FINAL REPORT March 8, 2013

FOULING-RESISTANT MEMBRANES FOR ADDITIVE-FREE TREATMENT OF RENDERING FACILITY WASTEWATER

Principal Investigator: Scott Husson, Professor Department of Chemical and Biomolecular Engineering 127 Earle Hall Clemson University Clemson, SC 29634 Phone: 864-656-4502 Fax: 864-656-0784 E-mail: shusson@clemson.edu

Date Submitted: March 7, 2011

Project Start Date: October 1, 2011

Duration of Project: 12 months + 5 month no-cost extension

Lay Summary: Rendering wastewater presents many challenges to the classical primary treatment technologies and flotation systems. Dissolved air flotation (DAF) is the most popular technology for primary treatment of rendering facility wastewater, but it has limitations. Perhaps most notably, the cost of coagulants and flocculants needed for primary treatment by DAF can be high. Motivated by the need for a more reliable and cost-effective method to treat rendering facility wastewaters, the overall objective of this work was to evaluate membrane ultrafiltration (UF) with fouling-resistant membranes as an alternative method to DAF.

In this study, we evaluated the separation performance of a new class of membranes developed in our laboratory for treatment of impaired wastewaters containing dispersed oils. These membranes were used to treat high-strength wastewaters (COD > 29000 mg/L, total solids > 11000 mg/L) provided by a Carolina By-Products/Valley Proteins, Inc. Separations were conducted without the chemical and polymer additives used in treatments by DAF. Membrane performance was evaluated by measuring productivity (i.e., the volume of filtrate per membrane area per time), capacity (i.e., the total volume processed per unit membrane area before the membrane must be cleaned), and effluent water quality (COD, turbidity, total dissolved solids, and pH). Membrane surfaces were characterized by electron microscopy and infrared spectroscopy pre- and post-filtration to determine the extent of fouling, and to evaluate the use of a cold water rinse to clean the membranes.

The results of experimental work are highly encouraging. We demonstrated that separations can be conducted *without addition of polyacrylamide*, which is used in DAF to improve separation. Ultrafiltration with a low-permeability membrane (0.09 L/($m^2 \cdot h$)/kPa) reduced turbidity 650-fold (nearly 100%), COD by 80%, and total solids by 90%. After a short start-up, average flux was constant over a 120-hour filtration test period, without the need for intermittent cleaning. While low-permeability membranes were able to treat rendering wastewaters with high solids, results using high-permeability membranes (O(1 L/($m^2 \cdot h$)/kPa)) were not encouraging. Their use would require further development to prevent internal, irreversible fouling. Not unexpectedly, the UF membranes used to reduce turbidity and COD did not reject salts or low molecular weight organic compounds as indicated by the residual total solids concentrations following filtration. Ultrafiltration membranes are not used for salt rejection in water treatment applications; rather, they provide an initial purification step that would need to be followed by a polishing step such as nanofiltration or reverse osmosis to recover clean water for direct discharge or beneficial use.

In addition to experimental work, a preliminary cost analysis was done to compare the operating costs (energy and consumables) of the membrane ultrafiltration process to DAF. The comparison was done based on data for a DAF unit with an 82,000-gallon capacity tank and 160 gallons per minute flow rate. Assuming a conservative membrane lifetime of 1 year, the operating costs were found to be \$0.95 per 1000 gallons of water for membrane ultrafiltration primary treatment compared to \$3.20 per 1000 gallons of water for DAF primary treatment. In addition to the significantly lower projected operating costs for the membrane process, there are likely to be other economic benefits associated with the removal of chemical additives from the process.

This project provided a training ground for one PhD student and one undergraduate researcher. It was the basis for one publication and provided preliminary data that were used in proposals requesting over \$390K in funding to develop membranes for treating high-strength wastewaters.

Objective(s): In prior work, our laboratory developed a special procedure to coat the surface of filtration membranes with an extremely thin polymer film that improves their resistance to fouling and allows them to be cleaned by a chemical-free water rinse step. The polymer coating is bound to the membrane by chemical reaction and will not leach off the surface. Treatment by our membranes is done without the chemical and polymer additives that are used commonly in treatments by dissolved air flotation. We evaluated the use of these polymer-coated membranes to treat rendering facility wastewater. Our four objectives were to

- 1. Test membrane performance using water samples provided by Carolina By-Products. Measure the productivity (i.e., the volume filtered per unit area of membrane per time), capacity (i.e., the total volume that can be processed per unit membrane area before the membrane must be cleaned), and effluent water quality parameters [*completed*]
- 2. Develop and optimize membrane cleaning protocols. Our cleaning step uses a cold water rinse only no chemical additives are used [*completed*, *but more could be done on membrane development based on our findings (vide infra)*]
- 3. Characterize the membrane surfaces pre- and post-filtration to determine the extent of fouling. Use two analytical techniques to evaluate the effectiveness of our chemical-free cleaning procedure to reverse membrane fouling. Scanning electron microscopy will allow 'visualization' of the membrane surface. Infrared spectroscopy will provide information about the chemical nature of the foulant species [*completed*]
- 4. Perform a preliminary cost analysis for operating a membrane separation process in place of the current dissolved air flotation process. This preliminary analysis will consider only relative costs of energy and consumables [*completed*]

Project Overview:

1. Introduction

According to the National Renderers Association, animal by-products from the slaughter of animals and poultry contributed to the production of an estimated 8.4 million metric tons of rendered products in the United States in 2011 [Swisher, 2012]. The rendering industry recycled these animal by-products into inedible tallow and grease, edible tallow and lard, and processed animal protein meals. While rendering processes convert this large mass of inedible materials into marketable products, they also produce large volumes of high-strength industrial wastewater containing significant amounts of total suspended solids (TSS), fats, oils and greases, and proteins [Colic, 2006; Sindt, 2006]. Removing such materials from rendering facility wastewater results in a more efficient recycling process and helps to comply with regulatory agencies. New regulations encourage primary treatment to reduce the amount of TSS, fats, oils, greases, and biological oxygen demand (BOD)/chemical oxygen demand (COD) in the effluent.

Rendering wastewater presents many challenges to the classical primary treatment technologies and flotation systems. It contains high levels of contaminants, up to 500 times higher than typical municipal or industrial wastewater influents. Depending on what is processed, the influent to the rendering facility wastewater treatment system can change hourly, daily, or weekly. The space available for the wastewater treatment system is often limited. Wastewater treatment produces large volumes of sludge with low solids content that have to be dewatered before recycling of fats, oils, greases or proteins is possible. Finally, the cost of coagulants and flocculants needed for primary treatment can be high. For example, dissolved air flotation (DAF) flocculant cost is roughly US \$3.00/1000 gallons of wastewater.

DAF is the most popular technology [Johns, 1995; O'Brien et al., 2005] for primary treatment of rendering facility wastewater, but it has limitations. Oftentimes, chemicals must be added to the wastewater to adjust the pH and improve flocculation of the solids to increase the removal efficiency. Long residence times require large dimension DAF tanks. Air solubility also limits the amount of dissolved gas and thus bubble availability, making treatment of wastewater with a high content of fats, oils, greases and TSS highly inefficient. Furthermore, aeration causes oxidative damage and degradation of fat and protein components [Abboah-Afari and Kiepper, 2012]. These limitations of DAF make it necessary to develop alternate methods to treat rendering facility wastewater.

Membrane technology is an economically competitive alternative or addition to traditional wastewater treatment technologies. Unlike other physical/chemical wastewater treatment operations, membrane separators provide a positive barrier to reject solids present in wastewater streams [Cheryan and Rajagopalan, 1998]. Thus, membrane separations can be conducted without chemical addition. Furthermore, membrane units can operate on a variable concentration waste stream. Thus, modest fluctuations in the feed concentration, a common feature of rendering facility wastewater, will not require process adjustments. Eliminating chemical agents for pH adjustment and polymer coagulation agents for solids flocculation is expected to provide economic benefit by reducing operating costs. Surprisingly, few studies are reported on the use of membranes for primary treatment of rendering plant wastewaters. One important example is provided by Abboah-Afari and Kiepper [2012], who reported on the efficiency of membrane filtration on pre-DAF poultry processing wastewater.

Although membranes can treat wastewaters with high solids loading, their use is hindered by declining permeate flux experienced as a result of fouling. The flux decline is due to the accumulation of rejected dissolved solids, suspended solids and other components on the membrane surface. One pertinent example is provided by O'Brien et al. [2005] who used a 0.2 µm pore size membrane as part of a membrane bioreactor system to treat rendering plant wastewater. Routine membrane cleaning was required as the membrane was susceptible to fouling. Fouling of conventional membranes can be irreversible or resistant to cleaning, hence making the original flux unrecoverable [Hilal et al., 2005; Peng and Tremblay, 2008]. It is necessary to develop new membranes and methods of their use for limiting fouling during treatment of rendering plant wastewater. That is the important focus and novelty of our work.

Our group has developed a special procedure to modify the surface of filtration membranes to improve their resistance to fouling during the treatment of oily waters and to allow them to be cleaned by a chemical-free water rinse step [Tomer et al., 2009, Wandera et al., 2011, 2012]. The strategy is to tailor membrane surface chemistry by grafting block copolymers comprising polymers known to provide fouling resistance (poly(ethylene glycol)) (PEGMA)) and temperature-responsiveness (poly(N-isopropylacrylamide) (PNIPPAm)). Polymer grafting from the membrane surface provides an additional resistance to flow, but, in return, it is possible to

decrease the rate of flux decline and reverse foulant accumulation using a chemical-free wash step or mild chemical cleaning. Limiting fouling during the filtration of rendering wastewater would reduce energy costs associated with pumping since, with low degrees of fouling, the transmembrane pressure to maintain constant flux (volume/area·time) would stay constant. Providing a mechanism for chemical-free or mild chemical cleaning would increase membrane lifetime because the harsh chemicals used to restore flux in more conventional membranes degrade the membrane material over time. Combined, the costs associated with membrane replacement, energy, and cleaning solutions comprise roughly 50% of total operational cost of an ultrafiltration plant [Kulkarni et al., 1982]. Reductions in these costs are expected to have significant economic benefits in addition to those gained by elimination of chemical additives used in conventional treatment methods like DAF.

The objectives of this study were to test the performance of our advanced, fouling-resistant and cleanable membranes using highly impaired waters (COD > 29000 mg/L, total solids > 11000 mg/L) provided by a rendering facility, to characterize the membrane surface pre- and post-filtration to determine the extent of fouling, and to evaluate the use of a cold water rinse to clean the fouled membranes. Cross-flow membrane filtration experiments using wastewater provided by Carolina By-Products/ Valley Proteins, Inc. were carried out, and membrane performance was evaluated by measuring productivity (i.e., the volumetric filtrate flux), capacity (i.e., the total volume processed per unit membrane area before the membrane must be cleaned), and effluent water quality (COD, turbidity, total dissolved solids (TDS), and pH). Membrane fouling was detected using scanning electron microscopy (SEM) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). Cleaning involved membrane relaxation (where filtration was paused) followed by a cold water rinse.

In addition to experimental work, a preliminary analysis was done to compare the costs of energy and consumables for the membrane ultrafiltration process to those for DAF.

2. Materials and methods

2.1 Materials

Commercial, M-series GE Septa[™] cross-flow UltraFilic ultrafiltration (UF) membranes with a nominal molecular weight cut-off (MWCO) of 100 kDa were purchased from GE Osmonics, Inc. (Minnetonka, MN). To avoid fouling, M-series UltraFilic membranes are engineered to be extremely hydrophilic [Hodgins and Samuelson, 1990; Nicolaisen, 2002]. Another set of commercial, UF cellulose acetate (CA) membranes were provided by Hydration Technology Innovations (HTI), LLC (Albany, OR).

The following chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used as received, unless stated otherwise: 2,2'-bipyridyl (bipy, >99%), 2-bromoisobutyryl bromide (2-BIB, 98%), copper(I) chloride (CuCl, >99.995%), copper(II) chloride (CuCl₂, 99.99%), neutral aluminum oxide (~150 mesh, 58 Å), tris(2-dimethylaminoethyl)amine (Me₆TREN, >98%, ATRP Solutions, Inc., Pittsburgh, PA). COD digestion vials (high range, 20–1500 mg/L) were purchased from Hach Company (Loveland, CO). The vials contained mercuric sulfate, chromic acid, silver sulfate, sulfuric acid and deionized water. N-hexane, methanol and water were purchased as HPLC grade solvents from Fisher Scientific (Fair Lawn, NJ). Sodium hydroxide

(NaOH, anhydrous, >97%) was purchased from Alfa Aesar (Ward Hill, MA).

Poly(ethylene glycol) methacrylate (PEGMA) macromonomer ($M_n \approx 360$ g/mol) containing monomethyl ether hydroquinone (650 ppm) inhibitor was purchased from Sigma-Aldrich. The inhibitor was removed before use by passing the PEGMA through a column of neutral aluminum oxide. N-isopropylacrylamide (NIPAAm, 97%) was purchased from Sigma-Aldrich and purified by re-crystallization from n-hexane.

2.2 Rendering facility wastewater

Polyacrylamide-free wastewater prior to DAF was collected from Carolina By-Products/Valley Proteins, Inc. (Ward, SC). The wastewater was stored in plastic containers at ~ 2 °C until filtration. Wastewater samples were stored for a maximum time of 6 weeks. Due to changes in weather conditions and differences in the animal by-products processed by the plant, the properties of the wastewater varied greatly depending on the time of the year or even just the day of the week. Indeed, one of the difficulties of treating rendering wastewater using conventional, non-membrane treatment methods is that its properties tend to fluctuate hourly, daily, or weekly. Table 1 shows the characteristics of three different wastewater samples (I, II, III) collected from the plant on three different occasions.

Table 1. Properties of different samples of rendering facility wastewater. Uncertainty values for pH, TDS, and turbidity represent uncertainties associated with the measurement device for single measurements. Uncertainty values for total solids represent the propagated uncertainty for single mass and volume measurements used in Equation 1. Uncertainty values for COD represent the standard errors based on three measurements for each water sample analyzed.

Water Sample	Ι	II	III	
pH	5.20 ± 0.05	5.25 ± 0.05	5.46 ± 0.05	
TDS (mg/L)	1750 ± 5	3460 ± 5	1830 ± 5	
Total Solids (mg/L)	11000 ± 200	35000 ± 500	47000 ± 600	
COD (mg/L)	29000 ± 80	42000 ± 100	97000 ± 1800	
Turbidity (NTU)	650.00 ± 0.05	>1000	>1000	

2.3 Membrane modification

The CA membranes were immersed in methanol for 15 min to remove any structural preservatives and then rinsed thoroughly with HPLC water to remove methanol. These membranes were hydrolyzed in 0.10 M aqueous NaOH solution to obtain regenerated cellulose membranes. Each 19 cm \times 14 cm membrane was immersed in 150 ml of the 0.10 M aqueous NaOH solution at 25 °C. Hydrolysis time was used as a variable to study the degree of hydrolysis (DH) (i.e., the degree of conversion of acetate groups to hydroxyl groups). At the end of the desired hydrolysis time, the membranes were removed from the NaOH solution and washed thoroughly with HPLC water. The hydrolyzed CA membranes were activated by 5.0 mM 2-BIB and then modified further by room temperature surface-initiated atom transfer radical polymerization (ATRP) of PNIPAAm (NIPAAm(0.05 M)/Cu(I)/Cu(II)/Me₆TREN: 100/1/0.2/2.4) for 1 h and then PPEGMA (PEGMA (0.1 M)/Cu(I)/Cu(II)/bipy: 200/1/0.2/2.4) for 3 h. All formulations were prepared in 4:1 (v/v) solvent mixturea of HPLC water and methanol. Further modification details were given elsewhere [Wandera et al., 2011, 2012].

GE UltraFilic membranes are polyacrylonitrile (PAN)-based membranes that have been highly hydrophilized through treatment with a solution containing uncharged, hydrophilic substituted amide groups [Hodgins and Samuelson, 1990]. An FTIR spectrum of the membrane (vide infra) suggests the presence of a large number of hydroxyl groups that can be utilized for surface modification. Thus, the membranes were activated by reaction of the hydroxyl groups with 1.0 mM 2-BIB and then modified further by ATRP of PNIPAAm for 1 h and then PPEGMA for 3 h, as described above.

2.4 Membrane filtration

Cross-flow (CF) membrane filtration experiments using unmodified and modified membranes were carried out using polyacrylamide-free wastewater to measure productivity and capacity of the membranes. Measurements were done using a Septa[®] CF II medium/high foulant membrane cell system (GE Osmonics, Minnetonka, MN). The membrane cell system accommodates a 19 cm \times 14 cm flat sheet membrane and presents an effective membrane test area of 140 cm². The wastewater was circulated using a Hydra-Cell pump (Wanner Engineering, Inc., Minneapolis, MN). The feed container was a 5 gallon B268 high density polyethylene tank (12 ¼ inch (L) \times 12 ¼ inch (W) \times 8 ¼ inch (H)) that was purchased from Ronco Plastics (Tustin, CA). It was customized with one ½ inch National Thread Pipe (NPT) opening at the bottom, two $\frac{3}{8}$ inch NPT openings at the top of one side face, and one 2 inch NPT vent with a cap on the top face. Experiments were carried out using a transmembrane pressure (TMP) selected depending on the membrane that was being tested to achieve high productivity and to limit membrane fouling. Permeate flux values were calculated from the permeate volumes collected at different times.

Membrane cleaning to detach accumulated foulants was initiated when the flux reached a defined lower limit. Cleaning involved membrane relaxation (where filtration was paused for 30 min) followed by a cold water rinse step. Filtration with rendering wastewater was repeated after the cleaning to determine the percentage recovery of the original permeate flux achieved by the membrane cleaning step and, hence, evaluate the effectiveness of the cleaning method.

2.5 Membrane physicochemical characterization

2.5.1 ATR-FTIR

Attenuated total-reflectance Fourier-transform infrared spectroscopy was used to characterize surface chemical properties of the pristine, hydrolyzed, PNIPAAm-modified and PNIPAAm-*b*-PPEGMA-modified membranes. The ATR-FTIR technique was used also to characterize surface chemical properties of the membranes before and after filtration, as well as membranes after filtration and cleaning. These measurements were done to detect membrane fouling and the degree to which cleaning removed organic foulants. Spectra were obtained using a Thermo-Nicolet Magna 550 FTIR spectrometer (Thermo Fisher Technologies Inc., Fair Lawn, NJ) equipped with a diamond ATR accessory. Measurements were done according to a procedure detailed elsewhere [Singh et al., 2005].

2.5.2 SEM

Scanning electron microscopy was used to provide information on the surface pore morphologies of the unmodified and modified membranes. To study membrane fouling, SEM was utilized to "visualize" membrane surfaces, both unmodified and modified, before and after filtration, as

well as membranes after filtration and cleaning. Images were obtained using a variable-pressure Hitachi FE-SEM SU 6600 (Hitachi High Technologies America, Inc., Schaumburg, IL). Representative 0.5 cm² samples of the membranes were attached with carbon tape to aluminum stabs prior to the SEM measurements. The SEM measurements were performed at an accelerating voltage of 20 kV and magnifications of 2000x and 5000x.

2.5.3 Water quality analysis

2.5.3.1 pH and TDS

The pH and total dissolved solids concentration of the feed and permeate were measured using a multiple parameter SympHonyTM meter (VWR International, LLC, Radnor, PA). The meter was calibrated using standard solutions with known pH values (catalog numbers 1493-32, 1500-16, 1550-16, 1600-16, 1615-16) or salt concentrations (catalog numbers 2236.10-32, 2244.50-32, 2241-32) purchased from Ricca Chemical Company (Arlington, TX).

2.5.3.2 COD

Chemical oxygen demand of a sample is a measure of the moles of a specific oxidant that reacts with the sample under controlled conditions. Dichromate ion (Cr_2O7^{2-}) was used as the specific oxidant in this work. The COD of the feed and permeate were measured using the closed-reflux, colorimetric method. In principle, when a sample is digested, the dichromate ion oxidizes COD material in the sample and this reaction reduces chromium from its hexavalent (VI) state to the trivalent (III) state. Both of these chromium species are colored and absorb in the visible region of the spectrum. Thus, measurements of color change can be used to determine the COD content of a sample.

Water samples were diluted by a factor of up to 100 using DI water to ensure that the samples had COD within the detection range (20–1500 mg/L) of the digestion solution vials. Diluted water samples (2 mL) were analyzed for COD by micropipetting into the COD digestion solution vials, sealing the vials, and mixing the contents by shaking the vials thoroughly by hand for 30 s. Digestion was done by placing the sealed vials in the wells of a Model 45600 COD Reactor (Hach Company, Loveland, CO), and heating them at 150 °C for 2 h. Samples were allowed to cool slowly by allowing them to stand in the wells of the reactor for at least 3 h to avoid precipitate formation. Once the wells of the reactor had cooled to room temperature (ca. 20–25 °C), the vials were removed and their contents were mixed by shaking thoroughly by hand for 30 s to combine condensed water and clear insoluble matter from the walls of the vials. The suspended matter was left to settle for at least 30 min to ensure a clear optical path through the vials. All measurements were done in triplicate. Absorbance of the vial contents was measured at 600 nm using a Spectronic 20D Spectrometer (Milton Roy, Ivyland, PA). COD was determined from a calibration plot that was prepared using standardized COD solutions (catalog number 22539-29, Hach Company, Loveland, CO).

2.5.3.3 Total solids

Total solids in a sample refer to the material residue left in the vessel after evaporation of the sample and its subsequent drying in an oven at a defined temperature and atmospheric pressure. Total solids include total suspended solids (TSS), which are the solids retained by a specified filter, and total dissolved solids (TDS), which are the solids that pass through the filter. The measurement principle involves evaporating a known volume of well-mixed sample in a weighed

dish and drying it to a constant weight in an oven at 103 to 105 °C and atmospheric pressure. The increase in weight over that of the empty dish divided by the sample volume represents the total solids content.

A clean aluminum foil dish was heated at ~105 °C and atmospheric pressure for 1 h, and then cooled and stored in a desiccator filled with Drierite (anhydrous calcium sulfate) purchased from W. A. Hammond Company Ltd. (Xenia, OH) until needed for measurement. The dish was weighed immediately before use. Five milliliters of well-mixed sample were pipetted into the preweighed dish. The sample was evaporated to dryness in an oven at ~105 °C for 24 h to ensure a constant dry weight, cooled in the dessicator and then weighed. Total solids content was calculated using Equation 1.

Total solids (mg/L) =
$$\frac{(m_f - m_i)}{V}$$
 (1)

where m_f is the mass of the dish plus dried residue (mg), m_i is the mass of the dish only (mg), and V is the sample volume.

2.5.3.4 Turbidity

Turbidity was measured using a MICRO 100 Laboratory Turbidimeter (HF Scientific, Fort Myers, FL). This turbidimeter has been designed for simple and quick measurement of turbidity. The MICRO 100 measures and records the turbidity of a sample in nephelometric turbidity units (NTU) and it has a measurement range of 0–1000 NTU. The meter was calibrated using a calibration kit containing TOC standards (catalog number 39957, HF Scientific, Fort Myers, FL)

2.6 Preliminary operating cost estimation

Preliminary cost analysis compared the costs of energy and consumables for dissolved air filtration to those of membrane ultrafiltration using the HTI membrane. Capital, labor, and maintenance costs were not included in this analysis. The comparison was done based on data for a DAF unit with an 82,000-gallon capacity tank and 160 gallons per minute flow rate. Included were the energy cost for pumping the wastewater using average energy price of \$0.193/kilowatthour from the U.S. Bureau of Labor Statistics (U.S. Bureau of Labor Statistics, 2012), DAF chemical additives costs, annual replacement membrane module costs provided by Hydration Technology Innovations (Wandera, 2013), and membrane cleaning costs.

Estimation of pumping energy costs required the pump break horsepower (BHP) as an input. BHP was determined using a head-capacity curve diagram (McCabe and Smith, 1976) for a centrifugal pump operating at 160 gal/min flow rate with a total head ranging from 140 to 620 kPa (47–210 ft of liquid) and a pump efficiency of 60%.

Sizing of the HTI membrane modules was done assuming a steady-state operating permeability of $0.09 \text{ L/(m^2 \cdot h)/kPa}$, which was measured in the long-term cross-flow filtration work using a transmembrane pressure of 280 kPa. We used membrane lifetime as a variable to show the effect it has on overall annual operating costs. Although we demonstrated that these membranes could operate at steady state for 5 days at 280 kPa without cleaning, our cost estimate assumes that a chemical enhanced backwash will be performed every 3 days using 600 mg/L hydrochloric acid solution. The cost for this solution was estimated using the ICIS pricing guide (ICIS pricing, 2013). The downtime for cleaning was taken into account in these calculations.

3. Results and discussion

3.1 Experimental work

Husson and coworkers have designed advanced anti-fouling and self-cleaning membranes for treatment of oily 'produced' waters using surface-initiated ATRP from commercial thin-film polyamide nanofiltration membranes [Tomer et al., 2009] and regenerated cellulose UF membranes [Wandera et al., 2011, 2012]. Membranes were fabricated by grafting bi-functional block copolymer (PNIPAAm-*b*-PPEGMA) nanolayers from the membrane surfaces. These membranes were shown to be effective at separating emulsified oils from large volumes of oily water at high flux.

In this study, the performance of these membranes for treatment of wastewaters generated in rendering facilities was evaluated and compared to performance of commercial UF membranes designed for wastewater treatment. Specifically, we measured the productivity and capacity of our modified membranes and commercial UF membranes using impaired waters provided by Carolina By-Products/Valley Proteins, Inc. Other aspects of this work involved characterizing the effluent water quality parameters, characterizing the membrane surfaces pre- and post-filtration to determine the extent of fouling, evaluating membrane cleaning by a water rinse, and estimating the costs for energy and consumables.

3.1 Membrane modification and characterization

The first step to modify CA membranes involved hydrolysis using aqueous NaOH to generate hydroxyl groups that could be activated for surface-initiated ATRP of PNIPAAm-*b*-PPEGMA. Figure 1 shows the ATR-FTIR spectra of the CA membranes before and after hydrolysis. Spectrum A represents a pristine CA membrane. Spectra B, C, D, E, and F represent CA membranes hydrolyzed in aqueous 0.1 N NaOH for 1 to 5 h. On hydrolysis, peaks at 1740 and 1220 cm⁻¹ that are characteristic of the stretching vibration of the C=O bond and the stretching and bending modes of the C–O single bond, respectively, decreased in intensity, while the broad peak centered at 3400 cm⁻¹ characteristic of intra- and intermolecular hydrogen bonding by O–H groups increased. The change in intensity of the peak at 1740 cm⁻¹ was used to estimate the degree of hydrolysis (DH) with time using Equation 2, which was presented previously by Luo et al. [2003],

$$DH = 1 - \frac{\left(A_{1740}/A_{1640}\right)_{t}}{\left(A_{1740}/A_{1640}\right)_{0}} \quad (2)$$

where A_{1740} and A_{1640} represent the absorption intensities (in absorbance units) at 1740 and 1640 cm⁻¹, respectively. Subscripts 0 and t represent the initial time and hydrolysis time, respectively. The intensity of the peak at 1640 cm⁻¹ did not change with increasing hydrolysis time so it was used as the reference. The DH increases steadily with hydrolysis time for approximately the first 2 h and then levels off at 0.82 ± 0.07 (see Figure 2). According to Chen et al. [2002], CA is known to have to both crystalline and non-crystalline regions. Crystalline regions account for roughly 20–25% of CA, which leaves roughly 75–80% amorphous CA. Since crystalline regions of CA are more resistant to hydrolysis, it is not surprising that the rate of hydrolysis slowed substantially after reaching a DH of 0.75 ± 0.06 at 3 h. At this point, most of the amorphous CA available for reaction has been hydrolyzed, leaving crystalline CA that is slow to hydrolyze.



Figure 1. ATR-FTIR spectra for a pristine cellulose acetate membrane (A), and membranes hydrolyzed with 0.1 M aqueous NaOH for 1 h (B), 2 h (C), 3 h (D), 4 h (E), and 5 h (F). The broad peak centered at 3400 cm⁻¹ is characteristic of intra- and intermolecular hydrogen bonding by O–H groups while peaks at 1740 and 1220 cm⁻¹ are characteristic of the stretching vibration of the C=O bond and the stretching and bending modes of the C–O single bond, respectively.



Figure 2. Dependence of degree of hydrolysis of cellulose acetate membranes on hydrolysis time during reaction with 0.1 N aqueous NaOH solution. Four DH values were estimated at each hydrolysis time and symbols in the figure represent the average of those values. The error bars represent the standard errors of the average of those values.

A CA membrane that had been hydrolyzed for 1 h giving a DH of 0.44 ± 0.04 was activated by 5.0 mM 2-BIB and then modified further by surface-initiated ATRP of PNIPAAm-*b*-PPEGMA.

Figure 3 shows the ATR-FTIR spectra of the hydrolyzed CA membrane (A, bottom), the hydrolyzed CA membrane following PNIPAAm modification (B, middle), and the hydrolyzed CA membrane following PNIPAAm-*b*-PPEGMA modification (C, top). Following polymerization, increases in intensity of peaks at 1640 and 1544 cm⁻¹ are characteristic of amide carbonyl groups and N-H bending of PNIPAAm. Peaks in the range 1370–1430 cm⁻¹ also increased and these are assigned to symmetrical and asymmetrical deformation bands associated with the isopropyl group in PNIPAAm. There was a slight increase in the peak at 1740 cm⁻¹, which is attributed to the carbonyl group of PPEGMA. While it is difficult to use FTIR to observe the modification with PPEGMA, our previous work demonstrated that water flux decreases upon addition of the PPEGMA block [Wandera et al., 2011, 2012] giving indirect evidence of successful modification.



Figure 3. ATR-FTIR spectra for (A, bottom) cellulose acetate membrane following 1 h hydrolysis, (B, middle) hydrolyzed cellulose acetate membrane following PNIPAAm modification, and (C, bottom) hydrolyzed cellulose acetate membrane following PNIPAAm*b*-PPEGMA modification. Peaks at 1640 and 1544 cm⁻¹ are characteristic of amide carbonyl groups and N-H bending of PNIPAAm. Peaks in the range 1370–1430 cm⁻¹ are assigned to symmetrical and asymmetrical deformation bands associated with the isopropyl group in PNIPAAm. The peak at 1740 cm⁻¹ is attributed to the carbonyl group of PPEGMA.

GE UltraFilic membranes are engineered to be highly hydrophilic [Hodgins and Samuelson, 1990; Nicolaisen, 2002]. Inspection of Figure 4 spectrum A (bottom) for the unmodified membrane shows a broad peak centered at 3400 cm⁻¹, which can be assigned to hydroxyl groups participating in both inter- and intramolecular hydrogen bonding [Liang and Marchessault, 1959]. Therefore, it was possible to modify the GE UltraFilic membranes by grafting PNIPAAm-*b*-PPEGMA nanolayers by surface-initiated ATRP from the hydroxyl groups. Figure 4 spectrum B (middle) represents the PNIPAAm-modified membrane. Spectrum C (top) represents the PNIPAAm-*b*-PPEGMA-modified membrane. Results were similar to those following polymerization from CA membranes. Increases in intensity of peaks at 1660 and 1535 cm⁻¹ and peaks in the range 1370–1450 cm⁻¹ support successful grafting of PNIPAAm. A slight increase in the peak at 1735 cm⁻¹ supports grafting of PPEGMA.



Figure 4. ATR-FTIR spectra for (A, bottom) unmodified GE UltraFilic membrane, (B, middle) GE UltraFilic membrane following PNIPAAm modification, and (C, bottom) GE UltraFilic membrane following PNIPAAm-*b*-PPEGMA modification. The broad peak centered at 3400 cm⁻¹ is assigned to hydroxyl groups participating in both inter- and intramolecular hydrogen bonding. Peaks at 1660 and 1535 cm⁻¹ are characteristic of amide carbonyl groups and N-H bending of PNIPAAm. Peaks in the range 1370–1450 cm⁻¹ are assigned to symmetrical and asymmetrical deformation bands associated with the isopropyl group in PNIPAAm. The peak at 1735 cm⁻¹ is attributed to the carbonyl group of PPEGMA.

Further inspection of spectra A and B of the PNIPAAm-modified and PNIPAAm-*b*-PPEGMA modified membranes shows shoulders in the peak at 3400 cm⁻¹ associated with hydroxyl group hydrogen bonding. According to earlier work by Coleman and Moskala [1983], when processing polymers containing hydrogen bonded hydroxyl groups (self-associated), there is always sufficient energy to disrupt a significant number of hydrogen bonds, yielding a higher concentration of unassociated (free) hydroxyl groups, with a peak assignment at 3500 cm⁻¹. Therefore, in the case of UltraFilic membranes, it appears that surface modification disrupts intermolecular hydrogen bonds among hydroxyl groups, yielding some fraction of non-hydrogen bonded hydroxyl groups. The observable outcome is a shoulder in the peak assigned to hydroxyl group hydrogen bonding.

Critical to any membrane surface modification is that it preserves the structural properties of the base membrane. SEM images in Figure 5 for unmodified and PNIPAAm-*b*-PPEGMA modified UltraFilic membranes support that the surface modification used in this work preserves the mechanical and dimensional stability of the base membrane. Earlier work by our group [Bhut et al., 2008] showed the same outcome for cellulosic membranes.



Figure 5. SEM images for (A) unmodified and (C) PNIPAAm-*b*-PPEGMA-modified UltraFilic membranes at 2000× magnification with a scale bar of 20 μ m. Images B and D are the corresponding membranes at 5000× magnification with a scale bar of 10 μ m. These images suggest that surface modification preserves the mechanical and dimensional stability of the base membrane.

3.2 Membrane performance

The performance of the membranes was evaluated by measuring their productivity and capacity. Measurements were done using cross-flow membrane filtration experiments with unmodified and modified membranes. The feed solutions were polyacrylamide-free wastewater samples (I, II, and III in Table 1). Polyacrylamide is a coagulant used by the processing facility to improve efficiency in DAF. Wastewater was collected prior to its addition to demonstrate the performance of our membranes without chemical addition. Performance metrics that were evaluated include volumetric filtrate flux, the total volume of water that was processed per unit membrane area before the membranes had to be cleaned, and effluent water quality (COD, turbidity, TDS, and pH). Membrane cleaning was carried out when the flux dropped below 10% of the initial flux. This value was selected arbitrarily. Intermittent membrane cleaning was necessary in just one set of experiments since, in other experiments, the flux never dropped

below 10% of the initial flux even after several days of filtration. The goal here was to maximize overall productivity by limiting membrane fouling through surface modification. Recognizing that fouling is inevitable even with modification, a secondary aim was to decrease the frequency and duration of the membrane cleaning steps to achieve maximum possible membrane performance.

Hydrolyzed CA, PNIPAAm-*b*-PPEGMA-modified CA, unmodified UltraFilic and PNIPAAm-*b*-PPPEGMA-modified UltraFilic membranes were tested using the three different rendering wastewater samples and their performance metrics were compared. Since the water quality of the three samples was different, comparisons were made among membranes that had been treated with the same water sample. A constant TMP was selected depending on what type of membrane was being test to achieve high productivity and limit fouling.

Figure 6 shows permeate flux measurements (permeate flux versus time) by cross-flow ultrafiltration for a CA membrane following 1 h hydrolysis, and a hydrolyzed CA membrane that was modified further by grafting PNIPAAm-b-PPEGMA using surface-initiated ATRP. Filtration was carried out using rendering facility wastewater Sample I over a 5 day period at a constant TMP of 280 kPa. Not surprisingly, permeate flux at the start of the experiment was much lower for the polymer modified membrane than for the hydrolyzed membrane since polymer grafting from the membrane surface provides an additional resistance to flow. However, the polymer-modified membrane maintained a constant permeate flux throughout the 5 day period. Even for the hydrolyzed membrane, the initial decline in flux during the first 12 hours is typical for cross-flow ultrafiltration. During ultrafiltration, particles that are smaller than the membrane pores adsorb to the inner surfaces of the pores leading to internal, adhesive fouling that usually is irreversible. Larger macro-particles are rejected and accumulate on the membrane surface, leading to cake formation that usually is reversible, nonadhesive fouling [Hilal et al., 2005; Taniguchi et al., 2003]. For low MWCO membranes (less than 100 kDa), internal pore fouling dominates early in the filtration run but there is a rapid transition to cake formation that dominates later in the run. For membranes with MWCO greater than 100 kDa, there is a longer period of transition from internal pore fouling to cake formation [Taniguchi et al., 2003]. The results in Figure 6 indicate an initial decline in flux caused by the initial internal fouling, followed by a stable flux after the transition to cake formation, forgoing the need for intermittent cleaning. A similar finding was observed in our previous work with produced water [Wandera et al., 2011, 2012].

Figure 7 shows permeate flux measurements by cross-flow ultrafiltration for an unmodified UltraFilic membrane carried out using rendering facility wastewater Sample I over a 12-day period at a constant TMP of 70 kPa. Despite a much higher initial permeate flux, this membrane maintained ~50% of its initial permeate flux even after 12 days of continuous filtration without intermittent cleaning. This result was not surprising since UltraFilic membranes are designed to be highly hydrophilic to limit membrane fouling. Abboah-Afari and Kiepper [2012] also found stable flux with this membrane during short-term (2 h) treatment of poultry processing wastewater.



Figure 6. Rendering facility wastewater sample I flux measurements by cross-flow filtration at a TMP of 280 kPa using a 1 h hydrolyzed CA membrane and a 1 h hydrolyzed CA membrane that has been modified further by surface-initiated ATRP of PNIPAAm-*b*-PPEGMA.



Figure 7. Rendering facility wastewater sample I flux measurements by cross-flow filtration at a TMP of 70 kPa using an unmodified UltraFilic membrane.

The performance of PNIPAAm-*b*-PPEGMA-modified UltraFilic membranes for filtration of rendering facility wastewater was evaluated and compared to unmodified UltraFilic membranes. Figure 8 shows rendering facility wastewater Sample II permeate flux data

obtained by cross-flow filtration for unmodified and modified UltraFilic membranes using a TMP of 140 kPa. The symbols represent average values measured for two filtration runs carried out using two different membranes. Immediately evident is the severe flux decline compared to results in Figure 7. There may be two reasons for the difference in flux decline. Firstly, wastewater Sample II had a markedly higher solids content and COD than wastewater Sample I. Secondly, the TMP was double the value used to collect the initial data reported in Figure 7. Higher solids content and higher TMP both lead to more rapid accumulation of foulant material at the membrane surface, which accelerates fouling. Flux data show that there was an increase in initial permeate flux after membrane modification, which is opposite to what might be expected from intuition. However, PEG is known to have good hydration properties and has been used for surface modification of membranes to increase permeate flux [Nie et al., 2004]. Thus, it is not surprising that flux might increase upon modification with PPEGMA. Both membranes showed a similar rate of flux decline. However, the total volume of permeate processed through the modified membranes was $\sim 26\%$ higher than the total permeate that was processed through the unmodified membranes before membrane cleaning (after 72 h of operation).



Figure 8. Rendering facility wastewater Sample II flux data obtained by cross-flow filtration for unmodified and modified UltraFilic membranes using a TMP 140 kPa. A second filtration run was carried out for each of these membranes after a membrane cleaning step, indicated by letter R in the legend.

The permeate recovery of both unmodified and modified UltraFilic membranes was determined after a membrane cleaning step that involved membrane relaxation for 30 min and a cold water rinse. Permeate flux recovery was low for all membranes. Several studies show that the effectiveness of membrane cleaning depends on the type of cleaning solution, its concentration, pH, temperature and ionic strength; while the mass transfer of the foulants from the fouling layer to the bulk solution is mainly controlled by the cross-flow velocity,

cleaning time and temperature [Mohammadi and Kazemimoghadam, 2007; Porcelli and Judd, 2010a, 2010b; Salahi et al., 2010; Zondervan and Roffel, 2007]. Therefore, all these parameters would have to be considered to optimize membrane cleaning.

The recovered flux value was the same for both membranes, which suggests that internal pore fouling played an important role towards flux decline. As explained earlier, internal pore fouling dominates early in the filtration run and then transitions to cake formation. Our results suggest that the higher solids content and COD of Sample II, together with the higher TMP used to collect data in Figure 8, led to more severe internal pore fouling that contributed substantially to rapid flux decline. Since internal pore fouling is known to be irreversible [Hilal et al., 2005], it explains why we attained the same low flux recovery for both modified and unmodified membranes. Our membrane cleaning step was only able to remove portions of the cake layer. This conclusion also is consistent with the ATR-FTIR data that are discussed later that indicate that some foulant was removed from the surface.

Despite the differences in wastewater quality for samples used to test performance of hydrolyzed CA and UltraFilic membranes, it is useful to compare filtration results. The initial permeability for the hydrolyzed CA membrane used in Figure 6 was 0.09 L/(m²·h)/kPa, while the value for the unmodified UltraFilic membrane in Figure 8 was 1.2 L/(m².h)/kPa. Thus, it can be interpreted that the CA membrane has a much smaller effective pore size, which rejects foulant species at the surface and limits the degree of internal fouling. From filtration measurements, internal fouling does appear to be more significant for the UltraFilic membranes than for the CA membranes. However, going further and comparing the pure water permeabilities to commercial membranes, we see that the modified UltraFilic membranes have much higher permeabilities (1.9 L/(m²·h)/kPa versus 0.14-0.57 L/(m²·h)/kPa for commercial membranes used removal of organics such as GE SeptaTM, GE Osmonics; Liqui-Flux[®], Membrana GmbH; DowTM, Dow Water Solutions). This suggests that there may be benefit to increasing the degree of grafting from the UltraFilic membranes to partially fill in the pores, thereby improving solute rejection and limiting internal fouling, while maintaining competitive permeabilities.

The membrane surfaces pre- and post-filtration were characterized to determine the extent of membrane fouling. Two analytical techniques were used to evaluate the effectiveness of our chemical-free cleaning procedure to reverse membrane fouling. The ATR-FTIR technique was used to provide information about the chemical nature of the foulant species on the membrane surface, while SEM was utilized to "visualize" membrane surfaces to detect fouling. Both of these techniques have been shown to be effective in detecting the level of membrane fouling [Loh et al., 2009; Mondal and Wickramasinghe, 2008; Tang et al., 2007]. Mondal and Wickramasinghe [2008] highlighted the value of using multiple characterization techniques with different depths of penetration to properly evaluate membrane fouling.

Figure 9 shows the ATR-FTIR spectra for PNIPAAm-*b*-PPEGMA-modified UltraFilic membranes. Spectrum A (bottom) represents a pristine membrane. Spectrum B (middle) represents a membrane after filtration with rendering facility wastewater Sample II but before membrane cleaning. Spectrum C (top) represents a membrane following filtration and membrane cleaning. Figure 10 shows the spectra for unmodified membranes. These results show significant changes in the chemical nature of the both the unmodified and modified

membrane surfaces post-filtration, before membrane cleaning. ATR-FTIR is a surfacesensitive technique. The evanescent wave created by internal reflection of an IR beam in an optically dense crystal extends $0.5-5 \mu m$ (depending on the wavenumber) beyond the crystal surface and into the sample [Perkin Elmer, 2005]. Also, the evanescent wave decays exponentially with distance into the sample. Therefore, the peaks associated with the base membranes diminish in intensity as the membranes become fouled. If the foulant layer thickness exceeds the penetration depth of the evanescent wave, then the peaks associated with the membrane disappear, as in Spectrum B of Figure 9. Protein fouling was detected by Amide I and II peaks at 1560 and 1440 cm⁻¹ that remained in the fouled membrane spectra. So it can be said that some amount of the foulant material was protein and that the thickness of the foulant layer exceeded the penetration depth of the evanescent wave. Spectra of the cleaned membranes (C) showed that our cleaning protocol was successful in partially restoring the unmodified and modified membrane surfaces to their original surface chemical nature since all of the peaks associated with the base membranes reappeared. Recall, however, that flux measurements showed significant membrane fouling and low percentages of initial flux recovery for both the unmodified and modified UltraFilic membranes. The ATR-FTIR spectra support our idea that flux decline in this membrane system was dominated by internal pore fouling. The membrane cleaning step was partially effective in removing the reversible foulant cake layer formed on the membrane surface, but it was not effective in dealing with the irreversible internal pore fouling. Removing some portion of the cake layer increased the intensity of the peaks associated with the base membrane surfaces.



Figure 9. ATR-FTIR spectra for (Spectrum A, bottom) PNIPAAm-*b*-PPEGMA modified UltraFilic membrane, (Spectrum B, middle) modified membrane after filtration with rendering facility wastewater sample II but before membrane cleaning, and (Spectrum C, top) after membrane cleaning. Peaks at 1560 and 1440 cm⁻¹ in Spectrum B are characteristic of Amide I and II bonds, which indicate protein fouling.



Figure 10. ATR-FTIR spectra for (Spectrum A, bottom) pristine UltraFilic membrane, (Spectrum B, middle) unmodified UltraFilic membrane after filtration with rendering facility wastewater sample II but before membrane cleaning, and (Spectrum C, top) after a membrane cleaning step.

Figure 11 shows the SEM images for unmodified (A–C) and PNIPAAm-*b*-PPEGMA-modified (D–F) UltraFilic membranes pre-filtration, after filtration with rendering facility wastewater Sample II but before membrane cleaning, and after membrane cleaning. All images show membranes at 2000x magnification. Comparison of images for unmodified and modified membranes indicated that filtration with rendering facility wastewater led to significant fouling. Significant fouling was still observed after membrane cleaning with a water only rinse. FTIR spectra showed that some fraction of the cake layer was removed by cleaning, based on the reappearance of membrane peaks. SEM images, however, show that not the entire cake layer was removed. This further supports the argument for a targeted future study to optimize the membrane cleaning protocol.

Table 2 shows data from the permeate quality measurements after filtration of rendering facility wastewater using all of the test membranes. CA membranes were used for filtration of wastewater Sample I, while UltraFilic membranes were used for filtration of wastewater Sample II. For all membranes, there were minimal changes in the pH and TDS by treatment, but we observed substantial reduction in turbidity and COD. The turbidity was reduced by nearly 100% for all the membranes tested. COD was reduced 70-84% for all the membranes tested. The low removal of TDS is explained by the fact that salts are the primary contributor to TDS, and uncharged UF membranes are not designed for salt rejection.



Figure 11. SEM images for (image A) unmodified UltraFilic membrane, (image B) unmodified UltraFilic membrane following filtration with rendering facility wastewater sample II but before membrane cleaning, and (image C) after membrane cleaning at 2000x magnification. Images (D–F) are the corresponding images for modified UltraFilic membranes. Scale bar is 20 µm in all images.

Table 2. Permeate quality after filtration of rendering facility wastewater (sample I used for CA membranes and sample II for UltraFilic membranes). Uncertainty values for pH, turbidity, and TDS represent uncertainties associated with the measurement device for single measurements. Uncertainty values for COD represent the standard errors based on three measurements for each water sample analyzed.

Membrane	pН	Turbidity	TDS	COD
		(NTU)	(mg/L)	(mg/L)
Hydrolyzed CA	5.30 ± 0.05	1.00 ± 0.05	1680 ± 5	5300 ± 50
Polymer-modified CA	5.29 ± 0.05	2.00 ± 0.05	1650 ± 5	4800 ± 200
Unmodified UltraFilic	5.21 ± 0.05	0.32 ± 0.05	3100 ± 5	12800 ± 240
Polymer-modified UltraFilic	5.19 ± 0.05	0.07 ± 0.05	3142 ± 5	12700 ± 80

3.2 Cost analysis work

Figure 12 compares the estimated costs of energy and consumables for dissolved air filtration to those for membrane ultrafiltration using the hydrolyzed CA membrane from HTI. Data are presented for total annual operating costs to run a 160 gal/min process, as well as cost per 1000 gallons treated. In this analysis, the transmembrane pressure was set to be 280 kPa, which was shown experimentally to provide steady-state flux over a 5-day period using this membrane. In this figure, membrane lifetime was varied from 6 months to 2 years. As a point of reference, the manufacturer suggested lifetime for the membrane modules is 2 years (Wandera, 2013).

For all cases studied, the operating costs for membrane ultrafiltration were substantially lower than DAF. Chemicals were the largest cost center for DAF, representing nearly 94% of the overall treatment cost, compared to less than 2% of the overall cost for membrane ultrafiltration. Membranes were the largest cost center for the ultrafiltration process. Not surprisingly, anything that can extend membrane lifetime (e.g., reducing the frequency of cleaning by making the surface fouling-resistant) will have a direct economic benefit.

Figure 13 compares the operating costs as a function of transmembrane pressure assuming a 1 year membrane lifetime. This pressure was varied from 140 kPa to 620 kPa, represents the upper limit of the manufacturers recommended pressure range for the support membrane that is used. Sizing of the membrane modules was done assuming a steady-state operating permeability of $0.09 \text{ L/(m^2 \cdot h)/kPa}$, which was measured in the long-term cross-flow filtration work using a transmembrane pressure of 280 kPa. Therefore, we have confidence in the values given at or below pressures of 280 kPa. The values presented for pressures of 420 kPa and 620 kPa assume that steady-state operation can be achieved at these operating pressures. (We have no experimental data to validate that it can.)

Again, the membrane ultrafiltration process had substantially lower operating costs than DAF. Anything that can increase the steady-state membrane flux (e.g., preventing fouling or using higher cross-flow velocities) will have a direct economic benefit.

Based on Figure 13, assuming a 1 year lifetime and steady-state operation at 280 kPa (shown experimentally), we estimate the operating cost for primary treatment by membrane ultrafiltration to be \$0.95/1000 gal compared to \$3.20/1000 gal for DAF.







Figure 13. Operating cost comparisons for membrane ultrafiltration and dissolved air flotation. (TOP) Total annual operating costs. (BOTTOM) Cost per 1000 gallons treated. Membrane lifetime was assumed to be 1 year in this figure. Sizing of the membrane modules was done assuming a steady-state operating permeability of 0.09 L/($m^2 \cdot h$)/kPa and pressures ranging from 140 to 620 kPa.

4. Conclusions

In this project, we investigated the use of fouling-resistant membranes that were designed for treatment of oily water in the treatment of highly impaired wastewaters generated by a rendering facility. Low molecular weight cutoff membranes showed stable permeate fluxes for long periods of time without the need for intermittent cleaning, characteristic of systems with low degrees of internal fouling. For 100 kDa molecular weight cutoff membranes, flux decline was more severe. While polymer-modified membranes processed ~26% more permeate than unmodified membranes in this case, flux recovery after a membrane cleaning step was low and similar for unmodified and modified membranes, characteristic of high degrees of internal fouling. ATR-FTIR spectra and SEM images support these conclusions.

All membranes showed minimal changes in the permeate pH and TDS but there was significant reduction in permeate turbidity and COD. There was nearly 100% reduction in turbidity and over 70% reduction in COD. Low molecular weight cutoff ultrafiltration membranes can be used to treat rendering wastewaters with high solids loading to reduce their turbidity and COD. Use of more open ultrafiltration membranes would require further development. In either case, there is the need for a polishing step such as reverse osmosis to allow direct discharge or beneficial use of the treated water.

Preliminary cost analysis compared the costs of energy and consumables for dissolved air filtration and membrane ultrafiltration. Assuming a conservative membrane lifetime of 1 year, and an operating pressure of 280 kPa, which was shown experimentally to yield steady-state flux, the operating cost for the membrane ultrafiltration process was estimated to be \$0.95 per 1000 gallons of wastewater. This represents 30% of the cost of DAF for the same process.

In addition to the significantly lower projected operating costs for the membrane process, there are likely to be other economic benefits associated with the removal of chemical/polymer additives from the process (e.g., higher quality end products).

Two important factors that were not studied in this work are cross-flow velocity and the solids concentration in the retentate. Both factors impact productivity (i.e., permeate flux). Higher cross-flow velocity is expected to increase flux at the expense of increased pumping costs. A higher solids concentration reduces the degree of dewatering needed after the unit, but will reduce flux. Future work should be done to evaluate the effects that these two factors have on productivity using the hydrolyzed CA ultrafiltration membrane that was used to perform the preliminary cost analysis.

5. References

Abboah-Afari, E., Kiepper, B.H., Membrane filtration of poultry processing wastewater: I. Pre-DAF (Dissolved air flotation), Appl. Eng. Agric. 28 (2012) 231–236.

Bhut, B.V., Wickramasinghe, S.R., Husson, S.M., Preparation of high-capacity, weak anionexchange membranes for protein separations using surface-initiated atom transfer radical polymerization, J. Membr. Sci. 325, (2008) 176–183.

Chen, Y., Xiong, X.-P., Yang, G., Zhang, L.-N., Lei, S.-L., Liang, H., Characterization of regenerated cellulose membranes hydrolyzed from cellulose acetate, Chinese J. Poly. Sci. 20

(2002) 369–375.

Cheryan, M., Rajagopalan, N., Membrane processing of oily streams. Wastewater treatment and waste reduction, J. Membr. Sci. 151 (1998) 13–28.

Coleman, M.M, Moskala, E.J., FTIR studies of polymer blends containing the poly(hydroxyl ether of bisphenol A) and poly(ɛ-caprolactone), Polymer 24 (1983) 251–257.

Colic, M., A new approach to wastewater treatment, Render, June (2006) 18–19.

FTIR Spectroscopy– Attenuated Total Reflectance (ATR), Perkin Elmer Life and Analytical Sciences, 2005, Retrieved 05.25.2012.

Hilal, N., Ogunbiyi, O.O., Miles, N.J., Nigmatullin, R., Methods employed for control of fouling in MF and UF membranes: A comprehensive review, Sep. Sci. Technol. 40 (2005) 1957–2005.

Hodgins, T.L., Samuelson, E., Hydrophilic article and method of producing same, US 4906379, 1990.

ICIS Pricing, Hydrochloric acid.

http://www.icispricing.com/il_shared/Samples/SubPage110.asp (accessed Feb. 2013).

Johns, M. R., Developments in wastewater treatment in the meat processing industry: a Review, Biores. Tech. 54 (1995) 203–216.

Kulkarni, S.S.; Funk, E.W.; Li, N.N. Applications and economics. In *Membrane Handbook*; Ho, W.S.W. and Sirkar, K.K. (Eds.); Kluwer Academic, Boston, 1992.

Liang, C.Y., Marchessault, R.H., Infrared spectra of crystalline polysaccharides. I. Hydrogen bonds in native cellulose. J. Polym. Sci., 37 (1959), 385–395

Loh, S., Beuscher, U., Poddar, T.K., Porter, A.G., Wingard, J.M., Husson, S.M., Wickramasinghe S.R., Interplay among membrane properties, protein properties and operating conditions on protein fouling during normal flow microfiltration. J. Membr. Sci. 332 (2009) 93–103.

McCabe, W. L., and J. C. Smith. *Unit Operations of Chemical Engineering*. New York: McGraw-Hill, 1976.

Mohammadi, T., Kazemimoghadam, M., Chemical cleaning of ultrafiltration membrane in the milk industry, Desalination 204 (2007) 213–218.

Mondal, S., Wickramasinghe, S.R., Produced water treatment by nanofiltration and reverse osmosis membranes, J. Membr. Sci. 322 (2008) 162–170.

Nicolaisen, B., Developments in membrane technology for water treatment, Desalination 153 (2002) 355–360.

Nie, F.-Q., Xu, Z.-K., Ye, P., Wu, J., Seta, P., Acrylonitrile-based copolymer membranes containing reactive groups: Effects of surface-immobilized poly(ethylene glycol)s on anti-fouling properties and blood compatibility, polymer 45 (2004) 399–407.

O'Brien, C.A., Scholz, M., McConnachle, G.L., Membrane bioreactors and constructed wetlands for treatment of rendering plant wastewater, Water Environ. J. 19 (2005) 189–198.

Peng, H., Tremblay, A.Y., Membrane regeneration and filtration modeling in treating oily wastewaters, J. Membr. Sci. 324 (2008) 59–66.

Porcelli, N., Judd, S., Chemical cleaning of potable water membranes: A review, Sep. Purif. Technol. 71(2010a) 137–143.

Porcelli, N., Judd, S., Chemical cleaning of potable water membranes: The cost benefit of optimization, Water Research 44 (2010b) 1389–1398.

Salahi, A., Mohammadi, T., Abbasi, M., Rekabdar, F., Chemical cleaning of ultrafiltration membrane after treatment of oily wastewater, Iran. J. Chem. Eng. 7 (2010) 17–28.

Sindt, L.G., Environmental issues in the rendering industry, In Essential rendering, edited by D. Meeker, (2006) 245–258. Washington DC: National Renderers Association

Swisher, K., Industry savors record prices and growing global demand, Render, April 2012. Tang, C.Y., Kwon, Y.-N., Leckie, J.O., Probing the nano- and micro-scales of reverse osmosis membranes—a comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR and streaming potential measurements, J. Membr. Sci. 287 (2007) 146–156.

Taniguchi, M., Kilduff, J.E., Belfort, G., Modes of natural organic matter fouling during ultrafiltration, Environ. Sci. Technol. 37 (2003) 1676–1683.

Tomer, N., Mondal, S., Wandera, D., Wickramasinghe, S.R., Husson, S.M., Modification of nanofiltration membranes by surface-initiated atom transfer radical polymerization for produced water filtration, Sep. Sci.Technol. 44 (2009) 3346–3368.

Wandera, D. Hydration Technology Innovations, Albany, OR. Personal communication, 2013. Wandera, D., Wickramasinghe, S.R., Husson, S.M., Modification and characterization of

ultrafiltration membranes for treatment of produced water. J. Membr. Sci. 373 (2011) 178-188.

Wandera, D., Himstedt, H. H., Marroquin, M., Wickramasinghe, S.R., Husson, S.M., Modification of ultrafiltration membranes with block copolymer nanolayers for produced water treatment: the roles of polymer chain density and polymerization time on performance, J. Membr. Sci. 403–404 (2012) 250–260.

Singh, N., Husson, S.M., Zdyrko, B., Luzinov, I., Surface modification of microporous PVDF membranes by ATRP, J. Membr. Sci. 262 (2005) 81–90.

U.S. Bureau of Labor Statistics. SAN FRANCISCO CONSUMER PRICE INDEX: AVERAGE ENERGY PRICES." U.S. Bureau of Labor Statistics, 12 Nov. 2012. Web. 18 Dec. 2012.

Zondervan, E., Roffel, B., Evaluation of different cleaning agents used for cleaning ultrafiltration membranes fouled by surface water, J. Membr. Sci. 304 (2007) 40–49.

Impacts and Significance: Unlike other physical/chemical wastewater treatment operations, membrane separators provide a positive barrier to reject solids present in wastewater streams. Thus, membrane separations can be conducted without addition of the chemicals used in dissolved air flotation. Furthermore, membrane units can operate on a variable concentration waste stream. Thus, fluctuations in the feed concentration will not require process adjustments. Eliminating chemical agents for pH adjustment and polymer coagulation agents for solids flocculation will provide economic benefit by reducing operating costs.

In this project, we showed in experimental work that

- ultrafiltration (UF) with a low-permeability (0.09 L/(m²·h)/kPa) membrane can reduce turbidity by 650-fold, *without addition of polyacrylamide*;
- ✤ COD was reduced by 80% and total solids were reduced by 90%;
- ★ stable permeate flux was observed over a 120-hour period, without intermittent cleaning

Preliminary analysis compared the costs of energy and consumables for dissolved air filtration and membrane ultrafiltration. The comparison was done based on data for a DAF unit with an 82,000-gallon capacity tank and 160 gallons per minute flow rate. Assuming a conservative membrane lifetime of 1 year, and an operating pressure shown experimentally to yield steadystate flux, the operating costs were found to be

♦\$3.20 per 1000 gallons of water for DAF primary treatment

\$\$0.95 per 1000 gallons of water for membrane ultrafiltration primary treatment

In addition to the significantly lower projected operating costs for the membrane process, there may be other economic benefits associated with the removal of chemical/polymer additives from the process (e.g., higher quality end products).

Publications: Wandera, D.; Husson, S.M. Assessment of fouling-resistant membranes for additive-free treatment of high-strength wastewaters. *Desalination*, 309, 222-230 (2013).

Wandera, D. Design of advanced fouling-resistant and self-cleaning membranes for treatment of oily and impaired waters. PhD dissertation, Clemson University, Clemson, SC, August 2012.

Outside funding: (PENDING) Husson, S.M. (PI) Antimicrobial, fouling-resistant membranes for treatment of agricultural and brackish waters. US-Israel Binational Agricultural Research & Development Fund, \$150,000.

(DECLINED) Husson, S.M. (PI) Collaborative research: Magnetic field-responsive nanolayers for water treatment. Environmental Engineering sub-program of the National Science Foundation, \$241,187.

Future Work: Two important factors that were not studied in our earlier work are cross-flow velocity and the solids concentration in the retentate. Both factors impact productivity (i.e., permeate flux). Higher cross-flow velocity is expected to increase flux at the expense of increased pumping costs. A higher solids concentration reduces the degree of dewatering needed after the unit, but will reduce flux. Future work should evaluate the effects of these two factors on productivity using the ultrafiltration membrane that was used in the preliminary cost analysis. Understanding and, ultimately, being able to predict how these conditions impact permeate flux is important because flux ultimately determines the area of membrane that is required to process the wastewater, and membrane cost represents the largest annual operating cost analysis. Knowing their effects would lend additional confidence to the operating cost analysis.

Acknowledgments: I would like to thank my two students, Dr. Daniel Wandera and Charlie Grimsley, who carried out the laboratory work and preliminary economic analysis for this project. We are grateful for the financial support of this work by the Animal Co-Products Research and Education Center at Clemson University with funding from the Fats and Protein Research Foundation. We thank Carolina By-Products/ Valley Proteins Inc. for supplying the wastewater for testing. We are grateful to Dale Robertson, Plant Manager at Valley Proteins, Inc. Ward Division for providing operating data needed for completing the preliminary economic analysis. We thank Hydration Technology Innovations for providing cellulose acetate ultrafiltration membranes, as well as price data for the membrane ultrafiltration modules.