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**Enhanced ammonia recovery from wastewater by Nafion membrane with highly porous
honeycomb nanostructure and its mechanism in membrane distillation**

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Abstract

Removing nitrogen from wastewater by conventional treatment methods requires substantial energy, only to release it back to the atmosphere as gaseous nitrogen. Herein, we investigated the applicability of membrane distillation (MD) in resource recovery from sludge digestate by controlling the volatility and pressure of the vapor transport across the membrane to concentrate ammonia in the permeate stream. A mixture of Nafion ionomer and Multiwall Carbon Nanotubes (MWCNTs) were incorporated into a Poly(vinylidene fluoride-co-hexafluoropropene; PVDF-HFP) nanofiber matrix to fabricate a nanoporous honeycomb Nafion membrane featuring high recovery and increased mechanical strength. Theoretical modelling was conducted to predict the expected performance of the fabricated Nafion membrane under different operation conditions and to reveal the mechanism behind the enhanced recovery of Nafion membranes in the MD process. The resultant Nafion (8%)/MWCNT (2.5%)/PVDF-HFP nanofibrous membrane showed up to three times higher ammonia recovery compared to the commercial PVDF membrane from a feed with an ammonia concentration of 300 mg/L. The theoretical analysis quantitatively revealed that the Nafion containing membrane can not only suppress the negative effect of membrane's structural resistance on the ammonia recovery efficiency but also enhance the efficiency. In addition, we also uncovered that the effect of Nafion on ammonia recovery efficiency was maximized when the Nafion 8% membrane was employed. This study demonstrated an innovative and realistically applicable MD treatment process for recovering resource, which integrates low-grade heat and has scaling-up potential for wastewater treatment plants.

Keywords: Nafion membrane; Ammonia recovery; Nafion coating; Membrane Distillation; Modeling.

1. Introduction

The inextricable linkages and challenges of the water-energy-food nexus have inspired scientists to explore innovative technologies that can help achieve global sustainable development [1]. In terms of the water and wastewater industry, the efforts so far have led to a paradigm shift from traditional end-of-pipe treatment to the development of new technologies with the potential to reuse and recover resources from wastewater. As part of this paradigm shift, this research sets out to propose an alternative separation technique for the recovery of ammonia through recovery, a major pollutant in agricultural as well as municipal and industrial wastewater, from wastewater streams. Nitrogen recovery by conventional treatments as shown in **Table. S2** which can be costly and are often unable to meet stringent discharge standards [2,3]. If recovered properly, ammonia can be used as ammonia-based fertilizers [4] and contribute not only to environmental sustainability but also become an additional source of profit that can lower the cost of wastewater treatment.

Over the recent decade, membrane distillation (MD) has been gaining attention as an emerging method for separating ammonia from the waste stream or for treating anaerobically-digested effluents [4–9]. MD allows volatile NH_3 gas to pass across a microporous hydrophobic membrane to concentrate ammonia in the permeate stream under acidic conditions. Previous studies have commonly noted the pH level and temperature of ammonia-containing feed wastewater as major factors that affect the mass transfer coefficient and solubility of ammonia [7–9]. In other words, increasing the pH and temperature of the feed wastewater favours the dissociation of ammonia from the aqueous phase to produce volatile ammonia molecules, which can be recovered by MD. Moreover, Yang et al. employed the vacuum membrane distillation

technology coupled with carbonate presence for ammonia recovery without pH adjustment, and high recovery efficiency was achieved through the pH polarization and buffering effect [10].

However, among the many studies conducted on different MD configurations - direct contact MD, air gap MD, sweep gas MD, and vacuum MD - for understanding the selectivity and mass transfer of ammonia in the MD process, most have reported on MD performance using polytetrafluoro-ethylene (PTFE) or polypropylene (PP) membranes. Despite the fact that separation performance is greatly affected by membrane properties, only a few studies have introduced new and innovative membranes for ammonia recovery in MD. He et al. applied the PP hollow fiber membrane in vacuum membrane distillation process for ammonia recovery from biogas slurry [11]. Yang et al. developed an innovative interlayer-free cobalt-doped silica membrane for wastewater treatment and ammonia recovery which achieved a high recovery efficiency [12]. Thus, this study concentrates on developing an ideal membrane for ammonia recovery that has the benefits of high liquid entry pressure (hydrophobicity), high permeability (high porosity and high surface to volume ratio), less fouling, high chemical reliability, and high thermal stability.

In particular, Nafion, a copolymer of perfluorosulfonic acid (PFSA) and tetrafluoroethylene (Teflon®), has been widely used in the fuel cell industry for several decades. Recently, Nafion was employed for gas sorption and separation in many studies and the gas permeation properties of Nafion have started to generate great interest. Mukaddam et al. demonstrated the good permeation properties of Nafion membrane for mixed gas transferring [13]. Dai et al. applied the Nafion membrane for N_2/CO_2 separation which achieved an excellent gas isolation efficiency [14]. Furthermore, Nafion has notable advantages in the removal of volatile compounds and water vapor due to its thermal/mechanical/chemical stability and has a

high selectivity for ammonia in particular [15]. Yang et al. developed a Nafion based dryer for water vapor removal in peroxy radical chemical amplification which attained an accurate measurement of peroxy radicals [16]. Moreover, the sulfonic acid functional group make Nafion strongly acidic which is suitable for ammonia adsorption and recovery. However, a major issue in deploying a Nafion polymer membrane is that it is prone to deterioration from mechanical stress [17].

Therefore, the present study aimed to achieve the following three objectives. First, we aimed to fabricate a suitable and innovative nanofiber Nafion membrane for MD operation by incorporating MWCNT nanoparticles as reinforcement to improve the mechanical stability of Nafion. Secondly, we set out to quantify the efficiency of Nafion membranes in ammonia recovery by investigating the ammonia recovery efficiency of Nafion membranes containing various Nafion concentrations (0-8%) in a DCMD system. In this process, we minimized the water vapor flux generated by the transmembrane temperature difference to enable an accurate measurement of ammonia recovery efficiency, which is primarily driven by concentration difference-based diffusion. Lastly, we set out to explain the enhanced ammonia recovery under different Nafion concentrations, pH levels, and temperatures through a theoretical modeling on the ammonia mass transfer resistance across the boundary layers adjacent to the Nafion membrane.

2. Materials and methods

2.1 Nafion composite membranes

The Nafion composite membranes were fabricated by electrospinning. First, the polymer solution was prepared by mixing polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP, hereinafter PH; $M_w=455,000 \text{ g mol}^{-1}$), lithium chloride (LiCl) as additives, and N-dimethylformamide (DMF) and acetone as solvents, all purchased from Sigma-Aldrich. Pristine multiwall carbon nanotubes (MWCNTs, internal diameter = about 5–30 nm; BET surface area = $155 \pm 5 \text{ m}^2/\text{g}$; purity 90% and bulk density = $0.04\text{--}0.08 \text{ g/cm}^3$), purchased from Carbon Nano-material Technology Co., Ltd., Korea and functionalized using previously developed methods [18,19], were mixed with Nafion (Nafion®PFSA, Dispersions D520 5%, Dupont™) ionomer at the desired concentrations to reinforce the electrospun membranes and achieve the desired membrane mechanical strength.

Specifically, 2 wt % F MWCNTs were added to the 15 wt% PH precursor solution (PH: DMF: acetone=15:59.5:25.5) mixed with the required mass of Nafion D520 PFSA ionomer (0~8%). The dope solution then underwent magnetic stirring at 65°C overnight, followed by sonication for 1.5 hours [20]. Finally, the membranes were fabricated via electrospinning under an applied voltage of 16 kV at a flow rate of 1 ml/h over a tip-to-collector distance of 15 cm. A commercial PVDF membrane (hereafter, PVDF membrane) with a pore size of $0.45 \mu\text{m}$ purchased from Millipore Company (Durapore® Membrane Filters, Merck Millipore Ltd) was used as the reference membrane to compare with the electrospun three Nafion membranes (hereafter, Nafion 0%, Nafion 6%, Nafion 8% membranes) on their MD performance.

2.2 Membrane characterization

The surface morphology of the membranes was analyzed by FE-SEM (Quantum 450 FEG, FEI, USA) conducted with ImageJ. A capillary flow porometry (Porometer, POROLUX™

100, Germany) was used to observe the pore sizes and liquid entry pressures (LEP) of the membranes, and a tensile strength test was conducted to measure the mechanical properties of the membranes using tensile strength measurements (Lloyd-Ametek LS1 material testing machine, USA). To obtain more specific information on the functional group of the membranes, Fourier transform infrared spectroscopy (FTIR) was performed. The IR spectra (700-4000 cm^{-1}) of the membranes were collected under the attenuated total reflectance (ATR) mode of FTIR spectrometer (Iraffinity-1, Shimadzu, Japan) with a 2 cm^{-1} resolution. The water contact angle (CA) was measured by a CA meter (KRUESS GmbH DSA25S). The zeta potential of the membrane surface was analyzed by the streaming current method using an electro kinetic analyzer (Surpass Anton Paar, Austria). Three membrane coupons were analyzed, and three spots on each membrane were measured by the membrane characterization methods used in this study.

2.3 Feed water and Experimental set-up

Supported and inspired by the concerns of the Hong Kong's Drainage Service Department (DSD) regarding the high nitrogen concentration in the sludge digestate of Hong Kong's sewage treatment plants, this study simulates the ammonia concentration (300 mg/L) of the digestate at Hong Kong's Shatin Sewage Treatment Works (STSTW) in investigating the recovery of ammonia using the Nafion membranes. The detailed experimental set up is given below.

Fig. 1. Schematic configuration of the DCMD setup (1: Permeate solution, 2: Digital balance connected to a computer, 3: Thermometers, 4: Heat exchanger, 5: Pumps, 6: Flat-sheet membrane module, 7: Flow meters, 8: Feed solution, 9: Hotplate).

The batch mode DCMD experiments for ammonia recovery were conducted using the laboratory fabricated Nafion membranes (**Fig. 1**). Each batch of DCMD experiments was operated for exactly 24 hours. The diameter of the membrane flow channel was 2.5 cm with an effective membrane surface area of 9.8 cm^2 ($6.1 \text{ cm} \times 1.6 \text{ cm}$). The feed and permeate solutions were circulated continuously in counter directions at the same flow rate (500 ml/min, 1.02 m/min). The ammonia concentration of the feed solution was maintained at 300 mg/L by dissolving 1.783 g of ammonia chloride (NH_4Cl) in an initial deionized (DI) water volume of 2.0 L, and its pH was adjusted to 7, 9, 12 using 4M NaOH. The feed solution was heated to the desired operating temperatures of 45°C , 55°C , and 65°C , while the permeate solution (diluted sulfuric acid with $\text{pH}=2$) was maintained either at the same temperature of feed (no temperature gradient across membranes to study the effect of varying pH level on ammonia transfer) or at 25°C (temperature gradient across membrane to study the effect of varied temperatures on both ammonia and water vapor transport).

The water flux ($\text{L}/\text{m}^2\cdot\text{h}$) was measured in real-time with a data-logging system connected to a balance in the permeate side. Ammonia recovery efficiency was determined by ammonia recovery efficiency (%), which was calculated by measuring the ammonia concentration in the initial feed and final permeate solutions. To measure the ammonia concentration, the total nitrogen (TN) in solution was detected first by a TOC-L analyzer (Shimadzu, Japan), and the ammonia concentration was converted based on the TN value. All DCMD experiments in this study were conducted in triplicate.

176

177 **3. Theoretical approach**178 **3.1 Mass transfer of ammonia gas across the membrane**

179 The ammonia gas transportation across the porous membrane follows the dusty gas model
 180 which includes Knudsen and viscous diffusions in a series network [1,5,19,21,22] and can be
 181 expressed as follows:

$$182 \quad N = K_{OV} \Delta C$$

183 (1)

184 where, N is the molar flux [$\text{mol}/\text{m}^2\text{s}$], K_{OV} is the overall mass transfer coefficient [m/s], and ΔC is
 185 the ammonia solution concentration difference across the membrane [mol/m^3].

186 The overall mass transfer coefficient can be calculated as follows:

$$187 \quad K_{OV} = \frac{V_0}{At} \ln \left(\frac{c_0}{c_t} \right)$$

188 (2)

189 where, K_{OV} is the overall mass transfer coefficient [m/s], V_0 is initial feed volume [l], A is the
 190 effective membrane area [m^2], t is the time [s], and c_0 [mol/m^3] and c_t [mol/m^3] are the ammonia
 191 concentrations at start-up and time t , respectively.

192 $1/K_{OV}$ [s/m] is the function of the feed side boundary resistance $1/K_f$ [s/m], membrane
 193 resistance $1/K_m$ [s/m], and the mass transfer resistance reducer K_N [s/m] which is the Nafion
 194 factor on the ammonia gas transportation across the membrane (if the membrane has no Nafion,
 195 K_N is 0), and can be expressed as follows:

$$\frac{1}{K_{OV}} = \frac{1}{K_f} + \frac{1}{K_m} - K_N \quad (3)$$

Membrane resistance $1/K_m$ is a function of Knudsen diffusion as follows:

$$\frac{1}{K_m} = \left(\frac{8r\varepsilon}{3\delta\tau} \sqrt{\frac{1}{2\pi RT}} \right)^{-1} \quad (4)$$

In this study, it is assumed that $1/K_f$ is independent from the effects of $1/K_m$ and K_N . Therefore, the feed side boundary resistance $1/K_f$ in Eq. (5) can be experimentally calculated based on the PVDF membrane without the Nafion factor as follows:

$$\frac{1}{K_f} = \frac{1}{K_{OV}} - \frac{1}{K_m}, \text{ if } K_N = 0 \quad (5)$$

When the Nafion membrane is employed in the DCMD process, the Nafion factor can be calculated from Eq. (6) as follows:

$$K_N = \left(\frac{1}{K_f} + \frac{1}{K_m} \right) - \frac{1}{K_{ov}} \quad (6)$$

3.2 Mass transfer mechanism for water vapor across the membrane

In the MD process, the transmembrane temperature difference generates a partial water vapor pressure difference between the liquid–vapor interfaces to work as the driving force that moves the water vapor across the membrane. Thus, the water vapor flux (J , $\text{kg/m}^2\text{h}$) can be expressed as follows:

$$J = m_{transfer} (p_{f,m} - p_{p,m}) \quad (7)$$

$$m_{transfer} = (R_K + R_M)^{-1} + R_p^{-1} \quad [\text{kg/m}^2\text{sPa}] \quad (8)$$

213 where, $R_K^{-1} = C_K (M_w / RT_m)^{0.5}$ [s/m], $R_M^{-1} = C_M (DM_w / P_{aM} RT_m)$ [s/m] and
 214 $R_P^{-1} = C_P (P_m M_w / \mu RT_m)$ [s/m]. C_K , C_M , and C_P represent the structural parameter of Knudsen
 215 diffusion ($C_K = r\varepsilon / \tau\delta$), molecular diffusion ($C_M = \varepsilon / \tau\delta$), and Poiseuille flow ($C_P = r^2\varepsilon / \tau\delta$),
 216 respectively. P_m is the mean water vapor pressure inside the membrane, P_{aM} is the log-mean air
 217 pressure at both sides of the membrane, and $P_m = (P_{f,m} + P_{p,m}) / 2$ [Pa]. The binary diffusion
 218 coefficient D can be expressed as $D = 1.19 \times 10^{-4} (T_m^{1.75} / P_m)$ [m²/s], which is taken from the
 219 Fuller-Schettler-Giddings empirical equation.

220 In this study, the NH_3 concentration in the feed and H_2SO_4 concentration in the permeate
 221 are relatively small, thus, the partial transmembrane water vapor pressures of the feed and
 222 permeate sides are assumed to be the partial water vapor pressure of pure water, which can be
 223 evaluated with the Antoine equation as follows:

$$224 \quad P_{w,m} = \exp \left(23.1964 - \frac{3816.44}{T - 46.13} \right) [\text{Pa}] \quad (9)$$

225 The mean permeate flux over the membrane's length L is evaluated as:

$$226 \quad J_m = \frac{1}{L} \int_0^L J(z) dz \quad [\text{kg/m}^2\text{h}] \quad (10)$$

227 3.3 Heat transfer mechanism

228 The heat transfer process in DCMD consists of the heat transferred across the boundaries
 229 of (i) the feed side (Q_f), (ii) permeate side (Q_p), and (iii) through the membrane (Q_m). This is
 230 well explained and validated in our previous paper [19,23–28].

231 (i) Heat transferred across the boundaries of the feed side:

$$Q_f = h_f (T_f - T_{f,m}) \quad (11)$$

where, h_f is the convection heat transfer coefficient of the bulk feed side [W/m²K], T_f is the bulk feed temperature [K], and the $T_{f,m}$ is the temperature of liquid/vapor interface at the feed side [K].

(ii) Heat transferred across the boundaries of the permeate side:

$$Q_p = h_p (T_{p,m} - T_p) \quad (12)$$

where, h_p is the convection heat transfer coefficient of the bulk permeate side, T_p is the bulk permeate temperature, and $T_{p,m}$ is the temperature of liquid/vapor interface at the permeate side.

(iii) Heat transferred through the membrane:

$$Q_m = \left[J \Delta H + \frac{k}{\delta_m} (T_{f,m} - T_{p,m}) \right] \quad (13)$$

where, J is the water vapor flux, ΔH is the thermal enthalpy for evaporation [J/kg], k is the thermal conductivity of the membrane [W/mK], and δ_m is membrane thickness [m].

At a steady state, if there is no heat transfer to ambient air, all heat transfer quantities in the DCMD process should be equal and can be expressed as follows:

$$Q = Q_f = Q_m = Q_p \quad (14)$$

The detailed equations for the convection heat transfer coefficient, Reynolds number, Prantl number, and the transportation behavior can be found in previous studies [19,24,27].

4. Results and discussion

4.1. Nafion composite membrane

4.1.1 Structural membrane characteristics

The Nafion composite electrospun membranes were effectively fabricated with pore sizes and membrane thicknesses similar to the commercial membrane for easy comparison. The characteristics of the membrane used in this study are summarised in Table 1. The nanocomposite surface modification of nanofibers based on our previous electrospinning methods [20,29,30] rendered higher porosities, controllable honeycomb porous structures, and higher hydrophobicities in the resultant membranes compared to the PVDF commercial membrane, which mean that our laboratory-fabricated membranes are highly suitable for MD.

Table 1. Characteristics of the membranes used in this study.

Membranes	PVDF	Nafion 0%	Nafion 6%	Nafion 8%
Material	Commercial PVDF	15%PH/2.5% CNT	15%PH/2.5%CNT/ Nafion 6%	15%PH/2.5%C NT/ Nafion 8%
Mean pore size (μm)	0.45 ± 0.03	0.54 ± 0.02	0.48 ± 0.02	0.42 ± 0.01
Thickness (μm)	104 ± 0.23	106 ± 0.12	104 ± 0.27	104 ± 0.19
Porosity (%)	69.2 ± 0.92	89.2 ± 1.21	88.9 ± 0.78	89.7 ± 1.02
Tensile strength (MPa)	7.11 ± 0.78	6.62 ± 0.92	6.77 ± 0.69	6.86 ± 0.55
LEP of water (bar)	1.35 ± 0.08	1.27 ± 0.11	1.35 ± 0.13	1.39 ± 0.06

Although MD is not a pressure driven process, improvement of mechanical strength could allow membranes to become more robust against deformation during long-term operations.

Therefore, membranes with better mechanical strength can achieve more stable MD performance [31,32]. Furthermore, greater mechanical strength could reduce the tendency of membrane pores to expand, thereby preventing water from being captured in the pores between the fiber layers and causing an increase in mass transfer resistance [33–36]. Thermal stability is important to membranes applied in MD, specifically, the membrane must be able to tolerate temperatures beyond 60 degrees. The membrane's thermal conductivity value is also of concern, as lower thermal conductivity can allow for a stable temperature gradient between the feed and permeate sides which enables stable water flux and efficient MD performance [37,38].

Fig. 2 provides an image of the Nafion composite nanofibers and their effects on the fiber structure and pore network [29]. Adding Nafion to the polymer solution containing CNTs formed nanoporous honeycomb Nafion sphere. Moreover, the cross-section SEM images of Nafion honeycomb membrane was shown in **Fig. S3**. To determine the diameter of the nanofibers in the membranes, the SEM images were analysed using the ImageJ software program by setting the scale between the pixels and the real distance and manually measuring one hundred individual fibers. The average and distribution of the nanofiber diameters of the Nafion membranes are presented in **Fig. 3**. The Nafion 6% and 8% membranes resulted in smaller nanofiber diameters compared to the Nafion 0%; their lowest average came out to be 300 nm, contributing to the relatively smaller pore sizes and porosities compared to the commercial PVDF and Nafion 0% membranes (Table 1). The Nafion 6% and 8% membranes' smaller nanofiber diameters also led to the membranes' higher LEP, which is determined by the hydrophobic membranes' pore sizes and shapes and indicates their resistance to wetting issues. High LEP values are ideal for MD membranes and can be obtained by using materials with low surface energy and minimizing the membrane's pore size [39].

Fig. 2. FE-SEM images of (a) the Nafion 0% membranes, (b) the Nafion 6% membrane, and (c) the Nafion 8% membrane.

Fig. 3. The average and distribution of the nanofiber diameters of (a) the Nafion 0% membrane, (b) the Nafion 6% membrane, and (c) the Nafion 8% membrane.

4.1.2. Contact angle

The electrospun Nafion membranes exhibited higher CAs than the commercial PVDF membrane as shown in **Fig. 4**. However, when Nafion was increased to 8%, the CA value decreased from 148.5° to 135.9° . This is because Nafion's unique ionic properties are a result of

incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone [40,41]. Several studies have shown that Nafion has wide channels, is less branched, and has a small sulfonate group separation, which means it is strongly hydrophilic and flexible [42,43]. Interestingly, despite the decrease in CA, there was an even more significant decrease in pore size which resulted in an increase in LEP. In order to improve the surface hydrophobicity, 2% fluorinated MWCNT was added during Nafion membrane fabrication which allows it to achieve a high contact angle of 138.7° for better antifouling and antiwetting properties in the 8% Nafion membrane.

Based on the Cantor-Laplace equation, the LEP of a porous membrane is proportional to the contact angle, liquid surface tension, and the inverse of the maximum pore size [47]:

$$LEP = \frac{-2B\gamma\cos\theta}{r_{\max}}$$

(16)

where, B and r are the shape factor and the radius of the membrane pore, respectively, γ is the surface tension of the wetting liquid, and θ represents the contact angle between the membrane sample and the wetting liquid.

b

Fig. 4. Contact angles of the fabricated membranes incorporating different Nafion concentrations.

4.1.3 Membrane surface Chemical structure

Fig. 5 shows the FTIR spectra of the commercial PVDF and the Nafion 0%, 6% and 8% membranes. All membranes with PVDF bases show absorption peaks at 1400, 1178 and 877 cm^{-1} which correspond to the stretching vibration of C–H bonds, the symmetrical stretching of C–F bonds, and the skeletal vibration of C–C bond[44–46], respectively. The absorption peaks at 1060 cm^{-1} found from the Nafion membrane (Nafion 6%, and 8%) can be attributed to the $-\text{SO}_3\text{H}$ groups [47,48].

Fig. 5. FTIR spectra of (a) the commercial PVDF membrane, (b) the Nafion 0% membrane, (c) the Nafion 6% membrane, and (d) the Nafion 8% membrane.

The zeta potentials of the commercial PDVF and Nafion membranes were measured under different pH levels ranging from 2 to 11, and the results are presented in **Fig. 6**. All membranes showed negative surface charge. Since Nafion's zeta potential depends on its concentration, the zeta potential of the Nafion-incorporated membranes (Nafion 6 and 8%) were more sensitive to the variations in pH, decreasing sharply with increasing pH, than the other two membranes (PVDF and Nafion 0 %). The Nafion 8% membrane possessed the lowest charge of -143 mV at around pH 11, which may be attributed to the micelle-like structure of Nafion aggregates that causes structural changes in the Nafion molecules at higher concentrations [49]. Thus, a higher negative charge occurred with increasing Nafion concentration. After membrane fabrication with Nafion, the overall membrane surface carried a greater negative charge which can attract ammonium ion to the membrane surface and accelerate the ammonia evaporation

337 process.

338
339 **Fig. 6.** Comparison of the zeta potentials of all membranes (commercial PVDF and Nafion) as a
340 function of pH.

341 4.2 Nafion membranes' performance

342 We tested the Nafion honeycomb porous membranes' performances in recovering
343 ammonia from the feed solution using direct contact membrane distillation (DCMD) under 1)
344 different pH levels, 2) feed and permeate temperature, and 3) Nafion concentrations. The
345 ammonia recovery process by DCMD is demonstrated in **Fig 7**. During MD process, besides the
346 highly negative surface charge and acidity of the Nafion membrane, which accelerates the
347 evaporation of ammonia, the porous honeycomb structure with nanosized pores also contributes
348 to ammonia recovery. The Nafion spheres can attract the ammonia gas, allowing for fast transfer
349 through the nanosized pores by capillary effect. Thus, the recovery efficiency (65 °C, pH=12) of

the 8% Nafion membrane was enhanced more than two times from the Nafion 0% membrane.

Figure 7. Schematic diagram of the ammonia recovery process by DCMD.

4.2.1 Effect of feed solution pH

DCMD experiments were conducted with the Nafion membranes to evaluate the effects of feed (ammonia) solution pH and Nafion concentrations on the ammonia recovery efficiency. The same temperature was maintained for both the feed and permeate solutions ($\Delta T=0$) at 45°C, 55°C, and 65°C to investigate the single effect of pH on ammonia recovery without water vapor flux.

As shown in **Fig. 8**, enhanced ammonia recovery was observed with increased feed solution pH. Among the Nafion membranes, the Nafion 8% showed the best performance at pH 12 with its ammonia recovery efficiency increased up to 59.74%, about 3 times higher than that of the PVDF (18.6%~22.0%) and 2.7 times higher than that of the Nafion 0% (22.2%~24.1%). The pH difference caused a difference in ammonia vapor pressure which, in turn, affected the movement rate of ammonia; the greater the amount of ammonia passing through the membrane,

the higher the ammonia recovery efficiency. In an alkaline environment ($\text{pH} > 9.3$), a substantial portion of the dissolved ammonia and ammonia ions dissociate instantly in an aqueous solution to form NH_3 and convert to ammonia molecules, a reaction which can be expressed chemically as follows [50]:

The greater dissociation reaction of NH_4^+ to the right side with increasing pH leads to the release of ammonia molecules, and thus, the vapor pressure of feed solutions containing ammonia becomes higher than that of initial concentration of feed solution, leading to an increase in the ammonia recovery efficiency [21,51,52].

Fig. 8. The ammonia recovery efficiency of the four membranes, PVDF and Nafion 0, 6, and 8%, under the same feed and permeate temperatures (45 °C, 55 °C, and 65 °C) when feed solution pH is adjusted to (a) pH 7, (b) pH 9, and (c) pH 12.

The amount of ammonia in an aqueous solution can be removed by control of two factors, such as temperature and pH value. Comparing with pH adjustment, the temperature adjustment cannot improve the ammonia evaporation and recovery efficiency effectively, since the dissolved ammonia dissociates immediately to form unstable NH_4^+ in the solution [5]. In fact, increasing the temperature of both the feed and permeate sides from 45 °C to 65 °C did not significantly affect the ammonia recovery efficiency in the Nafion membranes. Overall, the ammonia recovery efficiency in the DCMD system with the Nafion membranes was clearly determined by the solution pH, which had a positive effect on the average flux and the ammonia recovery efficiency as evidenced by the results shown in **Fig. 8**.

To summarize, in the DCMD system with Nafion membranes, the recovery of ammonia was more influenced by the ammonia dissociation resulting from increasing the feed pH than from increasing the feed temperature. Also, the recovery of ammonia was more efficient when increasing the Nafion concentration (**Fig. 8**) because the Nafion membrane accelerated the

transport of the diffused ammonia [53,54]. The interaction mechanisms between Nafion and ammonia are further explained in section 4.3 which touches upon the mass transfer coefficient.

4.2.2 Effect of permeate temperature on flux and ammonia recovery

To investigate the effects of disparate feed and permeate temperatures on the ammonia recovery efficiency, the feed temperature was changed ($\Delta T \geq 20$) to 45°C, 55°C, and 65°C, while the permeate temperature was kept constant at 25°C. The average fluxes of the four membranes under varied feed temperatures (45°C, 55°C, and 65°C) and pH levels with a constant 25°C permeate temperature are presented in **Fig. 9**. Under the single variable of feed temperature with various feed solution pH, the feed temperature influenced the average permeate flux significantly. The increase in the feed temperature from 45 to 65 °C resulted in a 21 LMH rise in the average flux of the 8% Nafion membrane. Also, membranes with higher Nafion percentage achieved higher flux; when Nafion concentration was increased from 0% to 8% (pH=12, 65°C), the average permeate flux increased from 32.3 LMH to 46.5 LMH. In comparison, the commercial PVDF membrane under its optimum operating condition (feed pH value of 12 and temperature of 65°C) had a flux of only 23.8 LMH.

Fig. 9. The average fluxes of the four membranes under three feed temperatures (45°C, 55°C, and 65°C) and 25°C permeate temperature with feed solution pH: (a) 7, (b) 9, and (c) 12.

The initial fluxes of the four membranes were proportional to the feed temperature (**Fig. 9**), indicating that the increase in the vapor pressure at the feed side is the direct result of the increase in feed temperature. The increase in vapor pressure facilitates the transfer of the ammonia vapor through the micropores, which is driven by the transmembrane vapor pressure difference. As can be seen in **Fig. 10**, other important trends can be observed in the ammonia

recovery efficiency of the membranes. When the feed solution was adjusted to pH 7, the ammonia recovery efficiency of the Nafion 8% membrane at feed temperatures 45°C, 55°C, and 65°C were 4.5%, 5.5%, and 6.2%, respectively; but when the feed solution was adjusted to pH 9, its ammonia recovery efficiency increased drastically under all three feed temperatures, 45°C, 55°C, and 65°C, to 27.2%, 29.2%, and 31.3%, respectively (**Fig. 10 (a) and (b)**). Also, when DCMD was conducted under different feed and permeate solution temperatures, the Nafion membranes exhibited higher ammonia recovery efficiency than when the feed and permeate side were maintained at the same temperatures (**Fig. 8 and 10**).

The Nafion 8% membrane showed the highest ammonia recovery efficiencies when the feed solution was pH 12 (**Fig. 10 (c)**), recording 62.7%, 64.1%, and 66.2% at feed temperatures of 45°C, 55°C, and 65°C, respectively. These values represent a maximum 10.8% increase compared to the values from the DCMD experiments under same feed and permeate temperatures. It appears that a greater temperature difference between the feed and permeate sides promotes the ammonia vapor diffusion in the feed solution as well as within the membrane module, thereby contributing to a higher mass transfer coefficient. Another consideration is the endothermic nature of ammonium ion dissociation, which would increase the presence of volatile ammonia in the feed solution [55]. Furthermore, both concerning the temperature and pH effect on the flux as well as ammonia recovery efficiency, the ammonia concentration in permeate side is shown in **Table. S6**.

Fig. 10. The ammonia recovery efficiency of the four membranes, PVDF and Nafion 0, 6, 8%, under three feed temperatures (45°C, 55°C, and 65°C) and a consistent permeate temperature of 25°C when feed solution pH is adjusted to (a) pH 7, (b) pH 9, and (c) pH 12.

Although the feed temperature notably influenced the ammonia recovery efficiency, the experimental results indicate that Nafion concentration has a much significant influence. As shown in **Fig. 11**, the DCMD system performance with the Nafion 0% membrane at feed

solution pH 12 was less than 24%. Also, the rates of increase in ammonia recovery at higher feed temperatures were observed to be about 2% with little change even with higher Nafion concentration. However, the Nafion 6% and 8% membranes showed notably higher ammonia recovery efficiencies, by a maximum of 51.4% for the Nafion 6% and a maximum of 66.2% for the Nafion 8% compared to the Nafion 0%. In addition, the mass balance table of ammonia before and after MD process are also demonstrated in **Table. S1**. The ammonia recovery efficiency under both same and different temperature of feed and permeate side are summarized in **Table. S3 and S4** for better comparison.

Moreover, in terms of the ammonia recovery in high strength wastewater, the extra experiments were conducted with a feed solution of ammonia (300 ppm), NaCl (3.5% wt) and bovine serum albumin (BSA, 1000 ppm). The synthetic wastewater was considered as ammonia containing high strength wastewater which was applied for MD treatment with an 8% Nafion membrane under 65 °C and pH =12. During MD treatment of this high strength wastewater, the ammonia recovery efficiency was reduced as the foulant attachment covered and blocked the pores leading to increased ammonia transfer resistance as shown in **Fig.S2**. Owing to the higher contact angle of 8% Nafion membrane with better anti-fouling function, the ammonia recovery efficiency is less affected by the fouling issue than commercial PVDF membrane. Finally, an ammonia recovery efficiency of 59% was achieved by the 8% Nafion membrane after 24 hours MD treatment of high strength wastewater.

In short, the increase in ammonia vapor diffusion and transmembrane vapor pressure caused by higher feed temperature was accommodated well by higher Nafion concentrations in the membrane, promoting the transfer of the ammonia vapor via the membranes' micropores

through its intrinsic properties such as high permeability to ammonia [53,54]. Furthermore, this phenomenon was significantly enhanced by increasing the pH of the feed solution. In sum, the results show that ammonia in aqueous solutions can be effectively and efficiently recovered when a Nafion membrane is used with the DCMD system in more alkaline conditions. Moreover, the physical and chemical stability of Nafion membrane was demonstrated by the post-MD FTIR, LEP and tensile strength detection which shown in **Fig. S1 and Table S5**.

Fig. 11. The ammonia recovery efficiency of the Nafion membranes as function of feed temperature under alkaline feed condition (pH 12).

4.3 Influence of Nafion on the membrane's ammonia recovery efficiency

To quantitatively analyze the effect of the Nafion on the membrane's ammonia recovery efficiency in the DCMD process, the Nafion factor K_N was estimated using Eq. (6). Here, K_{OV} was calculated using Eq. (2) based on the experimental results, K_m using Eq. (4), and K_f using

Eq. (5).

Table 2. Variations of K_{OV} , K_m , K_f , and K_N using the commercial PVDF membrane and Nafion membranes (0 to 8%) when the feed and permeate solutions were maintained at the same temperatures (45°C, 55°C, and 65°C) and the feed solution pH adjusted from 7 to 12.

Commercial PVDF under different feed pH (7, 9 and 12)				
	$1/K_{OV}(10^6\text{s/m})$	$1/K_m(10^6\text{s/m})$	$1/K_f(10^6\text{s/m})$	$K_N(10^6\text{s/m})$
S45	1.594/0.353/0.194	0.007/0.007/0.007	1.587/0.347/0.187	-
S55	1.499/0.339/0.190	0.007/0.007/0.007	1.492/0.332/0.183	-
S65	1.487/0.335/0.185	0.007/0.007/0.007	1.480/0.328/0.178	-
Nafion 0% membrane under different feed pH (7, 9 and 12)				
S45	1.580/0.321/0.158	0.002/0.002/0.002	1.579/0.319/0.157	-
S55	1.482/0.312/0.157	0.002/0.002/0.002	1.480/0.310/0.156	-
S65	1.459/0.304/0.156	0.002/0.002/0.002	1.457/0.302/0.154	-
Nafion 6% membrane under different feed pH (7, 9 and 12)				
S45	0.904/0.215/0.072	0.001/0.001/0.001	1.579/0.319/0.157	0.676/0.105/0.086
S55	0.874/0.212/0.071	0.001/0.001/0.001	1.480/0.310/0.156	0.607/0.100/0.086
S65	0.852/0.210/0.070	0.001/0.001/0.001	1.457/0.302/0.154	0.607/0.094/0.086
Nafion 8% membrane under different feed pH (7, 9 and 12)				
S45	0.878/0.124/0.049	0.002/0.002/0.002	1.579/0.319/0.157	0.702/0.197/0.109
S55	0.831/0.123/0.049	0.002/0.002/0.002	1.480/0.310/0.156	0.651/0.189/0.108
S65	0.806/0.121/0.048	0.002/0.002/0.002	1.457/0.302/0.154	0.653/0.182/0.108

Table 2 shows the variations of $1/K_{OV}$, $1/K_m$, $1/K_f$, and K_N using the commercial PVDF membrane and Nafion membranes (0 to 8%) when the feed and permeate solutions were

maintained at the same temperatures (45°C, 55°C, and 65°C) and the feed solution pH adjusted from 7 to 12. In all experimental and simulation matrices, $1/K_{OV}$ decreases with an increase in the feed and permeate temperatures and the feed pH; meanwhile, $1/K_m$ insignificantly decreases with an increase in the feed and permeate temperatures. Here, $1/K_m$ does not take the feed pH into account. According to the predicted results, when the Nafion 0% membrane is employed, $1/K_f$ dominantly determines $1/K_{OV}$, and $1/K_m$ insignificantly affects the overall mass transfer coefficient.

The simulation model employed, which is Eq. (1)-(6) regarding the mass transfer coefficient of ammonia recovery, was validated with the reference data, and the maximum error percentage was 2.5% [5]. All the theoretical study has been conducted based on the experimental data to investigate the Nafion effect as a reducer of the mass transfer resistance. The predicted $1/K_{OV}$, $1/K_f$, and $1/K_m$ trends well-matched the report from published literature [5]. Furthermore, $1/K_{OV}$ and $1/K_f$ decrease greatly as the feed pH increases, compared to when the feed and permeate temperatures are increased. Thus, the temperature adjustment can only negligibly affect the ammonia recovery efficiency without the partial vapor pressure difference. Meanwhile, for the Nafion 6% and 8% membranes, $1/K_{OV}$ is significantly smaller compared to the Nafion 0% membrane. When the 8% Nafion coated membrane was employed with inlet feed and permeate temperature of 65°C and a feed pH of 12, the overall mass transfer resistance for ammonia recovery efficiency was reduced to a maximum of 69.2%, meaning that the Nafion coated membrane reduced the overall mass transfer resistance.

Comparing the effect on mass transfer resistances between the influence of Nafion and feed pH, the influence of feed pH on the reduction of the mass transfer resistance is much higher than the influence of the Nafion, clearly indicating that the influence of the feed pH is the

dominant factor in the reduction of mass transfer resistance. Furthermore, the influence of the hydrophobic membrane on the mass transfer resistance, $1/K_m$, did not affect the increase of the mass transfer resistance due to the application of this high performance hydrophobic membrane. The estimated absolute value of K_N of the Nafion 8% membrane is higher than that of the Nafion 6% membrane as shown in **Table. 2**.

Table 3. Variations of $1/K_{OV}$, $1/K_m$, $1/K_f$, and K_N using the Nafion membranes (0 to 8%) when the feed temperature is controlled from 45°C to 65°C and the permeate temperature is maintained at 25°C under feed pH ranging from 7 to 12.

Commercial PVDF under different feed pH (7, 9 and 12)				
	$1/K_{OV}(10^6\text{s/m})$	$1/K_m(10^6\text{s/m})$	$1/K_f(10^6\text{s/m})$	$K_N(10^6\text{s/m})$
D45	1.431/1.231/1.066	0.007/0.007/0.007	1.425/1.224/1.060	-
D55	0.341/0.305/0.297	0.007/0.007/0.007	0.334/0.298/0.290	-
D65	0.189/0.174/0.157	0.007/0.007/0.007	0.182/0.168/0.150	-
Nafion 0% membrane under different feed pH (7, 9 and 12)				
D45	1.415/0.318/0.155	0.002/0.002/0.002	1.414/0.316/0.153	-
D55	1.321/0.265/0.152	0.002/0.002/0.002	1.320/0.263/0.150	-
D65	1.004/0.240/0.141	0.002/0.002/0.002	1.002/0.238/0.140	-
Nafion 6% membrane under different feed pH (7, 9 and 12)				
D45	0.864/0.209/0.067	0.001/0.001/0.001	1.414/0.316/0.153	0.551/0.109/0.088
D55	0.772/0.178/0.060	0.001/0.001/0.001	1.320/0.263/0.150	0.549/0.087/0.091
D65	0.675/0.142/0.054	0.001/0.001/0.001	1.002/0.238/0.140	0.329/0.097/0.087
Nafion 8% membrane under different feed pH (7, 9 and 12)				
D45	0.846/0.122/0.039	0.002/0.002/0.002	1.414/0.316/0.153	0.569/0.196/0.115
D55	0.691/0.113/0.038	0.002/0.002/0.002	1.320/0.263/0.150	0.630/0.152/0.114
D65	0.618/0.104/0.036	0.002/0.002/0.002	1.002/0.238/0.140	0.386/0.136/0.106

Table 3 shows the variations of $1/K_{OV}$, $1/K_m$, $1/K_f$, and K_N using the commercial PVDF membrane and Nafion membranes (0 to 8%) at the inlet feed temperature ranging from 45°C to 65°C and a consistent permeate temperature of 25°C, with feed pH ranging from 7 to 12. The K_{OV} value of the Nafion 0% membrane was higher than the commercial PVDF membrane as with the results in Table 2, since the electrospun Nafion 0% membrane can obtain a higher porosity than the commercial membrane.

The change of transmembrane temperature insignificantly affected the values of $1/K_m$, and the values of $1/K_f$ also showed a similar trend. Similar to the results in Table 2, $1/K_{OV}$ decreases with an increase in the Nafion containing percentage, inlet feed temperature, and feed pH. However, $1/K_{OV}$ decreases more noticeably compared to the results of Table 2 under the same feed and permeate temperature condition, indicating that the partial vapor pressure difference between the feed and permeate sides, which is the driving force of the MD process, also affects the ammonia recovery efficiency. The reduction of the mass transfer resistance with Nafion effect increases maximum 75% at the 65°C and 25°C of inlet feed and permeate temperatures, respectively, and 12 of feed pH. The maximum reduction of mass transfer resistance with MD mode is 5% higher than without MD mode at S65 and 12 of feed pH (refer the Table 2).

In summary, the quantitative comparison study on the effects of the inlet temperature, feed pH, and Nafion containing percentage on the ammonia recovery efficiency revealed that the feed pH is discovered that the most important factor for improving the ammonia recovery efficiency. Also, the Nafion factor increased with an increase in the Nafion containing percentage and, surprisingly, showed higher performance at low feed pH than at higher feed pH. The overall

results showed that mass transfer resistance can be lowered by controlling the inlet temperature, feed pH, and Nafion containing percentage by increasing the driving force (water vapor pressure difference) of the MD process.

5. Conclusions

DCMD experiments were performed with the Nafion membrane using different feed and permeate temperatures, and several different feed pH conditions to investigate the membrane's potential for recovering ammonia. The results are summarized as follows.

1. Nafion was successfully coated on the E-PH membrane with the porous honeycomb structure, and Nafion-incorporated membranes exhibited better performance for recovering ammonia than the commercial PVDF membrane. Moreover, ammonia recovery using the DCMD system can be enhanced by adjusting the Nafion concentration of the membrane.

2. The ammonia recovery efficiency increased when the feed solution pH was increased in this study.

3. The Nafion concentration level in the membrane had a much greater effect on ammonia recovery than the feed temperature adjustment. When applying the Nafion membrane to the DCMD system, the optimum conditions in terms of Nafion concentration and feed temperature, etc. should be considered to create a synergy effect for ammonia recovery.

4. The theoretical analysis conducted in this study revealed that the Nafion factor can not only reduce the transfer resistance of the membrane but also contribute to the quantitative enhancement of the overall mass transfer associated with the ammonia recovery efficiency. Furthermore, the combination of the partial vapor pressure difference, which is the driving force

of MD process, and the Nafion containing membrane can be expected to render a significant increase in the ammonia recovery efficiency.

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Conflict of interest

The authors declare no competing financial interests.

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Highlight

1. Nafion-MWCNT composite PVDF membrane was fabricated by an electrospinning method.
2. Nafion-incorporated membranes exhibited three times higher ammonia recovery than a commercial PVDF membrane.
3. Nafion membranes suppress the negative effect of membrane structural resistance on ammonia recovery efficiency.
4. Nafion's effect on ammonia recovery efficiency was maximized when the Nafion 8% membrane was employed.