

**CAN NANOFILTRATION AND ULTRA-LOW PRESSURE REVERSE OSMOSIS
MEMBRANES REPLACE RO FOR THE REMOVAL OF ORGANIC
MICROPOLLUTANTS, NUTRIENTS AND BULK ORGANIC CARBON?
– A PILOT-SCALE INVESTIGATION**

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ABSTRACT

The scope of this project was to determine if low pressure membranes such as nanofiltration (NF) and ultra-low pressure reverse osmosis (ULPRO) membranes can meet water quality requirements necessary for indirect potable reuse while meeting acceptable operational parameters such as feed pressure, permeate flux, and flux decline. A total of 12 NF and ULPRO membranes were screened in this study and one ULPRO and one NF membrane were selected for a pilot-scale assessment (19 gpm) at a water reuse facility. Results of this study suggest that ULPRO and NF membranes can achieve similar removal efficiencies for the selected trace organics, nitrogen and bulk parameters tested as commonly employed RO membranes. While providing a similar water quality, these membranes can be operated at significantly lower feed pressures. These results suggest that ULPRO and NF membranes are viable for water reuse projects where a high permeate quality is required.

KEYWORDS

Indirect potable reuse, organic micropollutants, nanofiltration, nitrogen, reverse osmosis

INTRODUCTION

High-pressure membrane technologies, especially reverse 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 was 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, California 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.

Performance of NF/ULPRO membranes during this study was based on flux and transmembrane pressure behavior and removal of Tier 1 (conductivity, TOC, UV absorbance, nitrate and ammonia), Tier 2 (dissolved organic nitrogen, pharmaceutically active compounds, endocrine disrupting compounds, disinfection by-products, and contaminant candidate list compounds, aliphatic amines), and Tier 3 compounds (N-nitrosodimethylamine – NDMA). Target compounds selected for this study represent the following physico-chemical properties: hydrophobic non-charged; hydrophobic negatively charged; hydrophilic non-charged; hydrophilic negatively charged; and hydrophilic positively charged compounds. The candidate compounds meeting these characteristics and selected for this study represent endocrine disruptors (e.g., 17 β -estradiol, estriol, testosterone, bisphenol A; pesticides (mecoprop, dichloroprop); DBPs (e.g., trichloroacetic acid, dichloroacetic acid, chloroform, bromoform, and NDMA), pharmaceuticals (e.g., ibuprofen, diclofenac, naproxen, gemfibrozil, phenacetine, caffeine, carbamazepine, and primidone), chlorinated flame retardants, aliphatic amines, and selected compounds appearing on the CCL (e.g., naphthalene). Candidate membranes for this study were selected from various manufacturers and represent a variety of RO, ULPRO, and NF membranes that are commercially available. A list of the candidate membranes that were considered for testing is presented in Table 1. The TFC-HR, a RO membrane currently employed in indirect potable reuse applications, was chosen as the benchmark membrane for which all other candidate membranes were compared to.

Table 1. Target membranes screened in this study

| | | | | | | | | |
|----------|---------------|---------|--------|--------------|--------------|---------|---------|---------|
| Membrane | TFC-HR | TFC-ULP | TFC-S | CTA | XLE | NF-90 | NF-200 | NF-270 |
| Vendor | Koch | Koch | Koch | Koch | Filmtec | Filmtec | Filmtec | Filmtec |
| Type | RO | ULPRO | NF | RO | ULPRO | NF | NF | NF |
| Membrane | TMG10 | NE-90 | RE-BLR | ESPA-2 | ESNA1 | | | |
| Vendor | Toray America | Saehan | Saehan | Hydranautics | Hydranautics | | | |
| Type | ULPRO | NF | RO | RO | NF | | | |

METHODOLOGY

A two-stage membrane laboratory-scale unit was employed for testing and screening all membranes (Figure 1). This 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. Experiments conducted with candidate membranes on the 2-stage testing unit were carried out with two feed water matrices, deionized water and secondary effluent. For deionized feed water matrices, NaCl and CaSO₄ were added to achieve 200 mg/L of hardness as CaCO₃ and a conductivity of 1200 μ s/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 μm 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.

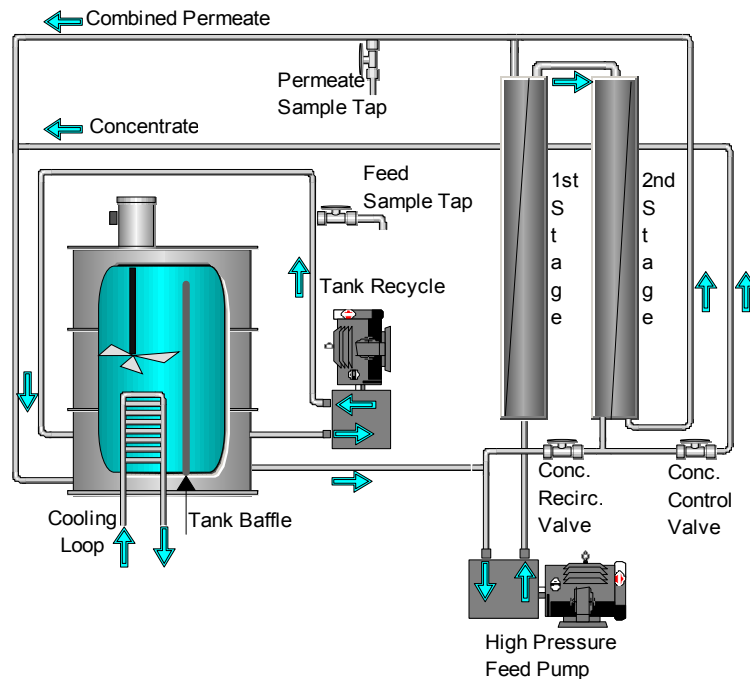


Figure 1. Schematic of the two-stage laboratory-scale membrane testing unit using 4040 spiral wound elements.

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 ($Q_{\text{perm}}/Q_{\text{feed}} * 100$) of 13-15 percent per element (26-30 percent total) and a permeate flux (gallons of permeate produced per day divided by the area of membrane (ft^2)) of 20-24 gfd. 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 percent was simulated which resulted in a permeate flux of 15-20 gfd. 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 these laboratory-scale experiments, two membranes were selected (NF-90 and TMG10) for pilot-scale testing at the West Basin Water Recycling Plant (WBWRP) in El Segundo, California. Detailed information in the membrane selection protocol and experimental results for the membrane screening were reported earlier (Bellona et al. 2005).

For this study, a 19-gpm pilot-skid was designed, constructed and installed at the WBWRP (Figure 2). 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 approximately 1,800 hours with non-nitrified feed water. The pilot-skid SCADA system continuously logged operational data during operation that allowed for the monitoring of flux decline, feed and concentrate pressure increases, and changes in conductivity rejection.



Figure 2. NF/RO Pilot-scale Skid employed during study

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 |
| Acetylsalicylic acid | PhAC | Transition ionic | 5 |
| Salicylic Acid | PhAC | Transition ionic | 5 |
| Tris(2-chloroethyl)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.

RESULTS AND DISCUSSIONS

Removal of Bulk Organics and Nitrogen

The two membranes selected during the laboratory-scale assessment (TMG10, Toray America; NF-90, Dow/Filmtec) were employed on the pilot-scale skid for approximately 2,800 hours and 1,400 hours, respectively. Samples for Tier 1 parameter (TOC, ammonia, nitrate) were collected weekly. Feed and permeate concentrations of TOC are presented in Figures 3 and 4. Both membranes were capable of achieving a TOC rejection exceeding 98 percent with final permeate concentrations of less than 0.3 mg/L. The current standard according to the California Department of Health Service proposed Groundwater Recharge regulations for TOC is less than 0.5 mg/L. Both candidate membranes would meet this requirement. Feed and permeate concentrations of ammonia for both membranes are plotted in Figure 5 and 6. Since the feedwater used in this investigation was a not nitrified microfiltered secondary effluent the nitrate concentrations were below 1 mg/N-L and no nitrate was detected in any permeate sample. While the TMG10 membrane consistently achieved permeate ammonia concentration of less than 1.7 mg/N-L, the NF-90 permeate exhibited ammonia concentrations of less than 2.8 mg/N-L. The current standard according to the California Department of Health Service proposed Groundwater Recharge regulations for total nitrogen TOC is not to exceed 5 mg/N-L. Both low-pressure membranes tested would be able achieving this requirement.

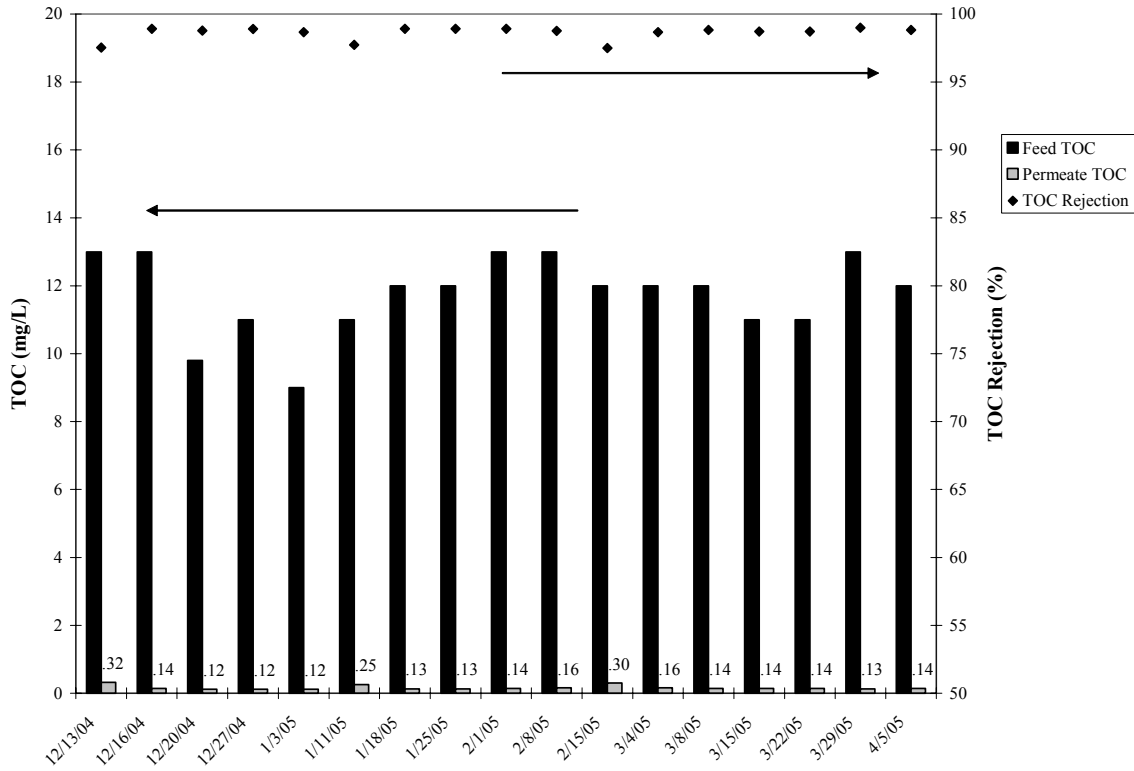


Figure 3. TOC feed and permeate concentrations and rejection of the TMG10 membrane

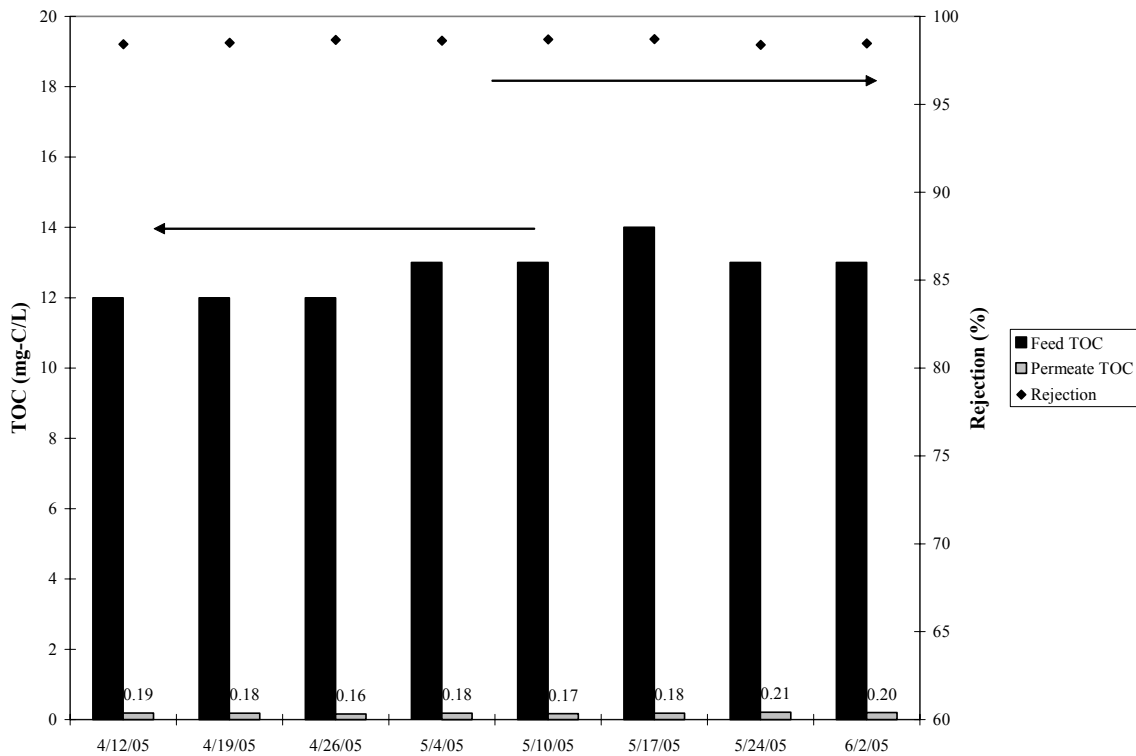


Figure 4. TOC feed and permeate concentrations and rejection of the NF-90 membrane

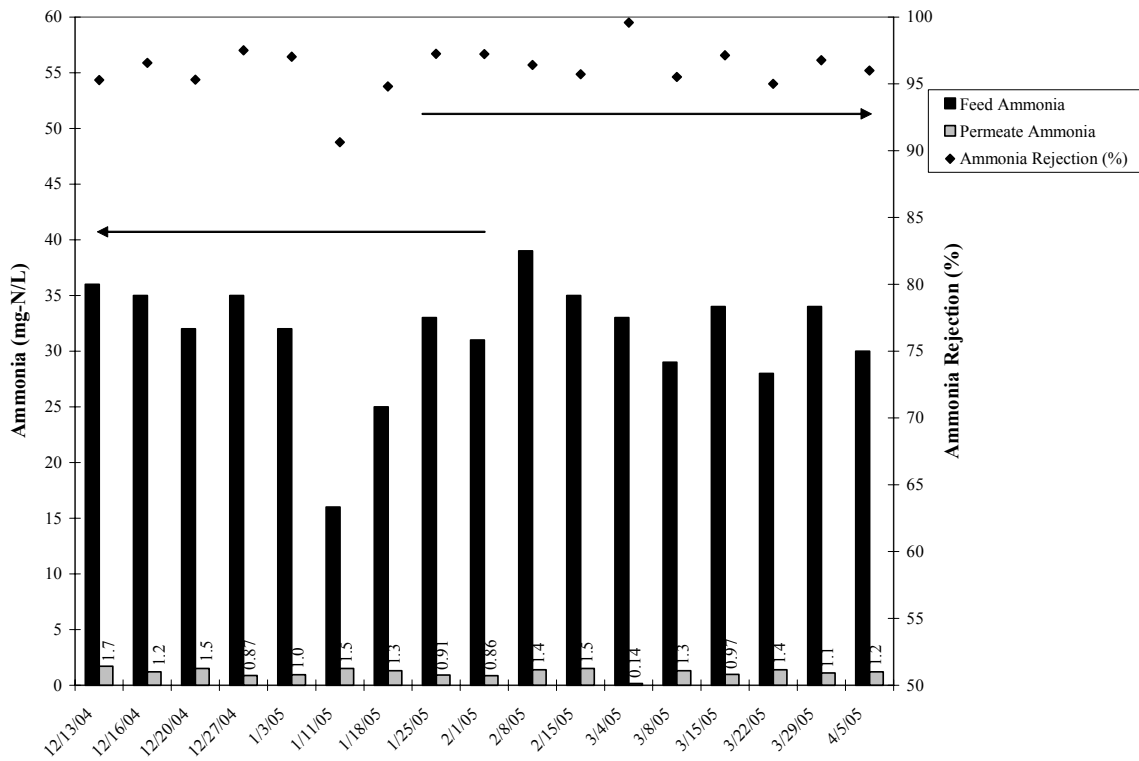


Figure 5. NH₄ feed and permeate concentrations and rejection of the TMG10 membrane

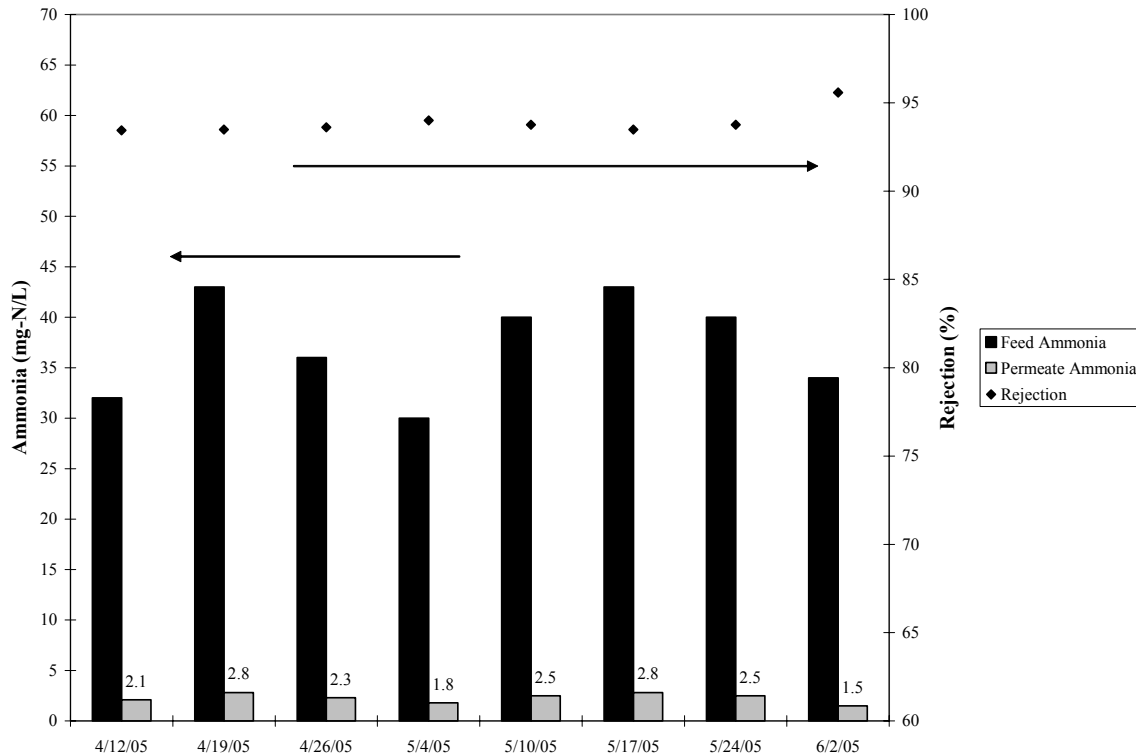


Figure 6. NH_4 feed and permeate concentrations and rejection of the NF-90 membrane

Removal of organic trace pollutants

Samples for organic trace pollutants (Tiers 2 and 3) were collected every sixth week from the feed and combined permeate of a 2.5-mgd RO train at the WBWRP employing the TFC-HR (Koch Membrane Systems, Inc.). None of the pharmaceutical residues and chlorinated flame retardants were quantified in any of the permeate samples collected during the course of this study. Table 4 summarizes the results of one sampling campaign for the full-scale TFC-HR in December 2004. In addition, samples were collected from the feed and the combined permeate of the pilot skid employing the TMG10 and NF-90. Again, while certain target compounds were present in the feed water, none of the pharmaceutical residues, chlorinated flame retardants and endocrine disrupting compounds (hormones, bisphenol A) was quantifiable in the membrane permeates. Table 5 summarizes feed and permeate concentrations of the TMG10 for two sampling campaigns in December 2004.

Table 4. Pharmaceutical residues and personal care product concentrations (Tier 2) in feed and combined permeate for full-scale train #3 (TFC-HR) for sampling campaigns in December 2004

| Analyte (ng/L) Samples (n) | Train #3 (TFC-HR) | |
|-------------------------------|--------------------------|------------------|
| | Combined Permeate | |
| | Campaign #1 | Feed Campaign #1 |
| | 3 | 2 |
| Phenacetine | n.d. | n.d. |
| Salicylic Acid | n.d. (1) - detect (2) | 69 |
| TCEP | n.d. - 15 | 307 |
| TCIPP | n.d. | 580 |
| Caffeine | n.d. | n.d. |
| Clofibric Acid | n.d. | n.d. |
| Propyphenazone | n.d. | n.d. |
| Ibuprofen | n.d. | 37 |
| Mecoprop | n.d. | n.d. |
| Dichloroprop | n.d. | n.d. |
| Gemfibrozil | n.d. | n.d. |
| Primidone | n.d. | 225 |
| TDCPP | n.d. | 368 |
| Naproxen | n.d. | n.d. |
| Fenofibrate | n.d. | n.d. |
| Ketoprofen | n.d. | n.d. |
| Diclofenac | n.d. | n.d. |
| Carbamazepine | n.d. | 420 |
| Bisphenol A | n.d. - detect | 205 |
| Recovery 1 (%) | 60 - 104 | 65 - 104 |
| Recovery 2 (%) | 120-150 | 115 |

Table 5. Pharmaceutical residues and personal care product concentrations (Tier 2) in feed and combined permeate for pilot skid (TMG10) for sampling campaigns in December 2004

PILOT (TMG10)

| | Feed Campaign 1 12/4/2004 | Feed Campaign 2 12/8/2004 | Combined Permeate Campaign 1 12/4/2004 | Combined Permeate Campaign 2 12/8/2004 |
|--------------------|------------------------------|------------------------------|--|--|
| Samples (n) | 5 | 6 | 4 | 4 |
| Analyte | ng/L | ng/L | ng/L | ng/L |
| Phenacetine | n.d. | n.d. | n.d. | n.d.(2) - 10 (1) - 142 (1) |
| Salicylic Acid | 85.2 | 109 | Detect (4) | n.d. (1) - Detect (3) |
| TCEP | 292 | 314 | n.d.(3) - Detect (1) | n.d. |
| TCIPP | 453 | 512 | n.d. (2) - Detect (2) | n.d. |
| Caffeine | 300 | 290 | n.d. | n.d. |
| Clofibric Acid | n.d. | n.d. | n.d. | n.d. |
| Propyphenazone | n.d. | n.d. | n.d. | n.d. |
| Ibuprofen | 169 | 142 | n.d. (3) - 27 (1) | n.d. (3) - Detect (1) |
| Mecoprop | n.d. | n.d. | n.d. | n.d. |
| Dichloroprop | n.d. | n.d. | n.d. | n.d. |
| Gemfibrozil | n.d. | n.d. | n.d. | n.d. |
| Primidone | 285 | 236 | n.d. | n.d. |
| TDCPP | 286 | n.d. | n.d. | n.d. |
| Naproxen | n.d. | n.d. | n.d. | n.d. |
| Fenofibrate | n.d. | n.d. | n.d. | n.d. |
| Ketoprofen | n.d. | n.d. | n.d. | n.d. |
| Diclofenac | n.d. | n.d. | n.d. | n.d. |
| Carbamazepine | 447 | 480 | n.d. | n.d. |
| Bisphenol A | n.d. | 260 | n.d. (1) - 25 (1) | n.d. (1) - Detect (1) |

Operational Conditions

Both membranes were operated at a flux of 12 gfd and a recovery of approximately 85 percent. Both membranes – as expected- exhibited an initial flux decline after start-up. The temperature corrected specific flux of the TMG10 declined from 0.17 to 0.11 gfd/psi after 4 weeks of operation (Figure 7). The NF-90 declined from 0.26 to 0.11 gfd/psi after 4 weeks (Figure 8). Both specific fluxes remained stable during the remainder of the test and were significantly higher than the specific flux of the TFC-HR employed on full-scale which was operated at 0.08 gfd/psi.

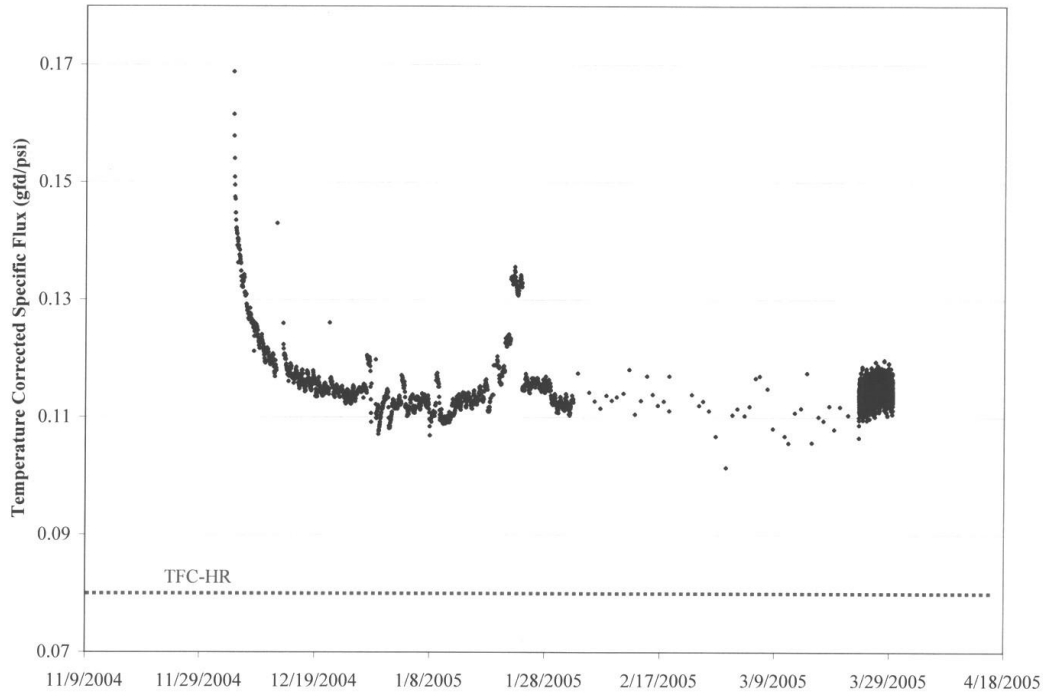


Figure 7. Temperature corrected specific flux for the TMG10

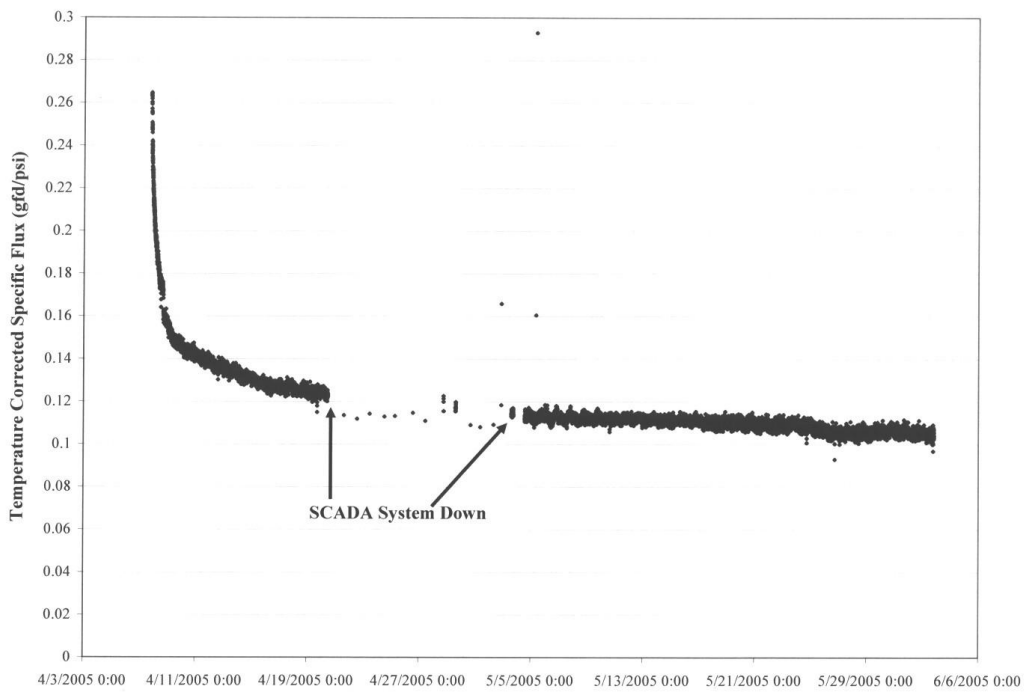


Figure 8. Temperature corrected specific flux for the NF-90

CONCLUSIONS

Results from this study showed that the new generation of ULPRO and NF membranes can achieve similar removal efficiencies for the selected trace organics, nitrogen and bulk parameters tested as commonly employed RO membranes. While providing a similar water quality, these membranes can be operated at significantly lower feed pressures. These results suggest that ULPRO and NF membranes are viable for water reuse projects where a high permeate quality is required.

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