

Performance of new generation membrane distillation membranes

Jianhua Zhang, Mikel Duke, Eddy Ostarcevic, Noel Dow, Stephen Gray and Jun-de Li

ABSTRACT

Membrane distillation has been a known desalination process for many years, but its commercial implementation has been hampered by low water fluxes and the need for low cost heat sources. With greater emphasis being placed on energy efficiency, membrane distillation coupled with waste heat or solar heat sources to drive the process is being reconsidered. In particular, the use of membrane distillation to treat brine concentrates is receiving renewed attention, as it results in increased water recovery and lower brine discharges, and high salt concentrations do not increase the driving force requirements for membrane distillation. In this paper, four different membranes, one made of polyvinylidene fluoride (PVDF) and three made of polytetrafluoroethylene (PTFE) of different pore sizes, were assessed the performance in membrane distillation under different hot feed flow rates and inlet temperatures. The results show that the PTFE membranes had a much higher flux than that of PVDF at the same operational conditions, and PTFE membranes of large pore size produced higher flux than that of the small pore size. The results also showed that increasing the flow rate of the hot feed and its inlet temperature increased the flux, but the rates of increase decreased with increasing flow rate and inlet feed temperature.

Key words | direct contact membrane distillation, membrane distillation, water desalination, water treatment

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INTRODUCTION

Membrane distillation (MD) is a membrane-based separation process. The driving force for MD is a difference in vapour pressure across the membrane, which is quite different from other membrane processes in which a total pressure difference, a concentration gradient or an electrical potential gradient is the driving force for mass transfer.

According to Smolders & Franken (1989), the membranes required for MD operation should have the following characteristics:

- the membrane should be porous;
- the membrane should not be wetted by process liquids;

- no capillary condensation should take place inside the pores of the membranes;
- only vapour should be transported through the pores of the membrane;
- the membrane must not alter vapour equilibrium of the different components in the process liquids; and
- for each component, the driving force of the membrane operation is a partial pressure gradient in the vapour phase.

Compared with other membrane separation operations, MD has distinct advantages, such as a virtually complete rejection of non-volatile components, lower operating

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pressure than pressure-driven membrane processes, much larger pores than RO membranes (and typically larger than in ultra-filtration membranes) that aren't nearly as sensitive to fouling, reduced vapour space compared to conventional distillation, and low operating temperature (40–80°C) of the feed (Tomaszewska 2000). Thus, the MD process can utilize low-grade heat to distil water at a relatively low temperature. It is a promising technique for water desalination and wastewater recycling in places where waste heat, solar or geothermal sources exist.

Figure 1 illustrates four configurations of MD system, based on the nature of the cold side of the membrane (Alklaibi & Lior 2005):

- Direct Contact Membrane Distillation (DCMD), in which the membrane is in direct contact only with liquid phases;
- Air Gap Membrane Distillation (AGMD), in which an air gap is interposed between the membrane and the condensation surface;
- Vacuum Membrane Distillation (VMD), in which the permeate vapour is drawn by vacuum from the liquid through the membrane and condensed, if needed, in a separate device; and
- Sweep Gas Membrane Distillation (SGMD), in which a stripping gas is used as a carrier for the produced vapour, instead of vacuum as in VMD.

Assuming fully developed MD technology, with a purified water production rate at 3,800 m³ per day, the total production cost of the DCMD desalination plant with heat recovery of 30% has total costs of \$0.782 m⁻³ in comparison with \$1.26 m⁻³ for reverse osmosis (RO) of the same capacity (El-Bourawi *et al.* 2006). In this paper we

focus on DCMD and present experimental results for the process using laboratory scale equipment and relate these results to membrane properties.

Heat transfer and mass transfer

Figure 2 shows the heat and mass transfer processes in DCMD. Temperature of the feed, T_f , drops across the feed side boundary layer to T_1 . The permeate temperature T_p increases across the permeate boundary layer to T_2 . The driving force is therefore T_1 to T_2 .

The DCMD process was developed in the late 1960s, but was not commercially adopted at that time, partly because membranes with characteristics suitable for MD were not available. Furthermore, the slow progress in development was also caused by negative opinions about the economics of the process (Hanbury & Hodgkiess 1985), which were performed using a non-optimal membrane and system. For instance, using typical data, the temperature polarization coefficient of DCMD defined in Equation (1) (Schofield *et al.* 1987) for their system was estimated to be 0.32. This means that when the temperature difference between the centres of the hot and cold channels was 10°C, the actual temperature difference across the membrane was only 3.2°C.

$$\tau = \frac{T_1 - T_2}{T_f - T_p} \quad (1)$$

In the 1980s, with the development of new membranes, MD research rose again and many novel MD modules were designed based on a better understanding of the mass and heat transfer processes in MD (Gryta *et al.* 1997).

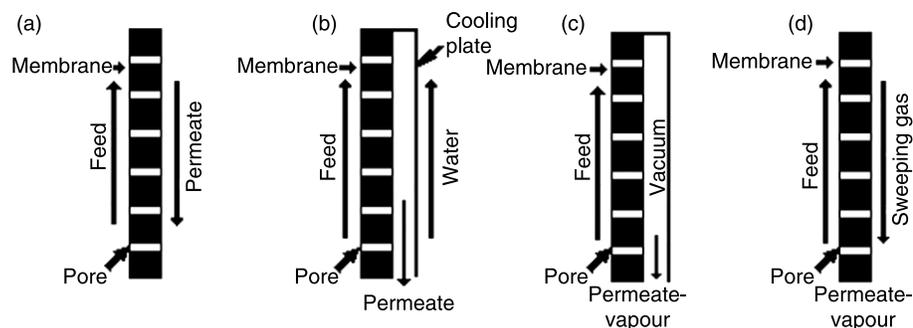


Figure 1 | Configurations of various MD system.

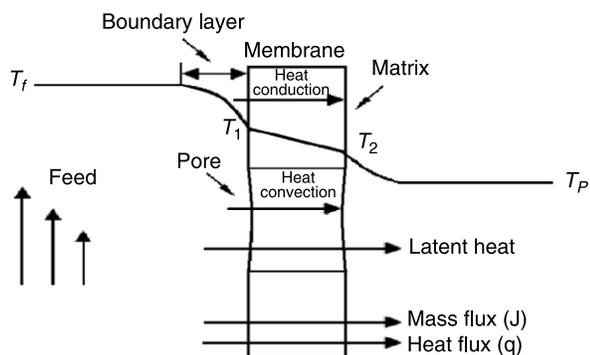


Figure 2 | Heat transfer and mass transfer through membrane.

Heat transfer

DCMD uses temperature difference as the driving force to cause mass transfer through the membrane. Thus DCMD performance relies on the complex relationships between simultaneous heat and mass transfers, which are in the same direction from the feed side to the permeate side.

The heat transfer from the feed side to the permeate side includes both sensible heat transfer and latent heat transfer. The sensible heat transfer across the membrane consists of heat conduction in the membrane matrix and heat conduction through the pores of the membrane via stagnant air or vapour while latent heat transfer is accompanied by the vapour mass transfer. In the feed side, heat needs to be transferred from the fluid to the surface of the membrane and in the permeate side heat needs to be transferred from the membrane surface into the fluid.

Mass transfer

The mass transfer in the DCMD process includes three steps. These are water vaporizes from liquid/gas interface of the feed, vapour passes through membrane pores by diffusion and convection, and vapour condenses on the permeate side.

The membrane employed in DCMD exerts its influence on transmembrane water flux in three ways. Firstly, water vapour molecules move only through the pores of the membrane, so the effective area for mass transfer is less than the total membrane area. Secondly, for most practical membranes, the membrane pores do not go straight through the membrane and the path for vapour transport is greater

than the thickness of the membrane. Thirdly, the inside wall of pores also increases the resistance to diffusion by decreasing the momentum of the vapour molecules. If the fluid dynamic conditions on both sides of a membrane could be considered good, mass transfer through the membrane may be the limiting factor in generating condensate in DCMD (Ding *et al.* 2003).

Schofield's model (Schofield *et al.* 1990) and Dusty-Gas model (Mason *et al.* 1967; Mason & Malinauskas 1983) are widely used for the mass transfer in DCMD. Both models suggest that mass transfer rate is proportional to the vapour pressure difference across the membrane (Schofield *et al.* 1990),

$$N = C(P_{T_1} - P_{T_2}) = C\Delta P. \quad (2)$$

where N is the mass transfer rate or flux, C is membrane distillation coefficient that can be obtained experimentally, and P_{T_1} and P_{T_2} are the vapour pressures at T_1 and T_2 , respectively. The above relationship shows that the flux in DCMD is an exponential function of temperature difference, due to the relationship between vapour pressure and temperature; and C is an important parameter to assess the performance of a membrane and depends on the characteristics of the membrane.

Characteristics of membrane

In MD, the membrane is not involved in the selective transport. Volatile compounds are transferred across the membrane according to vapour-liquid equilibrium principles, and the microporous material acts as physical barrier between two phases and sustains the interfaces where heat and matter are simultaneously exchanged. The properties of membranes used in membrane distillation ideally include:

- low thickness and tortuosity, since the permeate flux is inversely proportional to the diffusion length;
- reasonably small pore size, which is limited by the minimum Liquid Entry Pressure (LEP) of the membrane;
- low surface energy of the membrane material, or high hydrophobicity;
- low thermal conductivity of the membrane material, so heat loss due to sensible heat transfer can be minimized; and

- high porosity to reduce conductive heat flux and increase the water vapour transport coefficient through the membrane.

Materials used for membrane

Common materials used in MD are polytetrafluoroethylene (PTFE), polyethylene (PE), polyvinylidene fluoride (PVDF), and polypropylene (PP). The membrane porosity in the range of 0.06 to 0.85, pore size is in the range of 0.2 to 1.0 μm , and membrane thickness is in the range of 0.06 to 0.25 mm (Alklaibi & Lior 2005). The surface energies of these materials and thermal conductivities are listed in Table 1.

Among the membrane materials listed in Table 1, the PTFE membrane has the largest surface tension, good hydrophobicity, chemical stability and oxidation resistance; the PVDF membrane is easy to prepare, and has good hydrophobicity, heat resistance and good mechanical strength; the PP membrane has relative low oxidation resistance, and prone to fouling, but it is also hydrophobic and can be produced easily at low cost. Recently, new membrane materials, such as carbon nanotubes (Peng *et al.* 2007), which have high hydrophobicity and porosity, are being used as membrane materials to improve the performance of MD, but are still in the early stages of development for practical, low cost applications.

There are three common types of membrane configurations:

- hollow fibre membranes, mainly prepared from PP, PVDF or composite materials of PP (Song *et al.* 2007);
- capillary membranes, mainly prepared from PP (Gryta *et al.* 2000); and
- flat sheet membrane, mainly prepared from PP, PTFE, PVDF, etc.

Table 1 | Surface energy and thermal conductivity of some typical materials used in MD (Alklaibi & Lior 2005)

Membrane material	Surface energy (kNm^{-1})	Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)
PTFE	9.1	~0.27
PP	30.0	~0.17
PVDF	30.3	~0.19
PE	33.2	~0.33

Table 2 | Properties of membranes

Membrane	Effective area (cm^2)	Material	Nominal pore size (μm)	Provider
M _{p0.30}	14	PVDF	0.30	GE Osmonics
M _{t0.22}	14	PTFE	0.22	GE Osmonics
M _{t0.45}	14	PTFE	0.45	GE Osmonics
M _{t1.00}	14	PTFE	1.00	GE Osmonics

Compared to flat sheet membranes, hollow fibre and capillary membranes have relative large specific surface areas and high convective heat transfer coefficients, but they are limited by the manufacturing method and arrangement within the module (Gryta *et al.* 2000). In this paper, we provide results for DCMD using flat sheet PVDF and PTFE membranes, but additional results on hollow fibre membranes should be available by the time of presentation.

EXPERIMENTAL METHOD

Membranes and their properties

Table 2 lists four membranes used in the current experiments, all from GE Osmonics. One is PVDF, designed for microfiltration, and the other three are PTFE membranes with different pore sizes designed for MD. The properties presented in Table 2 were provided by the manufacturer.

Contact angle was measured as an indicator of hydrophobicity. This was performed by measuring the angle of water droplets resting on the membrane surface. Membrane active layer thickness was determined by removing the support and measuring membrane thickness was qualitatively estimated with micro callipers.

DCMD testing

Figure 3 shows a schematic diagram of the experimental setup. A flat-sheet DCMD configuration was applied to evaluate the four membranes. Flow rates were controlled by two pumps, one for the feed and the other for the permeate, and were varied in the range of 300–700 mL min^{-1} . The temperature of the hot feed water was controlled by a heater and was varied in the range of 45–70°C. A chiller was used to cool the permeate so that it can be recycled. The cold side

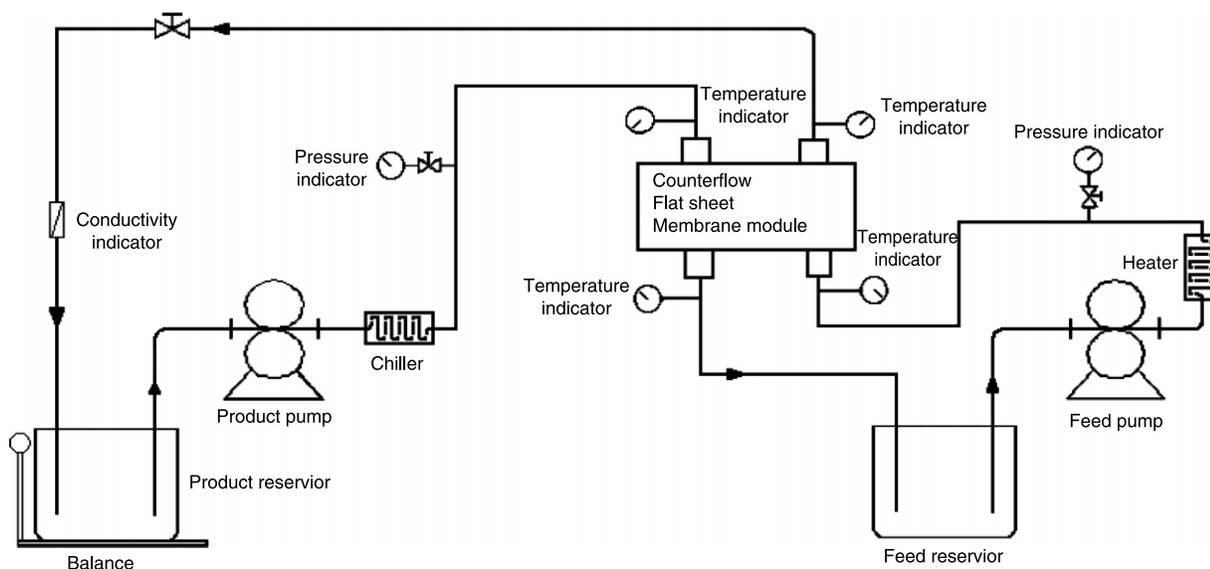


Figure 3 | Schematic diagram of the experimental setup.

was fixed at 20°C. For the hot feed, 100 g NaCl was dissolved in 10 L water (10 g L⁻¹). Water sourced for both the hot feed and the cooling fluid was deionised. Four temperature sensors were used to measure the temperature of the feed and permeate water at their respective inlets and outlets. Pressures for the hot feed water and cold permeate were monitored, and a conductivity indicator was used to measure the rejection rate. The flux was determined by measuring weight of the product reservoir over time. All the results presented here were measured over a period of 4 to 6 hours and no appreciable variation in flux was noticed during the measurement period.

RESULTS AND DISCUSSION

Membrane properties

The contact angle and membrane thickness is shown in Table 3. The M_{p0.30} membrane made from PVDF had a

Table 3 | Contact angle and membrane thickness

Membrane	Contact angle	Thickness of active layer (μm)
M _{p0.30}	90° ± 5	NA
M _{t0.22}	150° ± 10	6
M _{t0.45}	150° ± 10	11
M _{t1.0}	150° ± 10	48

lower contact angle and was more hydrophilic. The M_t series membranes made from PTFE were very hydrophobic, with contact angles similar for each pore size, at around 150°. The PVDF membrane (M_{p0.30}) active layer thickness could not be accurately determined.

Flux of the membranes at different flow rates

Figure 4 shows the measured fluxes at the temperature of hot side 60°C and cold side 20°C for the four membranes listed in Table 1. Permeate fluxes of all membranes increase with the increase of feed flow rate, but the tendency seemed to slow down at higher feed flow rates. A similar asymptotic trend of permeate flux with increasing feed flow rates was reported previously (Garcia-Payo *et al.* 2002; Matheswaran *et al.* 2007). M_{t1.0} showed the best performance at all flow rates, and gained the highest flux of 26.2 Lm⁻² hr⁻¹.

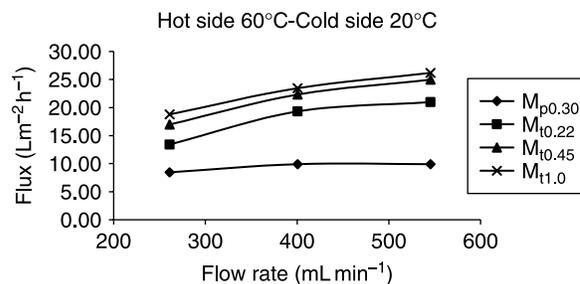


Figure 4 | Relation between flux and flow rate.

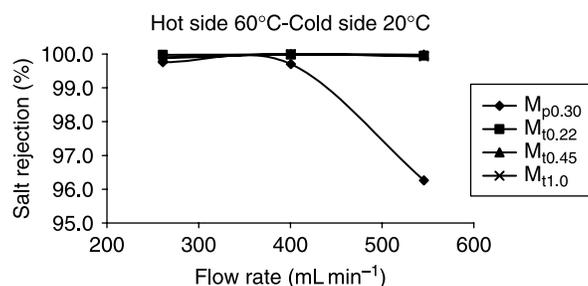


Figure 5 | Salt rejections related to flow rate.

The lowest flux was from $M_{p0.30}$, its highest flux was only around half of the lowest flux of the PTFE membrane $M_{t1.0}$.

Figure 5 shows the salt rejection rate with respect to flow rate for the four membranes. Salt rejections of all the new PTFE (M_t series) membranes are more than 99%, regardless the flow rates. Although salt rejection of the $M_{p0.30}$ was more than 99% at the low flow rate, it reduces to about 96% as the flow rate is increased to 550 mL min^{-1} . This may be due to the more hydrophilic property of the PVDF material, allowing wetting to occur at higher flow rates where pressure was highest. Alternatively defects in the membrane that act as large pores may be responsible for passing salt water at the higher pressures.

Mass transfer coefficients of the membranes were calculated from Equation (2) to assess the efficiency of each process under different conditions, wherein the mean vapour pressure difference was calculated by:

$$\Delta P = \frac{(P_{\text{hot-in}} + P_{\text{hot-out}}) - (P_{\text{cold-in}} + P_{\text{cold-out}})}{2} \quad (3)$$

where the $P_{\text{hot-in}}$, $P_{\text{hot-out}}$, $P_{\text{cold-in}}$ and $P_{\text{cold-out}}$ are the vapour pressures respectively at inlet and outlet temperatures of the hot side and cold side, ΔP is the mean pressure difference between the hot and cold side.

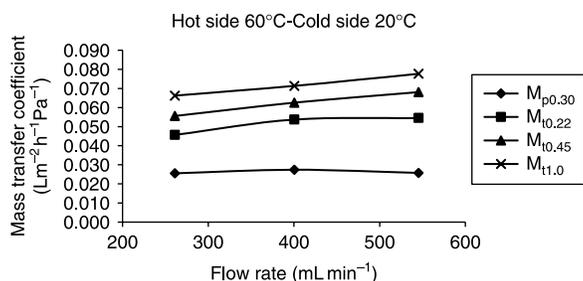


Figure 6 | Mass transfer coefficients with respect to feed flow rate.

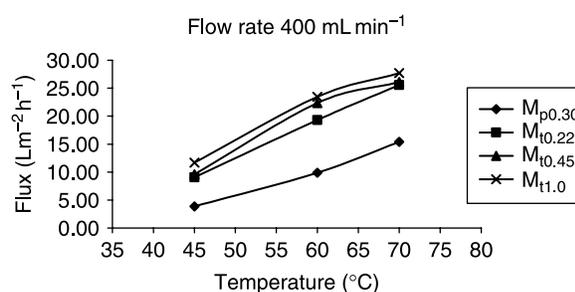


Figure 7 | Variation of flux with hot side inlet temperature at a constant flow rates.

The mass transfer coefficients of PTFE membranes increased almost linearly with respect to the feed flow rate, and are about double that of the PVDF $M_{p0.30}$. Compared with the novel M_t series PTFE membranes, $M_{p0.30}$ is less influenced by flow rate. Figure 6 illustrates the trend of the mass transfer coefficients of the different membranes. The PTFE membrane had better transport when pore size was larger, also when the membrane thickness was lower.

Temperature influence on flux of the membranes

The permeate flux of all membranes increased with raising temperature. Figure 7 shows the flux at different hot side inlet temperature at a feed flow rate of 400 mL min^{-1} . At a given temperature, all the new membranes had about twice the flux of the $M_{p0.30}$, with the highest value $27.7 \text{ Lm}^{-2} \text{ h}^{-1}$ obtained by $M_{t1.0}$ at 70°C . This flux is comparable to reverse osmosis membranes.

Figure 8 shows the salt rejection rate variation with hot side inlet temperature at 400 mL min^{-1} . It shows that all membranes had a good salt rejection of about 99% as represented in Figure 5, but $M_{p0.30}$ again showed a declining trend in recovery as the temperature was raised.

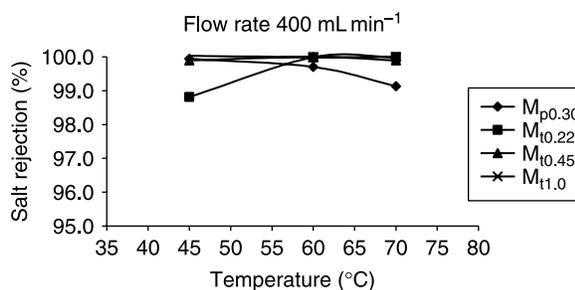


Figure 8 | Salt rejections related to temperature.

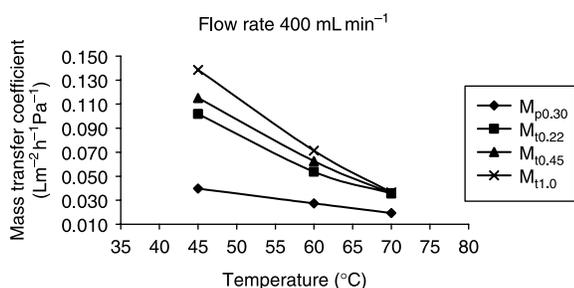


Figure 9 | Mass transfer coefficients with respect to temperature.

Again this decrease in recovery is consistent with the PVDF having a lower degree of hydrophobicity or defects in the membrane.

The mass transfer coefficients of new membranes shown in Figure 9 decreased as temperature increased and intersected at 70°C, and but still more than double that of the $M_{p0.30}$. The decreasing trend of the coefficient is partially caused by temperature polarization, which increases with the raising of feed temperature (Phattaranawik & Jiratananon 2001).

CONCLUSIONS

The performance of the new membranes in DCMD was assessed based on variation of temperatures and flow rates, and showed great potential as a desalination process. The new PTFE membranes have better operability than the PVDF membrane designed for microfiltration, and achieved a flux more than double that of the PVDC under the same conditions.

The contact angles of the new membranes are in the range of 140–160°, which is more than 1.5 times of $M_{p0.30}$, thus the PTFE membranes could be used at higher operation pressure without the risk of wetting because of the higher liquid entry pressure of the PTFE membranes.

Under certain conditions, permeate fluxes of the new membranes increased faster than the $M_{p0.30}$, when increasing the flow rate or temperature. This provides larger margin to improve the flux via adjusting process parameters in large scale applications.

The PTFE membranes also showed good salt rejection even under critical conditions of the microfiltration membranes. In comparison with 96% salt rejection of $M_{p0.30}$, all

PTFE membranes achieved nearly 100% salt rejection at feed flow rate of 550 mL min⁻¹, and no loss of rejection was found as temperature was increased.

Mass transfer coefficients were calculated to evaluate the efficiency of the process under different conditions. All new PTFE membranes have much higher mass transfer coefficients under various conditions than the PVDF membrane. Although sharp decline of mass transfer coefficient can be found as temperature increases because of the temperature polarization, this trend might be reduced by the optimisation of module by increasing τ . This may be achieved by using a spacer to increase the turbulence of flow as suggested by Phattaranawik & Jiratananon (2001).

Fluxes of up to 27 Lm⁻²h⁻¹ were obtained, which is comparable to the flux achieved in reverse osmosis systems. This suggests that membranes to support a commercially viable MD process are available, if issues around module design and long term operation of the MD process (fouling, wetting) can be resolved.

All the experimental results presented here were each measured for a period of four to six hours. Experiments of longer period are currently under consideration, as is the testing of MD on process waters.

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