21.5	119.1	0.96	21	6	109.09				
SE	5;00 pm 5/13	26	183.2	0.07	15	6	114.55				
SE	6;00 pm 5/13	27	38.6	24.10	285	7.1					
SE	11;00 pm 5/13	32	44.4	19.11	240	7.2					
SE	9;30 am 5/14	43.5	80.5	4.50	126	7					
SE	2;00 pm 5/14	48	150	0.28	90	6.9	114.55				
SE	2;30 pm 5/14	48.5	38.4	24.29	315	7.1					
SE	6;00 pm 5/14	52	42.2	20.86	288	7.2					
SE	11;00 pm 5/14	57	54.1	12.96	234	7.2	109.09				
SE	7;00 am 5/15	65	79.2	4.74	180	7.2					
SE	1;30 pm 5/15	71.5	148.5	0.30	144	7.1	103.64				
SE	3;30 PM 5/15	73.5	39.6	23.15	270	7.1					
SE	7;00 pm 5/15	77	46.9	17.29	225	7.2	103.64				
SE	2;00 am 5/16	84	57.2	11.44	144	7.2					
SE	12;00 pm 5/16	94	192.6	0.05	90	7.1	98.18				

Table A-24: Filtering Mode 24.2 ft/s @ 20 psi

Date	4/2/2003								
	Non-filtering mode								
	8.1 ft/s								
Experiment	10 PSI								
-									
Note:	Mixed liquor from 3/26/03 was used Spiked with NH4 and NaCO3								
		Time in			Alkalinity				
		Filtration			as				
	Sample	apparatus		Ammonia	CaCO3				
Sample	time	(hr)	SE (-mv)	as N (mg/l)	(mg/l)	pН			
	12:30								
S.E.	pm 4/2	0.5	43.2	19.1853855	195	7.2			
	8:30								
S.E.	pm 4/2	8.5	45.7	17.374258	174	7.1			
	11:00								
S.E.	am 4/3	23	50.3	14.4766483	150	7.1			
	9:30								
S.E.	pm 4/3	33.5	57.1	11.0543504	129	7.1			
	12:00								
S.E.	pm 4/4	48	67.6	7.28892231	105	6.9			
	9:00								
S.E.	pm 4/4	57	77.5	4.92185527	198	7.2			
	2:00								
S.E.	pm 4/5	74	162.9	0.1663618	180	7.2			
	2:30								
<u>S.E.</u>	pm 4/5	74.5	46.2	17.033089	192	7.2			
	6:30								
S.E.	pm 4/5	78.5	48.1	15.7966347	180	7.2			
	2:30								
S.E.	pm 4/6	98.5	57.3	10.9670061	153	7.1			
	10:30					_			
S.E.	pm 4/6	106.5	61.2	9.39523906	135	7			
	9:30 am	118 5		6 47100061		_			
S.E.	4/1	117.5	/0.6	6.47122061	111	1			
	7:00	107	0.2	2.06412074		6.0			
S.E.	pm 4//	127	83.6	5.86413274	90	6.9			
0 E	1:00	145	100 0	0.0770(015		(7			
5.E.	pm 4/8	145	182.3	0.07706815	63	6./			
O E	3:00	1 47	160	16 0656622		7			
5.E.	<u>pin 4/8</u>	14/	40.3	10.9030033	1/4	/			
СЕ	8:30 pm 4/9	150	50.1	14 5010442	100	71			
5.E.	pin 4/8	152	50.1	14.3919443	162	/.1			

Table A-25:	Non	Filtering	Mode	8.1	ft/s	@	10	psi
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Table A-25: (c	continued)
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	1:00 pm					
S.E.	4/9	169	55.5	11.7786185	147	7.1
	7:00 pm					
S.E.	4/9	175	59.9	9.89239051	135	7.1
	11:30					
S.E.	am 4/10	191.5	74.8	5.47820453	105	6.9
	8:00 pm					
S.E.	4/10	200	92.5	2.71483387	78	6.8
	9:00 am					
S.E.	4/11	213	181.6	0.07923789	62	6.7

Date	5/20/2003									
2400	Non-Filtering Mode									
	8.1 ft/s									
Experiment	20 PSI									
Note:	Mixed lique	Mixed liquor from 5/12/03 was used Spiked with NH4 and NaCO3								
		Time in			Alkalinity					
		Filtration		Ammonia	as					
~ .	Sample	apparatus		as N	CaCO3					
Sample	time	(hr)	SE (-mv)	(mg/l)	(mg/l)	рН				
	1:00									
S F	pm	0.5	47.1	17.040251		7.2				
5.E.	5/20	0.5	46.1	17.848251	213	1.2				
	5:00 pm									
SE	5/20	4 5	46.4	17 635183	105	7.2				
5.L.	12:30	ч.5	т. . т	17.055105	195	1.2				
S.E.	am 5/21	12	50.3	15.086058	189	7.1				
	12:00									
	pm									
S.E.	5/21	23.5	58.5	10.864585	165	7.1				
	7:00									
	pm									
S.E.	5/21	30.5	64.7	8.4766036	150	7.1				
	10:00									
	pm	22.5	(0)	7 12 (1 400		_				
S.E.	5/21	33.5	69	7.1361409	141	1				
	10:30									
SE	pm 5/21	34	383	24 389564	270	7.2				
0.12.	12.00	54	50.5	24.307304	270	1.2				
	nm									
S.E.	5/22	47.5	42.6	20.532677	234	7.2				
	11:00									
	pm									
S.E.	5/22	58.5	46.2	17.776944	204	7.2				
	11:30									
S.E.	am 5/23	71	52.6	13.759058	169	7.1				
	9:30									
C F	pm			11 700104						
S.E.	5/23	81	56.6	11.723194	156	7.1				

Table A-26: Non Filtering Mode 8.1 ft/s @ 20 psi

Table A-26: (continued)

	2.00					
S.E.	pm /24	97.5	71	6.5870664	111	7
	3:30					
	pm					
S.E.	5/27	170	42.2	20.864109	195	6.9
	10:00					
	pm					
S.E.	5/27	176.5	43.7	19.648134	186	7.3
	8:30 am					
S.E.	5/28	187	48.8	16.019697	174	7.2
	9:30					
	pm					
S.E.	5/28	200	56.5	11.770218	150	7.1
	1:30 pm					
S.E.	5/29	216	69	7.1361409	111	7
	11:00					
S.E.	pm 5/29	225.5	89.3	3.166168	0	6.8
	11:00					
S.E.	am 5/30	237.5	162.2	0.1710477	60	6.6

Date	6/2/2003								
	Non-Filtering Mode								
	8.1 ft/s								
Experiment	30 PSI								
•									
Note:	Mixed liquor from 5/12/03 was used Spiked with NH4 and NaCO3								
		Time in			Alkalinity				
		Filtration		Ammonia	as				
	Sample	apparatus		as N	CaCO3				
Sample	time	(hr)	SE (-mv)	(mg/l)	(mg/l)	pН			
	12:30								
S.E.	pm 6/2	0.5	53.5	13.272159	240	7.3			
	8:00								
S.E.	pm 6/2	8	59.8	10.313635	222	7.3			
	1:30								
S.E.	pm 6/3	25.5	68.2	7.3683792	189	7.2			
	6:30								
S.E.	pm 6/3	30.5	79.1	4.7628617	180	7.2			
	9:30 am								
S.E.	6/4	45.5	104.8	1.7023772	150	7.1			
	12:30								
S.E.	pm 6/5	72.5	52.4	13.869661	240	7.5			
	10:00								
S.E.	pm 6/5	82	57.9	11.128703	210	7.4			
	11:00								
S.E.	am 6/6	95	63.8	8.7875739	192	7.3			
	9:00								
S.E.	pm 6/6	105	75.2	5.5676529	174	7.2			
	1:00								
S.E.	pm 6/7	121	98.1	2.2260756	162	7.2			
~ ~	9:00								
S.E.	pm 6/7	129	149.3	0.2866769	159	7.1			
C F	12:00	1.00		11 (7() (7)		7.0			
5.E.	pm 6/9	168	56.7	11.6/635/	249	7.2			
Q F	9:30	177.5	50.0	10 070 42		7.2			
S.E.	pm 6/9	1//.5	59.9	10.2/243	225	1.2			
Q E	10:50	100 5	(0.5	6 0047029		7 1			
S.E.	am 0/10	190.5	09.3	0.994/238	201	/.1			
S E	10:00 m $6/10$	202	00 5	4 5022702	400	71			
5.E.	12:00	202	80.5	4.3032702	168	/.1			
Q E	12:00	216	1067	0 709 45		7			
S.E.	m 6/11	216	126.7	0./0845	143	/			

Table A-27: Non Filtering Mode 8.1 ft/s @ 30 psi

Date	6/11/2003								
Experiment	Non-Filterin	ng Mode 16.1	ft/s 20 PSI						
Note:	Mixed liquor from 5/12/03 was used Spiked with NH4 and NaCO3								
	Samula	Time in Filtration		Ammonia	Alkalinity as				
Sample	Sample	apparatus (hr)	SF (-mv)	as N (mg/l)	(mg/l)	nH			
Bampic	1.30 pm	(111)		(111g/1)	(IIIg/I)	pii			
S.E.	6/11	0.5	35.8	26.956795	345	7.3			
	9:30 pm								
S.E.	6/11	8.5	40.7	22.155338	321	7.3			
	12:30								
S.E.	pm 6/12	23.5	43.9	19.491451	276	7.2			
	6:00 pm	•	40.1	15.000450					
S.E.	6/12	29	49.1	15.828458	219	7.2			
SE	11:00 am 6/13	51.5	59.6	10 396541	169	71			
5.12.	2.00 am	51.5	57.0	10.370341	100	/.1			
S.E.	6/14	66.5	85.4	3.7011623	147	7			
	9:30 pm								
S.E.	6/15	110	161.7	0.1745059	120	7.2			
	10:00								
S.E.	pm 6/15	110.5	42.7	20.450645	210	7.2			
~ ~	11:00					_			
S.E.	am 6/16	123.5	50.5	14.965755	159	7			
S E	10:00	124.5	57.0	11 444067	400	6.0			
5.E.	1:00 pm	134.3	57.2	11.44490/	126	0.9			
SE	6/17	149 5	66.2	7 9825811	Q1	67			
5.1.	11:00pm	117.5	00.2	1.9023011	01	0.7			
S.E.	6/17	159.5	82.3	4.1901905	150	7.1			
	11:00 m								
S.E.	6/18	171.5	139.3	0.4278086	120	7			

Table A-28: Non Filtering Mode 16.1 ft/s @ 20 psi

Date	6/18/2003								
Experiment	Non Filtering Mode 4,5 GPM 20 PSI								
Note:	Mixed liquor from 6/11/03 was used Spiked with NH4 and NaCO3								
		Time in			Alkalinity				
	Samula	Filtration	SE (Ammonia	as CaCO3				
Sample	Sample time	apparatus (hr)	SE (- mv)	as N (mg/l)	(mg/l)	nH			
	12:30	(111)	m ()	(1119/1)	(1119/1)	P11			
	pm								
S.E.	6/18	0.5	51.1	14.610572	195	7.1			
	10:00								
	pm					_			
S.E.	6/18	10	62.5	9.2570026	126	7			
	12:00								
SE	6/19	24	1177	1 015735	60	67			
5.L.	2.00	24	11/./	1.013733	09	0.7			
	2.00 pm								
S.E.	6/19	26	162.4	0.1696837	63	6.7			
	8:00								
	pm								
S.E.	6/19	32	49.8	15.391063	222	7.2			
	2:30								
S E	AM	20 5	56.0	11 (20709	100	7 1			
5.E.	0/20	38.3	30.8	11.629708	180	/.1			
	AM								
S.E.	6/20	47.5	81.4	4.3439107	126	6.9			
	3:00								
	pm								
S.E.	6/20	51	115.9	1.091628	108	6.8			
	3:30								
Q F	pm	51.5	A 1 A	01 5 40 1 1		7 1			
S.E.	0/20	51.5	41.4	21.54311	210	/.1			
	8:30 nm								
S.E.	6/20	56.5	49.4	15.639501	172	7.1			

Table A-29: Non Filtering Mode 24.2 ft/s @ 20 psi

Table A-29: (continued)

	10:00					
	am					
S.E.	6/21	70	72.2	6.2781142	66	6.8
	4:00					
	pm					
S.E.	6/21	76	100.7	2.0060286	39	6.5

APPENDIX B

Ammonia Figures



Figure B-21: Ammonia Analysis during Accumulation of Nitrifying Organisms



Figure B-22: Ammonia Analysis of Filtering Mode at 8.1 ft/s and 10 PSI



Figure B-23: Ammonia Analysis of Filtering Mode at 8.1 ft/s and 20 PSI



Figure B-24: Ammonia Analysis of Filtering Mode at 8.1 ft/s and 30 PSI



Figure B-25: Ammonia Analysis of Filtering Mode at 16.1 ft/s and 20 PSI


Figure B-26: Ammonia Analysis of Filtering Mode at 24.2 ft/s and 20 PSI



Figure B-27: Ammonia Analysis of Non-Filtering Mode at 8.1 ft/s and 10 PSI



Figure B-28: Ammonia Analysis of Non-Filtering Mode at 8.1 ft/s and 20 PSI



Figure B-29: Ammonia Analysis of Non-Filtering Mode at 8.1 ft/s and 30 PSI



Figure B- 30: Ammonia Analysis of Non-Filtering Mode at 16.1 ft/s and 20 PSI



Figure B-31: Ammonia Analysis of Non-Filtering Mode at 24.2 ft/s and 20 PSI

APPENDIX C

Alkalinity Figures



Figure C-32: Alkalinity Analysis during Accumulation of Nitrifying Organisms



Figure C-33: Alkalinity Analysis of Filtering Mode at 8.1 ft/s and 10 PSI



Figure C-34: Alkalinity Analysis of Filtering Mode at 8.1 ft/s and 20 PSI



Figure C-35: Alkalinity Analysis of Filtering Mode at 8.1 ft/s and 30 PSI



Figure C-36: Alkalinity Analysis of Filtering Mode at 16.1 ft/s and 20 PSI



Figure C-37: Alkalinity Analysis of Filtering Mode at 24.2 ft/s and 20 PSI



Figure C-38: Alkalinity Analysis of Non-Filtering Mode at 8.1 ft/s and 10 PSI



Figure C-39: Alkalinity Analysis of Non-Filtering Mode at 8.1 ft/s and 20 PSI



Figure C-40: Alkalinity Analysis of Non-Filtering Mode at 8.1 ft/s and 30 PSI



Figure C-41: Alkalinity Analysis of Non-Filtering Mode at 16.1 ft/s and 20 PSI



Figure C-42: Alkalinity Analysis of Non-Filtering Mode at 24.2 ft/s and 20 PSI

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