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Gordon

2017

Wu, B., Christen, T., Tan, H. S., Hochstrasser, F., Suwarno, S. R., Liu, X., et al. (2017).
Improved performance of gravity-driven membrane filtration for seawater pretreatment:
Implications of membrane module configuration. *Water Research*, 114, 59-68.

<https://hdl.handle.net/10356/80772>

<https://doi.org/10.1016/j.watres.2017.02.022>

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available at: [<http://dx.doi.org/10.1016/j.watres.2017.02.022>].

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- > The pilot GDM reactor achieved a high flux at 18.6 L/m²h at 40 mbar
- > Reactor dimension influenced the propagation of bacteria and eukaryotes
- > Hollow fibre membrane flux increased with reduced packing density
- > Porous cake layers with less biopolymers and humics led to a high flux
- > Long-term operation of GDM benefited to remove AOC and biopolymers

Improved Performance of Gravity-Driven Membrane Filtration for Seawater Pretreatment: Implications of Membrane Module Configuration

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Abstract

As a low energy and chemical free process, gravity-driven membrane (GDM) filtration has shown a potential for seawater pretreatment in our previous studies. In this study, a pilot submerged GDM reactor (effective volume of 720 L) was operated over 250 days and the permeate flux stabilized at 18.6 ± 1.4 L/m²h at a hydrostatic pressure of 40 mbar. This flux was higher than those in the lab-scale GDM reactor (16.3 ± 0.2 L/m²h; effective volume of 8.4 L) and in the filtration cell system (2.7 ± 0.6 L/m²h; feed side volume of 0.0046 L) when the same flat sheet membrane was used. Interestingly, when the filtration cell was submerged into the GDM reactor, the flux (17.2 L/m²h) was comparable to the submerged membrane module. Analysis of cake layer morphology and foulant properties indicated that a thicker but more porous cake layer with less accumulation of organic substances (biopolymers and humics) contributed to the improved permeate flux. This phenomenon was possibly associated with longer residence time of organic substances and sufficient space for the growth, predation, and movement of the eukaryotes in the GDM reactor. In addition, the permeate flux of the submerged hollow fibre membrane increased with decreasing packing density. It is thought that the movement of large-sized eukaryotes could be limited when the space between hollow fibres was reduced. In terms of pretreatment, the GDM systems effectively removed turbidity, viable cells, and transparent exopolymer particles from the feed seawater. Importantly, extending the reactor operation time produced a permeate with less assimilable organic carbon and biopolymers. Thus, the superior quality of the GDM permeate has the potential to alleviate subsequent reverse osmosis membrane fouling for seawater treatment.

Key words: Eukaryotes; Gravity-driven membrane filtration; Membrane packing density; Optical Coherence Tomography; Seawater pretreatment; Stabilized flux

1. Introduction

Gravity-driven membrane (GDM) filtration has received increasing attention in treating/pretreating surface water (Peter-Varbanets et al., 2012; Peter-Varbanets et al., 2010), diluted wastewater (Peter-Varbanets et al., 2010), grey water (Ding et al., 2016), and seawater (Akhondi et al., 2015; Wu et al., 2016). In the GDM filtration process, the microfiltration (MF)/ultrafiltration (UF) membrane is located below water level at 40-100 cm (i.e., hydrostatic pressure of 40-100 mbar) and operated in a dead-end filtration mode. The presence of a microbial community in the feed water leads to formation of biofouling layers on the membrane, while the movement and predation behaviour of eukaryotic organisms in the biofouling layer perform “biological cleaning” to reduce biofouling resistance (i.e., form an open, heterogeneous, and porous fouling layer). When the dynamic development of such a “mini ecosystem” tends to be stabilized on the membrane, the permeate flux reaches a relatively constant level (Derlon et al., 2013; Derlon et al., 2012; Klein et al., 2016).

Compared to widely used biosand filter (i.e., biofilter with Schmutzdecke) that also employs the embedded biofilm to achieve high organic removal efficiency, the GDM filtration process does not require periodically physical cleaning. Compared to conventional pressurized or suction driven MF/UF processes, the GDM filtration process is free of chemical cleaning and require extremely low energy consumption (i.e., energy required for lifting water to the feed level is of the order of a few Wh/m³). The benign operating conditions and negligible cleaning chemicals should also lead to extended membrane lifetime.

However, the GDM filtration process has relatively lower permeate fluxes (typically < 10 L/m² h, ranging from 3.6 to 14.9 L/m² h) in the reported studies (Akhondi et al., 2015; Derlon et al., 2013; Derlon et al., 2012; Peter-Varbanets et al., 2010; Wu et al., 2016) compared to conventional MF/UF processes. Although GDM processes have been successfully employed

for decentralized drinking water treatment (Peter-Varbanets et al., 2012), the relatively low permeate flux does limit their wider applications, especially in large-scale, centralized drinking water and seawater treatment plants. To achieve the same productivity, the trade-off lies in more membrane area, which needs more space and capital cost (although this could be mitigated by less frequent membrane replacement).

To improve permeate flux of GDM filtration, several strategies have been examined. Our previous studies (Akhondi et al., 2015; Wu et al., 2016) employing GDM filtration for seawater pretreatment have illustrated that (1) the membrane achieved a higher flux at a higher operating temperature and greater hydrostatic pressure; (2) compared to UF membrane, the MF membrane tended to achieve higher permeate flux; (3) the submerged GDM-biofilm reactor achieved higher permeate flux than the small filtration cell. It has been recently reported that adding grazing metazoans (such as oligochaetes, nematodes) to the GDM filtration cell resulted in a permeate flux increase for treating surface water (Klein et al., 2016). Additionally, intermittent operation and periodical flushing protocols were applied for the GDM system to improve permeate productivity for decentralized household water treatment (Peter-Varbanets et al., 2012).

The previous work on GDM treatment of surface water and seawater has focused on flat sheet membranes. However, it is well known that hollow fibre membrane modules have a higher packing density than flat sheet membrane modules, and therefore, can achieve more productivity per unit of footprint (Judd, 2006). While the influence of flat sheet membrane properties on GDM performance in pretreating seawater has been investigated (Akhondi et al., 2015; Wu et al., 2016), the impact of hollow fibre membrane module configuration on GDM performance has not been reported.

This study focuses on the impact of reactor configuration (pilot-scale, lab-scale, and filtration cell), membrane configuration (submerged flat sheet membrane and hollow fibre membrane), and hollow fibre membrane packing density on GDM permeate flux development. Membrane fouling mechanisms and foulant characteristics for different GDM filtration scenarios are identified. The transformation and transportation of organic compounds in different GDM systems are also illustrated. Finally, the optimal GDM operation condition with regards to high productivity and superior permeate quality is proposed.

2. Materials and Methods

2.1. Feed seawater

Seawater was collected from the Tuas Spring Desalination plant, Singapore. As seawater was chlorinated before it was delivered to the collection tank, dechlorination of the seawater was performed before use. Sufficient sodium bisulphite (Acros Organics, USA) was added into the feed tank to ensure the free chlorine concentration to be zero (measured by a colorimeter, Thermo Fisher scientific, USA). The pH, conductivity, dissolved oxygen, and turbidity of the raw seawater are given in Table S1. The characteristics of the feed seawater for each testing system are summarized in Table S2.

2.2. Experimental setup and operating conditions

A pilot-scale GDM reactor (effective volume of 720 L and made of lightproof material, Figure 1a) was set up in a container at the Tuas Spring Seawater Desalination Plant, Singapore. A flat sheet membrane module (M1-P, at days 0-250) and an outside-in operated hollow fibre membrane module (M3-P, at days 65-205) were submerged into the reactor. The membrane modules were located 40 cm below the water level of the overflow line (i.e., a hydrostatic pressure of 40 mbar). The pilot GDM was operated in an intermittent filtration

mode (5-days off/2-days on) due to unavailable feed seawater at weekends during days 0-170 and in a continuous filtration mode during days 171-250. The temperature was $26\pm1^{\circ}\text{C}$.

The two parallel lab-scale GDM reactors (effective volume of 8.4 L and made of lightproof material, Figure 1a) were operated with flat sheet membranes (M1-L and M2-L) during days 157-201 and with hollow fibre membranes (M3-LL, M3-LM and M3-LH) during days 232-280 (the reactors were cleaned after the flat sheet membrane filtration experiments). The hydrostatic pressure was kept at 40 mbar by regulating the feed flow rate based on the permeate flow rate and the room temperature was at $21\pm1^{\circ}\text{C}$. The GDM filtration cell setup was described previously (Akhondi et al., 2015; Wu et al., 2016) and is shown in Figure 1b, while the filtration cells are shown in Figure 1c. These filtration experiments were performed at days 140-183 at a hydrostatic pressure of 40 mbar and a temperature of $21\pm1^{\circ}\text{C}$. In addition, two filtration cells (with the two feed outlets opened) were submerged into the pilot GDM and lab-scale GDM reactors during days 185-230.

Commercial membranes from different suppliers were used in this study. As the performance comparison of different membranes was not the purpose of this study, the names of the three tested membranes in this study were given as M1, M2, and M3, respectively. Detailed information of membranes and membrane modules is shown in Table 1. The permeate flux ($\text{L/m}^2 \text{ h}$, LMH) was calculated by dividing the weight of permeate generated during a certain period of filtration by the membrane area. To make a fair comparison, the permeate flux was normalized to a temperature of 27°C (yearly mean atmosphere temperature in Singapore) using Eq. [1]:

$$J_{27^{\circ}\text{C}} = \frac{J_T \mu_T}{\mu_{27^{\circ}\text{C}}} \quad \text{Eq. [1]}$$

where $J_{27^{\circ}\text{C}}$, J_T , $\mu_{27^{\circ}\text{C}}$, and μ_T represents the corrected permeate flux at 27°C , the measured permeate flux at temperature T , the water viscosity at 27°C and the water viscosity at

temperature T, respectively. The viscosity μ_T was calculated according to an empirical equation provided by the US EPA (EPA, 2005),

$$\mu_T = 1.784 - (0.0575 \cdot T) + (0.0011 \cdot T^2) - (10^{-5} \cdot T^3) \quad \text{Eq. [2]}$$

2.3. Cake layer fouling and irreversible fouling resistance

At the end of a filtration experiment, the total hydraulic resistance (m^{-1} , R_t) was calculated based on Darcy's law $R_t = \text{TMP}/(\mu_T J_T)$, in which μ_T is the permeate viscosity at temperature T, J_T is the measured permeate flux at temperature T and TMP is the transmembrane pressure (i.e., hydrostatic pressure). After that, the membrane was physically washed using distilled water (5 min) by ultrasonication to remove cake layer foulants. The resistance of the physically-cleaned membrane (defined as R_{ir+m}) was examined using distilled water at the hydrostatic pressure of 40 mbar. The clean membrane resistance (R_m) was measured using distilled water before seawater was fed into the system. The cake layer fouling resistance was derived from the difference between R_t and R_{ir+m} . The irreversible fouling resistance was achieved based on the difference between R_{ir+m} and R_m .

2.4. Analytical methods

The pH and conductivity of the feed seawater were determined by a pH/conductivity meter (Mettler Toledo, Switzerland). The dissolved oxygen (DO) of the feed seawater was determined by a DO meter (YSI, USA). The turbidity of the feed seawater was measured using a turbidity meter (Hach, USA). The dissolved organic carbon (DOC) of the feed seawater (after being filtered through a 0.45 μm hydrophilic filter) was monitored using a TOC analyzer (Shimadzu, Japan). Viable cells in the feed seawater and permeate were evaluated by measuring the intracellular ATP concentrations (Holm-Hansen and Booth, 1966;

Magic-Knezev and van der Kooij, 2004) using a luminometer (Hach, USA) following the manufacturer's manual.

The feed seawater, soluble foulants, and permeate seawater were filtered through a 0.45 μm hydrophilic filter and a liquid chromatography-organic carbon detector-organic nitrogen detector (LC-OCD-OND) was used to quantify their major soluble organic fractions with different sizes and chemical functions (Huber et al., 2011). On-line purified mobile phase was delivered by an HPLC pump (S-100, Knauer, Berlin, Germany) at a flow rate of 1.1 mL/min to an autosampler (MLE, Dresden, Germany) and the chromatographic column (TSK HW 50S, 3000 theoretical plates, Toso, Japan). The first detector after chromatographic separation was a non-destructive, fixed wavelength UV-detector (UVD 254 nm, type S-200, Knauer, Berlin, Germany) for analyzing organic carbon. For nitrogen detection, a side stream was diverted after UVD with a restricted flow rate of 0.1 mL/min (back pressure-driven).

Assimilable organic carbon (AOC) measurement was performed using flow cytometry (BD Biosciences, US) as described by Hammes et al. (Hammes et al., 2008; Hammes and Egli, 2005) with modification. In detail, the inoculants were prepared by filtering the feed seawater through a 10 μm glass fibre filter and incubating the filtrate at 30°C for at least 21 days to ensure complete consumption of the AOC in the feed seawater. The sample (10 mL) was filtered into a 40 mL vial with PTFE covers (EPA ASM Vial Kit, Thermo Scientific, USA) using a sterile 0.22 μm filter (Millex GP, Millipore, USA) and then sterilized in a water bath at 70°C for 30-40 min. The sample was inoculated with the prepared inoculants (0.5 mL) and incubated at 30°C. The cell number in the incubated sample was measured using a flow cytometry (BD, USA) daily till stationary stage. The detailed flow cytometry measurement protocol was described as follows: 0.5 mL of the incubated sample was stained with 0.5 μL of SYTO9 (Molecular Probes, USA). After keeping at room temperature for 30 min (at a dark

condition), the sample was transferred to a flat bottom well plate for flow cytometry analysis (the unstained sample was used as a control). The results were processed using proprietary software (CSampler, BD, USA). Counts in a defined region of a density plot were converted to an AOC concentration according to the relationship (94164 cells/L equivalent to 1 μ g carbon as acetate/L), which was achieved by using acetate (Sigma-Aldrich, USA) as the standard carbon source. Meanwhile, the negative control was performed using the sterilized sample without any inoculation as the sample and the positive control was performed by combining 5 μ L of mineral salt solution (1.53 g/L NH_4Cl , 2.88 g/L KNO_3 , and 0.34 g K_2HPO_4) and 10 mL of the sterilized sample with 0.5 mL of the inoculants.

Transparent exopolymer particles (TEP) content was measured using the method first introduced by Passow and Alldredge (Passow and Alldredge, 1995). In summary, the sample was filtered through a polycarbonate filter (Millipore, USA) with a pore size of 0.22 μm . The accumulated TEP on the membrane was subsequently stained with 3 mL of 0.02% aqueous solution of alcian blue in 0.06% acetic acid (Aldrich-Sigma, USA). Then the membrane was washed with distilled water to remove the excess dye. Four millilitre of 80% H_2SO_4 solution (Honeywell, Korea) was used to remove the complex of TEP and alcian blue from the polycarbonate membrane and to dissolve it for 2 hr without stirring. The absorption of the solution was measured at a wavelength of 787 nm using a spectrometer (Hach, USA) and the concentration of TEP was calculated based on a calibration with gum xanthan (Sigma-Aldrich, USA) as a standard.

2.5. Biofilm cake layer observation

An optical coherence tomography system (OCT, Thorlab, US) was used as a non-invasive approach to observe the *in situ* cross-sectional cake layer morphology through the cover glass window of the filtration cell. The cake layer thickness ($n=6$) was measured according to the

scale bar and the averaged value was calculated. The porosity of the cake layer was calculated according to the Carman-Kozeny equation (Derlon et al., 2012; Katsoufidou et al., 2005).

$$R_{cake\ layer} = \frac{75 (1-\varepsilon)^2}{2\varepsilon^3 r_p^2} H \quad \text{Eq. [3]}$$

Where ε (dimensionless) is the cake layer porosity, r_p (m) is the characteristic radius of the particles forming the cake layer (assuming 3 nm) (Akhondi et al., 2015), H (m) corresponds to the thickness of the cake layer.

The morphologies and movement behaviours of eukaryotic microorganisms derived from the biofilm cake layers and settlements in the GDM reactor were directly observed by an optical microscope (Axio Imager, Zeiss, Germany).

3. Results

3.1. Permeate flux development

The permeate flux development profiles of GDM filtration using different reactor and membrane module configurations over an operation period of 250 days are shown in Figure 2. Apparently, during the initial filtration period, a rapid drop in flux was observed and then the flux tended to be stabilized, regardless of reactor and membrane module configuration (it is noted that the membrane flux in the pilot GDM reactor was not monitored during the first day). This observation was similar to the findings in previous studies using seawater (Akhondi et al., 2015; Wu et al., 2016), surface water (Peter-Varbanets et al., 2010), grey water (Ding et al., 2016), and wastewater (Peter-Varbanets et al., 2010) as feed waters. In addition, a more fluctuating flux pattern was observed in the pilot GDM reactor compared to those in the lab GDM reactor and filtration cell. When the pilot GDM reactor was operated at

the intermittent filtration mode (5-days on/2-days off), the stabilized flux was at 20.9 ± 2.2 L/m²h (LMH) for the flat sheet membrane module (M1), which was slightly higher than during the continuous filtration mode (18.6 ± 1.4 LMH). However, there was almost no influence of intermittent filtration on the flux of the hollow fibre membrane module (15.2 ± 1.0 vs. 15.2 ± 1.7 LMH).

Figure 3 summarizes the stabilized permeate fluxes of different GDM operation scenarios. Compared to the hollow fibre membranes, the flat sheet membranes achieved slightly higher stabilized permeate fluxes in both pilot-scale and lab-scale GDM reactors. Although the clean water fluxes were significantly different (Table 1) for the two PVDF flat sheet membranes (i.e., M1 and M2), their respective stabilized permeate fluxes were relatively similar in both lab-scale GDM reactor and GDM filtration cell. For the same membrane M1, the permeate flux of the pilot GDM reactor was slightly higher than that of the lab-scale GDM reactor, both of which were significantly improved compared to that in the filtration cell. Furthermore, when the filtration cell was submerged into the pilot GDM reactor, it achieved a stabilized flux at 17.2 ± 0.8 LMH, which was comparable to that of the submerged membrane module in the GDM reactor.

In addition, increasing the hollow fibre packing density from 352 to 898 m²/m³ resulted in a slight decrease of the stabilized flux from 15.2 ± 1.7 to 12.7 ± 1.4 LMH. A further increase of the hollow fibre packing density to 1139 m²/m³ did not result in a significant change in the stabilized permeate flux (13.1 ± 1.2 LMH). At the highest packing density of 2151 m²/m³ tested in this study, the stabilized permeate flux reached the relatively lowest level of 8.5 ± 0.9 LMH.

3.2. Membrane fouling mechanisms

At the end of each filtration experiment, the membrane was physically cleaned by ultrasonication and the cake layer fouling and irreversible fouling resistances were examined. Figure 4 indicates that cake layer fouling was predominant for the gravity-driven flat sheet membranes (M1 and M2). In addition, the cake layer fouling resistance in the lab-scale GDM reactor (-L) was much lower than that in the filtration cell (-F), while irreversible fouling resistances in both GDM filtration systems were relatively comparable. For the hollow fibre membrane (M3), the major membrane fouling was ascribed to irreversible fouling. The contributions of cake layer fouling and irreversible fouling to the total fouling appeared to be independent of hollow fibre packing density when the packing density was below 1139 m²/m³. At a hollow fibre packing density of 2151 m²/m³, both cake layer and irreversible fouling resistances were higher than those at lower packing densities.

3.3. Cake layer morphology observation

The morphologies of cake layers on the membrane in the filtration cell system and the filtration cell submerged into the GDM reactor were examined by OCT, shown in Figure 5. The cake layer thickness and porosity, calculated based on the OCT images and Eq. 3, are shown in Figure 6. At the same filtration time, the biofilm cake layer in the filtration cell that was submerged into the GDM reactor was significantly thicker than that in the filtration cell system. Furthermore, the biofilm cake layer porosity at day 21 in the submerged filtration cell was higher than that at day 42 in the filtration cell system, although the cake layer thickness was the same in both filtration cells.

Furthermore, the morphologies (Figures 7a-g) and movement patterns (videos in the supplementary data) of several types of eukaryotic microorganisms derived from the cake layers and settlements in the GDM reactor were captured via a light microscope. Under the microscope, these eukaryotic microorganisms are transparent with round, rod, or filamentous

shapes. Their sizes range from less than a hundred micrometers to a few millimetres in length and from 20 to 100 μm in diameter. Compared to the filtration cell system in the previous study (Akhondi et al., 2015) and this study (data not shown), substantially more and a greater diversity of eukaryotic microorganisms were observed in the GDM reactor, especially for the larger-sized eukaryotes.

These eukaryotes display various movement patterns. For example, some types of eukaryotes move by curling and stretching, but with different speeds (eukaryotes shown in Figure 7a move quickly and those in 7b move slowly). The eukaryotes shown in Figures 7c-f move by rolling and circling (displacement is very limited). Figure 7g shows a type of eukaryotes which moves fast and in a random direction. In addition, filamentous organisms were observed in the cake layers as well as in the settlements in the GDM reactor (Figures 7h and i), which move in a gliding pattern.

These observations for GDM treatment of seawater agree with GDM treatment of surface water where it has been reported that the movement and predation behaviour of eukaryotic organisms can produce the porous, sponge-like structures of biofilm cake layers (Derlon et al., 2013; Derlon et al., 2012; Klein et al., 2016). Notably, the eukaryote shown in Figure 7a belongs to nematodes, which account for 80% of the abundance of multicellular organisms in terrestrial ecosystems and 90% in deep sea (Danovaro et al., 2008). The predation behaviours of nematodes have been reported to lead to permeate flux improvement. Klein et al. (Klein et al., 2016) illustrated that the addition of nematodes (*Plectus aquatilis*) into the GDM system resulted in a flux increase of 119-164% in comparison to the control system. In other studies, Jabornig and Podmirseg (Jabornig and Podmirseg, 2015) found that the nematodes could play an important role in flux stabilization in the fixed biofilm reactor. Follow-up investigations

are planned to investigate the eukaryotic diversity and identify the predominant eukaryotic organisms as “biofilm-scavenger” in the GDM system.

3.4. Characterization of organic substances in the cake layer foulants

To further identify the accumulated soluble organic substances in the cake layer foulants, the foulants were physically recovered from the M1 membranes in the filtration cell, lab-scale GDM reactor, and submerged filtration cell in the lab-scale GDM reactor, respectively. The characteristics of organic substances in the cake layer foulants are listed in Table 2. Apparently, the cake layer foulants in the filtration cell system (M1-F) contained a greater amount of TEP than those in the GDM reactor (M1-L) and the filtration cell submerged into the pilot GDM reactor (M1-SF), and the amount of TEP correlated negatively with the permeate flux. The DOC content of the cake layer foulants in the filtration cell system was comparable to that in the filtration cell submerged into the pilot GDM reactor, both of which were greater than that in the lab-scale GDM reactor. It should be noted that DOC are dissolved organic substances, smaller than 0.45 μm , while TEP is a component of the organic fraction larger than 0.22 μm .

The LC-OCD analysis of the soluble organic substances (less than 0.45 μm) further revealed that the cake layer foulants from the filtration cell system (M1-F) contained higher contents of biopolymers and humic substances than those in the submerged filtration cell system (M1-SF). In the GMD reactor, the cake layer foulants from the submerged flat sheet membrane module (M1-L) had slightly less biopolymers and significantly less humic substances, building blocks and low molecule substances compared to those from the submerged filtration cell (M1-SF). In addition, compared to the organic composition of the feed seawater (Table 3), a higher ratio of biopolymers was observed in the cake layer foulants derived from the three tested GDM systems, indicating the accumulation of biopolymers on the membranes. It is recalled that the permeate flux in the M1-L and M1-SF were comparable, both of which

were significantly higher than in the M1-F. Therefore, the LC-OCD results suggest that the amounts of biopolymers accumulated on the membrane were negatively correlated with the permeate flux of the GDM system.

Furthermore, the cake layer foulants derived from different GDM systems displayed diverse patterns of organic composition. In the filtration cell system (M1-F), the humic substances and low molecular weight neutrals were the predominant organic substances in the cake layer foulants, similarly to that submerged into the lab-scale GDM reactor. However, in the submerged membrane of the lab-scale GDM reactor, biopolymers and building blocks were the predominantly present foulants.

3.5. Permeate quality

A comparison of permeate quality of the pilot GDM reactor (250-day operation, samples taken from day 70 to 250) and lab-scale GDM reactor (44-day operation, samples taken from day 167-201) was performed and the details are shown in Table 3. The permeates of both pilot- and lab-scale GDM reactors had a very low level of turbidity, indicating almost free of particles. Both GDM reactors also significantly removed TEP (~41-85%), almost regardless of membrane properties (i.e., M1 and M2).

It is noted that the DOC contents in the feed (1.08 ± 0.16 mg/L, Table 3) and effluent (1.10 ± 0.10 mg/L, Table S3) of pilot GDM reactor were less than that in the permeate of the pilot (1.29 ± 0.33 mg/L, Table 3). This phenomenon was also observed in the previous studies (Akhondi et al., 2015; Chomiak et al., 2014; Wu et al., 2016), which was proposed to be possibly related to the hydrolysis of suspended organic material within the biofilm and carbon fixation activity within the microbial biofilm.

On the other hand, about 57% of AOC in the pilot GDM reactor was removed after long-term operation (p -value < 0.1), while the permeate in the lab-scale GDM reactor had almost

comparable AOC contents as the feed (p -value >0.1). The AOC in the feed of the lab reactor was much lower than that of pilot reactor, implying that storage of the seawater for the lab system might have contributed to degradation of AOC. The LC-OCD analysis revealed that less biopolymers, more building blocks and low molecular weight substances were found in the pilot GDM permeate compared to the feed, while in the lab-scale GDM reactor, the organic composition of the permeate was almost similar to the feed. In the pilot GDM reactor, the biofilms contributed to the removal of biopolymers. The increased amounts of building blocks and low MW substances in the permeate were noticed. It can be attributed to the biological hydrolysis products that were derived from biopolymers or particulate organics and could pass through the membrane.

4. Discussion

Previous studies have demonstrated the feasibility of low-energy, chemical-free gravity-driven membrane processes to pre-treat seawater as feed for reverse osmosis (SWRO) at a lab scale (Akhondi et al., 2015; Wu et al., 2016). In this study, long-term operation (250 days) of the pilot GDM reactor was performed. The permeate fluxes in the pilot reactor reached technically interesting values close to 20 LMH (flat sheet) and 15 LMH (hollow fibres). The fluxes showed some fluctuations (± 2 LMH) attributed to occasional detachment of the heterogeneous biofilm layers, as observed in our previous studies (Akhondi et al., 2015; Wu et al., 2016).

In addition, in the pilot GDM reactor, intermittent filtration tended to slightly improve the permeate flux of the flat sheet membrane, similarly to the conventional flat sheet membrane bioreactor (Christensen et al., 2016; Wu et al., 2010). The relaxation of membrane filtration contributes to the formation of porous and loosely-attached biofouling layers (Peter-Varbanets et al., 2012) and probably leads to more effective detachment of such biofouling

layers from the membrane. Unexpectedly, intermittent filtration could not further improve the permeate flux of the hollow fibre membrane (M3-P). This may be attributed to the fact that the fibres were not held tightly in the modules but had some degree of looseness (fibre length > module length, Figure 1d). The disturbance caused by feeding water could result in slight movement of the fibres, which may facilitate the self-removal of loosely-attached biofouling layers from the fibres during filtration cycles. Therefore, the intermittent filtration may not further benefit biofouling layer reduction during the idle period of filtration.

Interestingly, the permeate flux in the pilot GDM reactor was slightly higher than that in the lab-scale GDM reactor and both were much greater than that in the filtration cell when the same flat sheet membrane (M1) was used. To further explore this phenomenon, a filtration cell was submerged into the pilot GDM reactor (for flux comparison) and lab GDM reactor (for flux comparison, biofilm observation by OCT, and foulant analysis). Several observations were made: (1) the performances of the filtration cells were much better in the reactor and the permeate fluxes and cake layer fouling resistances of the filtration cells submerged into both GDM reactors were comparable to those of the submerged membrane modules (Figures 2-4); (2) the cake layer on the membrane in the submerged filtration cell was thicker and had a more porous morphology than that in the filtration cell system alone (Figures 5 and 6); (3) less soluble organic substances (especially larger-sized organic substances) were accumulated on the membrane in the submerged filtration cell than those in the filtration cell system (Table 2).

Previous studies (Akhondi et al., 2015; Wu et al., 2016) have shown that in the GDM filtration system, the bacteria utilize the organic substances in the feed seawater for their growth and then form biofouling layers on the membrane, while the movement and predation behaviour of eukaryotic organisms in the biofilm cake layer produce an open and spatially

heterogeneous structure and, as a result, the permeate flux is stabilized. It is evident that a part of the organic substances and almost all bacteria and eukaryotes from the feed seawater would be retained in the reactor or filtration cell because of membrane rejection. In this study, compared to the pilot (720 L) and lab-scale GDM reactor (8.4 L), the filtration cell had a very small feed-water-volume (0.0046 L). Accordingly, the hydraulic retention time (i.e., residence time, which is calculated by dividing reactor volume by permeate flow rate, Table S4) of the filtration cell (approximately 0.74 h) was much shorter than the pilot (~21.6 h) and lab-scale GDM reactors (~13.0 h for flat sheet and ~11.1 h for hollow fibre). This could lead to more accumulation of organic substances on the membrane due to less effective biodegradation in the GDM filtration cell. On the other hand, the limited space of the GDM filtration cell would not favour the propagation of microorganisms, especially eukaryotes, which could have resulted in a cake layer with lower porosity (Figure 6) and higher resistance (Figure 4). As the submerged filtration cell performed almost similarly to the submerged membrane module, this hints that the limited space did not restrict the predation and movement of some eukaryotes that were growing and propagating in the GDM reactor. The findings imply that reactor dimension and hydraulic retention time are important parameters influencing both organic accumulation and development of the ecosystem in the GDM system, which in turn affects permeate flux. Optimization of these two parameters should necessarily be considered in future in order to achieve higher productivity at fewer footprints.

In addition, for the hollow fibre membrane module, the packing density is another crucial parameter impacting GDM performance. As shown in Figure 7, the eukaryotes identified in the GDM reactor have sizes up to a few millimetres in length and 100 μm in diameter, some of which display active motion patterns (Videos in the supplementary data). Less packing density provides more space for these eukaryotes to move and predate the bacteria attached on the membrane, which benefits to flux improvement (Figures 2 and 3). While, once the

available space is enough for the movement of the eukaryotes, further expanding the space could not benefit to further increase permeate flux (Figure 1). It is noted that such findings were observed with the lab-scale hollow fiber modules where the membranes were aligned without any looseness. In case when some degree of looseness is present, the influence of hollow fibre density on permeate flux may not follow the same pattern. Further study on this issue will be performed in future.

To make a fair comparison, the permeate productivities per reactor volume of different GDM filtration scenarios were calculated based on their respective membrane packing density and flux (Figure 3; note: membrane cassette and installation fitting and piping are not considered into the calculation). As shown, hollow fibre membrane modules had a higher volumetric treatment capability compared to flat sheet membrane modules, which could be attributed to their substantially higher packing densities in spite of their lower flux values. Especially the hollow fibre membrane with a highest packing density ($2151 \text{ m}^2/\text{m}^3$) achieved the highest productivity (436 m^3 per day per m^3 of module volume). Compared to the two types of flat sheet membranes, the hollow fibre membrane had relatively higher clean membrane resistance and irreversible fouling resistance (Figure 4). These two parameters are associated with membrane properties and lowering these two resistances could be favourable to improve permeate flux. Therefore, the choice of suitable hollow fibre membrane materials, reduction of hollow fibre diameter, and installation of hollow fibre modules with a degree of looseness may be quite important in consideration for productivity improvement in large-scale GDM systems in order to economically compete against conventional UF processes for seawater pretreatment.

Furthermore, the GDM systems were able to remove almost all of the particles (i.e., turbidity), 94% of viable cells, and most of TEP (41-85%) (Table 3). Importantly, at

relatively long operation times (i.e., 250 days), the pilot GDM reactor appeared to remove considerable amounts of assimilable organic carbon (AOC) and biopolymers. This is possibly attributed to longer residence time of organic substances and the proliferation of bacteria in the reactor with time, leading to enhanced biodegradation capability. Previous studies have shown that AOC is a crucial indicator for assessment of biofouling potential of the seawater reverse osmosis processes (Naidu et al., 2013; Weinrich et al., 2016). Limited AOC in the permeate could be effective for reducing biofilm development on RO membranes (Weinrich et al., 2016). On the other hand, Dehwah et al. (Dehwah et al., 2015) further pointed out that TEP, natural organic matter, and bacterial concentrations in the pretreated seawater are important factors that can determine biofouling of RO membrane. The gel-like TEP helps in forming a conditioning layer on the membrane surface to promote bacterial attachment and AOC provides nutrients to bacteria for biofilm formation. Thus, the superior quality of the GDM permeate should facilitate control of RO fouling. Further work is in progress to quantify this effect.

5. Conclusions

In this study, we compared the permeate flux and quality, membrane fouling mechanisms, and foulant characteristics of different GDM systems (pilot-scale vs. lab-scale; submerged reactor vs. filtration cell; flat sheet vs. hollow fibre; hollow fibre packing density). The following conclusions can be drawn:

(1) Compared to the GDM filtration cell system, the submerged GDM reactor tended to achieve higher permeate flux values (e.g., $18.6 \pm 1.4 \text{ L/m}^2 \text{ h}$ for the pilot GDM reactor).

(2) The GDM reactor dimensions influenced the accumulation of organic substances and the propagation of bacteria and eukaryotes, but did not affect the movement and predation behaviour of the eukaryotes.

(3) The permeate flux of the submerged hollow fibre membrane increased with decreasing the packing density.

(4) The pilot GDM reactor tended to effectively remove AOC.

Acknowledgements

The Economic Development Board (EDB) of Singapore is acknowledged for funding the Singapore Membrane Technology Centre (SMTTC), Nanyang Technological University.

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Table 1. Characteristics of membrane and membrane modules used in this study

Membrane	Configuration	Materials	Pore size (μm)	Clean water flux (LMH) @ 40 mbar, 27°C	Reactor configuration	Membrane area (m ²)	Abbreviation
M1	Flat sheet	PVDF	0.08	182±1	Pilot-scale	0.9	M1-P
					Lab-scale reactor	0.0198	M1-L
					Filtration cell	0.0023	M1-F
					Filtration cell submerged into pilot and lab-scale reactor	0.0023	M1-SF
M2	Flat sheet	PVDF	0.22	280±15	Lab-scale	0.0198	M2-L
					Filtration cell	0.0023	M2-F
M3	Hollow fibre (outside-in)	PVDF	0.10	48±5	Pilot-scale	0.87 (352)*	M3-P
					Lab-scale	0.020 (898)	M3-LL
						0.020 (1139)	M3-LM
						0.028 (2151)	M3-LH

*The number in the bracket represents the packing density (m²/m³), which was calculated by dividing the membrane module area (m²) with the membrane module volume (m³).

Table 2. Characteristics of soluble organic substances in the cake layer foulants of the filtration cell (M1-F), lab-scale reactor (M1-L), and submerged filtration cell (M1-SF).

Membrane	M1-F	M1-L	M1-SF
TEP (>0.22 µm) (mg/m ²)	1135	59	179
DOC (<0.45 µm) (mg/m ²)	52	18	57
Biopolymers (µg/m ²)	12775 (24.6%)*	5643 (33.7%)	6848 (15.2%)
Humic substances (µg/m ²)	18556 (35.8%)	4000 (23.9%)	14560 (32.4%)
Building blocks (µg/m ²)	7645 (14.7%)	4664 (27.8%)	7942 (17.7%)
LMW neutrals (µg/m ²)	12925 (24.9%)	2450 (14.6%)	15590 (34.7%)
LMW acids (µg/m ²)	ND**	ND	ND

* The number in the bracket presents the ratio of the composition.

** ND represents ‘not detectable’.

Table 3. Feed and permeate water quality of pilot GDM reactor (samples taken from day 70 to 250) and lab-scale flat sheet GDM reactor (samples taken from day 167-201) (n>8).

	Pilot reactor feed	M1-P	Lab reactor feed	M1-L	M2-L
Turbidity (NTU)	3.08±2.76	~0	2.3±1.3	0.09±0.01	0.07±0.01
TEP (mg Gum Xanthan/L)	3.22±0.06	1.89±1.56	2.60±1.13	0.43±0.07	0.39±0.10
Bacterial amount (10 ⁴ CFU)	4.78±0.86	0.28±0.16	-	-	-
DOC (mg/L)	1.08±0.16	1.29±0.33	1.68±0.30	1.73±0.36	1.61±0.31
AOC (µg/L)	159±84	68±2	26±14	23±11	25±13
Biopolymers (µg/L)	69±15	47±15	81±36 (6.5%)*	112±35	92±21
Humic substances (µg/L)	522±61	504±39	612±72 (48.8%)	672±61	623±50
Building blocks (µg/L)	172±12	186±28	202±29 (16.1%)	219±47	192±25
LMW neutrals (µg/L)	309±149	509±283	359±94 (28.6%)	402±52	347±50
LMW acids (µg/L)	0±0	1.4±4.1	ND**	ND	ND

* The number in the bracket presents the ratio of the composition.
** ND represents ‘not detectable’.

Figure 1

Figure 1. Experimental setup. (a) Pilot and lab-scale GDM reactor; (b) GDM filtration cell system; (c) Filtration cell; (d) outside-in hollow fibre membrane module.

Figure 2

Figure 2. Permeate flux development (normalized at 27°C) in the different GDM filtration systems. (a) Pilot GDM reactor (flat sheet and hollow fibre membrane); (b) Lab-scale GDM reactor (flat sheet membrane); (c) Filtration cell (flat sheet membrane); (d) Lab-scale GDM reactor (hollow fibre membrane).

Figure 3

Figure 3. The stabilized permeate fluxes at different GDM filtration systems (normalized at 27°C). The numbers shown in brackets present the productivity per unit membrane module volume (1 m³). The membrane packing density of the flat sheet pilot module (m²/m³) was calculated assuming 2 sided membrane plates (dimension area of 1 m²) with a thickness of 5 mm and a space between the plates of 5 mm. PD represents packing density (m²/m³).

Figure 4

Figure 4. Cake layer and irreversible fouling resistances at different GDM filtration systems (See Table 1 for abbreviation descriptions).

Figure 5

Figure 5. Cake layer morphology observation by OCT. (a1-3) M1 membrane in the filtration cell; (b1-3) M1 membrane in the filtration cell that was submerged into the lab-scale GDM reactor.

Figure 6

Figure 6. The thickness and porosity of biofilm cake layers on the membranes in different GDM filtration cell systems.

Figure 7

Figure 7. Microscopic images of microorganisms derived from the cake layers on the M1-L and M2-L membranes (a-h) and settlements (i) in the lab-scale GDM reactor observed by a light microscope.

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