Transport phenomena and fouling in vacuum enhanced direct contact membrane distillation: Experimental and modelling

Gayathri Naidu^a, Wang Geun Shim^{a, b}, Sanghyun Jeong^{a, c}, YoungKwon Choi^a, Noredine Ghaffour^c

Saravanamuthu Vigneswaran^{a, *}

^a Faculty of Engineering, University of Technology Sydney (UTS), P.O. Box 123, Broadway, NSW 2007 Australia,

^b Department of Polymer Science and Engineering, Sunchon National University, 255 Jungang-ro, Sucheon-si, Jellanam-do 57922, Republic of Korea,

^c King Abdullah University of Science and Technology (KAUST), Water Desalination and Reuse Center (WDRC), Biological and Environmental Science & Engineering (BESE), Thuwal 23955-6900, Saudi Arabia

*Corresponding author: Tel +61-2-9514-2641; Fax +61-2-9514-2633; Email: Saravanamuthu.Vigneswaran@uts.edu.au

Abstract

The application of vacuum to direct contact membrane distillation (vacuum enhanced direct contact membrane distillation, V-DCMD) removed condensable gasses and reduced partial pressure in the membrane pores, achieving 37.6% higher flux than DCMD at the same feed temperature. Transfer mechanism and temperature distribution profile in V-DCMD were studied. The empirical flux decline (EFD) model represented fouling profiles of V-DCMD. In a continuous V-DCMD operation with moderate temperature (55 °C) and permeate pressure (300 mbar) for treating wastewater ROC, a flux of 16.0±0.3 L/m²h and high quality distillate were achieved with water flushing, showing the suitability of V-DCMD for ROC treatment.

Keywords: fouling; reverse osmosis concentrate; transfer mechanism; vacuum enhanced direct contact membrane distillation

Nomenclature			
J	Permeate flux (kg/m ² ·h)	r	Membrane pore diameter (m)
C	Mass transfer coefficient	η	Water vapor viscosity (kg/m/s)
P	Vapor pressure (Pa)	ε	Membrane porosity
T	Temperature (°C)	δ	Membrane thickness (m)
D	Diffusion coefficient (m ² /s)	τ	Membrane pore tortuosity
D _{WA}	Molecular diffusivity coefficient (m ² /s)	k ₀	Flux decline potential
M	Molecular mass of water (kg/kmol)	k ₁	Rate constant
R	Universal gas constant (kJ/kmol/K)	d	Flux decline kinetic constant
P _{total}	Total pressure inside the pore (Pa)	γ _w	Activity coefficient of water
P _α	Air pressure (Pa)	x _w	Mole fraction of water
P _{avg}	Average pressure of the membrane (Pa)		
P _w	Vapor pressure of pure water (Pa)	<i>Subscript</i>	
P _{reference}	Reference pressure (Pa)	f	Feed side
α	Dimensionless coefficient ratio	p	Permeate side
Q	Heat flux (kJ/m ² ·hr)	u	Flow velocity (m/s)
h	Heat transfer coefficient (W/m ² ·K)	E	Molecular diffusion

A	Thermal conductivity (kW/m·K)	P	Poiseuille flow diffusion
L	Membrane module length (m)	K	Knudsen diffusion
ρ	Fluid density (kg/m ³)	m	Membrane surface
C _p	Specific heat capacity of fluid	x	Transversal (x-direction)
λ	Latent heat of water	z	Axial (z-direction)
R _m	Membrane resistance (Pa.m ² .h/L)		
t	Time (s)		

1. Introduction

In recent times, membrane distillation (MD) has gained wide attention as an alternative water treatment technology with a capability of treating and concentrating solutions with high salinity [1-4]. The main benefits of MD are the production of high quality permeate utilizing vapor driven force compared to pressure driven technologies and low thermal requirement compared to conventional thermal technologies [2, 5]. On this basis of advantages of MD, it has been regarded as a viable alternative concentrate treatment technology [3, 4].

Presently, many wastewater reclamation plants (WRPs) around the world are progressively using reverse osmosis (RO) technology as a final polishing step due to its capability to maintain a high grade water standard [1, 6]. However, a substantially large volume of wastewater RO concentrate (ROC) is produced, generally comprising 20–25% of the feed stream volume [7]. For instance, two WRPs for biologically treated wastewater in New South Wales (Homebush bay and St. Marys WRPs) are using RO technology as a final treatment process. On a daily basis, around 2000 kL of water is treated by RO

in Homebush bay WRP, resulting in 300 kL/ day ROC while substantially larger volume of ROC (7000 kL/day) is produced from St.Marys WRP [8].

It has been well established that conventional methods such as coagulation and granular activated carbon (GAC) as well as advanced technologies such as, ozonation, electrochemical oxidation and photocatalysis are effective for treating ROC contaminants, specifically to reduce dissolved organics carbons as well as selective micro-pollutants prior to discharge from WRPs [1, 6, 7]. Nonetheless, these operations do not simultaneously reduce the ROC volume and its inorganic content.

In this regard, MD offers the possibility to concentrate pretreated ROC wastewater, while producing good quality distillate, making it a sustainable ROC treatment technology. Furthermore, the low salinity content of ROC wastewater (1-2 g/L), would enable MD to concentrate ROC to a high level. However, the aspect of scaling by the main ions such as Ca, Na, SO₄, and Cl present in ROC wastewater must be given due consideration to establish the feasibility of MD operation for ROC wastewater treatment.

Direct contact membrane distillation (DCMD) is the most commonly used MD configuration due to its application simplicity [9]. In general, high feed temperature is used to achieve higher water production (water flux) in DCMD system [10]. At a high feed temperature, higher heat and mass transfer occur from the feed side, across the boundary layer and membrane, and to the permeate side. Large quantity of heat is used to vaporize the molecules at the membrane surface. It results in a significant conduction and latent heat-loss resulting in temperature difference between the bulk solution and membrane surface. This phenomenon is known as temperature polarization. Alternatively, a larger vapor driving pressure in DCMD can be created by incorporating a vacuum on the permeate side, even at relatively low feed temperature ranges. This is referred to as vacuum enhanced DCMD configuration (V-DCMD). The advantages of V-DCMD have been highlighted in previous literatures [11, 12]. Cath et al. [11] demonstrated that the V-DCMD system achieved a 15% permeate flux increment (compared to DCMD)

with the reduction of permeate side pressure (increased vacuum) from 108 kPa to 94 kPa. Importantly, their study highlighted that on an economic aspect, the incorporation of vacuum did not incur significant additional cost due to the low pressure-gradient on the pump. Similarly, Naidu et al. [12] established the enhanced permeate flux performance of DCMD by 30% with reduced permeate pressure from 1000 mbar to 300 mbar using vacuum pump. However, this study observed a higher flux decline and fouling with V-DCMD compared to DCMD, even though a higher flux was attributed to the higher driving force in V-DCMD system.

Nevertheless, there are still limited researches on an in-depth understanding on the performance of a V-DCMD in comparison to DCMD. Generally, the mass transfer across the membrane for DCMD system consist of Knudsen diffusion, molecular diffusion, surface diffusion, and viscous flow [13]. In this study, experimental data of V-DCMD and DCMD performance were used to estimate the transport mechanism and related resistance based on the empirical models and resistance coefficient values. An alpha coefficient was incorporated to represent the mass transfer scenario of V-DCMD. At the same time, a 2-D dynamic model temperature profile along the membrane module was used to compare the temperature profile of the DCMD and V-DCMD configuration. Further, the fouling profile was represented by coefficient values based on empirical fouling model. A continuous experimental operation of V-DCMD with membrane water flushing was carried out to verify the effectiveness of this configuration for ROC wastewater treatment. Membrane fouling pattern and its reversibility on membranes were analysed using scanning electron microscope - energy-dispersive spectroscopy (SEM-EDX).

2. Materials and methods

2.1 Experimental set-up

Experiments for DCMD and V-DCMD were carried out with the same effective membrane area of 0.0168 m^2 ($0.21 \text{ m} \times 0.08 \text{ m}$). The dimensions of membrane cell channel were 21.0 cm (length), 8.0 cm (width), and 0.4 cm (height). The membrane cell was designed to hold a flat sheet membrane securely in the membrane cell under moderate pressure gradients without the need for physical supports such as spacers (**Fig. 1**). A polytetrafluoroethylene (PTFE) flat-sheet hydrophobic membrane (General Electrics, US) was used in this study. The porosity, normalized pore size, and membrane thickness as provided by the supplier were 70–80%, $0.22 \text{ }\mu\text{m}$, and $179 \text{ }\mu\text{m}$, respectively. The DCMD baseline study (with deionized (DI) water) was carried out at different feed temperatures ranging from 50 to 65 °C. Meanwhile the V-DCMD operation was carried out at different vacuum pressures (300 to 1000 mbar) at a feed temperature of 55 °C. For all operating conditions, flow rate in both feed and permeate sides was 1.1 L/min, which corresponds to a cross-flow velocity of 0.06 m/s.

2.2 Feed solution

The baseline experiments were carried out with 1.5 L of DI water. To study the performance of DCMD and V-DCMD for the treatment of ROC wastewater, a synthetic solution (1.5 L) was used. The synthetic solution comprised of 600 mg Na/L, 800 mg Cl/L, 90 mg Ca/L and 200 mg SO_4 /L, emulating the characteristics of the major ions present in wastewater ROC from WRPs [8].

2.3 Membrane characterization

The morphology of fouled (tested) membrane and cleaned membrane was observed using Zeiss Supra 55VP field emission scanning electron microscope (FE-SEM). The membrane specimens were dried in a

desiccator overnight prior to analysis. It was operated at 5 kV in conjunction with Bruker XFlash silicon drift energy-dispersive spectroscopy (EDS) detector. The EDS analysis was used to obtain information on chemical characteristics of the membrane.

3. Theory

3.1 Transfer mechanism in DCMD and V-DCMD

3.1.1 Mass transfer in DCMD

The overall permeate water flux, J for DCMD can be calculated using Eq. (1):

$$J = C(P_{fm} - P_{pm}) \quad (1)$$

where, C is the mass transfer coefficient, which can be described by different models, P_{fm} and P_{pm} are the vapor pressures on the feed and permeate side membrane surface, respectively.

The P_{fm} and P_{pm} were calculated using the Antoine equation at the respective temperatures of T_{fm} and T_{pm} , based on the Eq. (2) [9, 14]:

$$P = \exp\left(23.7836 - \frac{3782.89}{T - 42.85}\right) \quad (2)$$

For non-ideal binary mixtures, the pressure can be determined by Eq. (3), while the water activity of water or other solutions such as NaCl, γ_w , were determined using the correlation equation (Eq. (4)).

$$P = x_w r_w P_w \quad (3)$$

$$r_w = 1 - 0.5(1 - x_w) - 10(1 - x_w)^2 \quad (4)$$

where, x_w is the mole fraction of water, γ_w is the activity coefficient of water, and P_w is the vapor pressure of pure water.

Therefore in DCMD, mass transfer mechanism in the membrane is generally represented by the three mass diffusion models (Knudsen, molecular and Poiseuille) as described by Eq. (5) [13, 15]:

$$J = \left(\frac{1}{J_K} + \frac{1}{J_E} \right)^{-1} + J_p \quad (5)$$

where, J_K , J_E and J_p are vapor flux from Knudsen, molecular, and Poiseuille flow diffusion and they can be calculated using Eqs. (6) to (8):

$$J_K = C_K \cdot DP = 1.064 \frac{re}{dt} \sqrt{\frac{M}{RT}} (P_{fm} - P_{pm}) \quad (6)$$

where, J_K is the vapor flux through the membrane occurring from the Knudsen diffusion, C_K is the Knudsen mass transfer coefficient, r is the membrane pore diameter, ε is the membrane porosity, δ is the membrane thickness, τ is the membrane pore tortuosity, M is the molecular mass of water, and R is the universal gas constant.

$$J_E = C_E \cdot DP = \frac{P_{total} D_{WA}}{P_a} \frac{re}{dt} \sqrt{\frac{M}{RT}} (P_{fm} - P_{pm}) \quad (7)$$

where, J_E is the vapor flux through the membrane arising from molecular flow, C_E is the molecular mass transfer coefficient from molecular flow, P_{total} is the total pressure inside the pore (air pressure + water pressure), P_a is the air pressure (assuming almost 1.0 atm), and D_{WA} is the molecular diffusivity coefficient (subscripts 'w' and 'a' refer to water vapour and air).

$$J_P = C_P \cdot DP = 0.125 \frac{r^2 e}{dt} \frac{MP_{avg}}{hRT} (P_{fm} - P_{pm}) \quad (8)$$

where, J_P is the vapor flux through the membrane arising from Poiseuille flow, C_P is the Poiseuille-flow mass transfer coefficient, P_{avg} is the mean pressure of the membrane ($P_{avg} = (P_{fm} + P_{pm})/2$), and η is the water vapor viscosity.

3.1.2 Mass transfer in V-DCMD

V-DCMD mass diffusion model was represent by introducing a dimensionless coefficient ratio (α) based on the theory of Schofield et al. [16]. The α represented the membrane permeate pressure and was derived by using the average pressure between the bulk feed and permeate vacuum, and reference pressure, $P_{reference}$ as presented in Eq. (9):

$$\alpha = 1 - (P_{avg}/P_{reference}) \quad (9)$$

where, P_{avg} is $(P_{fm} + P_{pm}) / 2$ and $P_{reference}$ is atmospheric pressure (1,000 mbar).

By adding the α value to Eq. (1), the permeate flux for V-DCMD can be calculated using Eq. (10) [13, 16]:

$$J = \alpha^* C(P_{fm} - (P_{pm} - P_{pm}^* \alpha)) \quad (10)$$

3.2 Heat transfer and transport resistance

Heat transfer in DCMD and V-DCMD can be considered in three steps: i) convective heat transfer from the heated feed solution across the boundary layer to the membrane surface ($Q_f = h_f(T_f - T_{fm})$), ii) heat transfer across the membrane by conduction and heat assembling the vapor flow through the membrane pores ($Q_m = JH + h_m(T_{fm} - T_{pm})$), and iii) convective heat transfer from the membrane surface of the permeate side across the boundary layer to the bulk of permeate solution ($Q_p = h_p(T_{pm} - T_p)$) [9, 13]. The total heat transfer through the membrane, (Q_m) in DCMD and V-DCMD is by conduction across the membrane pores and latent heat due to molecule vaporization.

In this study, a two-dimensional (2D) dynamic model for flat sheet module was used to represent the heat transfer as presented by Shim et al. [15]. The model geometry represented the heat transfer of the feed and permeate channel thickness as FT and PT from 0 to 1, with 1 being closer to the membrane. Similarly, the heat transfer through the feed and permeate channel length (FL and PL, respectively) were presented by channel inlet ($L = 0$), centre ($L = 0.5$) and outlet ($L = 1$) as shown in **Fig. 2**.

The following assumptions were used: (i) non steady-state, (ii) constant physical properties of fluids and membrane, (iii) incompressible hot and cold flow, (iv) negligible momentum of permeate flow through the membrane, (v) negligible heat loss to the ambient environment, (vi) negligible concentration polarization of the feed solution, (vii) no chemical reaction and (viii) negligible membrane fouling. To solve the 2-D dynamic model equations, the orthogonal collocation method and the variable

coefficients ordinary differential equation integrator were used [15, 17, 18]. The main thermal equations with the initial and boundary conditions for representing the 2D dynamic model were expressed using Eqs. (11) to (16):

$$\frac{\partial T_i}{\partial t} = \frac{A_z}{rC_p} \frac{\partial^2 T_i}{\partial z^2} - u_i(x) \frac{\partial T_i}{\partial z} + \frac{A_x}{rC_p} \frac{\partial^2 T_i}{\partial x^2} \quad i = \text{feed or permeate} \quad (11)$$

$$T_i(0, x_i, z) = T_{i,in} \quad (12)$$

$$A_F \frac{\partial T_i}{\partial x} \Big|_{x=di} = \pm \left(QI + A_m \frac{(T_F - T_P)}{d_m} \right) \quad (13)$$

$$\frac{\partial T_i}{\partial x} \Big|_{x=0} = 0 \quad (14)$$

$$A_z \frac{\partial T_i}{\partial z} \Big|_{z=0} = -rC_p u_i (T_i \Big|_{z=0^-} - T_i \Big|_{z=0^+}) \quad (15)$$

$$\frac{\partial T_i}{\partial z} \Big|_{z=L} = 0 \quad (16)$$

where, A_z , A_x , A_m , ρ , u , C_p , Q , and λ are the axial thermal conductivity of fluid, transversal thermal conductivity of fluid, thermal conductivity of membrane, fluid density, flow velocity and specific heat capacity of fluid, heat water flux and latent heat of water, respectively.

3.2.1 Transport resistance

The resistance on the membrane was calculated from Eq. (17) [11, 19].

$$R_m = \frac{P_{fm}}{J \bullet P_{pm}} = \frac{P_{(FT = 1, FL = 0.5)}}{J \bullet P_{(PT = 1, PL = 0.5)}} \quad (17)$$

where, J is the water flux, P_{fm} and P_{pm} are the vapor pressure at the surface of membrane at feed and permeate sides. The vapour pressure at the membrane feed and permeate sides were derived from the average temperature profile values from the 2-D model.

3.3. Flux decline coefficients

The EFD model is a simple flux decline models where EFD coefficients can be evaluated from experimental results using nonlinear regression [20]. The equation, Eq.18 consists of three flux-decline coefficients (k_0 , k_1 and d):

$$\frac{J_t}{J_0} = \frac{1}{1 + k_0(1 - e^{-k_1 t}) + dt} \quad (18)$$

where, k_0 is the given flux decline potential, which is dimensionless, k_1 is the rate constant, which represents how quickly flux decline occurs, and d is the flux decline kinetic constant. The unit of both k_1 and d is min^{-1} .

4. Results and discussion

4.1 Transfer mechanism in DCMD and V-DCMD

Transfer mechanisms in DCMD and V-DCMD were investigated using experimental data and mass diffusion model.

4.1.1 DCMD mass transfer

The DCMD performance was examined by varying the feed temperature from 50 °C to 65 °C (**Table 1**). The results showed a permeate flux increment of around 1.8 times (9.0 ± 0.2 to 16.0 ± 0.5 LMH) with a 15 °C of feed temperature increment. Permeate flux increased linearly with feed temperature (**Fig. 3**). This indicated that the feed temperature mainly contributed to higher driving force (larger vapour pressure gradient), increasing the mass transfer which corresponds to the high permeate flux pattern. Similar trends have been described in other studies [9, 14].

In DCMD, mass transfer can be divided into three steps: i) mass transfer in feed boundary layer, ii) mass transfer across the membrane, and iii) mass transfer in permeate boundary layer. Here, the mass transfer in permeate boundary layer is not taken into account since the mole fraction of the transporting species in the permeate stream is approximately equal to one. In addition, the essential models employed to describe the mass transfer across the hydrophobic porous membrane: a) viscous flow, b) Knudsen diffusion (due to the larger mean free path of vapor molecules than the membrane pore size), c) molecular diffusion (due to concentration gradient across the membrane) and d) Poiseuille flow model (due to the momentum transfer to the membrane area). The vapor molecule motions (comparison between the mean free path and pore diameter) are the distinction factor between these models. In DCMD configuration, viscous flow can be negligible, as both feed and permeate aqueous solutions are brought into contact with the membrane under atmospheric pressure, maintaining a constant total pressure at approximately 1 atm [13].

As can be seen from **Fig. 3**, the experimental flux fitted well with the calculated flux using the DCMD mass diffusion model based on Eq. (5).

4.1.2 V-DCMD mass transfer

A baseline study with DI water was conducted to analyse the effect of vacuum incorporation on the permeate side of the DCMD configuration (here, V-DCMD). Even at a feed temperature of 55 °C, an increase in permeate flux (approximately 1.4 times higher) was achieved in the V-DCMD operation as the permeate pressure reduced from 1000 to 300 mbar (**Table 1**).

The mass transfer mechanism of V-DCMD can be linked to the concept of deaerated DCMD system as described by previous researchers [13, 16, 21]. Based on their studies, it was deduced that a substantial flux increase can be achieved by degasing/deaerating the liquids in the DCMD system, creating a lower liquid pressure because MD membranes have larger pores than the mean free path of the water molecules. The presence of non-condensable gasses between the membrane surfaces hinders the diffusion of water vapor resulting in lower fluxes. By lowering the liquid pressure, the gas pressure/partial pressure within the membrane pores substantially reduced. Similarly, a study on air gap MD reported on achieving three times higher flux upon removing non-condensable gases [22]. In line with this, Schofield et al. [16] proposed an empirical model with Knudsen/Poiseuille transition for representing deaerated DCMD, where a coefficient value of dimensionless pressure (P/P_{ref}) was incorporated in the flux equation.

In this study, for the first time, the theory of Schofield et al. [16] was applied to represent the scenario of V-DCMD mass diffusion model by introducing a α , a dimensionless coefficient ratio to represent the membrane permeate pressure as presented in Eq. (9). **Fig. 4 shows a good correlation between the α value and the permeate (bulk) pressure.** The α value was incorporated to calculate the V-DCMD permeate flux as presented in Eq. (10). Using Eq. (10), the V-DCMD fluxes at two different

permeate vacuum pressures (260 and 200 mbar) were predicted (**Fig. 5**). This verified the model fitting to the experimental permeate flux.

In V-DCMD, it was possible to obtain more than 30% higher permeate flux in comparison to DCMD at the same feed temperature. This was attributed to the partial elimination of stagnant air from the pores, which effectively reduced the resistance for vapor diffusion across the membrane as well as increased convective mass transport in the pores by enhanced total pressure gradient in the pore [11]. In this condition (V-DCMD), the dominant mass transport was most likely Knudsen/Poiseuille transition and minimally molecular diffusion, as molecular diffusion depends on the partial pressure of air in the membrane pores and in the V-DCMD system, minimal air is present within the membrane pores [13]. On the other hand, the DCMD system mass transfer is a combination of Knudsen/Poiseuille as well as molecular diffusion. The resistance of water vapour diffusion through the membrane air pores in the DCMD most likely resulted in lower permeate flux compared to the V-DCMD. As such, the α coefficient represented the reduced partial pressure and increased vapour diffusion in V-DCMD.

4.2 Heat transfer and transport resistance

4.2.1 Temperature profile

In V-DCMD, the partial elimination of stagnant air from the pores has been implied to reduce convection heat loss in the membrane [11]. To represent this phenomenon, in this study, a theoretical temperature distribution profile generated from the 2D model was used to represent the water vapor's heat transport mechanism in the V-DCMD (and the DCMD) (**Fig. 2**). To obtain an accurate temperature distribution profile, the experimental operation parameters used are as follows: feed temperature (T_F) = 55 °C and 65 °C, permeate temperature (T_P) = 25 °C, feed and permeate velocity = 0.06 m/s, membrane pore diameter (r) = 0.22 μ m; counter current flow module; parabolic for laminar flow.

Fig. 6 shows the temperature variation across and along the flow channels on the feed and permeate side at different feed temperature and vacuum pressures. Additionally, the temperature variation is presented in **Fig. 7** as a line scatter for comparison of the temperature pattern between the different configurations. The temperature profiles were obtained at assumed steady state condition. Temperature boundary layers were evidently formed in both feed (F) and permeate (P) channels which became more prevalent as water flowed through the channels. At the channel inlet (entrance) (FT and $PT = 0$, and FL and $PL = 0$), the water stream showed a uniform temperature distribution. As the water was channelled along the membrane, the evaporation of feed water reduced the temperature near the membrane (FT and $FL = 1$), while the condensation of hot vapor on the permeate side increased the permeate stream temperature near the membrane (PT and $PL = 1$). These created temperature gradients/boundary layers as can be evidently seen in **Fig. 6** and **Fig. 7**, showing the feed and permeate temperature difference across the membrane, respectively.

A lower evaporation and condensation in DCMD (at 55 °C and 1,000 mbar) resulted in a more uniform temperature distribution near the membrane (**Fig. 6a**). Specifically, across the membrane ($FT = 0$ to 1) of DCMD (at 55 °C and 1000 mbar), 14.4 °C and 20.4 °C temperature difference occurred at $FL = 0.5$ and $FL = 1$, respectively (**Fig. 7a**). This represented the temperature losses near the membrane. Meanwhile in V-DCMD (at 55 °C and 300 mbar), an increased mass transfer (higher evaporation and condensation) may have resulted in slightly higher temperature variation near the membrane (lower membrane feed temperature and a higher membrane permeate temperature) (**Fig. 6b**). Specifically, across the membrane ($FT = 0$ to 1), for V-DCMD (at 55 °C and 300 mbar), 16.7 °C and 22.9 °C temperature difference occurred at $FL = 0.5$ and $FL = 1$, respectively (**Fig. 7a**). The results showed that, at the same feed temperature of 55 °C, V-DCMD (300 mbar) could achieve at least 30% higher flux

increment compared to DCMD with only slightly higher heat transfer losses compared to 1,000 mbar, establishing the advantages of vacuum incorporation to DCMD.

Likewise, in DCMD operation, to obtain the similar permeate flux (16.0 ± 0.5 LMH) as that of V-DCMD (at 55 °C and 300 mbar), a higher DCMD feed temperature setting (65 °C) had to use at 1,000 mbar. At the same time, a number of MD studies have carried out detailed energy evaluation. These studies have reported energy consumption in the range of 65-90 W for low vacuum consumption (200-300 mbar) [23, 24]. On the other hands, Criscuoli et al. [25] reported a 200-220 W increment in energy consumption with an increase of the feed temperature by 20 °C in a DCMD system.

Further, at this DCMD condition (65 °C and 1000 mbar), an increased mass diffusion at higher feed temperature had likely resulted in elevated resistance (air pores resistance) at the membrane surface. Significant temperature loss appeared to have occurred near the membrane surface due to latent and conduction heat loss (**Fig. 6c**) as compared to V-DCMD (at 300 mbar and 55 °C). Specifically, for DCMD (at 65 °C and 1000 mbar), across the membrane (FT = 0 to 1), 19.1 °C and 27.2 °C temperature difference occurred at FL = 0.5 and FL =1 (**Fig. 7b**). It is worth highlighting that the higher permeate flux achieved with V-DCMD was attributed to both higher driving force and removal of non-condensable gases. However, fast velocities in feed and permeate side can be reduced the effect of non-condensable gases. Further investigations must be carried out to identify the more significant flux increment contributor between these two factors.

4.2.2 Transport resistance

In MD process, the transport resistance consists of i) feed boundary layer resistance, ii) permeate boundary layer resistance and iii) membrane resistance (R_m) (without the presence of fouling layer). In DCMD system, resistance in feed boundary layer is associated to temperature polarization effect and at

higher feed temperature, this effect becomes more prevalent, enhancing feed boundary layer resistance. Contrarily, a higher feed temperature (higher driving force) will reduce membrane resistance, as resistance in membrane surface is associated with pore resistance across the membrane surface which is proportional to vapour molecular diffusivity. Vapour molecular diffusion is a function of driving force [19]. For this reason, at similar feed temperature of 55 °C, R_m is a useful indicator to compare the transport resistance of DCMD and V-DCMD as presented in Eq. (17).

In DCMD (1,000 mbar), increased feed temperature from 55 °C to 65 °C, resulted in reduced R_m from $0.030 \pm 0.001 \text{ Pa.m}^2.\text{h/L}$ to $0.020 \pm 0.003 \text{ Pa.m}^2.\text{h/L}$ (**Table 2**). This is related to the higher driving force at higher temperature on the membrane surface, increasing the vapour molecular diffusion. Meanwhile, at similar feed temperature of 55 °C, a significantly lowered R_m value ($0.005 \pm 0.002 \text{ Pa.m}^2.\text{h/L}$) was achieved with V-DCMD (at 300 mbar), compared to DCMD (at 1000 mbar), clearly indicating the lower resistance/hindrance of vapor molecular diffusion through membrane in V-DCMD configuration. The reduction of air/gas pressure within the pores of the membrane coupled with higher driving force by incorporating the vacuum, would result in lower hindrances of molecular diffusion and increased diffusion through the membrane pores. This would enhance the permeate flux in the V-DCMD, verifying the concept discussed in **Section 3.2**. Overall, the results of the transport mechanism and temperature profile established the advantages of V-DCMD over DCMD.

4.3. Flux decline coefficients

Several studies employed the blocking filtration laws proposed by Hermia [26] to describe fouling behaviour for dead-end filtration mode. Hermia's model has been applied for cross flow mode application with some modification [27, 28]. A previous DCMD study showed that fouling with a mixture of humic and calcium feed solution corresponded well to Hermia's cake filtration model [19].

Experiments were carried out with three different feed solutions of i) NaCl alone, and ii) NaCl with CaSO₄ representing constituents of wastewater ROC. The permeate flux at different times (DCMD transport mechanism). However, Hermia's blocking filtration models did not fit well to the experimental data obtained in this study. This could be because rapid fouling occurs in MD when the membrane surface (or pore) was blocked, which was the main difference between MD compared to other membrane processes. Ramezaniapour and Sivakumar [28] highlighted that the permeate flux decline in MD processes does not show the first order exponential decay generally represented for other membrane processes.

On the other hand, the experimental fouling flux profiles of V-DCMD (at 300 mbar) and DCMD (at 1000 mbar) were fitted well with the empirical flux decline model (EFD) used in the study (Eq. (18)) as presented in **Fig. 8**. Three flux-decline coefficients (k_0 , k_1 , and d) were obtained by fitting experimental and simulated plots. Two flux-decline coefficients (d and k_0) show the total qualitative capacity of flux decline through the correlation analysis results. The coefficient k_1 represents a kinetic flux-decline trend. A sensitivity test showed that the coefficient k_1 was the most sensitive with the changes of its reference value (Ref = 1.0) (**Fig. 9**). No changes were observed with k_0 and d coefficient values. The k_1 value showed a good relationship with the flux ratio (J/J_0) with a inverse pattern of k_1 value with J/J_0 ratio (**Table 3**). Thus, k_1 value is a good indicator to determine the flux decline in the MD process.

At F_t of 55 °C, both DCMD (1000 mbar) and V-DCMD (300 mbar) showed a closely similar flux decline ratio, between the ranges of 0.73 to 0.82, for all feed solutions (**Fig. 8** and **Table 3**). In fact, the V-DCMD achieved slightly lower flux decline ratio than DCMD. This could probably be related to the low inorganic concentration of the wastewater ROC feed solution and operating at low feed temperature, resulting in low scaling development, which minimally influenced the flux pattern. Hence, in these operating conditions, the slight flux decline occurrence could be attributed to NaCl concentration

polarization effect that increased the mass transfer resistance across the membrane. The lower flux decline ratio of the V-DCMD could therefore be attributed to its efficient mass transfer and lower membrane resistance compared to DCMD. In line with this, Martinetti et al. [29] observed only slightly higher flux decline with V-DCMD (480 mbar) compared to V-DCMD (880 mbar) at a temperature gradient of 20 °C for treating saline reverse osmosis brine containing ions such as Ca and Mg. On the other hand, at a temperature gradient of 40 °C, a significant flux decline was observed at these respective vacuum pressures and with saline brine containing higher ion contents; verifying that a higher temperature gradient and presence of high ion contents are the main contributing factors for flux decline related to scaling in V-DCMD.

4.4. Continuous V-DCMD operation for ROC wastewater

A continuous operation of V-DCMD was carried out with a synthetic ROC wastewater solution (2.2 g/L) to validate a lower fouling tendency in V-DCMD. Only a 25-29% flux decline was observed even when the initial volume of feed solution reduced by a fourth (volume concentration factor, VCF = 4.0) (**Fig. 10a**). Thereafter, the membrane in V-DCMD was rinsed with DI water (100 mL) for removing salts deposited on the membrane surface, followed by another (2nd) cycle of V-DCMD operation with same synthetic ROC wastewater. The test was done for three cycles and each cycle lasted for 4h. The TDS concentration in permeate remained constantly low at 8 to 10 $\mu\text{S}/\text{cm}$ (more than 98% removal) throughout the operation. This indicates that V-DCMD produced a good quality of permeate with a short DI water flushing. At the end of the operation (after finishing the 3rd cycle), SEM-EDX analyses on the membranes before and after cleaning were carried out. The inorganic ions of Ca, S and NaCl (salt) were presented on the used membrane while minimal ions were detected on the membrane after the cleaning (**Fig. 10b**). As V-DCMD process is not a pressure-operated system, the inorganic crystals did not

strongly adhere onto the MD membrane. Hence, with simple DI water flushing, most of the salts deposited on the membrane were removed as observed in **Fig. 10b**. The flux was restored in the subsequent experiments (with DI water flushing), suggesting that the flux decline most probably was attributed to concentration polarization effect and scaling was mostly reversible in V-DCMD operation. Similar trends of evolving flux decline with time associated with an increased Na concentration in the feed solution have been observed in other MD studies [28, 30]. Therefore, this present study established the effectiveness of V-DCMD for producing good quality water while reducing the volume of ROC wastewater.

5. Conclusions

The performance of V-DCMD (operated under vacuum pressure applied at the permeate side) was evaluated in terms of transport mechanism and fouling analysis. This study showed that the V-DCMD is a more promising option compared to the DCMD (operated under atmospheric pressure) due to following advantages:

- The V-DCMD (300 mbar) enhanced the permeate flux by 37.6 % compared to the DCMD configuration at the same feed temperature (55 °C). This may be due to the reduced partial pressure in the pores of the membrane as well as the removal of non-condensable gases within the membrane pores, enabling a higher diffusion of water vapor through the membrane;
- The V-DCMD mass transport mechanism was explained by incorporating a dimensionless coefficient (α) into the empirical DCMD mass transport model;
- The simulated temperature profile distribution showed a reduced temperature loss in the V-DCMD compared to the DCMD, which indicated a better energy efficiency in the V-DCMD configuration;
- In terms of projected energy consumption, for achieving a similar permeate flux of 16.0 ± 0.3 LMH, V-DCMD (at 55 °C and 300 mbar) would theoretically require less energy consumption than DCMD (at 65 °C, 1,000 mbar);
- The V-DCMD showed a lower membrane resistance compared to the DCMD. This was associated with reduced resistance of water vapor diffusion through the membrane pores in the V-DCMD;
- The fouling profile of the V-DCMD was well represented by empirical flux decline model;
- V-DCMD operation was able to maintain a stable flux in continuous operation of ROC wastewater solution, enabling to produce good quality distillate while reducing the ROC volume.

The permeate flux was recovered upon flushing the membrane with DI water which removed most salts deposited on the membrane (as observed in the EDX analysis). This reflected the suitability of V-DCMD application for ROC produced from wastewater reclamation plant.

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Table 2 Comparison of fluxes and membrane resistances of DCMD and V-DCMD.

Table 3 Comparison of flux decline ratio J/J_0 with flux decline coefficient value.

Table 1 Permeate fluxes of DCMD and V-DCMD (feed and permeate= DI water, feed and permeate velocity= 0.06 m/s, permeate temperature 25 °C).

Permeate vacuum pressure (mbar)	Permeate Flux (LMH)			
	Average feed temperature (°C)			
	50	55	60	65
1,000 (no vacuum)	9.0 ± 0.2	11.0 ± 0.9	14.0 ± 0.2	16.0 ± 0.5
800	-	13.0 ± 0.4	-	-
600	-	14.0 ± 0.8	-	-
300	-	16.0 ± 0.3	-	-

Table 2 Comparison of permeate fluxes and membrane resistances of DCMD and V-DCMD.

Configuration	Feed Temperature (°C)	Permeate pressure (mbar)	Flux (LMH)	R_m (Pa.m ² .h/L)
DCMD	55	1000	11.0 ± 0.9	0.030 ± 0.001
DCMD	65	1000	16.0 ± 0.5	0.020 ± 0.003
V-DCMD	55	300	16.0 ± 0.3	0.005 ± 0.002

Table 3 Comparison of flux decline ratio J/J_0 with flux decline coefficient value.

MD configuration	Feed solution	J/J_0	k_1
DCMD (1000mbar)	NaCl	0.78	-6.41E-04
	NaCl + CaSO ₄	0.73	-9.79E-02
V-DCMD (300mbar)	NaCl	0.82	-6.93E-03
	NaCl + CaSO ₄	0.74	-3.23E-02

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Fig. 2. 2D model of simulated DCMD with counter current flow across the membrane, with feed and permeate membrane channel thickness, FT and PT from scale 0 to 1 (0 being furthest (do you mean farthest?) from the membrane, 1 being closest to the membrane) and channel length, FL and PL, where L=0 (channel inlet), L=0.5 (centre) and L= 1 (outlet).

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Feed

Permeate

(a) $F_t = 55^\circ\text{C}$, 1000mbar

(b) $F_t = 55^\circ\text{C}$, 300 mbar

(c) $F_t = 65^\circ\text{C}$, 1000mbar

Fig. 6. Temperature distribution profile along the membrane module channel length and thickness of feed and permeate side of V-DCMD (300 mbar) and DCMD (1000 mbar) at F_t of 55 °C and 65 °C. (channel thickness, from scale 0 to 1 (0 being furthest from the membrane, 1 being closest to the membrane; and channel length, from scale 0 = inlet, 1= outlet).

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(channel thickness, from scale 0 to 1 (0 being furthest from the membrane, 1 being closest to the membrane; and channel length, from scale 0 = inlet, 1 = outlet).

(a)

(b)

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