Pilot-scale Study Investigating the Performance of Reverse Osmosis and Nanofiltration Membranes for the Removal of Organic Micropollutants, Nutrients and Bulk Organic Carbon

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Introduction

High-pressure membrane technologies, especially reverses osmosis, have been widely used in indirect potable water reuse projects due to their high removal efficiency for unregulated and unidentified organics, as well as nutrients and bulk organic carbon (Drewes et al., 2003). Recent developments in membrane manufacturing have resulted in "lower pressure" membranes such as ultra-low pressure reverse osmosis (ULPRO) and nanofiltration (NF) membranes. The focus of this project is to determine if membranes operating at lower pressures can meet water quality requirements necessary for indirect potable reuse while meeting acceptable operational parameters such as feed pressure, permeate flux, and flux decline. For this purpose, a 19 gpm membrane pilot-skid was constructed and installed at the West Basin Water Recycling Plant (WBWRP) in El Segundo, CA in order to test the performance of two candidate "lower pressure" membranes in treating non-nitrified and nitrified wastewater effluents for indirect potable water reuse applications.

In order to select two candidate membranes for pilot-skid testing, a laboratory testing protocol was developed to investigate the viability of commercially available RO, ULPRO and NF membranes for treating wastewater effluents during indirect potable reuse projects. Parameters relevant to indirect potable reuse projects were chosen as criteria for the evaluation and identification of membranes that could be used to efficiently treat wastewater effluents. The testing protocol evaluated membranes based on the rejection of relevant solutes and constituents present in wastewater effluents (TOC, nutrients (NH_3 and NO_3^-), conductivity, and selected trace organics), as well as operational performance (specific flux, and flux decline due to fouling).

Based on the results from the membrane testing, membranes were ranked in order of how well they performed and the highest ranking membrane was chosen for installation on the pilot-skid operated at the WBWRP. The purpose of this paper is to present the membrane testing protocol used to evaluate the candidate membranes and the selection criteria that were used to select membranes for installation on the pilot-skid operated at the WBWRP.

Candidate Membranes, Testing Equipment and Analytical Methods

Candidate Membranes

Candidate membranes for this study were selected from various manufacturers and represent a variety of RO, ULPRO, and NF membranes that are commercially available. The TFC-HR, a RO membrane, was chosen as the benchmark membrane for which all other candidate membranes were compared to. A list of the candidate membranes that were considered for testing is presented in Table 1.

Table 1. Candidate membranes

Membrane	**TFC-HR**	**TFC-ULP**	**TFC-S**	**CTA**	**XLE**	**NF-90**	**NF-200**
Vendor	Koch	Koch	Koch	Koch	Filmtec	Filmtec	Filmtec
Type	RO	ULPRO	NF	RO	ULPRO	NF	NF
Membrane	**TMG10**	**NE-90**	**RE-BLR**	**ESPA-2**	**TMG20-430**		**MX07**
Vendor	Toray America	Saehan	Saehan	Hydranautics	Toray, Japan		Osmonics
Type	ULPRO	NF	RO	RO	ULPRO		NF
Membrane	**NF-270**	**ESNA**					
Vendor	Filmtec	Hydranautics					
Type	NF	NF					

Fouling Apparatus

A fouling apparatus was constructed in order to investigate the fouling potential of candidate membranes relative to one another. The fouling experimental design used during this study has been commonly used by researchers studying membrane fouling performance and mechanisms in laboratory studies (Balannec et al. 2002, Cho et al. 2000, DiGiano et al. 2000, Lee et al. 2004, Seidel et al. 2002, and Zhu et al.1997). Two cross-flow flat-sheet membrane units (Sepa II, Osmonics, Figure 3) were employed in membrane fouling experiments. The unit consists of two rectangular plate-and-frame cells having a membrane surface area of 139 cm^2 and a cross-sectional flow area of 0.90 cm^2. A picture of the fouling set-up is presented in Figure 1. 50 Liters of the WBWRP microfiltered secondary effluent was used as feed water during fouling tests where two flat-sheet membrane specimens were fouled in parallel. The pH of feedwater was adjusted to 6.0 using HCl and kept constant during the fouling experiments. Applied feed pressure was 60 psi. The feedwater flow rate for each membrane unit was kept at 1,000 mL/min equaling a crossflow velocity of 0.19 m/s. The experiments were operated in recycling mode in which concentrate and permeate were recirculated into the feedwater tank. Feedwater temperature was kept at 22.5±1.5^oC by a stainless steel water cooling loop immersed in the feed solution. The duration of fouling experiment lasted nine days (218 hours) for all membranes to ensure that the membranes reached a relatively stable extent of fouling before experiment was terminated.

Figure 1. Picture of the fouling apparatus

2-Stage Membrane Testing Unit

A two-stage membrane laboratory-scale unit was employed for testing all membranes (Figure 2). The membrane unit employed two single element (4040 spiral wound) vessels arranged in a two-stage array. A baffled stainless steel feed tank (200 liters) was used to supply the feed water to the high-pressure pump (Figure 2). Experiments conducted with candidate membranes on the 2-stage testing unit were carried out with 2 feed water matrices, deionized water and secondary effluent. For deionized feed water matrices, NaCl and $CaSO_4$ was added to achieve 200 mg/L of hardness as $CaCO_3$ and a conductivity of 1200 µs/cm. For all 2-stage membrane experiments a feed water pH of 6.1-6.3 was maintained using HCl. Secondary effluent used for feed water was 0.04 um microfiltered prior to membrane experiments. During all 2-stage membrane experiments, a vertical mixer and a tank recycle pump was used to insure proper mixing. During operation, combined permeate and concentrate flows from the membrane unit were recycled to the stainless steel tank. The return lines were situated so as to maximize mixing and hydraulic retention time before returning to the system feed. A stainless steel cooling loop was used to maintain a constant feed water temperature (23° C) during membrane experiments.

Membrane performance was evaluated in two flow regimes: flow through and internal recycle. For all 2-stage membrane experiments, the feed flow was set at 9.2 gpm. Flow through mode simulates the first stage of a membrane treatment unit, with a system recovery (Q_{perm}/Q_{feed} *100) of 13-15 percent per element (26-30 % total) and a permeate flux (gallons of permeate produced per day divided by the area of membrane (ft^2)) of 20-24. During the internal recycle mode, an internal concentrate recycle loop was used to simulate higher recoveries and bulk concentrations found in the second stage of a full-scale membrane treatment plant. During internal recycle experiments a recovery of 80% was simulated which resulted in a permeate flux of 15-20. When the internal recycle valve was open, a portion of the combined concentrate flow is diverted to the pump inlet and the system feed flow becomes a combination of flow from the feed container and combined concentrate flow. By reducing the feed flow from the feed container and maintaining the permeate flow achieved during flow through experiments, higher system recoveries can be simulated.

During membrane experiments, feed samples were withdrawn from the tank recycle line, and permeate samples were taken from the permeate line before return to the feed tank. A LabView SCADA system was used to collect data for: feed flow, permeate flow, concentrate flow, feed conductivity, permeate conductivity, concentrate conductivity, feed pressure, and temperature. Data collected by the SCADA system was used to compare operational performance among candidate membranes.

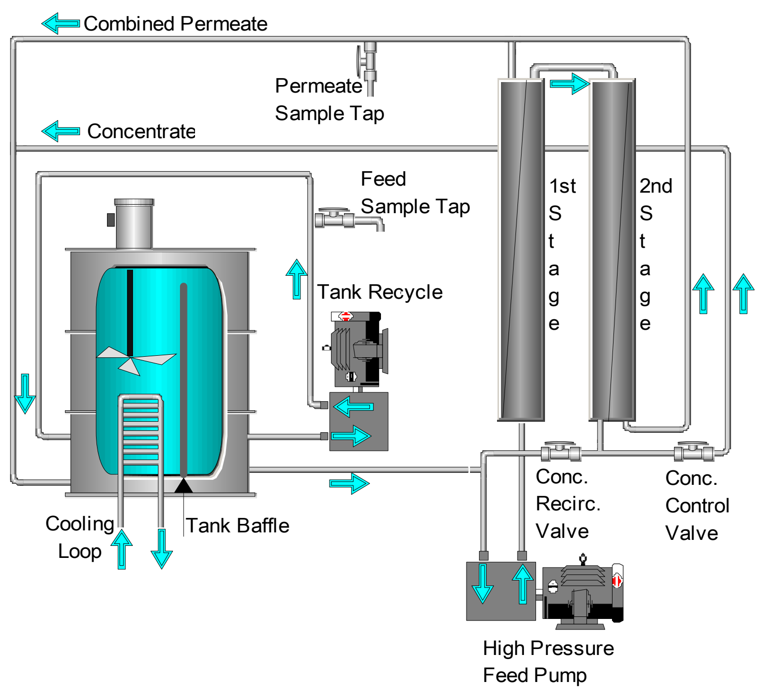

Figure 2. Schematic of the two-stage membrane testing unit using 4040 spiral wound elements.

Analytical Procedures

TOC and Nutrients

Total organic carbon was measured with a Sievers 800 Total Carbon Analyzer and UV-254 was measured with a UV spectrophotometer. Nitrate was measured using Hach method 10020 and Ammonia was measured using Hach method 8038. The method and detection limit for TOC, UV-254, nitrate and ammonia analysis is presented in Table 2.

Table 2. TOC and nutrient analysis method, and detection limit.

Parameter	Method	Detection limit
Total organic carbon (TOC)	Standard Method 5310C	0.06 mg/L
UV absorbance (UVA-254)	Standard Method 5910B	0.06 1/m
Ammonia	Hach 8038	0.02 mg/L N
Nitrate	Hach 10020	0.5 mg/L N

Trace Organic Analysis

The selection of target trace organic used during this study was based on solute characteristics relevant to drinking water augmentation projects using water of impaired quality: solute water solubility (polarity/ hydrophobicity), rejection behavior (e.g., molecular geometry and charge), resistance to biodegradation, and associated potential adverse human health effects. The analysis of the selected trace organics was performed using a method published by Reddersen and Heberer (2003). One liter samples collected during 2-stage membrane experiments were extracted with C-18 material (Solid phase extraction (SPE)), eluted, derivatized and analyzed by GC-MS. A list of compounds that were analyzed by this method is presented in Table 3. Compounds are grouped according to physico-chemical properties including charge and hydrophilicity/hydrophobicity. The criteria for hydrophilicity/hydrophobicity used during this study was: compounds with a Log K_{ow} greater than 3 are considered hydrophobic, compounds with a Log K_{ow} between 1 and 3 are considered transition compounds, and compounds with a Log K_{ow} less than 1 are considered hydrophilic. Compounds considered ionic are negatively charged at the feed water pH (6.1-6.3) used during 2-stage membrane experiments.

Table 3. Trace organics used during candidate membrane experiments

Analyte	Compound Type	Grouping	Limit of Detection (ng/L)*
Caffeine	PhAC	Hydrophilic neutral	20
Clofibric acid	PhAC	Hydrophilic ionic	5
Dichloroprop	Pesticide	Hydrophilic ionic	5
Diclofenac	PhAC	Hydrophilic neutral	1
Fenofibrate	PhAC	Hydrophobic neutral	10
Gemfibrozil	PhAC	Transition ionic	10
Ibuprofen	PhAC	Transition ionic	2
Ketoprofen	PhAC	Transition ionic	5
Mecoprop	Pesticide	Hydrophilic ionic	5
Naproxen	PhAC	Transition non-ionic	2
Propyphenazone	PhAC	Transition non-ionic	2
Carbamazepine	PhAC	Hydrophobic non-ionic	2
Phenacetine	PhAC	Hydrophilic non-ionic	25
Primidone	PhAC	Hydrophilic non-ionic	1
Acetylsalicyclic acid	PhAC	Transition ionic	5
Salicylic Acid	PhAC	Transition ionic	5
Tris(2-chlroethyl)phosphate (TCEP)	Flame Retardant	Transition non-ionic	25
1,3-dichloro-2-propanol phosphate (TDCPP)	Flame Retardant	Transition non-ionic	25
Tris(2-chloroisopropyl)phosphate (TCIPP)	Flame Retardant	Transition non-ionic	10
Bisphenol-A	Plasticizer	Hydrophobic non-ionic	5

*The limit of detection (LOD) is defined as the concentration (ng/L) at which the signal for the three ions for each individual compound is greater than baseline noise by 3 times.

Testing Protocol

<u>Operational Parameters</u>

Permeate Flux and Conductivity Rejection

For each membrane candidate, two operational performance experiments were conducted on the two-stage membrane laboratory scale unit. Data collected by the SCADA system during these two-stage membrane experiments were used to compare operational performance between the candidate membranes. Immediately following the installation of virgin elements onto the two-stage membrane unit, verification experiments were conducted in order to verify that the performance of the membrane specimens used during testing matched manufacturer performance data sheets. During these experiments, feed water was prepared to replicate the conditions used during manufacturer testing and the membrane unit was operated so to replicate manufacturer testing conditions. Following the verification experiment, membrane performance experiments were conducted in accordance to the testing protocol with different feed water matrices (DI and secondary effluent) and different flow regimes (internal recycle and flow through). The SCADA system was used to collect system performance data during these experiments in order to assess and compare membrane operational performance with different flow regimes and different feed water matrices.

Fouling Tendency

Fouling experiments were conducted on the candidate membranes according to the fouling protocol detailed above. Fouling experiments were run for approximately 220 hours and the permeate flux was monitored over the entire experiment. For fouling tendency experiments, the extent of membrane fouling was described by permeate flux decline. Permeate flux decline is defined as the percentage of reduced permeate flux compared to initial permeate flux, that is

$$\text{Permeate flux decline (\%)} = (1-J/J_o) \times 100 \qquad (1)$$

Where J_o is initial permeate flux taken at filtration time of 30 minutes and J is the permeate flux at filtration time t.

The permeate flux decline for a specific membrane was used to calculate a value called the adjusted specific flux, which is described further in the next section.

Adjusted Specific Flux

Flux performance of the candidate membranes was evaluated by considering the specific flux (gfd/psi) observed during two-stage experiments and the flux decline measured during flat-sheet fouling experiments. The unadjusted membrane specific flux value was measured at the end of the flow through two-stage unit experiments, using non-nitrified microfiltered secondary effluent as feed water. This value was chosen, because it most closely represented the conditions used during the flat-sheet fouling experiments and the feed water of the WBWRP. The flux decline was measured during the flat sheet fouling experiments, and was used to correct the virgin membrane specific flux in order to characterize the fouling potential of a specific membrane and the permeate flux that could be expected with a specific membrane on pilot- or full-scale. These two terms were incorporated into a single term, called "adjusted specific flux" (2) in order to make a comparison among the target membranes, and also to compare with the performance of the TFC-HR membrane, which is commonly used during indirect potable reuse applications. This method of comparison allows for some membrane fouling during operation, as long as the "adjusted specific flux" was not reduced to below the specific flux of the TFC-HR membrane. The "adjusted specific flux" is defined as the difference between the specific flux and the flux lost due to fouling (equation 1). Although the fouling experiments did not simulate actual hydrodynamic or pressure conditions (1 L/min and 60 psi) found in pilot or full-scale systems, the membranes were tested under the same conditions, and it is assumed that the measured flux decline is relative, allowing the use of this data for comparison of the candidate membranes. The adjusted specific flux for a particular membrane is calculated with the following equation

$$\text{Adjusted Specific Flux} = \text{Specific Flux} * (1 - J/J_o) \qquad (2)$$

where J/J_o is the flux decline that was measured during fouling experiments.

<u>Nutrient and TOC Rejection</u>

Nutrients

Membranes were evaluated for rejection of inorganic nitrogen species, relevant to differing wastewater operational conditions for nitrogen conversion and removal. Membrane rejection for both ammonia and nitrate was used to determine a membrane's potential for meeting federal drinking water quality requirements, as well as defining membrane specificity for rejection of nitrified or non-nitrified waters. In order to evaluate the rejection of ammonia and nitrate by candidate membranes, experiments with the 2-stage unit were conducted with deionized and secondary effluent as feed water. When necessary, feed water was spiked with ammonia and nitrate to achieve concentrations of 40 mg/L as nitrogen. Experiments were run in both flow through and internal recycle flow regimes with both feed water matrices for approximately three hours after which samples were taken from the feed, concentrate and permeate lines. Samples were analyzed for ammonia and nitrate and concentrations were used to calculate the percent rejection for a particular membrane.

TOC

During flow through and internal recycle flow regime experiments using secondary effluent as feed water, samples were taken from the feed, permeate and concentrate lines for TOC analysis. The percent rejection for a specific membrane was then calculated.

Trace Organic Rejection

2-stage membrane experiments were conducted in order to assess the removal of select trace organics by candidate membranes. These experiments were performed with both feed water matrices (DI and secondary effluent) and under both flow regimes (flow through and internal recycle). Before two-stage membrane rejection experiments were started, selected trace organic solutes were spiked to the feed water at a nominal concentration of 300 ng/L. Permeate and feed samples were taken in triplicate after one hour and analyzed by GC-MS after SPE and derivatization to determine rejection performance.

Selection Criteria

Operational performance was assessed by comparing "adjusted specific flux values" for the membranes tested, which is presented in Equation 2. Nitrogen rejection was assessed using the laboratory-scale deionized feed water experimental data at the end of the flow through experiments. If the membrane exhibited more than 92 percent rejection for both ammonia and nitrate (based on a feed concentration of 40 mg/L N), the membrane is considered to have sufficient nitrogen rejection to meet federal drinking water requirements of 10 mg/L N with feed concentrations up to 40 mg/L N. This does not reflect compliance with California Groundwater Recharge Draft Regulations limit of 5 mg/L total nitrogen, which should be considered when selecting membranes for compliance in that state. If the membrane has more than 92 percent rejection for ammonia, but not for nitrate, the membrane might be considered acceptable for treating only non-nitrified feed waters. If the membrane has more than 92 percent rejection for nitrate, but not for ammonia, then the membrane might be considered acceptable for treating only fully nitrified feeds. For the purpose of this study, it was necessary to select a membrane that has 92 percent rejection for both nitrate and ammonia. Trace organic rejection was assessed using the number of detections in membrane permeates from the laboratory-scale membrane experiments. Permeate concentrations of any compound above the limit of detection (LOD) were considered detects for ranking purposes.

Membranes with adjusted specific flux values less than the adjusted specific flux value for the TFC-HR and ammonia or nitrate rejection less than 92 percent were not considered for further selection. Membranes that meet the initial criteria are then ranked according to performance in each of four categories: operational performance ("adjusted specific flux"), ammonia rejection, nitrate rejection, and trace organic detections above the limit of detection (LOD, signal to noise exceeding 3:1). Ranking was done using whole number integers, with the best performing membrane receiving a value of 1, the second receiving a value of 2, and continuing with the next whole number integer in series for the remaining membranes. Membranes that performed similarly to one another were given the same ranking, with the next best membrane receiving the next available ranking. Ranking in each category was summed, and the membrane with the lowest summed score was chosen for pilot-scale testing at the WBWRP. A flow schematic of the selection process is presented in Figure 3.

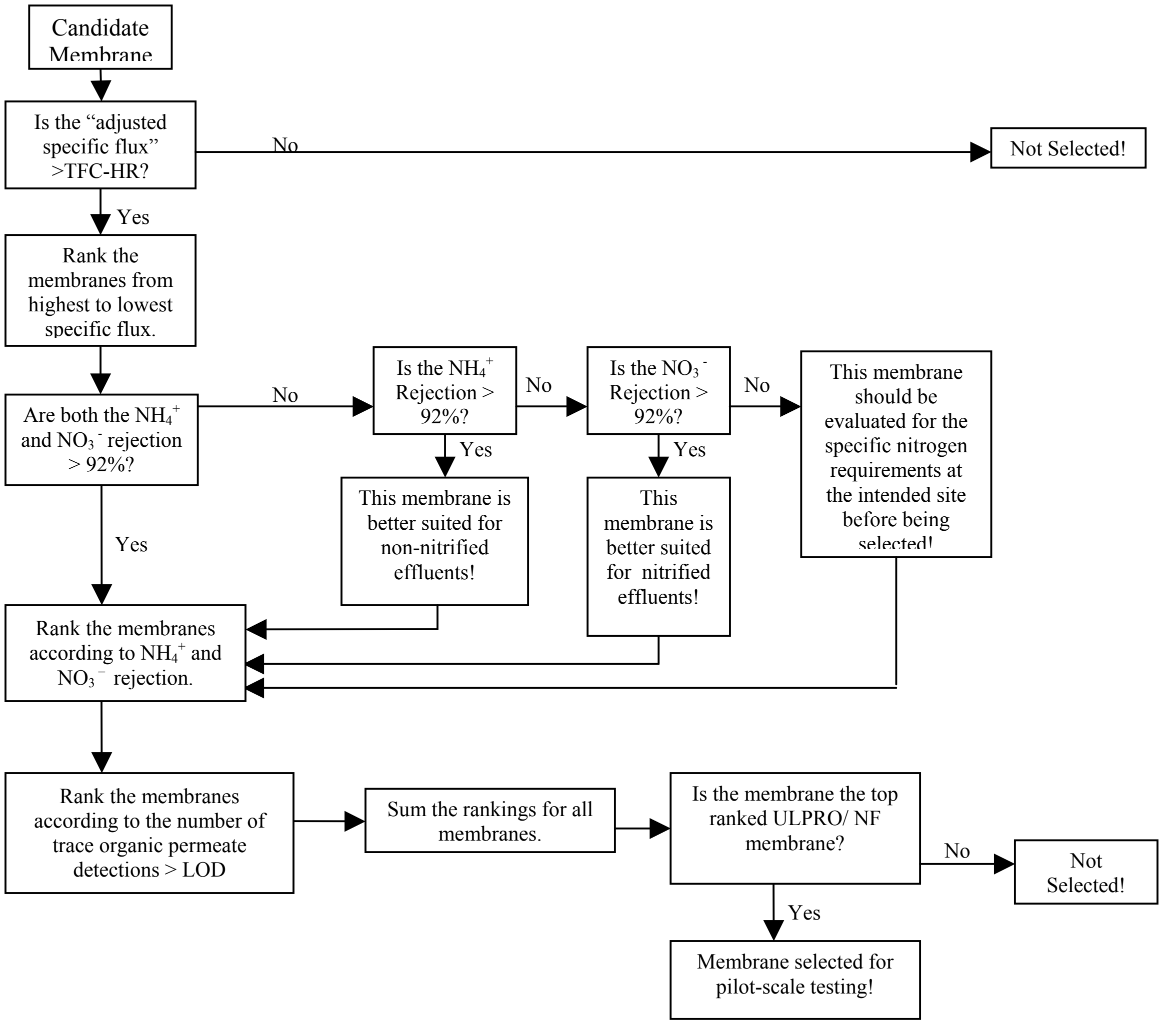

Figure 3. Flow schematic used for selection of candidate membrane for installation on pilot-skid.

Pilot-Skid Description

For this study, a 19-gpm pilot-skid was designed, constructed and installed at the West Basin Water Recycling Plant (WBWRP) in El Segundo, California. The pilot-skid was designed to mimic a full-scale 2-stage membrane treatment train for the treatment of secondary and tertiary treated effluents for indirect potable reuse applications. The skid is configured in a 2:2:1:1 pressure vessel array and a 3:4:3:4 element array with fourteen 4040 elements in the first stage and seven 4040 elements in the second stage. Candidate membranes selected for installation onto the pilot-skid were tested for 3 months with non-nitrified feed water and an additional 3 months with denitrified feed water. The pilot-skid SCADA system continuously logs operational data during operation that allows for the monitoring of flux decline, feed and concentrate pressure increases, and changes in conductivity rejection that will occur with membrane fouling. In addition, sampling campaigns will be conducted to evaluate the rejection of TOC, nitrate, ammonia, select hormones, disinfection by-products, and select trace organics.

Results and Discussion

In order to pick the first candidate membrane for installation on the pilot-skid operated at the WBWRP, the testing protocol was implemented using commercially available ULPRO membranes. Using the data generated during the testing protocol with the ULPRO membranes, the selection criteria outlined in this document was used to select the first membrane for installation on the pilot-skid. The protocol allowed for a clear ranking of the different membrane products that were tested and an ULRPO membrane was selected and installed on the pilot-skid.

Three ULPRO membranes were tested in accordance with the testing protocol and the ranking for the membranes are summarized in Table 4. The membrane ULPRO #1 received the best ranking for the operational parameter (adjusted specific flux), ammonia rejection, and nitrate rejection and was second for trace organic permeate detections. When the rankings were summed, the ULPRO #1 membrane had the lowest value and was chosen for installation on the pilot-skid.

Table 4. Rankings for ULPRO membranes during testing protocol.

Membrane	**Operational Ranking**	**NH_4^+ Rejection Ranking**	**NO_3^- Rejection Ranking**	**Trace Organics Detections Ranking (>LOD)**	**Sum of Ranking**
ULPRO #1	1	1	1	2	5
ULPRO #2	3	2	2	1	8
ULPRO #3	2	2	3	3	10

Table 5 presents a comparison of select parameters obtained during laboratory testing with the ULPRO #1 membrane (using secondary effluent as feed water and the flow through regime) and during pilot-skid operation with the ULPRO #1 membrane. The testing protocol effectively evaluated the performance of the ULPRO #1 membrane on the pilot-skid in respect to TOC rejection, ammonia rejection, and increases in feed pressure due to fouling. Trace organic rejection data could not be completed for this comparison, but will be presented at the 2005 Awwa Membrane Technology Conference in Phoenix, AZ.

Table 5. Comparison of parameters from ULPRO #1 during laboratory testing and pilot-skid testing.

Parameter	**ULPRO #1Testing Protocol**	**ULPRO #1 Pilot-Skid**
TOC Rejection (%)	96	97.3
Ammonia Rejection (%)	95	94.5
Conductivity Rejection (%)	99.3	97.5
Feed Pressure Startup (psi)	141	135
Feed Pressure after fouling period (psi)*	159[#]	157[$]

*The change in feed pressure is the result of fouling and represents the feed pressure needed to maintain a permeate flux equal to the initial permeate flux.

#The fouling protocol was operated for 219 hours.

$The pilot-skid feed pressure stabilized after 200 hours and has been stable for over 600 hours.

Conclusions

This paper summarizes a comprehensive laboratory testing protocol that can be used for the selection of NF/ULPRO candidate membranes for pilot- and full-scale applications. For indirect potable reuse applications, it is necessary to investigate the viability of a specific membrane in terms of operational performance and the rejection of compounds and constituents present in wastewater effluents. The testing protocol was used to select an ULPRO membrane for installation on the pilot-skid operated at the WBWRP in El Segundo, CA. The protocol allowed for a clear ranking of the different ULPRO membranes tested and the selection of a membrane based on operational and rejection performance.

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