The feasibility of nanofiltration membrane bioreactor (NF-MBR)+reverse osmosis (RO) process for water reclamation: Comparison with ultrafiltration membrane bioreactor (UF-MBR)+RO process

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Abstract: This study examines the feasibility of a novel nanofiltration membrane bioreactor (NF-MBR) followed by reverse osmosis (RO) process for water reclamation at 90% recovery and using an ultrafiltration MBR (UF-MBR)+RO as baseline for comparison. Both MBRs adopted the same external hollow fiber membrane configurations and operating conditions. The collected permeates of the MBRs were subsequently fed to the respective RO systems. The results showed that the NF-MBR (operated at a constant flux of 10 L/m²h) achieved superior MBR permeate quality due to enhanced biodegradation and high rejection capacity of the NF membrane, leading to lower RO fouling rates (~3.3 times) as compared to the UF-MBR. Further analysis indicated that the cake layer fouling that caused the cake-enhanced osmotic pressure (CEOP) effect contributed predominantly to the transmembrane pressure (TMP) increase in the NF-MBR, while irreversible pore fouling was the major reason for UF membrane fouling. Furthermore, it was found that the biopolymers (i.e., organics with MW >10 kDa) were the main components present in the foulants of the NF/UF membranes and RO membranes. The analysis indicated that the NF-MBR+RO system at recovery of 90% has comparable energy consumption as the UF-MBR+RO system at recovery of 75%. Our findings proved the feasibility of the NF-MBR+RO for water reclamation at a high recovery rate.

Highlights:

- A novel NF-MBR+RO system for high recovery water reclamation was developed
- The high-flux NF-MBR achieved excellent permeate quality in treating domestic wastewater
- Fouling mechanisms and foulant characteristics in the NF-MBR+RO and UF-MBR+RO system were illustrated
- Energy consumption between the NF-MBR+RO and UF-MBR+RO system was compared

**The Feasibility of Nanofiltration Membrane Bioreactor (NF-MBR)+Reverse Osmosis (RO)
Process for Water Reclamation: Comparison with Ultrafiltration Membrane Bioreactor (UF-
MBR)+RO Process**

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Abstract

This study examines the feasibility of a novel nanofiltration membrane bioreactor (NF-MBR) followed by reverse osmosis (RO) process for water reclamation at 90% recovery and using an ultrafiltration MBR (UF-MBR)+RO as baseline for comparison. Both MBRs adopted the same external hollow fiber membrane configurations and operating conditions. The collected permeates of the MBRs were subsequently fed to the respective RO systems. The results showed that the NF-MBR (operated at a constant flux of $10 \text{ L/m}^2\text{h}$) achieved superior MBR permeate quality due to enhanced biodegradation and high rejection capacity of the NF membrane, leading to lower RO fouling rates (~ 3.3 times) as compared to the UF-MBR. Further analysis indicated that the cake layer fouling that caused the cake-enhanced osmotic pressure (CEOP) effect contributed predominantly to the transmembrane pressure (TMP) increase in the NF-MBR, while irreversible pore fouling was the major reason for UF membrane fouling. Furthermore, it was found that the biopolymers (i.e., organics with MW $>10 \text{ kDa}$) were the main components present in the foulants of the NF/UF membranes and RO membranes. The analysis indicated that the NF-MBR+RO system at recovery of 90% has comparable energy consumption as the UF-MBR+RO system at recovery of 75%. Our findings proved the feasibility of the NF-MBR+RO for water reclamation at a high recovery rate.

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1. Introduction

Water scarcity resulted from global population growth, rapid urbanization and growing economic activity is one of the major problems in the 21st century. Besides surface water, groundwater, and seawater, water reclamation has become an important alternative for indirect or direct potable use (Bartels et al., 2005).

Universally, water reclamation refers to the treatment of used or wastewater to the quality suitable for water recovery by reverse osmosis (RO) process. For example, the NEWater concept in Singapore involves the pretreatment of effluent from conventional activated sludge (AS) process by a low-pressure membrane process such as microfiltration/ultrafiltration (MF/UF) prior to RO (Qin et al., 2006). Alternatively, the effluent from a membrane bioreactor (MBR) can be directly used as feed water to RO (Chen et al., 2012; Qin et al., 2006). MBRs have become a more viable option for wastewater treatment compared to AS process due to its advantages in terms of better effluent quality, smaller footprint, better disinfection, and reduced sludge production (Yamamoto, 2001). In addition, the successful integration of MBR and RO demonstrated a more consistent removal performance and lower RO fouling rates compared to the AS+MF/UF+RO process for water reclamation (Qin et al., 2006).

Typically, in wastewater reclamation processes, the recovery levels of RO are 75 to 85% using two or more stages of RO in series (Wetterau et al., 2011). Although promising technologies are available to achieve over 90% of recovery, such as semi-batch RO process or known as closed circuit desalination (CCD) (Septon and Efraty, 2016; Warsinger et al., 2016; Werber et al., 2017), energy-efficient reverse osmosis (EERO) (Chong Loo and Krantz, 2015; Chong Loo Fane et al., 2015), the practical recovery level is limited by membrane fouling, including inorganic scaling such as calcium phosphate, calcium carbonate and silica, organic fouling and biofouling (Antony et al.,

2011; Kent et al., 2011; Moreno et al., 2013; Ridgway et al., 1984; Zhao et al., 2010). Usually antiscalants or disinfecting agents are added to RO feed water to reduce RO fouling, however, some antiscalants could enhance the biofouling potential in RO systems (Antony et al., 2011) and disinfecting agents may eventually cause the degradation of membranes in long run (Antony et al., 2010). Emerging technology such as flow reversal (FR) technology is an attractive option for scale control which works by periodically switching the flow direction in the RO pressure vessel arrays to disturb the kinetics of nucleation/crystallization (i.e. scaling) process (Lu et al., 2012). It has been demonstrated to be effective for calcium sulfate and calcium carbonate scaling, but its efficiency on other types of fouling is not well established.

One avenue to prevent RO membrane fouling is to improve the quality of RO feed water. Despite the use of MF/UF or MF/UF-MBR, dissolved organic carbons (DOCs) and scale forming solutes/ions can easily pass through the membrane owing to the relatively large pore sizes of MF/UF membranes. In particular, conventional MBR has its own limitations in removing a wide range of trace organic carbons (TrOCs) such as pesticides, endocrine disrupting chemicals (EDCs), hormones and pharmaceutically active compounds (PhACs) (Tadkaew et al., 2011). Several studies have found that hydrophobic TrOCs can be adsorbed to the biomass, resulting in longer retention time in the bioreactor, thus increasing the removal efficiency. In contrast, hydrophilic TrOCs such as carbamazepine and diclofenac were found to be persistent in both AS and MBR process (Radjenović et al., 2009; Tadkaew et al., 2011; Wijekoon et al., 2013). Furthermore, these compounds are almost not retained by MF/UF membranes.

To achieve high quality permeate, the integration of high retention membrane separation processes, such as membrane distillation (MD), forward osmosis (FO) and nanofiltration (NF) with biological reactor to form MD-MBR, FO-MBR (known as OMBR) and NF-MBR configurations, respectively,

has been explored in recent years (Choi et al., 2002; Cornelissen et al., 2008; Goh et al., 2013; Luo et al., 2015; Qiu et al., 2016). The key differences between high retention MBRs and conventional MBRs are summarized in Table 1.

Insert Table 1

Such high retention MBRs have enhanced biodegradation of refractory organics due to prolonged residence time as well as effective rejection of inorganic compounds (i.e. Ca^{2+}). However, there remain several technical challenges in high retention MBRs, such as salt accumulation, low permeate flux (i.e. $< 10 \text{ L/m}^2 \text{ h}$), and membrane stability (W. C. L. Lay et al., 2010; Luo et al., 2016; Luo et al., 2014). Specifically, in the FO-MBRs, the setbacks include (i) reversed salt diffusion effect that results in the loss of draw solutes and requires constant topping up of draw solutes to maintain the flux; (ii) salinity increase in the bioreactor due to salt accumulation and reverse salt diffusion as well as concentration decrease of the draw solution due to solute diffusion would reduce the net driving force for water permeation, thus causing the flux to decline over time; (iii) elevated salts could increase the soluble microbial products (SMP) and extracellular polymeric substances (EPS) in the mixed liquor that cause greater membrane fouling (Luo et al., 2017); (iv) requires additional steps (i.e. RO or other processes) to separate the draw solution and water. More importantly, the combined FO-MBR and RO process cannot reduce the energy requirement for water production compare to the conventional MBR+RO process due to the trade-off between FO and draw solution recovery processes (Shaffer et al., 2015). While in MD-MBR, the requirement of waste heat and membrane wetting are still the bottlenecks.

Compared to MD-MBRs and FO-MBRs, NF-MBRs are more feasible. This is attributed to the facts that (i) NF is a pressure driven process similar to MF/UF, which is less complicated compared to FO or MD; (ii) NF has lower monovalent salt rejection, thus resulting in a lower salt accumulation in the bioreactor. The maximum salt concentration factor can be controlled by regulating the ratio of

sludge retention time/hydraulic retention time (SRT/HRT, refer to Figure S1 in the Supplementary Data for details) (W. C. Lay et al., 2010); (iii) NF application for surface and groundwater treatment is rather mature with a large number of full-scale installations. However, it shall be noted that the NF-MBR for wastewater treatment is still in its infancy. In previous attempts on NF-MBRs, an extremely low flux of 0.042 L/m²h or equivalent to 0.5 L/m²h·bar was attained with a commercial cellulose acetate NF (Choi Fukushi et al., 2007; Choi et al., 2002; Choi et al., 2006; Choi Lee et al., 2007). The low permeability or high operating pressure required to obtain a decent flux has made the NF-MBR less attractive. However, the novel low-pressure hollow fiber NF membrane, previously developed by the Singapore Membrane Technology Centre (SMTC) for water softening application, may be applied to overcome this challenge. The novel NF membrane possesses a positively charged thin film selective layer with a pure water permeability of ~ 17 L/m²h·bar, molecular weight cut off (MWCO) of < 500 Da, and rejections of Mg²⁺ and Ca²⁺ ~ 90% and Na⁺ < 15% (Liu et al., 2015; Rajabzadeh et al., 2014). Most of the commercial membranes in the market (as summarized in Table S1 in the Supplementary Data) require operating pressures of > 5 bar, but our membrane only requires < 2 bar to achieve this performance. The very low rejection of Na⁺ ion while maintaining high rejection of the divalent ions is the key to achieve such a low operating pressure condition.

In this study, we aim to develop a high-flux NF-MBR (i.e., 10 L/m²h) using the SMTC's in-house fabricated low-pressure hollow fiber NF membrane (with inside-out configuration), and integrate the NF-MBR with a RO process for high recovery water reclamation (i.e., 90% of recovery). The main objectives of this study are (1) to evaluate the performance of an NF-MBR+RO for high recovery water reclamation, (2) to illustrate the membrane fouling mechanisms and examine foulant characteristics in the NF-MBR and RO membranes, and (3) to estimate the energy consumption of the NF-MBR+RO at different recovery levels. An UF-MBR+RO system was used as a baseline for

comparison. This study provides meaningful information for further improvement and scale-up of the NF-MBR+RO system.

2. Materials and methods

2.1. UF-MBR, NF-MBR and RO set-ups and operations

Two identical lab-scale moving bed biofilm membrane bioreactors (hereinafter referred as MBR) employing side-stream ultrafiltration (defined as UF-MBR) and nanofiltration (defined as NF-MBR) membrane modules respectively were set up as shown in Figure S2 (Supplementary Data). Each bioreactor had a total effective working volume of 7.0 L, and filled with 117 pieces of K3 bio-carriers (i.e., filling ratio of 10%). The dimension of a bio-carrier is $12 \times \varnothing 25$ (mm, $W \times D$) with a surface area of $500 \text{ m}^2/\text{m}^3$ (Ping Yin Chemical Packing, China). No activated sludge was inoculated in the bioreactors. The aeration rate of bioreactors was set at 3 L/min. The sludge retention time (SRT), hydraulic retention time (HRT), pH and temperature of bioreactors were kept at 30 d (i.e., 0.233 L of sludge was discharged daily, accounting for only 3% of the feed flow, so the recovery of NF-MBR was assumed to be ~100%), 22 h, 6.8 ± 0.5 , $20 \pm 0.5^\circ\text{C}$, respectively. The bioreactors were continuously with municipal wastewater collected from Ulu Pandan wastewater treatment plant of Singapore (after sieving with a 1 mm opening mesh). The permeate flux of both MBRs was maintained at $10 \text{ L}/\text{m}^2\text{h}$ via a mass flow controller installed on the permeate stream. The pressures of feed, retentate and permeate were recorded by digital pressure transducers (Ashcroft, USA) connected to a data logging system (LabVIEW, National Instrument, USA). The operating parameters of UF-MBR and NF-MBR and the characteristics of the municipal wastewater are summarized in Tables 2 and 3, respectively.

Insert Table 2

Insert Table 3

In this study, SMTC's in-house fabricated polyethersulfone (PES) hollow fiber UF membrane and low-pressure hollow fiber NF membrane with PES as substrate were used and their characteristics are summarized in Table 4. Each membrane module consisted of 25 hollow fibers (0.46 m in length; a total effective area of 0.031 m²) and filtration was performed in an inside (lumen)-out (shell) configuration. Periodic physical membrane cleaning was performed when the transmembrane pressure (TMP) reached the pre-set upper limit due to membrane fouling. After flushing the lumen side of the hollow fiber membrane with tap water at 500 mL/min for 2 min, backwashing was performed (15 min) by using distilled water at a pressure of 0.5 and 2 bar for UF and NF membrane, respectively. When the desired TMP was not achieved after membrane cleaning, the fouled membrane module was replaced with a new module. In the NF-MBR, three new NF membrane modules were used in series, hereinafter, defined as NF1, NF2, and NF3; while in the UF-MBR, two new UF membrane modules were used in series, hereinafter defined as UF1 and UF2.

Insert Table 4

Two identical RO systems were used to study the fouling potential of the permeates from the two MBRs. The details of the RO system (Figure S3, Supplementary Data) were described previously (Suwarno et al., 2016; Wu et al., 2013). Briefly, the RO setup comprised of a feed tank, a high-pressure pump (Hydra Cell D-03-S, USA), a cooling device equipped with temperature controller (PolyScience 9106, USA), a flat sheet RO test cell, a back pressure regulator (SS-4R3A, Swagelok), a mass flow controller (LIQUI-FLOW L30, Bronkhorst, Netherlands), pressure transducers (EUTECH Instruments, USA), and conductivity meters (EUTECH Instruments, USA). The RO membrane (BW-30, DOW FilmTec, USA) with an effective membrane area of 0.0186 m² was

employed in the RO test cell. The crossflow rate of the RO system was maintained at 18 L/h (i.e., equivalent to a crossflow velocity of 0.10 m/s) and the permeate flux was kept at 20 L/m²h by the mass flow controller. In this study, the RO concentrate and RO permeate were recirculated to feed tank and the test solution in the feed tanks was replenished daily.

2.2. Analytical measurement

2.2.1. Water quality parameters

The feed water, mixed liquor and permeate of the MBRs were sampled twice weekly for analysis. The supernatant of the feed water and mixed liquor was obtained by centrifuging for 10 min at 4000 ×g and then filtering through 0.45 µm membrane filter before analysis. Total organic carbon (TOC) and total nitrogen (TN) were determined by a TOC/TN-V analyzer (Shimadzu, Japan). Chemical oxygen demand (COD), ammonia, nitrite, nitrate and total phosphorus (TP) were measured using the colorimetric method with a spectrophotometer (DR 3900, HACH, USA). Concentrations of cations (i.e. Ca²⁺, Mg²⁺) were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer, USA). The extracellular polymeric substances (EPS) content was determined by analyzing the concentrations of polysaccharides and proteins in the MBR permeate. The polysaccharides concentration was determined according to the phenol-sulfuric acid method with glucose as a standard and absorbance measurement at 490 nm using a spectrometer (HACH, USA) (Dubois et al., 1956). The protein concentration was determined by Bradford method with bovine serum albumin (BSA) as standard and absorbance measurement at 595 nm (Bradford, 1976).

Liquid chromatography-organic carbon detector (LC-OCD) analyzer (LC-OCD Model 8, DOC-LABOR, Germany), a size-exclusion chromatography system coupled with organic carbon detection and organic nitrogen detection was used to quantify the dissolved organic fractions in the

sample. The organic matter was separated into major fractions based on their molecular weight and assign them into different fraction group such as biopolymers (typically MW > 10 kDa), humic substances (MW ~ 500 Da), building blocks (MW ~ 300 Da), low molecular weight organics acids (MW ~ 200–250 Da), and neutrals (MW < 200 Da). Details of the LC-OCD system and analysis were described in the literature (Huber et al., 2011).

2.2.2. Total biomass concentration

Total biomass concentration in the bioreactor was defined as the sum of mixed liquor suspended solids (MLSS) and total attached growth biomass on the bio-carriers. The attached growth biomass on the bio-carrier was extracted by sonication (10 min) and vortex (1 min). The total attached growth biomass was estimated by multiplying the attached growth biomass extracted per bio-carrier and the total number of bio-carriers in the bioreactor. The MLSS and biomass concentration were measured according to Standard Methods (American Public Health et al., 2005).

2.2.3. Membrane autopsy

At the end of the membrane filtration tests, membrane modules were removed from the setup for autopsy studies. The foulants were detached from the membrane surfaces by soaking the membranes in 30 mL of Milli-Q water and then ultrasonication for 30 min and vortex for 1 min (Jeong et al., 2013). The foulant solution was centrifuged for 10 min at 4000 ×g and then filtered through 0.45 µm membrane filter, and the filtrates (i.e., soluble foulants) were used for EPS and LC-OCD analysis.

3. Results and Discussion

3.1. MBR performance

3.1.1. Overall reactor performance

Both NF-MBR and UF-MBR were operated for 60-80 days. The accumulation of dissolved organics and divalent ions was observed in the NF-MBR (Figure 1). For example, after 60 days of operation (i.e., both reactors tended to be stable based on the constant total organic removals as shown in Figure 2), the concentrations of DOC (~116 mg/L), conductivity (~ 2212 $\mu\text{S}/\text{cm}$), Ca^{2+} (~267 mg/L), Mg^{2+} (~108 mg/L) and PO_4^{3-} (~71 mg/L) in the NF-MBR were approximately 5.3, 2.4, 8.3, 13.5, and 2.8 times of that in the UF-MBR (DOC at ~22 mg/L, conductivity at ~ 930 $\mu\text{S}/\text{cm}$, Ca^{2+} at ~32 mg/L, Mg^{2+} at ~8 mg/L, and PO_4^{3-} at ~25 mg/L), respectively. The concentration of Ca^{2+} , Mg^{2+} , and PO_4^{3-} increased gradually and reached an equilibrium level at around day 10 due to high rejection properties of the NF membranes (NF1). On day 38 a new NF membrane (NF2) resulted in a further increase of conductivity, Ca^{2+} , Mg^{2+} , and phosphate concentrations, and no equilibrium was reached before day 52. On day 52, a new NF membrane with higher rejection properties, NF3, was used. This has resulted in a further build-up of Ca^{2+} , Mg^{2+} , and PO_4^{3-} concentrations in the NF-MBR. The retention and accumulation of slowly-biodegradable and non-biodegradable organic compounds were inevitable in the high retention NF-MBRs (Figure 1). This finding was similar to the reported studies in the NF-MBR, FO-MBR and MD-MBR (Choi Lee et al., 2007; Phattaranawik et al., 2008; Qiu et al., 2016).

Insert Figure 1

The total attached growth biomass on the bio-carriers in NF-MBR and UF-MBR were maintained at 399 ± 96 and 407 ± 79 mg/L, respectively; whereas the MLSS in the reactors were kept at 503 ± 69 and 513 ± 96 mg/L, respectively (Figure S4 and S5, Supplementary Data). Despite the total biomass was

relatively low (~ 1 g/L), the NF-MBR and UF-MBR achieved excellent biodegradation of DOC at 80.5 $\pm$ 8.2% and 76.7 $\pm$ 9.5%, respectively (detailed mass balance calculation was presented in the Supplementary Data). This implied that the elevated salts level (i.e., Ca^{2+} , Mg^{2+}) in the NF-MBR did not show significant negative impact on the biodegradation of organics; instead slightly greater biodegradation rate was observed (Figure S6, Supplementary Data). This could be attributed to two factors. First, previous studies had pointed out the microorganisms derived from municipal wastewater could tolerate high salt concentration of up to 10 g/L without acclimation (Jang et al., 2013). Interestingly, the presence of additional salt (<10 g/L) could improve the biodegradability of organic carbon due to stimulatory effect on microorganisms (Ng et al., 2005). Second, a longer retention time of the slowly-biodegradable organic substances could enhance their degradation.

Figures 2a and 2b show the COD and DOC levels in the permeates and removals of both MBRs, respectively. The NF-MBR produced the permeate containing 0.5 to 2.5 mg/L of DOC, much lower than the permeate of UF-MBR, i.e., in the range between 7.0 to 9.5 mg/L. The overall COD and DOC removal rates in the NF-MBR were 99.6 $\pm$ 0.8% and 97.5 $\pm$ 1.8%, significantly higher than those in the UF-MBR (93.4 $\pm$ 3.0% and 81.3 $\pm$ 6.9%, respectively).

Insert Figure 2

In addition, the permeate qualities of NF-MBR and UF-MBR were compared as shown in Figure 3. In general, due to better retention of the NF membrane, the permeate of NF-MBR had lower concentrations of proteins (~ 12 times lower), polysaccharides (~ 1.6 times lower), Ca^{2+} (~ 2.3 times lower), Mg^{2+} (~ 5.2 times lower), and PO_4^{3-} (~ 1.4 times lower) compared to that of the UF-MBR. The improved quality of the NF-MBR permeate (i.e., RO feed water) is expected to contribute to less fouling in the subsequent RO process.

270 3.1.2. TMP profiles of MBRs

271 Figures 4a and 4b illustrate the TMP profiles of the NF-MBR and UF-MBR, respectively, under a
272 continuous filtration mode with periodic water flushing and backwashing. In the NF-MBR, from
273 Day 0 to 38, the periodical cleaning of NF membrane (i.e., NF1) was performed when the TMP
274 reached to 1.5 times of the initial TMP. During the early stage of operation (Day 0-12), a gradual
275 increase in TMP was observed. This could be attributed to (i) an increase in osmotic pressure due to
276 the build-up of predominantly rejected inorganic divalent ions (Ca^{2+} , Mg^{2+} , PO_4^{3-} , etc.) and organic
277 molecules in the bioreactor (Figure 1); and (ii) the cake formation due to the deposition of
278 suspended and colloidal particles, soluble microbial products and microorganisms on the membrane
279 surface that increased the overall resistance and possibly the cake enhanced osmotic pressure
280 (CEOP) effect (Tang et al., 2011).

282 In detail, after first backwashing cleaning of NF1 on Day 7, the TMP could not return to the original
283 value of ~100 kPa, mainly due to a continuous increase in osmotic pressure (i.e., as indicated by the
284 increase of conductivity, Figure 1). After an additional 6 days of filtration, the second backwashing
285 was performed when the TMP reached ~220 kPa, the TMP could not return to its original value and
286 was even higher than the value after first cleaning. In the third cycle (Day 13-19), the TMP rise was
287 more notable, hence, pure water flushing was performed to remove the loosely bound cake layer
288 before backwashing. Nevertheless, a rapid fouling rate of ~ 150 kPa/day was observed in the 4th
289 cycle (Day 20-22) and the TMP reached the upper limit of ~ 350 kPa. Meanwhile, the constant flux
290 could not be attained and dropped from 10 L/m²h to 8.5 L/m²h (data not shown). The duration of 2

subsequent cycles became shorter (3-4 days). Also, it was observed that when the TMP exceeded ~250 kPa, the fouling rates increased exponentially (for the last 3 cycles). This could be attributed to the formation of a more compressed cake layer at a high operating pressure of ~ 400 kPa (Teychene et al., 2011), which was not effectively removed by the employed cleaning method.

A new cleaning protocol in an attempt to prolong the NF membrane lifespan was adopted in the operation of NF2. It was hypothesized that more frequent hydraulic physical cleaning was beneficial in removing the limited cake layer (i.e., the TMP rise was low) by shear and uplift forces. To prevent the cake compression or collapse under a high-pressure condition, a combination of water flushing and backwashing (i.e., pure water flushing for 2 min before backwashing for 15 min) was performed when the TMP reached an upper limit of 200 kPa. After implementing the new cleaning protocol, the cycle duration was reduced to around ~1.5-2.5 days. Unexpectedly, a sudden jump in TMP to ~320 kPa at Day 12 occurred due to unattended operation over the weekend. Thus, the membrane was replaced. In NF3, frequent hydraulic physical cleaning was performed, i.e., cycle duration of 1 to 3 days (when TMP reached an upper limit of 200 kPa). The lifespan of NF3 could be prolonged to ~26 days without any chemical cleaning.

On the other hand, in the UF-MBR with a periodically water flushing and backwashing, the TMP increased from an initial value of ~10 kPa to 40 kPa within 25 days during start-up period (for UF1) and ~ 37 days during the stabilization period (For UF2). The TMP profile of UF2 was compared to the TMP profile of NF3 (from 150 kPa to ~250 kPa in 26 days). In general, the UF membrane was cleaned every 3-5 days, which had lower cleaning frequency compared to the NF membrane.

3.1.3. Fouling mechanism

To further clarify the membrane fouling mechanisms in the NF-MBR and UF-MBR, the membrane pure water permeability (PWP) was measured (at a fixed pressure of 100 kPa) after each physical cleaning cycle (Figure 5a). A gradual decline of the NF membrane PWP over time was noticed, which means predominance of cake layer fouling and slow build-up of irreversible fouling. On the other hand, the UF membrane experienced (i) a dramatic drop in the PWP in the first cycle, and (ii) a continuing loss in the PWP in the following cycles. Overall, the irreversible fouling has caused 90% loss in PWP after 7 cycles. These observations implied that the membrane fouling mechanisms in the NF-MBR and UF-MBR appeared to be dissimilar. The fouling experienced by the NF-MBR was highly reversible by physical cleaning due to the formation of cake layers on the NF membrane (it is noted that the NF membrane with pore size distribution ranging from 200-300 Da). In contrast, irreversible fouling was predominant in the UF-MBR as internal pore blocking and pore plugging were likely to take place in the UF membrane (Fu et al., 2016). Despite the NF-MBR had greater amount of potential foulants than UF-MBR (Table 5) and they had different fouling mechanisms, both membranes exhibited approximately similar final value of irreversible fouling resistance (i.e., $R_{irr} = R_{after\ physical\ cleaning} - R_{membrane}$) as shown in Figure 5b. The results suggest that both membranes may have very similar amount of attached foulants that cannot be easily removed by the employed physical cleaning. Upon examining the TMP and resistance data, the additional pressure (i.e. ΔTMP , Figure S7 in the Supplementary Data) required in the UF-MBR was mainly to overcome the increase in irreversible fouling. Conversely, the main contribution for additional pressure in NF-MBR was due to the CEOP effect.

Insert Figure 5

Nevertheless, effective periodically physical cleaning strategies (backwashing and flushing) could help extend the operation lifespan of NF membrane by preventing the collapse and compression of

cake layer, which may eventually lead to irreversible fouling. This finding allows us to further improve NF-MBR performance by optimizing physical fouling control methods, such as employing two-phase flow cleaning protocol using periodical air and water cleaning (Wibisono et al., 2014).

3.1.4. Organic foulant analysis

Table 5 describes the organic fractions in the feed, mixed liquor, permeate of both MBRs. The contribution ratio of each organic fraction to the DOC was presented in Figure 6. In general, the biopolymer fraction (typically MW >10 kDa), accounting for ~24 % of the total DOC in the feed, was removed effectively in both MBRs (>98.5%). The UF-MBR removed less humic substances (59%), building blocks (70%), and LMWs (76%) than the NF-MBR (all >95%). It was noted that humic substances (MW ~500 Da), building blocks (MW ~300 Da), LMWs (MW ~200-250 Da) had smaller sizes than the UF membrane pore size (~50 kDa). Partial removal of these substances by the UF membrane could be due to the retention by cake layer formed on the membrane or adsorption in the membrane pores (Aslam et al., 2017). Furthermore, humic substances are the second abundant organic fractions (~19%) in the NF foulants. The humic substances are relatively stable and could chelate with calcium ions to form calcium enhanced organic fouling layer. Such fouling tends to be more difficult to be removed by physical cleaning (Sutskover-Gutman et al., 2010). The high rejection of organic substances by the NF membrane resulted in their accumulations in the NF-MBR with concentration factors of 2.1, 6.0, 4.9, and 2.5 for biopolymers, humic substances, building blocks, and LMWs, respectively. The difference in the concentration factors could be due to the difference in biodegradability of these compounds. For example, biopolymers and LMWs were more easily biologically degraded than humic substances and building blocks. This finding was similar to the observation in the high retention FO-MBR (Qiu et al., 2016).

Insert Table 5

3.1.5 Correlation between organic fractions in mixed liquor and membrane fouling

In the UF-MBR, majority of the foulants were biopolymers (75.7% or 159.2 mg/m²) due to the high retention property of the UF membrane towards large MW biopolymers. However, it shall be noted that despite the smaller amount of the low MW fractions, i.e., building blocks and LMW, in the foulant, the impact of these components towards the overall resistance could be more critical than the biopolymer fraction due to the effect of pore plugging that resulted in irreversible fouling (Chen et al., 2016). On the other hand, in the NF-MBR, the foulants were comprised of 56.6% biopolymers (128.1 mg/m²), 19.2% humic substances (43.4 mg/m²), 7.6% building blocks (17.2 mg/m²), and 16.7% LMWs (37.8 mg/m²). In addition, by comparing the ratio of organic fractions in the mixed liquor and foulants, it was noticed that the NF membrane was more prone to fouling caused by biopolymers than other organic fractions. Furthermore, both extracted foulants from the UF2 and NF3 membranes have comparable amount of DOC and organic fractions, which was consistent with the fouling resistance tendency (Figure 5).

3.2. RO performance

3.2.1 TMP Profiles of ROs

After about 20 days of operation of both MBRs, the permeates of UF-MBR and NF-MBR were collected and directly fed to the respective RO systems to assess the RO performance. At recovery of ~ 0% (i.e., the permeate was fully returned to the RO feed tank), the permeate of UF-MBR caused more severe fouling on the RO membrane (~3.7 times higher) compared to the permeate of NF-MBR (Figure 7a). The higher fouling rate observed in the RO system fed with UF-MBR permeate was corroborated by the presence of higher amount of soluble organic compounds (Figure

3 and Table 5). This could result in more organic fouling by adsorption of organics onto the membrane surface (i.e., formation of conditioning film), which subsequently initiated the bacterial deposition (Suwarno et al., 2016). Furthermore, these organic compounds could serve as the carbon sources to promote the biofilm formation on the RO membrane.

In another attempt to simulate the membrane fouling at a high recovery of 90%, the collected MBR permeate was concentrated by discharging the RO permeate until the concentration equivalent to 90% recovery was attained. Subsequently, the test was performed with a full recycle of permeate back to the feed tank to assess the membrane fouling. As shown in Figure 7b, the initial TMP increased from 5.3 to 8.5 bar and from 4.5 to 7.0 bar when the recovery ratio was increased from 0 to 90% for the UF-MBR and NF-MBR, respectively. The lower initial operating pressure required for the concentration process in the NF-MBR could be attributed to its superior permeate quality with less divalent ions and dissolved organics (Figure 3 and Table 5). At a high recovery rate of 90%, TMP increase rate ($dTMP/dt$) for the RO system fed with the UF-MBR and NF-MBR permeate was at ~ 0.30 and 0.094 bar/day, respectively. Obviously, the membrane fouling at 90% of recovery ratio is more severe compared to that at 0% of recovery ratio. Nevertheless, with the improved quality of the RO feed water, the fouling rate of the RO membrane in the NF-MBR+RO was ~ 3.3 times lower than that in the UF-MBR+RO. The lower fouling tendency could translate into energy saving and operation cost saving (e.g., chemical cleaning) associated with fouling.

Insert Figure 7

3.2.2. Foulant analysis

Shown in Figure 6, in the RO fouling test with UF-MBR permeate, the ratio of biopolymers in the RO foulant was 43.9%, significantly higher than that in the permeate (1.7%), which suggested a

greater tendency of their accumulation onto the RO membrane. Meanwhile, the ratios of building blocks (24.6%) and LMWs (31.5%) were comparable to those in the permeate (22.1% and 29.0% respectively). In addition, on the RO membranes, no humic substance (i.e., non-detectable) were observed. Similarly, in the NF-MBR+RO system, a high ratio of biopolymers (40.7%) in the RO foulants was observed. The biopolymers appeared to be the major component of the RO foulants despite both permeates had different compositions and very low amount of biopolymers. The possible mechanism is the transformation of smaller organic molecules to the larger biopolymers through aggregation or bio-conversion (such as producing extracellular polymeric substances) (Jeong et al., 2013). Future studies on this aspect will be performed.

3.2.3. Correlation between organic fractions in MBR permeate and RO fouling

It was found that the amounts of biopolymers, building blocks, and LMWs were ~ 5 to 6 times higher in the RO foulant with the UF-MBR permeate than those with the NF-MBR permeate (Table 5). The autopsy results agreed well with the TMP profiles in Figure 7. Thus, the removal of organic fractions was crucial to the sustainable operation of downstream RO processes. In fact, in a recent work (Katsuki Kimura et al., 2016), where an NF membrane was used to pretreat the MF/UF-MBR effluent prior the RO process, has shown that (1) severe membrane fouling occurred only in the co-presence of organics and silica; (2) the removal of the organic matter from the RO feed water could significantly reduce the RO membrane fouling.

3.3. Comparison of energy consumption of NF-MBR+RO and UF-MBR+RO

Energy consumption is an important aspect in evaluating the feasibility of NF-MBR+RO process for high recovery water reclamation. In MBR+RO processes, aeration energy and pump energy are practically the two major contributors to the total energy demand. The total aeration energy is the

sum of power consumption of blowers for membrane (only for submerged membrane configuration) and biological process. Based on the typical values applied in the aerobic MBRs, normalized biological aeration demand of 10 Nm³ air/m³ product (Qin et al., 2007) and a specific membrane aeration demand of 0.3 Nm³/m²h (Judd and Judd, 2006) were chosen. A power consumption of 0.019 kWh/Nm³ air for coarse bubble aeration was taken for calculation (Maere et al., 2011). Pump energy usage was evaluated using the pump power requirement equation (Judd and Judd, 2006):

$$P = \frac{Q\rho gH}{1000\xi} \quad (1)$$

where P is the pump energy demand (kW), Q is the volumetric liquid flow rate (m³/s), ρ is the pumped fluid density (kg/m³), g is gravitational field strength (9.8 N/kg), H is water head (m, which is equivalent to ~10 times of the feed pressure (bar)), and ξ is pump efficiency (assuming 80% in this study).

Table 6 summarizes the total energy consumption (kWh/m³ product) of the submerged UF-MBR+RO and side-stream NF-MBR+RO at a RO recovery rate of 75% or 90% respectively. It is noted that if the RO membrane is operated at recovery of 90% in the submerged UF-MBR+RO systems, additional RO pre-treatment (i.e., MBR post-treatment, such as activated carbon adsorption process (Wang et al., 2014) or low-pressure NF process (K. Kimura et al., 2016)) is generally necessary in order to achieve consistent RO performance. Thus, this scenario is not discussed in this study.

In the NF-MBR+RO system, increasing the RO recovery rate from 75% to 90%, the energy consumption only inclines from 0.732 to 0.739 kWh/m³, both are slightly lower than that of the submerged UF-MBR+RO (0.770 kWh/m³) at 75% of recovery rate. This signifies the feasibility of NF-MBR+RO for high recovery water reclamation process. It is worth noting that the capital cost of

446 NF-MBR+RO may be higher than UF-MBR+RO due to relatively lower NF permeate flux (10
447 L/m²h) and larger NF membrane area is required. A decrease in capital cost of NF-MBR+RO could
448 be foreseen with improved permeability by developing novel NF membranes and advanced NF
449 membrane fouling control strategies.

450 *Insert Table 6*

451 **4. Conclusions**

452 In this study, a novel NF-MBR+RO system for high recovery water reclamation was developed and
453 compared with a UF-MBR+RO system. The following conclusions can be drawn:

454 (1) The NF-MBR achieved higher organic and inorganic removal than the UF-MBR. The extended
455 retention time could enhance the biodegradation of retained organics in the reactor.

456 (2) The fouling experienced by the NF-MBR was highly reversible in which the PWP can be
457 restored by physical cleaning, while irreversible fouling was predominant in the UF-MBR.

458 (3) The subsequent RO membrane fed with the NF-MBR permeate displayed better performance
459 than that with the UF-MBR permeate due to lower organic/inorganic substances present in the NF-
460 MBR permeate.

461 (4) In both NF-MBR+RO and UF-MBR+RO, biopolymers were identified as the predominant
462 organic foulants in the MBR and RO processes.

463 (5) The calculated energy consumption of the NF-MBR+RO system at 90% recovery was
464 comparable to that of the UF-MBR+RO at 75% recovery, which proves the feasibility of NF-
465 MBR+RO for high recovery water reclamation.

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Table 1. A comparison of conventional and high retention MBRs (Luo et al., 2014)

Table 2. Operating parameters of the UF-MBR and NF-MBR

Table 3. Characteristics of the municipal wastewater (n=25)

Table 4. Properties of the UF and NF membranes (Liu et al., 2015)

Table 5. Concentrations of dissolved organic fractions in the feed, mixed liquor, permeate and foulants of the MBRs and ROs.

Table 6. A comparison of energy consumption (kWh/m³ product) for NF-MBR+RO and UF-MBR+RO at different recovery ratios.

Table 1. A comparison of conventional and high retention MBRs (Luo et al., 2014)

	Conventional MBR MF/UF-MBR	MD-MBR	High retention MBR FO-MBR	NF-MBR
Membrane	Hydrophilic porous MF/UF	Hydrophobic porous MF	Dense FO (usually TFC type)	Dense NF (usually TFC type)
Driving force	Hydraulic pressure	Vapour pressure	Osmotic pressure	Hydraulic pressure
NaCl rejection (%)	Negligible	~ 100	~ 100	40 – 90
TOC in permeate (mg/L)	3 – 10	< 0.8	< 3	1 – 4
Organic micropollutants rejection	low	high	high	high
Permeate flux (L/m ² h)	10 – 30	1.2 – 15	< 10	< 2.5
Additional step	-	Heat source is required	water/draw solute separation	-

Table 2. Operating parameters of the UF-MBR and NF-MBR

Parameter	MBRs
HRT (h)	22
SRT (d)	30
Flux (L/m ² h)	10
Organic loading Rate (g COD/L.day)	0.43
F/M Ratio (g COD/g MLSS.d)	0.43
Crossflow velocity of side stream membrane unit (m/s)	0.20
pH	6.3 – 7.3
Aeration (L/min)	3.0
Dissolved oxygen level (mg/L)	5.5 – 6.5
Biocarrier filling ratio (%)	10

Table 3. Characteristics of the municipal wastewater (n=25)

Parameter	Value
tCOD (mg/L)	389.8 ± 169.9
sCOD (mg/L)	124.9 ± 45.1
DOC (mg/L)	48.3 ± 13.9
Ca ²⁺ (mg/L)	28.9 ± 3.5
Mg ²⁺ (mg/L)	7.9 ± 1.2
Na ⁺ (mg/L)	105.2 ± 6.9
TN (mg/L)	40.7 ± 6.1
NH ₄ -N (mg/L)	40.9 ± 4.5
NO ₃ ⁻ N (mg/L)	0.3 ± 0.2
NO ₂ ⁻ N (mg/L)	N.D.
PO ₄ ³⁻ (mg/L)	23.6 ± 3.2
Conductivity (μs/cm)	859.5 ± 18.9

Note: tCOD: total chemical oxygen demand; sCOD: soluble chemical oxygen demand; DOC: dissolved organic carbon; TN: total nitrogen; TP: total phosphorus; N.D.: not detectable.

Table 4. Properties of the UF and NF membranes (Liu et al., 2015)

	UF membrane	NF membrane
Material	PES	Glutaraldehyde (GA) crosslinked layer-by-layer polyelectrolyte with PES UF as substrate
Pore size (MWCO, Da)	50,000	200-300
Active Layer	N.A.	Lumen side
ID/OD (mm)	0.9/1.4	0.9/1.4
Ca ²⁺ Rejection (%)	N.A.	91.8
Mg ²⁺ Rejection (%)	N.A.	98.4

Note: MWCO: Molecular weight cut-off; ID: inner diameter; OD: outer diameter; N.A.: not applicable.

Table 5. Concentrations of dissolved organic fractions in the feed, mixed liquor, permeate and foulants of the MBRs and ROs.

		DOC	Biopolymers	Humic substances	Building blocks	LMW
	Feed (mg/L)	35.6	8.4	7.8	5.0	8.2
UF-MBR + RO	Mixed Liquor (mg/L)	16.7	7.7	4.1	2.0	2.8
	UF permeate (mg/L)	8.0	0.1	3.2	1.5	2.0
	UF foulant ^a (mg/m ²)	201.2	159.2	N.D. ^e	37.6	13.4
	RO foulant ^b (mg/m ²)	104.5	45.3	N.D.	25.4	32.5
NF-MBR + RO	Mixed Liquor (mg/L)	109.5	17.8	46.9	24.3	20.9
	NF permeate (mg/L)	0.9	N.D.	0.1	0.1	0.4
	NF foulant ^c (mg/m ²)	198.3	128.1	43.4	17.2	37.8
	RO foulant ^d (mg/m ²)	22.6	7.0	N.D.	4.6	5.6

^a UF2 membrane was removed for autopsy at the end of cycle.

^b RO membrane was operated for ~8 days, after which a TMP of 6.5 bar was reached (equivalent to ~ 20% increase in TMP).

^c NF3 membrane was removed for autopsy at the end of cycle.

^d RO membrane was operated for ~26 days, after which a TMP of 6.5 bar was reached (equivalent to ~ 20% increase in TMP).

^e N.D. represents "not detectable".

Table 6. A comparison of energy consumption (kWh/m³ product) for NF-MBR+RO and UF-MBR+RO at different recovery ratios.

		Submerged UF-MBR+RO (75% recovery)	Side-stream NF-MBR+RO (75% recovery)	Side-stream NF-MBR+RO (90% recovery)
MBR	Feed pump	0.005	0.005	0.004
	Waste pump	0.0001	0.0001	0.0001
	UF/NF crossflow pump	-	0.231 ^a	0.193
	UF permeate pump	0.012	-	-
	Aeration (biological)	-	0.190	0.190
	Aeration (membrane)	0.447 ^b	-	-
RO	High-pressure pump	0.306 ^c	0.306	0.352 ^d
Total		0.770	0.732	0.739

^a Feed pressure of NF at 100% of recovery was set at 2.5 bar.

^b UF flux was set at 17 L/m²h.

^c Feed pressure of RO at 75% of recovery was set at 6.62 bar.

^d Feed pressure of RO at 90% of recovery was set at 9.12 bar.

Figure 1. DOC, Conductivity, Ca^{2+} , Mg^{2+} , and phosphate concentrations in the NF-MBR.

Figure 2. COD (a) and DOC (B) in the permeate of NF-MBR and UF-MBR.

Figure 3. Comparison of permeate quality of NF-MBR and UF-MBR.

Figure 4. TMP profiles in the (a) NF-MBR and (b) UF-MBR.

Figure 5. (a) Membrane water permeability and (b) irreversible fouling resistance after each cleaning cycle for UF2 and NF3. Note that the test period is 37 and 26 days for UF2 and NF3, respectively.

Figure 6. Contribution ratios of dissolved organic fractions in feed, mixed liquor, permeate and foulants of UF-MBR+RO and NF-MBR+RO.

Figure 7. TMP profiles of the RO systems fed with permeate from UF-MBR and NF-MBR at a concentration equivalent to (a) 0% recovery (b) 90% recovery. CP represents the concentration process to increase the concentration of the solution from 0 to 90% recovery equivalent.

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