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Theme: Wastewater-Energy Nexus: Emerging Energy-Neutral and Energy-Plus Processes for Wastewater Reclamation

Title: Membrane Distillation Bioreactor (MDBR) – a lower Green-House-Gas (GHG) option for industrial wastewater reclamation

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Abstract

A high-retention membrane bioreactor system, the membrane distillation bioreactor (MDBR) is a wastewater reclamation process which has the potential to tap on waste heat generated in industries to produce high quality product water. There are a few key factors which could make MDBR an attractive advanced treatment option, namely tightening legal requirements due to increasing concerns on the micropollutants in industrial wastewater effluents as well as

concerns over the electrical requirement of pressurized advanced treatment processes and greenhouse gas emissions associated with wastewater reclamation. This paper aims to provide a consolidated review on the current state of research for the MDBR system and to evaluate the system as a possible lower green house gas (GHG) emission option for wastewater reclamation using the membrane bioreactor-reverse osmosis (MBR-RO) system as a baseline for comparison. The areas for potential applications and possible configurations for MDBR applications are discussed.

Highlights

- MDBR as a lower GHG wastewater reclamation option is evaluated
- Conditions when GHG emission potential of MDBR < MBR-RO are discussed
- Wastewater reclamation performance of MDBR and MBR-RO are comparable
- Fouling is an issue in MDBR and MD but can be mediated

Keywords – Membrane Distillation Bioreactor, Green-House-Gas (GHG), industrial wastewater reclamation, biofouling, membrane distillation

1 Introduction

Freshwater makes up 2.5% of the earth's total water supply and of this, less than 1% is available for use by humans and the ecosystems (UNEP, 2008). With industrialization, twenty percent of the world's freshwater had already been extracted for industrial use by 2010 and many countries are extracting groundwater faster than it can be replenished (WWAP, 2012). Industries require different grades of water from low grade applications such as cleaning to high grade water required for heating and cooling applications (Leverenz and

Asano, 2011). Industrial wastewater reclamation typically includes an advanced water treatment process (eg. reverse osmosis (RO)) as a polishing step after the wastewater treatment process (eg. membrane bioreactor (MBR)) to recover high grade water (Fane et al., 2011). Life-cycle analyses have shown that in most cases, wastewater reclamation requires less energy than desalination of locally available resources (WEF, 2011). The reduction in energy consumption results in cost savings, which makes wastewater reclamation a more economically-feasible option for water production especially in cases where surface or ground water are not readily-available (Durham and Mierzelewski, 2003). In addition, increasing environmental awareness of the toxic and recalcitrant nature of industrial effluents has resulted in stringent trade discharge requirements in many countries. Advanced treatment technology is often required to remove emerging micropollutants from an effluent prior to discharge, leading to increased cost for effluent disposal and preference for wastewater reclamation (Tambosi et al., 2010).

Membrane processes have been used in industries to reclaim different grades of water for reuse (Leverenz and Asano, 2011). High quality water is often required for cooling and heating applications in industries (Table A.1 in Supplementary Information). To achieve the water quality suitable for cooling and heating applications, some industries have already started to use a combination of MBR and RO processes for simultaneous wastewater biodegradation and ions removal (Durham and Mierzelewski, 2003). Like the MBR-RO process, the high-retention membrane distillation bioreactor (MDBR) system is able to produce high quality product water with simultaneous biodegradation of organics (Phattaranawik et al., 2008). The MDBR combines a thermophilic bioprocess with the membrane distillation (MD) process, which works by transferring water vapor across a thermal gradient through a hydrophobic, microporous membrane to produce water. As such, only volatiles such as water vapor would be able to diffuse across the membrane. There is a

growing interest in tapping of waste heat for MD applications in industrial wastewater reclamation (Drioli et al., 2012) and the MDBR may find application in this niche area.

By reviewing the MDBR studies conducted to date, this paper aims to evaluate the potential of the MDBR as a lower green-house-gas (GHG) emission option for industrial wastewater reclamation in terms of its GHG emission potential and wastewater reclamation performance (in terms of the quality and quantity of produced water, as well as efficiency of biotreatment process) and sludge production. In this paper, the MBR-RO has been used as a baseline for comparison.

2 Overview of MDBR

The MDBR (Phattaranawik et al., 2008) is a system which couples the thermophilic bioprocess with the MD process (Figure 1). The basic principle behind the MD process is the creation of a vapor-liquid interface using a microporous hydrophobic membrane; water in the hot feed vaporizes on the membrane surface and diffuses down the vapor pressure gradient before it is condensed/removed (depending on the MD configuration) at the permeate/distillate side (Lawson and Lloyd, 1997). MDBR systems typically follow the direct contact membrane distillation (DCMD) configuration in which the condensing liquid is in contact with the membrane. Since the driving force for flux is vapor pressure gradient (which is related to temperature by the Antoine equation), the temperature difference between the feed and permeate should ideally be maintained at $> 30^{\circ}\text{C}$ and the feed temperature preferably at $> 50^{\circ}\text{C}$. Due to the requirement for elevated temperature, special thermophiles (microbes that proliferate at an optimal temperature of $45\text{-}60^{\circ}\text{C}$) have to be used (LaPara and Alleman, 1999) and the thermophilic bioreactor has to be operated at this temperature range (instead of $60\text{-}80^{\circ}\text{C}$ usually observed in MD systems).

Figure 2 shows the mass balance in a typical submerged MDBR system, which is similar to the MBR system where the hydraulic retention time (HRT) of the system is the reactor volume (V) divided by the volumetric flow rate of influent (Q_1), ie. $HRT = V/Q_1$ and the sludge retention time (SRT) is the volume of sludge in the reactor over the volume of sludge wasted per unit time and can be represented as $SRT = VX / Q_4X \approx V/Q_4$ (where X is the biomass concentration in the MDBR and Q_4 is the volumetric flow rate of the sludge wasting stream). The deviation arises when we consider the retention time of the non-volatiles (eg. small molecular weight organics). Since only volatiles would permeate across the hydrophobic membrane, the MDBR system should be able to retain all non-volatiles solutes (ie. salts), viable-but-not-culturable (VBNC) bacteria, as well as low-molecular weight organics (eg. potential carcinogens/emerging micropollutants). Unlike the UF/MF-MBR system, organics and ions will be accumulated in the system over time and this accumulation can be represented by the concentration factor (CF), which is equivalent to SRT/HRT (Phattaranawik et al., 2008). Since Q_4 is dependent on the membrane rejection efficiency (denoted by ϕ) of the system, CF can also be represented as $1 / (1 - \phi)$ (Lay et al., 2010). With complete theoretical retention of non-volatile organics in the retentate, the MDBR is able to increase the residence time of these organics for further degradation and decouple its organic retention time (ORT) from the HRT.

The idea of increasing the ORT for biodegradation of recalcitrant organics is not new. In 1994, Rautenbach and Mellis inserted the nanofiltration (NF) process after the bioprocess to recycle NF concentrate back to the bioreactor for further treatment (Rautenbach and Mellis, 1994). The process was patented as BioMembrat-Plus® process and was initially developed in cooperation with Wehrle AG, Emmendingen, Germany to treat dumpsite leachate. Rautenbach and Mellis proposed that this recycling process would increase the concentration and residence time of the recalcitrant organics, thereby increasing the biodegradability of

these recalcitrants which are difficult to degrade biologically and would not be degraded under the operating conditions of conventional bioreactors.

In the context of this review, only small molecular weight organic micropollutants that have been generated from anthropogenic sources and do not readily biodegrade due to certain physico-chemical characteristics of the micropollutant are considered to be recalcitrant organics. Some of these xenobiotics do not biodegrade unless specific abiotic (eg. wastewater conditions) and biotic (eg. types of microorganisms available) conditions are met (Knapp and Bromley-Challoner, 2003). Some of these micropollutants can be found in wastewater generated from industries such as textile, pharmaceutical, petrochemical, pulp and paper. Their recalcitrant nature and harmful impact on both the environment and human health makes the biodegradation and subsequent removal of these recalcitrant organics during the wastewater treatment process a challenging task (Maszenan et al., 2011). It is thus important to retain these recalcitrants and the MBR technology typically performs this task better than the conventional activated sludge process (CASP), thus explaining the increased use of MBRs in the treatment of industrial wastewaters from a number of industries, including food, pulp and paper, textile, tannery, landfill leachate, pharmaceutical and petrochemical (Lin et al., 2011). Yet despite its advantages over the CASP, the microfiltration(MF)/ultrafiltration(UF) membranes used in MBRs are still unable to retain most of the small molecular weight organics (Zhang et al., 2006a). While the RO process is increasingly used as an advanced treatment process to remove these small molecular weight organics, the micropollutants retained in the RO retentate are often not recycled for further degradation in the MBR. Effectively, this means that the ORT of these micropollutants is still coupled to the HRT of the MBR system. A comparison between the MBR-RO process and the MBR process is available in Table A.2 in the supplementary information.

On the other hand, high-retention MBRs (HRMBRs) such as the MDBR, nanofiltration MBR (NF-MBR) and the osmotic MBR (OMBR) decouples the ORT from the HRT, thus achieving the dual goals of retention and increasing the residence time of recalcitrant organics for further biodegradation in a single step (Lay et al., 2010). The other benefit of non-pressurized HRMBRs is that these systems can potentially utilize less electrical energy and hence, reduce the greenhouse gas (GHG) emission associated with wastewater reclamation process. The MDBR system can tap onto waste heat generated in the industry (Phattaranawik et al., 2008) and in view of the water-energy nexus, this makes the MDBR, a potentially attractive option in industrial wastewater reclamation. This is further discussed in the next section.

3 Evaluation of the MDBR

3.1 Electrical requirement and GHG emission potential

Inevitably, all thermal processes are energy-intensive but the MD/MDBR uses less thermal energy than its conventional thermal counterparts. In addition, instead of requiring high-grade electrical energy like pressurized membrane systems, it can utilize low grade waste heat (typically $< 200\text{ }^{\circ}\text{C}$) which is usually lost to the environment. The challenge is capturing this waste heat in industry and using it effectively. On-going efforts to reduce heat loss by membrane conduction in the MD system has led to the development of the vacuum-multi-effect MD process and the permeate gap MD, which could improve energy efficiency of MD systems (Winter et al., 2011). Efforts to improve thermal efficiency and water recovery through various process intensification strategies have helped to reduce the thermal requirement of the process. For example, the use of a cascade MD system integrated with a heat exchanger can improve the gain-output-ratio from 0.75 to 4.1 (Lee et al., 2011). While various configurations of combining MD with heat exchangers using waste heat or solar

thermal energy have been proposed (Lee et al., 2011; Cipollina et al., 2012), a gradual shift in research focus from using solar energy as a thermal source to tapping into the waste heat generated in industries has been observed recently (Hausmann et al., 2012). This is evident in the rise in recent projects focusing on applying MD processes in industry (Drioli et al., 2012; Technology, 2012). By combining MD and thermophilic bioprocess, the MDBR may provide more options (than MD) in the treatment and reclamation of industrial wastewater. Although higher aeration cost has been associated with the thermophilic aerobic bioprocess, full-scale aerobic thermophilic MBRs have been implemented in pulp and paper industry to close the water loop (Joore et al., 2001; Ramaekers et al., 2001). Aerobic thermophilic MBRs have found practical application in this water-intensive industry since it is not economical to cool down the hot effluent prior to biotreatment. Furthermore, tightening legal requirements have resulted in higher cost for effluent disposal (Jung and Pauly, 2011). With this in mind, the MDBR could find potential applications in niche areas where hot wastewater and waste heat are produced and the cost of disposing effluent makes treatment a more feasible option.

Despite the additional aeration requirement of the thermophilic bioprocess, a preliminary estimate shows that the electrical energy requirements of the MDBR could be about 10 - 30% lower than the MBR-RO (Table 1a). The additional energy cost of post-treating MDBR permeate has not been included in the estimate as it is presumed that the reclamation of industrial wastewater with low nutrients and non-volatile organics concentrations under optimal operating condition would produce water suitable for most industrial applications (Table A.2). In addition, the capital and energy cost of installing infrastructure to collect waste heat has not been included.

Since the main source of energy required for the MDBR is thermal (rather than electrical), a better way of comparing the MDBR and MBR-RO systems would be in terms of their green-

house-gas (GHG) emission potential. This evaluation criterion arises from the escalating interest in the topic of energy-water-climate nexus (WEF, 2011; King et al., 2013). Generally, water is required for electricity production and vice versa. In addition to the increasing scarcity of available freshwater and fuel, it is evident that the use of fossil fuels has resulted in green house gas (GHG) emissions, which in turn, accelerates climate change. Within the United States, 41% of the freshwater withdrawn by the nation is used by the thermoelectric sector (King et al., 2013). The power industry in the United States is also the biggest sector responsible for energy-related CO₂ emissions (EIA, 2011). This is because the main electricity producers in the United States are thermoelectric plants running on fossil fuels. Natural gas is the least polluting fuel, emitting an estimated 0.553 kg of CO₂ per kWh of electricity produced. In comparison, coal and oil respectively emit 75% and 43% more CO₂ equivalent per kWh of electricity produced than natural gas. In countries where electricity is mainly produced by non-GHG emitting sources such as hydropower in Norway (Raluy et al., 2004), the use of electricity in wastewater reclamation processes would not result in significant GHG emission. However, in countries where the main fuel source for electricity generation is coal (eg. Australia, China, Spain, Portugal), the GHG emission potential for MBR-RO systems would be higher due to the CO₂ emitted during power generation (Tarnacki et al., 2012). In such cases, the MBBR would be a lower GHG emitting wastewater reclamation option (Table 1b).

For countries which do not have access to non-GHG emitting renewable energy sources, reducing electrical consumption in processes such as industrial wastewater reclamation could help to reduce the reliance on fuel for electricity production and reduce its impact on climate change. To identify the actual industries and processes in which waste heat could be tapped for MBBR operation, waste heat characterization studies would first have to be conducted. In the United Kingdom, 25% of the total energy use is for industry particularly in the metal and

chemical sectors and as much as 18 to 40 TWh surplus heat generated from these industries has been estimated (Ammar et al., 2012b), indicating that there is indeed market potential to look into technologies which could tap on to this energy source.

While waste heat could also be captured for electricity generation (Ammar et al., 2012a) using a waste heat-to-power (WHP) system, the thermal energy would first need to be transformed into mechanical energy to drive the turbine before electricity can be generated to drive the MBR process. On the other hand, the grade waste heat can directly be used to heat up the wastewater in the MDBR process. Considering the losses incurred during the transformation processes (from thermal to electrical energy), the direct utilization of waste heat in the MDBR system would likely be more efficient than a MBR-RO-WHP system. In summary, the fundamental difference between the MDBR and MBR-RO system is the MDBR's ability to directly harness low-grade thermal energy, which reduces the reliance on electrical energy. The multiple transformative steps required for power generation made energy losses inevitable so the direct use of thermal energy in the MDBR would reduce energy losses associated with power generation. Due to the limited literature available on the MDBR, data from pilot-scale MD and thermophilic bioprocesses had been used to compare the electrical requirement between the MDBR and MBR-RO system. Admittedly, other issues such as off-site GHG generation during the construction phase can affect the total GHG emissions and this should be considered in future studies when actual data from full-scale MDBR plants are available for comparison.

3.2 MDBR as a wastewater reclamation option

3.2.1 *Flux performance*

The performance of the MDBR in wastewater reclamation is summarized in Table 2. From a wastewater engineering viewpoint, it is generally accepted that micro-organisms growing at an environmental temperature of $> 45\text{ }^{\circ}\text{C}$ are considered to be thermophilic (LaPara and Alleman, 1999). As biodiversity decreases with temperature increase, the MDBR is generally operated at $< 60\text{ }^{\circ}\text{C}$ in the temperature range of 53 to $58\text{ }^{\circ}\text{C}$. This poses a limitation on the absolute flux attainable in the MDBR system since the driving force in the MD process is vapor pressure gradient, which increases exponentially with temperature increase. In unfouled membranes, heat transfer through the boundary layers, the membrane thermal permeability, the partial pressure of air within the pores and the feed composition (for example, solute in the feed affects vapor pressure and film transfer coefficients) would affect the initial MD flux (Schofield et al., 1990). For dilute salt solutions, concentration polarization effects on vapor pressure reduction are small (Martínez-Díez and Vázquez-González, 1999) and are usually not considered in MDBR studies where salt concentrations in systems are typically $< 1\text{M NaCl}$. Heat and mass transfer mechanisms govern the permeation flux in MD and have been well-researched with numerous models developed (Schofield et al., 1987; Srisurichan et al., 2006; Gryta, 2008). Improving hydrodynamics via inclusion of baffles and increasing air flow rate has been shown to reduce boundary layer resistance in the feed side and result in higher initial flux in the MDBR (Goh et al., 2012a).

Like all membrane systems, the MDBR faces the challenge of flux decline due to fouling. Understanding the fouling phenomenon and its impact on the MD flux would aid in determining the significance of each factor and identifying the measures required to minimize

flux decline. Fouling in the MDBR system (and in the MD process) has proved to be more complex than the conventional MBR systems. First of all, it has at least 3 detrimental effects on flux, one of which is similar to MBRs while the other two are unique to the MDBR. The first factor is analogous to the effect of a fouling layer in a conventional MBR. Like the MBR system, the fouling layer could exert a mass transfer resistance to flow and may have caused some degree of pore closure or obstruction (Figure 3a).

Like the MBR system, the total mass transfer resistances when fouling occurs in the MDBR process would include resistances through the feed and permeate boundary layers (R_f and R_p , respectively), resistance due to fouling (R_b) and resistance in the membrane. The vapor transfers through the micro-porous, hydrophobic MF membrane via diffusion. The mass balance across the MD membrane can thus be summarized by Eq. 1 (Schofield et al., 1987; Srisurichan et al., 2006).

[Mass transfer through feed boundary layer] = [Mass transfer through fouling layer] = [Mass transfer through membrane] = [Mass transfer through permeate boundary layer]

$$J = \left(\frac{P_f - P_b}{R_f} \right) = \left(\frac{P_b - P_1}{R_b} \right) = \left(\frac{P_1 - P_2}{R_m} \right) = \left(\frac{P_2 - P_p}{R_p} \right) \quad \text{Eq. 1}$$

Fouling layer characteristics such as porosity would determine the relative contribution of its hydraulic resistance towards the overall mass transfer resistance. In a study where saline wastewater produced from animal intestines processing plant was treated by the DCMD process, protein precipitation and fouling contributed to 70% decrease in MD flux from 23.25 to 6.5 L/m².hr in a mere 55 hours (Gryta, 2008). The non-porous proteinaeous fouling layer thickness was estimated to be 90µm. The study estimated that 20% flux decline was due to its thermal resistance while 7-10% was contributed by concentration polarization (due to feed

concentration). The remaining 40% of the flux decline was assumed to be contributed by the hydraulic resistance of the non-porous fouling layer. On the other hand, a mere 15% decrease in flux for MD treatment of tap water was observed in the same study. The thin 8-12 μ m thick bicarbonate fouling layer appeared to be relatively porous. Based on its modeling results, the study concluded that the thin, porous layer only resulted in thermal and not hydraulic resistance.

Similar results were observed in a comparison study on fouling in MD and MDBR (Goh et al., 2013a). After 7 days of operation, the fouling layer thickness in both MD and MDBR systems were observed to be similar but the MD flux was 19% higher than the MDBR flux, indicating that the flux in the MD process is influenced not just by the fouling layer thickness but also the characteristics of the fouling layer (eg. Structure, composition, porosity, coverage, pore blocking). On the other hand, the heat transfer resistance of a 20 μ m thick fouling layer was estimated to be 2 magnitudes lower than that of the membrane, feed and permeate boundary layers, indicating that the main contributor to flux decline in this study is unlikely to be thermal resistance of the fouling layer but other factors such as hydraulic resistance. While convective transport could have taken place within the more porous parts of the biofilm (Costerton et al., 1994), the main component of a biofilm is the extracellular polymeric substance (EPS). The mechanism for mass transfer across the biofilm would likely comprise of diffusion through the hydrated EPS matrix and flow through a tortuous 'cake' layer. With a self-diffusion coefficient estimated 15% lower than that in bulk water (Vogt et al., 2000), the hydrated EPS matrix would have conferred a degree of mass transfer resistance.

The second effect of fouling in the MDBR system is heat transfer resistance and this is unique to the MD system. Figure 3b summarizes the temperature profile in a fouled MD

membrane. The hydrophobic membrane used in MD prevents aqueous solution penetration into membrane pores. This results in a vapor-liquid interface (denoted by the curves in Figure 3b) at the pore's entrance. For DCMD two boundary layers exist between the membrane surface and the feed and permeate side, namely the feed boundary layer and the permeate boundary layer. On the membrane surface of the feed side, the temperature (denoted as T_1) will be lower than the temperature in the bulk feed (T_f) depending on the heat transfer coefficient (h_f) at the feed-boundary layer and the amount of heat loss during vaporization (ΔH_v). Conversely, the temperature at the membrane surface on the permeate side (T_2) will be higher than temperature in the permeate (T_p) due to the heat transfer coefficient (h_p) at the permeate-boundary layer and the heat gain from latent heat of condensation. In the case of a fouled membrane, T_1 is also influenced by the heat transfer coefficient (h_b) in the fouling layer and the heat balance across the MD membrane can be summarized by Eq. 2.

[Heat transfer through feed boundary] = [Heat transfer through fouling layer] = [Heat transfer through membrane + Heat transferred by vapor] = [Heat transfer through permeate boundary]

$$h_f(T_f - T_b) = \left(\frac{k_b}{\delta_b} \right) (T_b - T_1) = \left(\frac{k_m}{\delta} \right) (T_1 - T_2) + J \Delta H_v = h_p(T_2 - T_p) \quad \text{Eq. 2}$$

Temperature polarization is the ratio of the net transmembrane temperature difference ($T_1 - T_2$) and overall temperature difference ($T_f - T_p$) (Schofield et al., 1987) and the temperature polarization coefficient (TPC) in Eq. 3 is often used to quantify the magnitude of the heat resistance in the boundary layers (and fouling layer in the case of fouled membranes) over the total heat transfer resistance (Curcio and Drioli, 2005). The TPC value can be an indication of the thermal efficiency of the system. If the thermal resistance of the fouling layer is significantly greater than the boundary layers, the TPC observed after fouling has occurred would be lower.

$$\text{TPC} = \left(\frac{T_1 - T_2}{T_f - T_p} \right) \quad \text{Eq. 3}$$

While thermal resistances are absent in the MBR system, it results in temperature polarization in the MDBR system, which reduces the effective temperature gradient across the membrane and lowers the flux. Depending on characteristics such as porosity and thickness, the fouling layer would have impeded convective heat transfer from the feed film boundary layer and heat transfer to the membrane surface would likely occurred via diffusion and conduction across the fouling layer (Flemming and Wingender, 2001; Incropera and DeWitt, 2002). Assuming the thermal conductivity of biofilms is 0.57~0.71W/m.K (Characklis, 1981), which is almost 75% lower than the thermal conductivity of inorganic deposits such as CaCO_3 and CaSO_4 (2.6 and 2.3W/m.K respectively (Green and Perry, 2008)), a fouling layer thickness in the magnitude of millimeter range would significantly reduce heat flux.

Temperature polarization has been cited in numerous journals to be a significant factor affecting net driving force in MD (Schofield et al., 1987; Lawson and Lloyd, 1997; Srisurichan et al., 2006) but temperature is not the direct driving force in MD; hence, TPC is not a direct coefficient for the driving force (vapor pressure gradient) in MD. For the same TPC value, the driving force of the MD may be different and hence, result in different fluxes (Gryta, 2008). This is illustrated in Table 3 where analysis of the experimental results from another paper (Srisurichan et al., 2006) shows that while the TPC before and after membrane fouling were similar, the MD flux differed significantly. MD fouling test had been conducted using 100mg/L humic acid + 0.755mM Ca^{2+} solution and a cake layer was formed after 9 hours of operation.

Even though the TPC has remained relatively constant at around 0.4, the permeation flux (J) has decreased by 21%. This brings us to the vapor pressure polarisation coefficient (VPC)

(Martínez-Díez and Vázquez-González, 1999), a direct coefficient for the driving force in MD. Unlike temperature, increase in vapor pressure polarisation can be directly correlated with decrease in permeation flux. VPC is represented by Eq. 4.

$$\text{VPC} = \left(\frac{P_1 - P_2}{P_f - P_p} \right) \quad \text{Eq. 4}$$

Note: P_f and P_p represent vapor pressure of water corresponding to the temperature of the bulk liquid.

The Antoine equation (Eq. 5) relates partial vapor pressure exponentially to temperature (in dilute solution) and the use of TPC as a surrogate measure of vapor polarization coefficient (VPC) would be appropriate only at lower temperatures or low feed/salt concentration, where the relationship between vapor pressure and temperature is relatively linear. As temperature and feed concentration increase, the deviation between TPC and VPC increases (Martínez-Díez and Vázquez-González, 1999).

$$\log P = A - \left(\frac{B}{T - C} \right) \quad \text{Eq. 5}$$

Where P = Pressure, T = Temperature, A , B , C are component specific constants

It can be concluded that while TPC is a good indicator of the heat transfer efficiency across the membrane, it should not be used exclusively to explain the entire flux decline phenomenon. Mass transfer resistance should also be taken into account in the evaluation of flux. This is especially so in a fouled membrane where fouling layer resistance may significantly limit mass transfer across the membrane. Since the flux is directly driven by the vapor pressure gradient at the interface between the liquid and the hydrophobic membrane (i.e., $J = \Delta P / R_m$) where J is the flux ($\text{kg/m}^2\text{h}$), R_m is the membrane resistance ($\text{kPa.kg/m}^2\text{h}$) and ΔP (kPa) is the difference between the vapor pressure on the feed and permeate side of the membrane in the MD/MDBR system, factors which could significantly reduce vapor

pressure should be considered. This brings us to the third detrimental effect of the fouling layer in the MD system, namely vapor-pressure depression.

In the MD process, the curvature of the evaporating surface can affect the vapor pressure and this becomes significant for pores smaller than 100 nm (Fisher and Israelachvili, 1981; Mitropoulos, 2008). A wetting liquid confined to a small hydrophilic pore would experience greater attractive force between the neighboring molecules (compared to that for a plane surface) due to the increased number of nearest neighboring molecules, thereby resulting in a vapor pressure depression (Skinner and Sambles, 1972; Heidenreich and Büttner, 1995). This is the Kelvin effect and the Kelvin equation is given by

$$\ln \frac{\bar{P}_A}{P_A^\circ} = -\frac{4\sigma V}{dRT} \quad \text{Eq. 6}$$

Where P_A° is the vapor pressure of the volatile solvent over a flat interface, $\bar{P}_A$ is the vapor pressure of the solvent in the pores from which liquid is evaporating, σ is the interfacial tension of water (N/m), V is the molar volume of the liquid (m³/mol), d is the pore diameter (m), R is the gas constant (8.314 Nm/K.mol), and T is the absolute temperature (K).

Earlier studies on the impact of the Kelvin effect on MD flux looked into employing hydrophilic polymeric layers on both sides of the hydrophobic membrane to reduce the “water-logging phenomenon” and increase condensation at the distillate side (Cheng and Wiersma, 1982; Cheng and Wiersma, 1983). Having a hydrophilic biofilm on the hydrophobic MD membrane is somewhat analogous to having a hydrophilic layer at the distilland side. A hydrophobic fouling layer (with a contact angle > 90°) will result in a vapor pressure enhancement and lead to higher flux while a hydrophilic fouling layer will lead to a vapor-pressure depression and reduce flux (Goh et al., 2013b). Using the evapoporometry method (Krantz et al., 2013) to determine the pore size distribution (PSD) of a biofouling

layer for the first time, the PSD of the biofouling layer in the MD process was estimated to reside in the < 10 nm range, which is the effective pore size range for the Kelvin effect to manifest (Goh et al., 2013b). Despite the relatively thin fouling layer (in 8–16 μm range), a significant 20-36% reduction in vapor-pressure was observed in the same study. This validated the hypothesis proposed in a previous seawater desalination study (Krivorot et al., 2011) that the extracellular polymeric matrix of a biofilm can reduce vapor-pressure and directly affect the driving force for water vapor mass transfer in an MD process.

From the membrane cleaning results, the bulk of the fouling in the MDBR seem to be inorganic carbonate (Khaing et al., 2010; Goh et al., 2012a). While a thin, non-continuous bicarbonate fouling layer may not contribute to significant mass transfer resistance (Gryta, 2008), both organic fouling (Wu et al., 1991; Hausmann et al., 2011) and inorganic crystallization (Tun et al., 2005; Chen et al., 2012) had been observed to result in flux tending to zero in the MD system. Inorganic foulants do not necessarily result in porous deposits. Inorganics can precipitate to form a continuous, impermeable layer on the membrane surface, which reduces the effective membrane area (Tun et al., 2005). Greater flux decline was observed in the MDBR system (as compared to the MD system) (Goh et al., 2013a), indicating that the bioprocess may play a role in accelerating flux decline. The self-accelerating fouling model can help to explain the combined effects of inorganic, organic and bio-fouling on flux decline in the MD/MDBR system (Goh, 2014). Like the MBR system, organics will first deposit on the membrane surface in the MDBR – this is the membrane conditioning phase. The rate of organic deposition may be dependent on operating conditions such as SRT (Goh et al., 2012b). This conditioning layer is likely to trigger more extensive fouling since it is a source of nutrients for the biofilm (Palmer et al., 2007). In addition to hydraulic resistance, heat transfer resistance and vapor pressure depression, the developing biofilm could hinder the back-diffusion of inorganic solutes (Herzberg et al., 2009), resulting

in the cake enhanced concentration polarization (CECP) phenomenon where inorganic solutes accumulate to concentrations beyond their solubility products. Studies have shown that the microbial EPS can affect CaCO_3 precipitation, either by trapping and concentrating the calcium ions or through the chemical interactions of ions with protein (Braissant et al., 2003; Ercole et al., 2007; Li and Yu, 2014; Lin et al., 2014). With inorganic precipitation and bacterial EPS forming impermeable crusts on the membrane surface, the effective membrane area would be reduced.

While fouling in the MDBR system can have more detrimental impact on flux than in the MBR systems, fouling and its impact can be controlled. Measures which have shown success in flux improvement and fouling control in the MBR systems have been demonstrated to be equally effective in the MDBR system. Periodic membrane cleaning were effective in minimizing fouling and stabilizing flux (Khaing et al., 2010). Similar successes have been observed with increase in air flow rate, inclusion of baffles and operating at the SRT of 30 days (Goh et al., 2012a). Through process optimization, a MDBR flux of $10 \text{ L/m}^2\text{.hr}$ was successfully achieved and maintained for > 120 hours (comparable to MBR-RO and OMBR (Zhang et al., 2012)). To compete with the MBR (typical flux of $10\text{-}30 \text{ L/m}^2\text{.hr}$) and RO ($20\text{--}25 \text{ L/m}^2\text{.hr}$ (for water reuse)) systems which has already been used in actual municipal and industrial applications (Table A.2), longer term performance studies, improvement of reactor design and development of better membranes are required to further improve the MDBR flux and reduce fouling.

3.2.2 *Permeate quality*

In the reclamation of synthetic wastewater, the MDBR is able to achieve a high overall organic removal efficiency of 99.9% (Goh et al., 2013a), which translates to an average

permeate concentration of around 0.8 ppm in terms of total organic carbon (TOC), which is better than the 6-10 ppm TOC observed in MBR filtration and comparable to the 20-200 ppb TOC observed in municipal wastewater reclamation using UF-MBR/RO (Qin et al., 2006; Tam et al., 2007). In terms of its performance in industrial wastewater reclamation, the MDBR is able to achieve a permeate quality of 1.5–4.3 mg/L TOC in petrochemical wastewater (Khaing et al., 2010), as compared to 30-500 ppm COD observed in MBR-treated effluent (Qin et al., 2007a; Lin et al., 2011). While the MBR system may be capable of treating industrial wastewater to meet current disposal requirement and produce water for basic uses in the industry (Qin et al., 2007b), the treated effluent would need to be further polished for applications that need high grade water (Table A.1). In view of the growing concerns with emerging micropollutant, it is likely that stricter discharge limits would be imposed on industrial effluents in the near future. On its own, the MBR would not be able to treat/remove hydrophilic and biologically persistent trace organic compounds effectively. Inserting an advanced treatment process such as NF/RO process can increase the overall removal efficiency (Alturki et al., 2010). The NF and RO processes remove most emerging micropollutants via three main mechanisms: steric hindrance (sieving effect), electrostatic interaction (charge effect) and hydrophobic/adsorptive interactions (Dolar et al., 2012; Cartagena et al., 2013). Slightly higher removal for greater varieties of organics is typically observed with RO membranes, as compared to NF membranes (Khan et al., 2004). These is because the main retention mechanism in RO membranes usually retains is steric-hindrance; ie., any micropollutants with the stoke's radius less than the molecular cutoff weight (MWCO) of the RO membrane will be retained. On the other hand, the main retention mechanism in NF membranes is electrostatic interaction. Neutral micropollutants with stoke's radius less than the membrane's MWCOs are thus not effectively retained by the NF membranes. In short, how effective the micropollutants are retained by the process is

dependent on the solute-membrane interactions, which would be dependent on the physico-chemical characteristics of the micropollutant and the membrane characteristics, as well as the fouling layer characteristics. Unlike the NF and RO processes which retain micropollutants via steric hindrance/electrostatic interaction, the MD process is able to retain all non-volatiles, which may imply theoretical retention of a greater range of micropollutants though further research is required to verify this.

For now, the permeate quality (in terms of TOC concentration) of the MDBR and MBR-RO are relatively comparable. While more studies are required to compare the performance of the MDBR and MBR-RO in industrial wastewater reclamation, it is likely that there are different niche areas for MD/NF/RO applications. To select the system most suitable for treating a particular industrial wastewater, factors such as the availability of waste heat, effluent quality requirement and the compatibility of the membrane process with the targeted solutes should be considered.

3.2.3 Performance of the biological process

One of the benefits of including biomass in the MD process is that the thermophilic bioprocess would biologically remove organics which would then delay membrane wetting. Despite the relatively low thermophilic biological TOC and total nitrogen (TN) removal efficiency of $88 \pm 3\%$ and $58 \pm 8\%$, respectively at the prolonged SRT of 110 days without pH control, the MDBR (when compared to the MD system) was still able to delay membrane wetting by 1.7~3.6 times (Goh et al., 2013a). Wetting in the MD system had lead to a 15 fold increase in TOC transmission and a reduction in organic removal efficiency from 99.9% to 99.1% (as compared to the MDBR system). Liquid surface tension, membrane contact angle and membrane pore size are three important factors which can affect membrane wetting

(Lawson and Lloyd, 1997; Curcio and Drioli, 2005). The higher TOC, TN and salts content in the MD retentate may have contributed to faster membrane wetting. Organic amphiphilic foulants such as proteins, lipids or fats have a high tendency to adsorb/deposit on the hydrophobic membrane surface. Preferential organics deposition onto the MD membrane may have led to the lower contact angle observed in the MD system (Goh et al., 2013a). High concentration of organic foulants, particularly protein, can also reduce the surface tension of the feed and result in faster membrane wetting (Aw, 2011). The situation could be exacerbated by salt crystals formation within the membrane pores, which would lead to progressive wetting of the membrane (Gryta et al., 2006; Gryta, 2008; Nghiem et al., 2011). Measures such as improving the biological removal efficiency, limiting the MDBR application to specific wastewaters with low concentrations of foulants, pre-treating the wastewater to remove the foulants prior to MDBR application can delay membrane wetting. On the other hand, another area to look into would be the development of membranes with greater hydrophobicity and chemical resistance (Drioli et al., 2012) to improve the working lifespan of the hydrophobic membrane. In general, no membrane wetting has been observed when PTFE membranes are used (Goh et al., 2012a) but the effect of repeated citric acid cleaning on the mechanical and hydrophobic characteristics of the membrane has not been evaluated. This is an important area to investigate as past studies have shown deterioration in PVDF membrane structure with repeated cleaning using hypochlorite solutions (Puspitasari et al., 2010; Hajibabania et al., 2012).

Compared to mesophilic conditions, thermophilic COD removal often appears to be lower with exceptions in the treatment of specific compounds such as long-chained fatty acids, which observe improved degradation at elevated temperature (Becker et al., 1999; Tripathi and Grant, 1999). Some of the reasons commonly cited for the lowered COD removal efficiency observed at elevated temperatures are summarized as follows:

i) Reduced colloidal COD removal: The lower COD removal efficiency may be attributed to reduced colloidal COD removal at thermophilic temperature (Vogelaar et al., 2002). These may be due to a few reasons. Floc-forming species and protozoa have been observed to be absent at temperature $> 40\text{ }^{\circ}\text{C}$ (LaPara and Alleman, 1999; Vogelaar et al., 2002). This is significant because protozoa consume small colloidal particles and floc formation plays an important role in the entrapment of colloidal particles for biological degradation. Interestingly, trace amount of *Acanthamoeba*, a genus under the Kingdom *Amoebozoa*, was found during a single sampling from the MDBR system; more studies are required to verify if this is a unique occurrence (Zhang, 2014). Variation in amount and type of EPS (soluble or bound) produced in the thermophilic and mesophilic sludge can also affect the floc size (Choudhary, 2005; Vogelaar et al., 2005; Visvanathan et al., 2007; Lin et al., 2009). Changes in polymer interactions and/or interplay with exo-enzymes (the soluble microbial products (SMP)) at varying temperatures may account for the difference in bioflocculation behaviour (and hence, floc size) between mesophilic and thermophilic activated sludge (Vogelaar et al., 2005). It was hypothesized that thermophilic sludge tend to release EPS into bulk solution (SMP) while mesophilic sludge excretes EPS to form bulk of the floc matrix (bEPS), resulting in the higher SMP, lower bEPS and smaller floc size commonly observed at thermophilic temperature (Vogelaar et al., 2005). The excess SMP production by the thermophilic sludge may have hindered bioflocculation, resulting in weaker floc structures that exhibit higher shear sensitivity (Mikkelsen and Keiding, 2002; Suvilampi et al., 2006; Li and Yang, 2007). Compared to the floc size range of 1 - 100 μm commonly observed in mesophilic MBR systems (Zhang et al., 2006a; Zhang et al., 2006b; Zhang et al., 2010), the floc size observed in the MDBR falls within the lower range of 0.3 to 30 μm (Goh, 2014).

ii) Reduced biodiversity and ability to degrade large range of COD: The poorer COD removal efficiency may also be attributed to the decrease in biodiversity at thermophilic

temperature and hence, inability to degrade the large range of compounds as the mesophilic counterparts (LaPara et al., 2000; LaPara et al., 2002). Phenotypic fingerprinting has shown that as temperature increases, the microbial community has shifted to become more selective and uses a narrower range of COD (Tripathi and Grant, 1999). Indeed, compared to the Shannon Weaver index of > 4.0 observed for all the mesophilic bacterial communities in the OMBR system operated at SRT of 20 days, the alpha diversity of all thermophilic bacterial communities in the MDBR (operated at SRT of 110 days, at unsteady state, without pH adjustment) were relatively low (Shannon=1.75~2.53) (Zhang, 2014). This is slightly lower than the Shannon index of > 3.0 reported in other thermophilic studies (Mardanov et al., 2010; Li et al., 2013). The combination of high temperature and accumulation of non-volatiles may have reduced the richness and diversity of the bacterial community (but not the eukaryotic community) in the MDBR, resulting in the slightly lower Shannon index observed. Species from the kingdom fungi were observed to dominate in the MDBR. In spite of the lower biodiversity in the MDBR, there may be a chance that these particular niche species could be suitable for biodegradation of specific recalcitrant micropollutants - further research is required to look into this.

iii) pH shift with temperature increase: Another potential factor which may affect COD removal at elevated temperature would be pH. pH was observed to increase to > 10 in the MDBR (Goh et al., 2013a). This pH increase phenomenon is not uncommon and has been observed in several thermophilic studies (Tripathi and Grant, 1999; Lasik M. et al., 2002; Cibis et al., 2004). Due to lower solubility of gases at elevated temperature, carbon dioxide would be stripped from the solution, which would result in the removal of carbonic acid from solution (Suzuki et al., 2002). Adjusting the retentate pH to the range of 7.5 - 8.5 appears to improve TOC removal (Wong, 2011). Similar observations have been made in other aerobic

thermophilic studies where optimal pH for COD degradation at elevated temperature was observed to be 7 (Lasik M. et al., 2002; Cibis et al., 2004; Krzywonos et al., 2008).

iv) Organic acids production at micro-aerobic conditions: Due to lowered oxygen solubility at elevated temperature, the presence of micro-aerobic environments within a thermophilic system may encourage the production of organic acids (such as acetic acids), leading to reduced organic removal efficiency (Chu et al., 1996; Cibis et al., 2004). Good mixing should minimize the micro-environments. This factor has not been evaluated though it should be noted that the dissolved oxygen (DO) in the MDBR had been consistently maintained at > 2 mg/L.

v) Nutrient deficiency: Supplying adequate amounts of nitrogen and phosphorus to the system is crucial in maximizing COD removal efficiency in the thermophilic system. Enrichment of the culture with ammonia nitrogen and phosphate phosphorus has increased COD removal from 51% to 84.2% (Cibis et al., 2006). Reducing the COD:N:P ratio from 126:3.7:1 to 853:6.1:1 in the MDBR system resulted in a significant reduction in biomass concentration from 1.3 g MLSS/L to < 0.5 g MLSS/L and a corresponding reduction in biological carbon removal was observed (unpublished results).

Another factor which could contribute to the relatively low biological organic removal observed at the SRT of 110 days could be inhibitory effects imposed by the accumulation of non-volatiles such as recalcitrant organics and salts in the MDBR system. While inorganics and organics are uptaken by cells for respiration / biomass growth, residual inorganics and recalcitrant organic by-products may accumulate in the MDBR retentate. Since the concentration factor increases with SRT (Table 2b), non-volatiles may accumulate to inhibitory levels in the MDBR at higher SRT. In one study utilizing synthetic wastewater, free ammonia (FA), salinity (NaCl), potassium, sulphate and heavy metals were identified to

be potential inhibitors that would most likely inhibit the aerobic thermophilic bioprocess (Koh, 2012). While the individual concentration of each potential inhibitor had not exceed the inhibitory limit, it is also not known if any synergistic / antagonistic effects are occurring between multiple inhibitors in the MDBR. More studies are required in this area.

The relatively low biological nitrogen removal observed in the MDBR studies may be due to the absence of nitrifiers at elevated temperature in conventional bioreactors (LaPara and Alleman, 1999; Juteau, 2006). In the absence of nitrification (the biological conversion of ammonium to nitrite and nitrate), biological nitrogen transformation in the thermophilic bioreactor would not proceed by the same nitrification-denitrification ($\text{NH}_4^+ \rightarrow \text{NO}_3^- \rightarrow \text{N}_2$) pathway as the conventional mesophilic bioreactor. There are limited studies on thermophilic nitrogen removal; the general consensus is that the main transformation pathway in the thermophilic bioreactor is ammonification ($\text{Organic N} \rightarrow \text{NH}_4^+$). Due to lower gas solubility at elevated temperature (Abeynayaka and Visvanathan, 2011), ammonia stripping will likely occur in the aerated MDBR system, preventing ammonium from accumulating to inhibitory levels. On the other hand, this would also result in the permeation of ammonia across the hydrophobic membrane into the product water, which would reduce the quality of the permeate. Measures such as pH adjustment and limiting MDBR treatment to feedwater with low nitrogen content can help to reduce ammonia permeation (Table 2c). Further research would be required to determine the effect of variable nitrogen loading, as well as to determine the range of feed COD:N:P ratio suitable for MDBR operation so that ammonia permeation can be minimized without compromising biological removal efficiency. The current permeate quality observed in the MDBR studies are within the range of 5–15 mg $\text{NH}_3\text{-N/L}$ for basic industrial water (Qin et al., 2007b). However, further post-treatment may be required to reduce the ammonium concentration to ≤ 1 mg $\text{NH}_3\text{-N/L}$ and ≤ 0.1 mg $\text{NH}_3\text{-N/L}$ respectively, for cooling water and boiler feed water applications (Levine, 2003).

Thermophilic nitrifiers and anammox microbes are not unheard of. Aerobic heterotrophic nitrifiers, *Bacillus* MS30, have been observed to be able to produce nitrite from ammonia and nitrate reduction at 65 °C (Mevel and Prieur, 1998, 2000). Thermophilic ammonia oxidizing archaea (AOA) have also been observed in recent studies (de la Torre et al., 2008; Reigstad et al., 2008; Weidler et al., 2008). Thermophiles from deep-sea hydrothermal vents have been observed to be able to reduce nitrate to nitrite (genera *Oceanithermus* and *Vulcanithermus*), ammonium (*Caldithrix*, *Caminibacter*, *Hydrogenimonas*, *Thermovibrio*) and molecular nitrogen (genus *Persephonella*) (Miroshnichenko, 2004). Thermophilic anammox microorganisms have also been discovered recently from deep sea hydrothermal vents (Byrne et al., 2008) and high temperature produced water (between 55 °C to 75 °C) from oilfields (Li et al., 2010). In addition, thermophilic nitrogen fixing methanoe archaea capable of converting dinitrogen to ammonium have also been observed (Capone, 2006; Mehta and Baross, 2006). The complexity of the nitrogen cycle within the thermophilic bioprocess, as well as the current lack of studies in this area, makes determining the thermophilic biological nitrogen removal mechanism within the MDBR a great challenge.

The inclusion of thermophilic nitrifiers/denitrifiers would likely reduce the ammonium concentration in the system but the biological nitrogen removal process in the MDBR has to be optimized so that the physical process of ammonia stripping and diffusion do not occur at a faster rate than ammonium removal by nitrification/ denitrification. To reduce ammonia permeation, research on the optimization of the biological nitrogen removal process would have to be carried out to significantly improve the biological nitrogen removal efficiency. Future work should also look into using techniques such as phylogenetic and functional marker genes to identify ammonia-oxidizing organisms in the MDBR. Conversely, there have been interests in recovering nutrients from the wastewater (Cornel et al., 2011). The production of nitrogen-based fertilizer from its base elements (for example, nitrogen or air) is

an energy-intensive process (Larsen et al., 2007). If recovering nitrogen from wastewater is a less energy-intensive option, it may be feasible to recover ammonia from the MDBR product water instead of nitrifying and denitrifying the ammonium in the wastewater into nitrogen gas.

Nevertheless, process optimization can play an important role in improving the biological removal efficiency in the MDBR. By adjusting the pH, SRT and the COD:N:P of the feedwater, a high biological removal efficiency of > 95% and > 75% for TOC and TN, respectively, can be achieved at the SRT of 10 and 30 days (Table 2c). A higher SRT of 110 days (compared to 10 or 30 days) likely resulted in greater accumulation of inhibitory substances, which led to lowered observed nitrogen removal efficiency in Table 2c. Maintaining the pH at the 7-8 range via pH adjustment appears to improve nitrogen removal efficiency (Table 2c) while reducing the COD:N:P ratio from 126:3.7:1 to 379:6:1 did not appear to have any adverse impact on nitrogen removal (unpublished results). Further process optimization, such as determining the optimal SRT where there is sufficient residence time for biodegradation of micropollutants with minimal side effects on the bioprocess and membrane process, would have to be conducted in future works.

3.2.4 Sludge production & disposal

The biomass concentrations observed in the MDBR (Table 2b) are typically lower than that observed in most mesophilic MBR studies (Zhang et al., 2006a; Zhang et al., 2006b). Net sludge yield has been observed to decrease with temperature increase in some cases (LaPara and Alleman, 1999; Suvilampi and Rintala, 2003; Krzywonos et al., 2008). This may be due to the higher maintenance energy and decay rate at elevated temperature (Prescott et al., 2002). Biomass decay rate has been observed to increase by a factor of 4, from 0.004 h⁻¹ to

0.017 h⁻¹, as temperature increased from 30 to 55°C (Vogelaar et al., 2003) and in some cases, the endogenous cell decay rate (k_d) have been reported to be one magnitude higher (in the range of 0.32 – 0.78 d⁻¹) than that observed at mesophilic temperatures (in the range of 0.03 – 0.08 d⁻¹) (LaPara, 1999). The lower yield implies that there is less sludge for disposal, which would result in some cost savings for the MDBR treatment plant.

4 Possible configurations for MDBR application

Without optimizing the existing MDBR system for biological nutrient removal, there are three possible configurations for the MDBR system (Figure 4). Waste heat input and heat recovery processes would be required to reduce the electrical energy requirement for the system. In the first configuration, the MDBR system can be used in its current form to treat industrial wastewater with high carbon and low nitrogen content. Depending on the quality of the permeate, the permeate could be used to close the water loop in the industry for uses such as feed water for cooling towers (if the permeate NH₄-N < 1ppm).

The benefit of this configuration is that no further post-treatment would be required but the disadvantage is that MDBR application would be limited by the industrial feed water quality and the use for the final product water. The second configuration allows MDBR to be applied to more types of wastewater (regardless of the nutrient content) but the drawback is that depending on the use of the product water, energy- and/or chemical-intensive post-treatment such as ammonia stripping or ion exchange (Wang et al., 2007; Chmielewska, 2012) would be required to remove ammonium from the permeate. The process and removal efficiency would be limited by the ammonium concentration in the permeate.

The third configuration considers an anaerobic MDBR system (instead of an aerobic one). Biogas can be recovered from the system for gas sparging and additional gas could be

required for energy use. The disadvantages would be the post-treatment required to recover ammonia and methane gas from the permeate (Smith et al., 2012). Methane loss through liquid phase in the anaerobic MBR had been reported to be as much as 30 % and 50 % at 35 °C and 15 °C, respectively (Smith et al., 2012). This is because the solubility of methane gas decreases as temperature increases, for example, methane solubility in water decreases by approximately 24% as temperature increases from 35 °C to 55 °C (Green and Perry, 2008). In the anaerobic MDBR, this reduction in methane gas solubility may be beneficial as most of the methane would likely exist in the gas phase, which is easier for extraction and recovery. In addition, the methane gas would pass into the permeate via the slower process of gas diffusion in the anaerobic MDBR while in the anaerobic MBR, the dissolved methane would be transported more quickly with the permeate across the porous MF/UF membrane via poiseuille flow. Depending on the operating pressure of the anaerobic MBR, it is likely that methane permeation in the anaerobic MDBR would be less than the anaerobic MBR. Studies are required to determine if the intrinsic benefits of thermophilic anaerobes for methane production can be exploited.

5 Conclusions

With the move towards zero liquid discharge, industrial interest in advanced wastewater treatment to reclaim high quality product water for reuse is increasing. Like the RO system, the MDBR is a high retention system and has the potential to produce high quality water. The GHG emission from the MDBR system is likely to be lower than the MBR-RO in situations where waste heat is available and a non-renewable energy (such as coal) is used to generate electricity. In terms of wastewater reclamation performance, short term studies have shown that the MDBR is capable of achieving a flux of 10 L/m².hr, which is comparable to the MBR-RO. Other than the ammonium concentration, the permeate quality for MDBR and

MBR-RO are comparable. In terms of biological removal efficiency, more studies are required to optimize the MDBR process and to further evaluate the performance of the MDBR using different industrial wastewaters.

The MDBR is still a budding technology which requires further research. Future work should look into understanding the biological nitrogen removal mechanism in the MDBR system and optimizing the biological nitrogen removal process to address the issue of ammonia permeation. While a flux of $10 \text{ L/m}^2\cdot\text{hr}$ has been achieved, further improvement in areas such as membrane fabrication, module and reactor design are required to achieve higher flux. Study into improving the antifouling properties of the membrane and improvements in module and reactor design are necessary to delay fouling and reduce cleaning frequencies. To achieve energy neutrality, future work should look at the anaerobic MDBR system to understand the biological removal efficiency of the system, the biogas generation and recovery rate to compare the performance of the anaerobic MDBR system against existing anaerobic MBR systems.

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Nomenclature

C	Substrate concentration (g/L)
d	Pore diameter (nm)
h_b	Heat transfer coefficient in biofilm or fouling layer ($\text{W/m}^2 \text{ K}$)
h_f	Heat transfer coefficient in feed boundary ($\text{W/m}^2 \text{ K}$)

h_m	Heat transfer coefficient in membrane ($\text{W/m}^2 \text{ K}$)
h_p	Heat transfer coefficient in permeate boundary ($\text{W/m}^2 \text{ K}$)
J	Permeation flux ($\text{kg/m}^2.\text{s}$)
k	Thermal conductivity of fluid (J/s.m.K)
k_b	Thermal conductivity of fouling layer (W/m.K)
k_m	Thermal conductivity of membrane (W/m.K)
P_1	Vapor pressure at membrane surface on the feed side (Pa)
P_2	Vapor pressure at membrane surface on the permeate side (Pa)
P_b	Vapor pressure at fouling layer (Pa)
P_f	Vapor pressure at bulk feed (Pa)
P_p	Vapor pressure at bulk permeate (Pa)
P_A°	Vapor pressure of volatile solvent over a flat interface (bar)
$\bar{P}_A$	Vapor pressure of solvent in the pores from which liquid is evaporating (bar)
Q	Volumetric flow rate (L/d)
R	Gas constant (8.314 Nm/K.mol)
R_b	Resistance in biofilm or fouling layer ($\text{Pa.m}^2 \text{ s/kg}$)
Re	Reynolds number ($d_h \rho v / \mu$)
R_f	Resistance in Feed boundary ($\text{Pa.m}^2 \text{ s/kg}$)

R_m	Resistance in membrane ($\text{Pa.m}^2 \text{ s/kg}$)
R_p	Resistance in permeate boundary ($\text{Pa.m}^2 \text{ s/kg}$)
R_t	Total resistance ($\text{Pa.m}^2 \text{ s/kg}$)
T	Absolute temperature (K)
T_1	Temperature at membrane surface on the feed side (K)
T_2	Temperature at membrane surface on the permeate side (K)
T_b	Temperature at on fouling layer surface (K)
T_f	Temperature in bulk feed (K)
T_p	Temperature in bulk permeate (K)
V	Reactor Volume (L)
V	Molar volume of liquid (m^3/mol)
X	Biomass concentration (gTSS/L)
δ	Membrane thickness (m)
δ_b	Fouling layer thickness (m)
σ	Interfacial tension of water (N/m)
ΔH_v	Heat of vaporization (J/kg)
ΔP	Difference between the vapor pressure on the feed and permeate side of the membrane (kPa)
ϕ	Membrane rejection efficiency

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List of Tables

Table 1. Comparison of electrical energy requirement and associated CO₂ emission between MBR-RO and MDBR systems

(a) Estimated electrical energy requirement for high grade water production by industrial wastewater reclamation

Estimated Energy Requirement (kWh/m ³)	Industrial wastewater with wasteheat source or heated wastewater (eg. petrochemical, pharmaceutical, pulp and paper)	
	Treatment via MBR-RO	Treatment via MDBR
Aeration		
For dissolved oxygen	0.3 ^a	0.42 ^b
For membrane cleaning	0.4 ^a	0.4 ^c
Thermal and Cooling		0.08 ^{d, e}
Pressure	MBR: 0.1 ^a RO: 0.5 ^a	--
Total	1 to 1.3	0.9

^a Upper Bound energy estimates based on wastewater reclamation using MBR-RO process (Pearce, 2008).

^b Assuming worst case scenario of 40% increase in aeration requirement due to thermophilic aerobic bioprocess (LaPara and Alleman, 1999)

^c Assuming similar air flow rate is required for membrane cleaning

^d Electrical requirement for cooling in a direct contact membrane distillation system (DCMD) is estimated to be 0.05kWh/m³(Al-Obaidani et al., 2008). Energy to heat up feedwater is excluded from this estimate as waste heat is assumed to be available.

^e An estimated 0.03kWh/m³ of backup thermal energy to maintain reactor temperature is included

(b). Comparison of electrical requirement and CO₂ emission associated with electrical requirement for MBR-RO and MDBR

Wastewater reclamation option	MBR-RO	MDBR
a) Direct CO ₂ emission from wastewater treatment process ^a	$\left[\frac{\text{kgCO}_2 \text{ emitted}}{\text{m}^3 \text{ water produced}} \right]$	
- Emission from 1 kg BOD/m ³ wastewater	0.36	0.45
- Emission contributed by biomass decay	0.12	0.22
b) Total direct CO ₂ emission from wastewater treatment process and electricity usage based on fuel source used in electricity generation ^b	$\left[\frac{\text{kgCO}_2 \text{ emitted}}{\text{m}^3 \text{ water produced}} \right]$	
Coal	1.78	1.57
Natural gas	1.18	1.17
Oil	1.48	1.37

^a Estimate based on equations developed in Ashrafi et al, 2014 and biokinetic constants compiled in LaPara and Alleman, 1999

^b Estimate based on electricity requirement of 1.3 kWh/m³ water for MBR and 0.9 kWh/m³ water for MDBR

Table 2. Summary table comparing existing MDBR studies in terms of (a) Flux, (b) Retentate Characteristics and (c) permeate quality

(a) Flux observed in existing MDBR studies

System	Type	Material	Membrane properties				Temperature		Crossflow velocity		Flux		Permeate Organics [ppm TOC]	Reference
			Nominal pore size [μm]	Porosity [%]	Thick-ness [μm]	Area [m^2]	Feed [$^{\circ}\text{C}$]	Pemeate [$^{\circ}\text{C}$]	Feed [cm/s]	Permeate [cm/s]	Initial [$\text{L}/\text{m}^2\cdot\text{hr}$]	Final [$\text{L}/\text{m}^2\cdot\text{hr}$]		
Submerged Aerobic	T	PVDF	0.22	-	-	0.62	58.5	45	-	-	1.5-2.5 (for 1 month)		1-1.7	(Phattaranawik et al., 2008)
Submerged Aerobic	T	PVDF	0.2	70	650	0.035	56	25	-	-	5.01-5.46 (for 15d)		< 0.2	(Phattaranawik et al., 2009)
	FS	PVDF	0.22	80	125	0.013			-	-	12.7	1.9	< 0.4	
	FS	PTFE	0.45	70	70	0.013			-	-	20.1	3.6	~ zero	
Submerged Aerobic	FS	PTFE	0.45	-	-	0.1	58	30	-	-	8.6	5.5 ^a	< 0.5	(Khaing et al., 2010)
Submerged Aerobic	FS	PVDF	0.22	-	-	0.019	55.5 $\pm$ 1	19.5 $\pm$ 1	5.1	1.2	8.37 $\pm$ 0.09	4.05 $\pm$ 0.59 (after 23 days)	< 1 (before membrane wetting)	(Goh et al., 2013a)
Crossflow Aerobic	FS	PVDF	0.22	-	-	0.0066	55.5 $\pm$ 1	19.5 $\pm$ 1	7.4	7.4	8.42 $\pm$ 0.27	3.17-3.68		(Goh et al., 2013b)
Submerged Aerobic	FS	PTFE	0.2	-	-	0.019	53 $\pm$ 1	25 $\pm$ 1	5.1	0.9	10.0 $\pm$ 0.4 (after 1 st hour)	2.9-4.2 ^a (after 30 days)		(Goh et al., 2012a)
		PTFE	0.2	-	-	0.019	55 $\pm$ 1	18 $\pm$ 1	3.8 – 6.4	1.5	9.2-11.7	10.1-10.3 ^b (over 120 hours)		

^a without membrane cleaning

^b with membrane cleaning

T – Tubular, FS – Flatsheet, PVDF - Polyvinylidene fluoride, PTFE - Polytetrafluoroethylene

(b). Summary of retentate characteristics observed in MDBR studies

Wastewater	SRT [d]	Organic loading rate kg/m ³ .day	MLSS [g/L]	Retentate		Reference
				pH	Conductivity	
Synthetic	35	1.44	2.2–3.2	8.04 – 8.48	4.02–4.5 S/m	(Phattaranawik et al., 2008)
Synthetic	137	4.54 ^a	5.3-5.6	6.44	3.04 S/cm	(Phattaranawik et al., 2009)
		1.46 ^b	1.4-1.6	6.82	2.26 S/cm	
Petro- chemical	30	Feed COD: 330-556 mg O ₂ /L	Not available	7.5 - 10.3	15-30 mS/cm	(Khaing et al., 2010)
Synthetic	110	0.35±0.03	5 - 6	10	15 mS/cm	(Goh et al., 2013a)
Synthetic	10	0.391± 0.014	0.8 ± 0.1	7 - 9	10.7±2.2 mS/cm	(Goh et al., 2012b)
	30		1.5 ± 0.1		11.6±2.7 mS/cm	

^a Tubular membrane module

^b Flatsheet membrane module

(c). Effect of varying conditions on permeate quality reported in existing MDBR studies

Feed Source	Feed COD:N:P	SRT	pH	Biological nitrogen removal [%]	Permeate Quality	References
		[d]			[mg NH ₄ -N/L]	
Synthetic wastewater	379:6:1	10	7 - 9	81±2 ^a	2 – 3.5 ^b	(Goh, 2014)
		30	7 - 9	78±3 ^a	3.7 – 6.1 ^b	
	126:3.7:1	110	9-10	58±8 ^c	8.97±0.41 ^d	
		110	7-8.5	67±9 ^c	7.78±0.71 ^d	
Petrochemical wastewater	3300:41:1 to 214:13:1	30	7.5 – 10.3	Not Available	0.5 – 1	(Khaing et al., 2010)

^a Measured after steady-state (similar retentate TOC and biomass concentration) has been achieved

^b Measured at the end of 30 days of MDBR operation

^c Measured during the first 30 days of MDBR operation (non steady-state bioprocess)

^d Measured on 7th to 15th day of MDBR operation

Table 3. Effect of fouling on TPC and mass flux*

Parameter	J	T _f	R _t	R _f	T _b	R _b	T ₁	R _m	T ₂	R _p	T _p	TPC
Before Fouling	31	70	943	434	57	0	57	390	36	119	20	0.42
After fouling	24	70	1203	481	59	216	53	390	33	115	20	0.4

*computed based on experimental data from Srisurichan et al. 2006

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Figure 1. Schematic diagram of a MDBR process

Figure 2. Mass balance diagram for a typical MDBR system (1- influent feed, 2 – MDBR/MBR, 3 – permeate stream, 4 – sludge wasting stream, 5- evaporation stream)

Figure 3. Schematic depicting (a) mass transfer (b) heat transfer through a fouled MD membrane in a DCMD process

Configuration 1

Configuration 2

Configuration 3

Figure 4. Configurations for MDBR system in wastewater reclamation

Supplementary information

Table A.1 Water quality guidelines for industrial application

Water quality parameter (in mg/L unless otherwise stated)	Cooling water (Levine, 2003)	Cooling tower (Qin et al., 2007a)	Boiler feed water (Levine, 2003)	Water for industrial use (Qin et al., 2007b)
Alkalinity (mg/L as CaCO ₃)	350		40-350	
Hardness (mg/L as CaCO ₃)	600		0.07-350	
pH	6.9-9.0		7-10	6.8–7.3
Total dissolved solids (TDS)	500	<1000	200-700	
Conductivity (µS/cm)				700–1600
Total suspended solids (TSS)	100	<5	0.5-10	
Turbidity, NTU	50			0.5–2.5
C-BOD ₅	25	<5	1-50	
COD	75		1-5	50–80
Ammonia, mgN/L	1	<5	0.1	5–15
Nitrate, mgN/L				5–10
Phosphate, mgP/L	4			
Aluminium	0.1		0.01-5	
Bicarbonate	24		48-170	
Chloride	500		Variable	
Iron	0.5		0.05-1	
Manganese	0.5		0.01-0.3	
Silica	50		0.7-30	
Sulphate	200		variable	

1 Table A.2 Comparison of MD and UF/MF MBR-RO processes (adapted from Phattaranawik
2 et al., 2008)

Parameters	UF/MF MBR - RO	MDBR
Membrane type	Hydrophilic preferred	Hydrophobic porous (eg. PVDF, PTFE)
Primary Driving force	Pressure gradient	Vapor pressure gradient (dependent on temperature gradient)
Phase in Pores	Liquid	Vapor, Gas
Operating temperature	Room (Mesophilic)	Elevated (Thermophilic)
Mechanism governing flux	Mass transfer	Heat and mass transfer
Mass transfer through membrane	MBR: Hagen-Poiseuille / Carman-Kozeny RO: Solution-Diffusion	Diffusion
Permeation	MBR: Solutes, bacteria, low-molecular weight organics RO: Molecules less than 150 Dalton	Volatiles (eg. NH ₃ , CO ₂)
Permeate Quality	MBR: Dependent on biological process (Typical permeate TOC of 3–10 ppm) RO: Organic concentration independent of biological process	Organic concentration is independent of biological process (<0.8ppm TOC) but NH ₃ and CO ₂ is dependent on biological degradation rate of nutrients
Organic Retention Time (ORT)	MBR: Equivalent to HRT RO: Equivalent to retention time in the RO concentrate or till organics degrade to volatile organics or CO ₂	Equivalent to SRT or till organics degrade to volatile organics or CO ₂
Parameters	UF/MF MBR - RO	MDBR
Membrane Retention properties	MBR: No retention of recalcitrant organics, non-volatiles solutes (ie. salts). <50% of small organic compounds, spores and small virus retained in MF RO: 98 - 99.9% retention of solutes and all VBNCs	100% theoretical retention of non-volatiles solutes (ie. salts) viable-but-not-culturable (VBNC) bacteria recalcitrant, low-molecular weight organics (potential carcinogens)
Salt Retention	MBR: Absent, RO: Present	Present

Parameters	UF/MF MBR - RO	MDBR
Flux	MBR: 10–30 L/m ² .hr (typical) RO: 20–25L/m ² .hr (for water reuse)	2–15 L/m ² .hr at 55°C
Problem of wetting	Absent	Present
Concentrating Factor (CF)	MBR: Absent (due to lack of retention of salt and low-molecular weight organics) RO: Same as MDBR	$CF = SRT / HRT$ $= 1 / (1 - \phi)$

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