

# Influences of Permeate Solution and Feed pH on Enhancement of Ammonia Recovery from Wastewater by Negatively Charged PTFE Membranes in Direct Contact Membrane Distillation Operation

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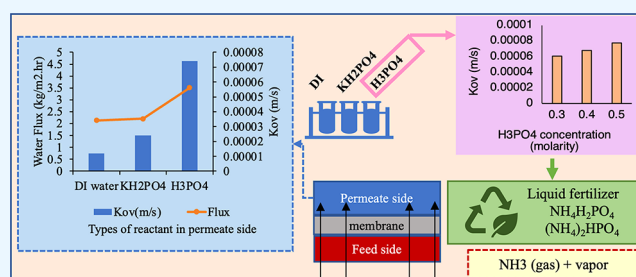
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**ABSTRACT:** This research investigated the feasibility of enhancing ammonia recovery from wastewater using a negatively charged poly(tetrafluoroethylene) (PTFE) membrane in a direct contact membrane distillation (DCMD) system. The influences of phosphate solution types (as the permeate solutions) and feed pH on ammonia recovery were analyzed. Three types of permeate solutions—DI water and two types of phosphate solutions ( $\text{H}_3\text{PO}_4$  and  $\text{KH}_2\text{PO}_4$ )—were investigated for recovery of ammonia gas on the permeate side. From the obtained results, the  $\text{H}_3\text{PO}_4$  solution was found to be the most suitable permeate solution to recover ammonia gas in the DCMD operation with the highest overall ammonia mass transfer coefficient of  $7.4 \times 10^{-5}$  m/s, compared to values of  $1.2 \times 10^{-5}$  and  $2.4 \times 10^{-5}$  m/s for DI water and  $\text{KH}_2\text{PO}_4$  solution, respectively. Moreover, an increase in the  $\text{H}_3\text{PO}_4$  concentration from 0.3 to 0.5 M in the permeate solution also could significantly enhance ammonia recovery. With an increase in the feed pH from 10.0 to 11.8, the ammonia recovery could be enhanced to 92.98% at a pH of 11.8. Liquid ammonium phosphate fertilizer could be produced by the DCMD system with the use of 0.5 M  $\text{H}_3\text{PO}_4$  solution. Therefore, the DCMD process using a negatively charged PTFE membrane with an appropriate permeate solution is one of the challenging processes for ammonia recovery from wastewater to promote the circular economy concept.



## 1. INTRODUCTION

Ammonia has been recognized as an important nitrogen pollutant that is found in various wastewater sources such as domestic, agriculture, and industrial discharges. The surplus amount of ammonia is the source of nutrient existence in water resources. The number of contaminated ammonia ions in a receiving water body may vary in accordance with their discharge sources. Eutrophication of surface water is caused by the enrichment of water by ammonia and other nutrients. The excessive growth of algae is one of the examples by ammonia solubility in water as well as its chemical reactivity.<sup>1</sup> Fish often suffer from ammonia toxicity in the water at higher pH due to the higher concentration of the un-ionized form of ammonia.<sup>2</sup> Moreover, un-ionized ammonia that is released into the atmosphere can also be oxidized by active chemical species, resulting in the formation of nitric acid. This results in acid rain, which increases the acidification of soil and water.

At present, more stringent regulations on residual ammonia concentration in effluents discharged from various pollution sources have been provided by the National Environmental Laws of Thailand to minimize the eutrophication problem. Currently, there are various ammonia removal technologies such as biological treatment, ion-exchange method, advanced oxidation process, adsorption, air stripping, membrane

processes, and so on. Indeed, there are many conventional approaches to removing ammonia from wastewater; however, a secondary waste stream is generated on the release of nitrate to water resources using traditional aerobic treatment processes. The technology of ammonia removal depends on the contamination level of wastewater to be treated, plant safety and regulatory considerations, and plant site.<sup>3–5</sup>

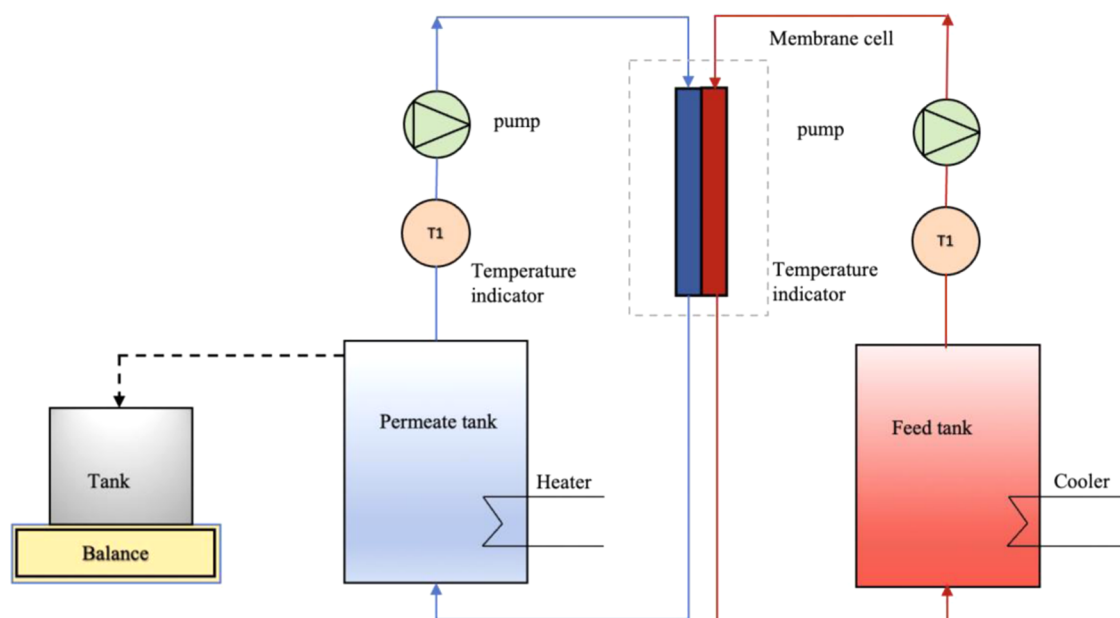
Membrane technology for nitrogen removal has seen improvements in the last two decades with new materials and developed processes. The application of the membrane process is intended for various fields of application with different purposes.<sup>6</sup> Membrane contactor technology can recover ammonia in the form of ammonium salts by a liquid–liquid or liquid–gas mass transfer system without dispersion from one state to another state.<sup>7</sup> In the membrane contactor, the receiving solution used is an acid to capture the ammonia passed through the membrane pore. Darestani et al.<sup>8</sup>

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**Figure 1.** Flow diagram of the DCMD experimental setup used in this study.

reviewed the study on membrane contactor research and summarized that the concentration of permeate acid could affect the removal of ammonia in the membrane contactor test. Unlike a membrane contactor, membrane distillation can drive the vapor molecules of more volatile compounds from the feed side to the permeate side by the temperature differences between the liquid phases on both sides of the MD membrane.<sup>2</sup> On the permeate side, the escaped vapors are condensed or removed in the vapor phase out of the membrane module. The higher feed temperature can result in a higher ammonia removal efficiency.<sup>9</sup>

Among the membrane distillation processes, the direct contact membrane distillation (DCMD) process normally uses distilled water for the condensation side to condense the escaped vapor. For ammonia removal purposes, some experiments also used an acidic solution on the permeate side to capture the volatile ions as the membrane contactor.<sup>10</sup> Sulfuric acid was used in membrane distillation for ammonia recovery from agricultural waste.<sup>11</sup> Qu et al.<sup>12</sup> proved that the highest ammonia transfer could be obtained when using  $\text{H}_2\text{SO}_4$  solution as the permeate solution in the DCMD system compared with the result of the membrane contactor and the ordinary DCMD process. Other permeate solutions such as  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$ , or a mixture of both were also proposed as stripping solutions for the membrane contactor process.<sup>13</sup> In recent years, the integration of the membrane with the adsorption process has also become an efficient way to remove ammonia during the filtration process. The ion-exchange mechanisms might be used in the treatment system.<sup>14</sup>

There are some previous research works on ammonia removal with membrane distillation using the acid on the permeate side. However, few studies have focused on the effects of types of phosphate solutions (as the permeate solutions) and feed pH on the enhancement of ammonia recovery by the negatively charged poly(tetrafluoroethylene) (PTFE) membrane in the direct contact membrane distillation (DCMD) system. The electrostatic interaction between the ammonium ion in the feed wastewater and the negative charge on the surface of the PTFE membrane might also be involved

in the driving force for ammonia mass transport through the DCMD system. A previous work on the adsorptive membrane filtration system with a negatively charged surface indicated that the membrane surface could also react with cations in the solution.<sup>15</sup>

This research work aims to investigate the effects of permeate solution type and feed pH on the enhancement of ammonia recovery from wastewater by a negatively charged PTFE membrane in the direct contact membrane distillation (DCMD) system. The mass transfer coefficients of the ammonia flux at different permeate solutions and feed pH values were also calculated to indicate the enhanced ammonia recovery performance. Finally, liquid fertilizer could be produced from the ammonia recovery using the DCMD system. Therefore, the DCMD process with an appropriate permeate solution and feed pH is one of the challenging processes for ammonia recovery from wastewater to promote the circular economy concept.

## 2. MATERIALS AND METHODS

**2.1. Experimental Setup.** The experimental setup flow diagram of the direct contact membrane distillation system is illustrated in Figure 1. The membrane was sandwiched between the feed compartment and the permeate compartment. The feed water was circulated as hot water, while the permeate water was circulated as cold water on the other side. Two peristaltic pumps were used to transport the water on each side. The accumulated permeate water was measured by the electronic balance from A&D Company (GX-6100) within the time interval. The operating condition of the DCMD system is shown in Table 1.

**2.2. Membrane.** The experiments were carried out in the direct contact membrane distillation system. A hydrophobic poly(tetrafluoroethylene) (PTFE) membrane (Sterlitech Corporation) was used in this direct contact membrane distillation study since the PTFE membrane has low surface energy compared with other hydrophobic materials.<sup>16</sup> It can give good wetting resistance and stability under different operation

**Table 1. Operating Condition of the DCMD Experimental Run**

parameters	values	unit
feed temperature	60	°C
permeate temperature	20	°C
feed flow rate	1	L/min
permeate flow rate	0.5	L/min

conditions.<sup>17</sup> The total membrane surface area is 140 cm<sup>2</sup>, and the pore size is 0.1 μm.

**2.3. Characterization of Membrane Surface Morphology.** The surface morphology and chemical composition of the origin membrane were assessed using scanning electron microscopy (SEM, S-3400N, Hitachi, Japan) in conjunction with energy-dispersive X-ray spectroscopy (EDX, Apollo X, EDAX). Scans were obtained with an electron accelerating voltage of 15 kV, a tilt angle of the specimen stage of 0°, a working distance of 10 mm, and a vacuum degree of 30 Pa. ζ-Potential measurements were performed by a ζ-potential instrument (Nano Brook ZetaPlus). The hydrophilicity of membrane active surfaces was evaluated by the water contact angle using a contact angle analyzer (CAM-PLUS IMAGE, C1221105, Tantec Inc.). The measurements were performed at three random locations for each membrane sample, with the average values reported in this research.

**2.4. Chemical and Analytical Methods.** The feed ammonia solution was prepared using ammonium chloride solution to obtain an ammonia concentration of 53 mg N/L, which is considered the maximum ammonia concentration range usually found in domestic wastewater in Thailand.

**2.5. Experimental Procedure.** The experimental runs were designed to obtain the mass transfer coefficient and to investigate the influence of feed pH and permeate phosphate solution on ammonia recovery by the negatively charged PTFE membrane in the DCMD system. The temperature was controlled by the hot water bulk (WNB-7 from memmert) and the chiller (Xi'an Heb Biotechnology Co., Ltd. (CCA-420)). Sodium hydroxide solution was also used to adjust the pH of the feed water. The pH measurement was carried out by a pH meter, and the nitrogen concentration was carried out by SEM (HI 4101 Ammonia Ion Selective Electrode). The molarity of ammonia on the permeate side was also investigated. The water temperature of the feed solution was kept at 60 °C and that of the permeate side was kept at 20 °C.

**2.5.1. Study on the Effect of Permeate Solution on Ammonia Recovery by the DCMD System.** In this experiment, DI water and two types of phosphate solutions were considered. The first permeate phosphate solution was a synthetic wastewater, prepared from a KH<sub>2</sub>PO<sub>4</sub> solution to have a maximum concentration of 15 mg P/L, which is in the typical phosphorus concentration range of 3–15 mg P/L, which was often found in treated domestic effluents.<sup>18,19</sup> The second phosphate solution was phosphoric acid, H<sub>3</sub>PO<sub>4</sub>, which is in the form of an acid solution. A previous technical report on the application of hollow-fiber membrane contactors for ammonia removal suggested the use of 0.33 M H<sub>3</sub>PO<sub>4</sub> for ammonia absorption.<sup>20</sup> In this study on permeate solution concentration, H<sub>3</sub>PO<sub>4</sub> solution was selected and the concentrations were varied to 0.3, 0.4, and 0.5 M to investigate the potential of ammonia recovery by the DCMD system. Also, DI water was used as another permeate solution to compare the performance of ammonia recovery with both permeate

phosphate solutions. The sample to detect the concentration of ammonia was taken at a regular time interval (every 30 min). The measured concentration was used to determine the mass transfer coefficient by the equations in Section 2.6.

**2.5.2. Study on the Effect of Feed pH on Ammonia Recovery by the DCMD System.** The feed ammonia solution was adjusted by NaOH to have different pH values of 10, 11, and 11.8. H<sub>3</sub>PO<sub>4</sub> solution with the concentration of 0.5 M was selected as the permeate phosphate solution. An increase in the feed pH was expected to enhance the ammonia stripping process; as a result, ammonia recovery might be enhanced.

**2.6. Theoretical Framework.** There are two forms of ammonia nitrogen in water: volatile ammonia and ammonium ion forms. The temperature and pH values of the aqueous solution are the main parameters for the removal of ammonium ions from wastewater. The ammonia solubility in water decreases on reducing the temperature. However, increasing only the temperature cannot release all of the dissolved ammonia because of the formation of an unstable ammonia ion, NH<sub>4</sub><sup>+</sup>. It can be seen in the following chemical equation.



At a temperature of 25 °C, the equilibrium constants for this reaction are  $K_1 = 1.8 \times 10^{-5}$  toward NH<sub>4</sub><sup>+</sup> formation and  $K_2 = 5.6 \times 10^{-10}$  toward un-ionized ammonia formation. As with the ammonia–ammonium equilibrium with the pH value, the ammonium ion form is more than the gaseous ammonia form while the condition of the pK<sub>a</sub> is lower than 9.3. When the solution pH is higher than the value of pK<sub>a</sub>, the solution tends to be enriched with gaseous ammonia. This may cause higher ammonia removal efficiency. It can be mentioned that the vapor pressure of the ammonia solution is greater than that of the water.<sup>21,22</sup>

The overall mass transfer coefficient of ammonia gas across the MD membrane,  $K_{\text{ov}}$ , can be calculated as

$$\frac{1}{K_{\text{ov}}} = \frac{1}{k_s} + \frac{1}{k_m} \quad (2)$$

where  $k_s$  and  $k_m$  are the mass transfer coefficients on the feed side and within the membrane pores, respectively. The mass transfer resistance on the permeate side can be neglected as the concentration of ammonia on the permeate side should be very close to zero due to the reaction with acid.<sup>23</sup> The mass flux of ammonia gas (NH<sub>3</sub>) across the MD membrane,  $M_{\text{NH}_3}$ , can be estimated as follows

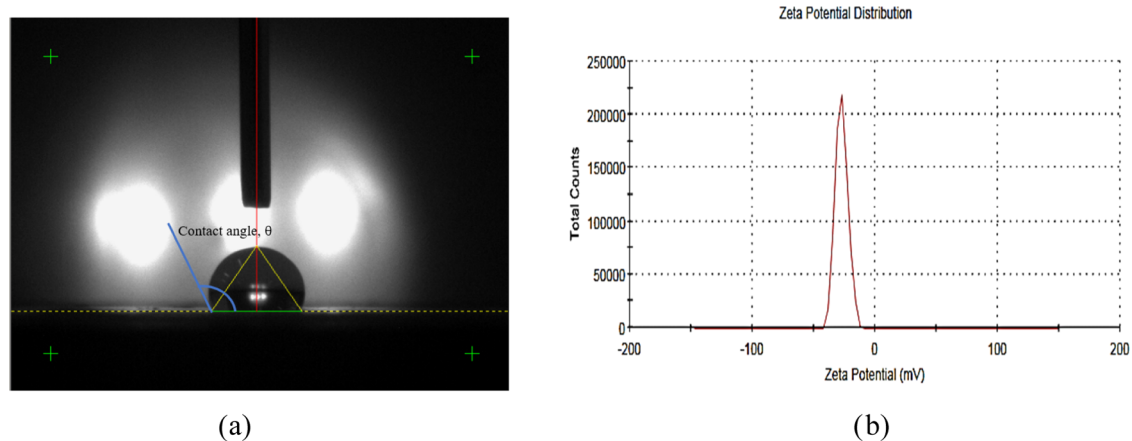
$$M_{\text{NH}_3} = K_{\text{ov}} C_f \quad (3)$$

$$-F_f dc = K_{\text{ov}} C_f dA \quad (4)$$

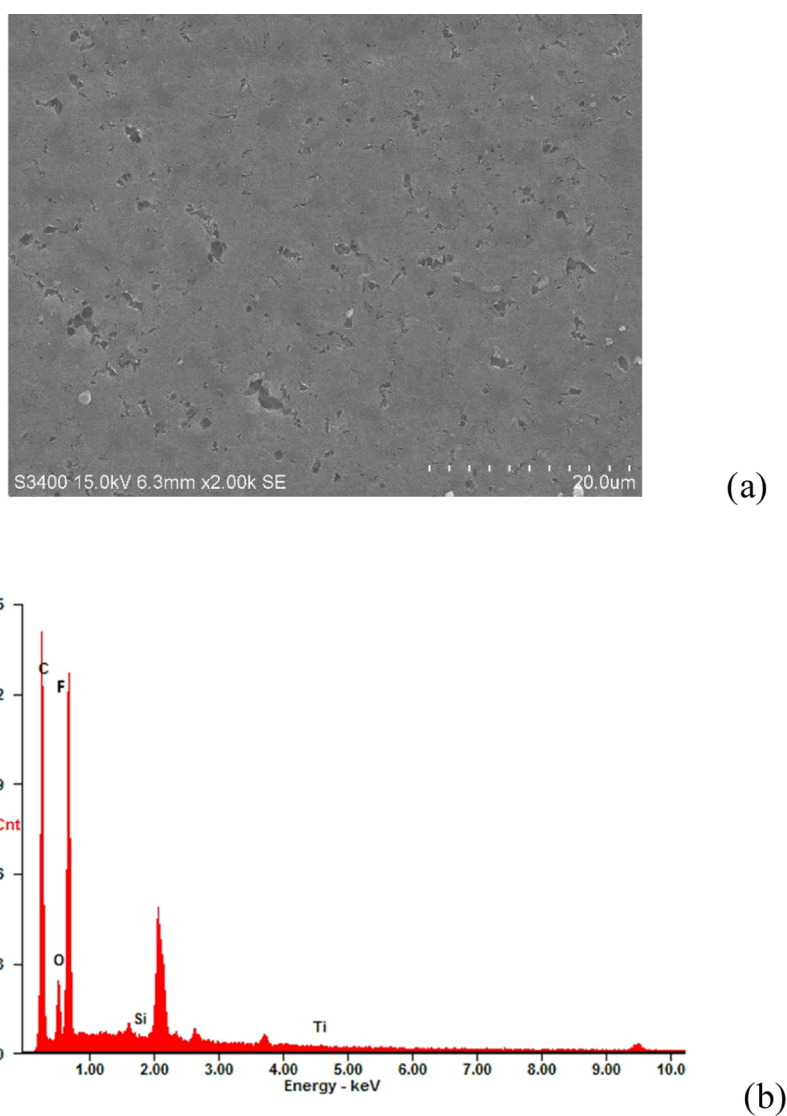
The ammonia recovery by the DCMD membrane was reported to follow first-order kinetics, as shown in the following equation<sup>2,12</sup>

$$\ln(C_0/C_t) = K_{\text{ov}} A t / V \quad (5)$$

where  $M_{\text{NH}_3}$  is the ammonia mass flux across the MD membrane;  $F_f$  is the flow rate of the feed;  $C_f$  is the concentration of NH<sub>3</sub> across the membrane on the feed side;  $C_0$  and  $C_t$  are the feed ammonia concentrations at the initial time and the ammonia concentration after time ( $t$ ) of the experiment, respectively;  $V$  is the initial liquid volume of the feed solution;  $A$  is the membrane area; and  $t$  is the time of the



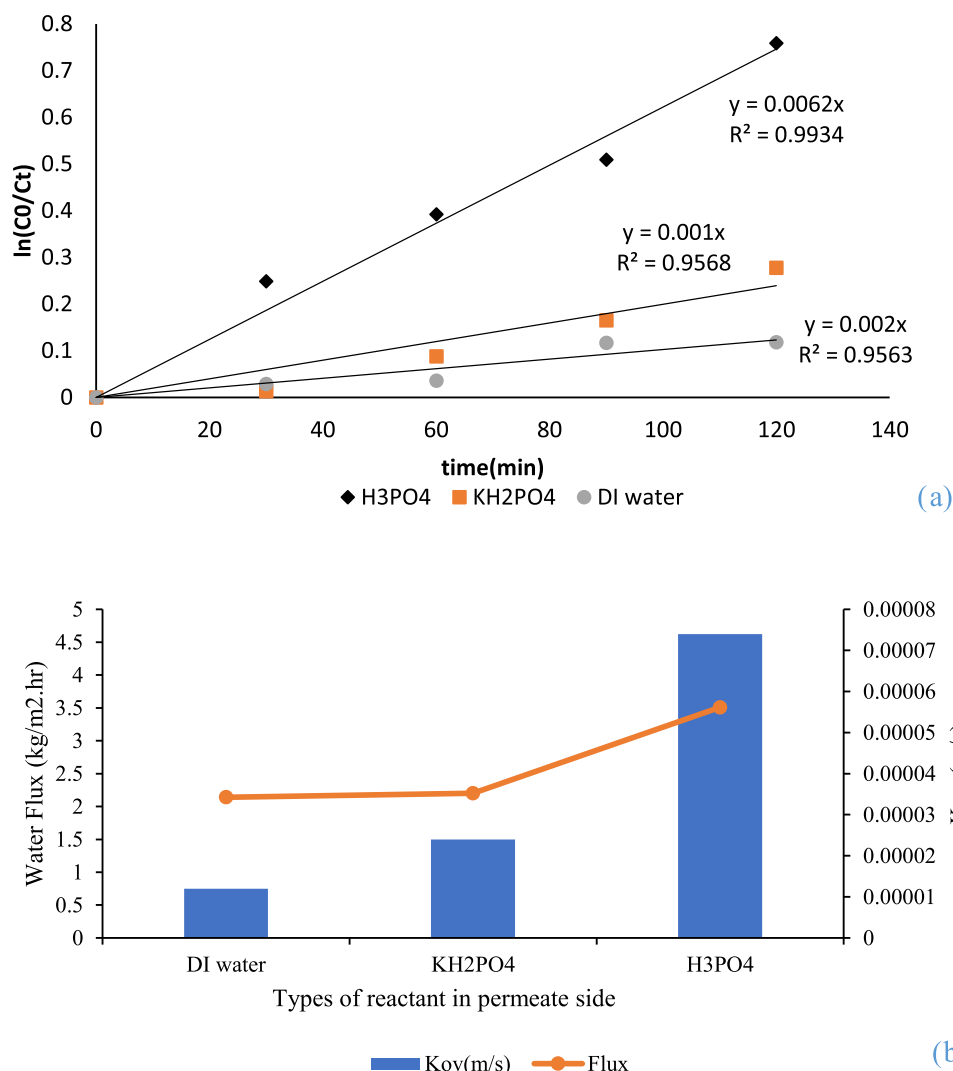
**Figure 2.** Characterization of the PTFE membrane surface for DCMD system operation: (a) contact angle measurement and (b)  $\zeta$ -potential measurement.



**Figure 3.** SEM-EDX measurement of the membrane surface: (a) SEM image and (b) EDX analysis.

experimental run. The overall mass transfer coefficient of the DCMD membrane for ammonia,  $K_{ov}$ , could be obtained from the experimental results of the DCMD membrane system.

Absorption of ammonia gas on the permeate side by phosphoric acid,  $H_3PO_4$ , as the permeate solution is an alternative method to recover ammonia gas as ammonium phosphate fertilizer. The dissociation of triprotic  $H_3PO_4$  acid in

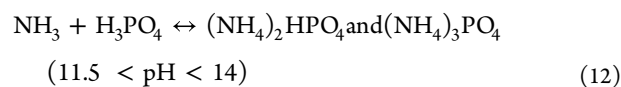
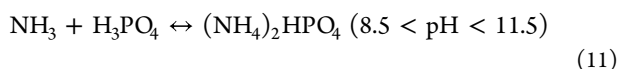
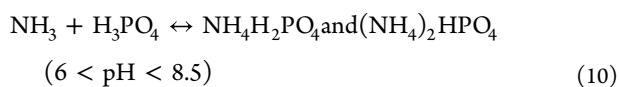
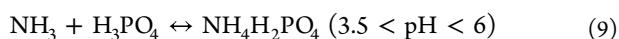


**Figure 4.** Influence of permeate solution type on the mass transfer coefficient,  $K_{ov}$ , and water flux: (a) relationships between  $\ln(C_0/C_t)$  and the filtration time for different permeate solution types; and (b) obtained value of  $K_{ov}$  and flux with different permeate solution types.

water plays an important role in fixing ammonia gas, which is shown below



The absorption reaction of ammonia gas with phosphoric acid as the permeate solution makes it possible to form this ammonium phosphate based on the aquatic phosphate chemistry principle.<sup>24</sup>



The performance of ammonia removal by the negatively charged PTFE membrane in direct contact membrane distillation was investigated. The removal efficiency of ammonia could be defined as

$$R (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (13)$$

where  $C_0$  and  $C_t$  are the ammonia concentrations at the initial time and after time ( $t$ ) in the feed wastewater, respectively.

The average permeate water flux is calculated as

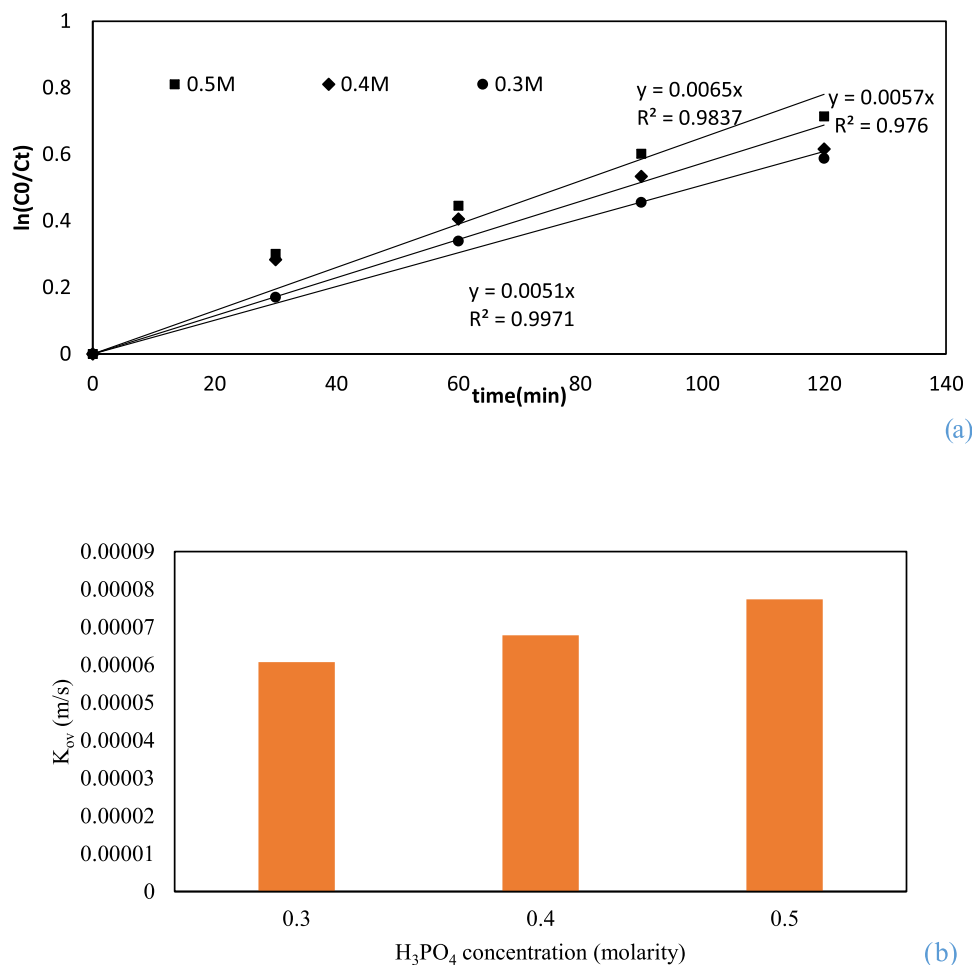
$$J = \frac{m}{A \cdot t} \quad (14)$$

where  $J$  is the water flux (kg/m<sup>2</sup>.s),  $m$  is the mass of water accumulation (kg),  $A$  is the membrane area (m<sup>2</sup>), and  $t$  is the operating time (s) during water accumulation.

**Table 2. Mass Balance of Ammonia Recovery in Different Permeate Solutions**

permeate solution	initial $\text{NH}_4^+$ (mg/L)	remaining $\text{NH}_4^+$ after 120 min (mg/L)	$\text{NH}_4^+$ loss <sup>a</sup> (mg/L)	$\text{NH}_4^+$ recovered in permeate (mg/L)	$\text{NH}_4^+$ removal efficiency <sup>b</sup> (%)	$\text{NH}_4^+$ recovery efficiency <sup>c</sup> (%)	ammonia flux (kg/m <sup>2</sup> -h)
DI	53	42	11	8.5	20.75	77.27	0.0013
$\text{KH}_2\text{PO}_4$	53	38	15	12.2	28.30	81.33	0.0018
$\text{H}_3\text{PO}_4$	53	24.5	28.5	26.5	53.77	92.98	0.0039

<sup>a</sup> $\text{NH}_4^+$  loss = initial  $\text{NH}_4^+$  – remaining  $\text{NH}_4^+$  after 120 min. <sup>b</sup> $\text{NH}_4^+$  removal efficiency = ( $\text{NH}_4^+$  loss/initial  $\text{NH}_4^+$ )  $\times$  100. <sup>c</sup> $\text{NH}_4^+$  recovery efficiency = ( $\text{NH}_4^+$  recovered in the permeate solution/ $\text{NH}_4^+$  loss)  $\times$  100.



**Figure 5.** Influence of  $\text{H}_3\text{PO}_4$  concentration on the obtained mass transfer coefficient ( $K_{ov}$ ): (a) relationship between  $\ln(C_0/C_t)$  and time at different  $\text{H}_3\text{PO}_4$  concentrations; and (b) obtained  $K_{ov}$  value as a function of  $\text{H}_3\text{PO}_4$  concentration.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of Membrane Surface Morphology

Contact angle measurement is the common parameter to determine the membrane hydrophobicity property. The contact angle is the angle between the surface of the wetted solid and a line tangent to the curved surface of the drop at the point of the three-phase contact. To investigate the hydrophobicity and wettability of the negatively charged PTFE membrane, the contact angle measurement was also done to analyze the hydrophobicity of the membrane. The contact angle measurement for the virgin membrane PTFE membrane is shown in Figure 2a. The active layer of the membrane surface had a contact angle of  $99.83^\circ$ , indicating the property of hydrophobicity of the membrane surface. The hydrophobic property of the membrane material made it reject water and nonvolatile components and allow the passage of ammonia gas through the membrane pore. The electrical potential of the

surface charge of the negatively charged PTFE membrane was measured by the  $\zeta$ -potential difference. The determination of the  $\zeta$ -potential is used to evaluate the surface charge of a membrane and the possible interaction between the particles (foulants) and the membrane surface. The  $\zeta$ -potential value of the membrane is  $-23.18$  mV, as shown in Figure 2b. The result shows that the membrane surface has a negative charge characteristic.

To investigate the morphology of membrane surfaces, scanning electron microscope (SEM) imaging was also undertaken. The surface of the membrane morphology was captured by SEM imaging. EDX measurement was also performed. The surface of the porous negatively charged PTFE membrane is shown in Figure 3a. The EDX result is also shown in Figure 3b.

The composition of elements on the surface of the negatively charged PTFE membrane is shown in Figure 3b.

**Table 3. Mass Balance of Ammonia Recovery at Different H<sub>3</sub>PO<sub>4</sub> Concentrations**

H <sub>3</sub> PO <sub>4</sub> conc. (M)	initial NH <sub>4</sub> <sup>+</sup> (mg/L)	remaining NH <sub>4</sub> <sup>+</sup> after 120 min (mg/L)	NH <sub>4</sub> <sup>+</sup> loss <sup>a</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> recovered in permeate (mg/L)	NH <sub>4</sub> <sup>+</sup> removal efficiency <sup>b</sup> (%)	NH <sub>4</sub> <sup>+</sup> recovery efficiency <sup>c</sup> (%)	ammonia flux (kg/m <sup>2</sup> -h)
0.3	53	30.3	22.7	19.9	42.83	87.67	0.003
0.4	53	29	24	21.2	45.28	88.33	0.0031
0.5	53	25.9	27.1	24.5	51.13	90.41	0.0036

<sup>a</sup>NH<sub>4</sub><sup>+</sup> loss = initial NH<sub>4</sub><sup>+</sup> – remaining NH<sub>4</sub><sup>+</sup> after 120 min. <sup>b</sup>NH<sub>4</sub><sup>+</sup> removal efficiency = (NH<sub>4</sub><sup>+</sup> loss/initial NH<sub>4</sub><sup>+</sup>) × 100. <sup>c</sup>NH<sub>4</sub><sup>+</sup> recovery efficiency = (NH<sub>4</sub><sup>+</sup> recovered in the permeate solution/NH<sub>4</sub><sup>+</sup> loss) × 100.

The main elements on the membrane surface were C (41.39%), O (6.76%), Si (14.53%), and F (37.34%).

**3.2. Effect of Permeate Solution Type on Ammonia Recovery by the DCMD System.** **3.2.1. Type of Permeate Solution.** In this study, three different permeate solutions (DI water, 0.3 M H<sub>3</sub>PO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> solution with a concentration of 15 mg P/L) were used to investigate the potential of ammonia recovery by the negatively charged PTFE membrane in the direct contact membrane distillation system. Typical DI water was used as the permeate solution to induce water vapor in DCMD for water recovery. The mass transfer coefficient of the DCMD system was also analyzed. According to eq 5, the relationships between ln(C<sub>0</sub>/C<sub>t</sub>) values and the interval time were plotted to obtain the overall mass transfer coefficient, as shown in Figure 4.

Figure 4a shows the first-order equation for the relationships between ln(C<sub>0</sub>/C<sub>t</sub>) and the time, and then, the mass transfer coefficient (K<sub>ov</sub>) was determined. The maximum slope was obtained with the H<sub>3</sub>PO<sub>4</sub> solution for ammonia recovery, as illustrated in Figure 4a. The overall mass transfer coefficient, K<sub>ov</sub>, was also calculated for each permeate solution. The K<sub>ov</sub> values for different permeate solutions were 1.2 × 10<sup>-5</sup> m/s for DI water, 2.4 × 10<sup>-5</sup> m/s for the KH<sub>2</sub>PO<sub>4</sub> permeate solution, and 7.4 × 10<sup>-5</sup> m/s for the H<sub>3</sub>PO<sub>4</sub> permeate solution under the same operating pH (pH 11.8). A previous work had reported that the K<sub>ov</sub> value of the DCMD using a H<sub>2</sub>SO<sub>4</sub> reagent solution (5.57 × 10<sup>-5</sup> m/s) was higher than that of DI water in the normal DCMD process (0.81 × 10<sup>-5</sup> m/s).<sup>12</sup> As can be seen in Figure 4b, the permeate water flux was different using different permeate solutions. The water permeate flux with DI water permeate showed the lowest value in this experiment. However, the permeate flux was the highest (3.51 kg/m<sup>2</sup>-h) when H<sub>3</sub>PO<sub>4</sub> solution was used as the permeate solution on the permeate side. The buffer solution of KH<sub>2</sub>PO<sub>4</sub> (2.2 kg/m<sup>2</sup>-h) resulted in nearly the same water flux as that of the DI water test (2.14 kg/m<sup>2</sup>-h). Therefore, the mobility of water vapor from the feed solution can be enhanced by the permeate solution on the permeate side. The ammonia recovery on the permeate side with different permeate solutions was calculated in the mass balance, as shown in Table 2. The remaining NH<sub>4</sub><sup>+</sup> on the feed side was different under the same operating time. During the experiment, a certain amount of NH<sub>4</sub><sup>+</sup> was lost. This could be due to the volatilization. However, most of the ammonia captured by the permeate solution and the recovery rate can be seen with the use of a H<sub>3</sub>PO<sub>4</sub> solution, resulting in the highest NH<sub>4</sub><sup>+</sup> recovery efficiency (92.98%) and a recovery rate of 28.5 mg/L at the end of the experiment.

This means that the H<sub>3</sub>PO<sub>4</sub> solution with an acidic pH range can absorb more amount of ammonia gas than DI water and the KH<sub>2</sub>PO<sub>4</sub> solution. Hence, NH<sub>4</sub><sup>+</sup> recovery efficiency depends on the type of permeate solution and its ammonia fixation capacity. Moreover, the reaction between the

ammonium ion and phosphate can form the ammonium phosphate compound in the permeate solution. Therefore, the H<sub>3</sub>PO<sub>4</sub> solution is considered the best permeate solution among the three permeate solutions considered in this study. Damtie et al.<sup>24</sup> reported that when the ammonia from the urine was surplus in the permeate acid solution, the pH level was increased. This could affect the ammonium transfer gradient.

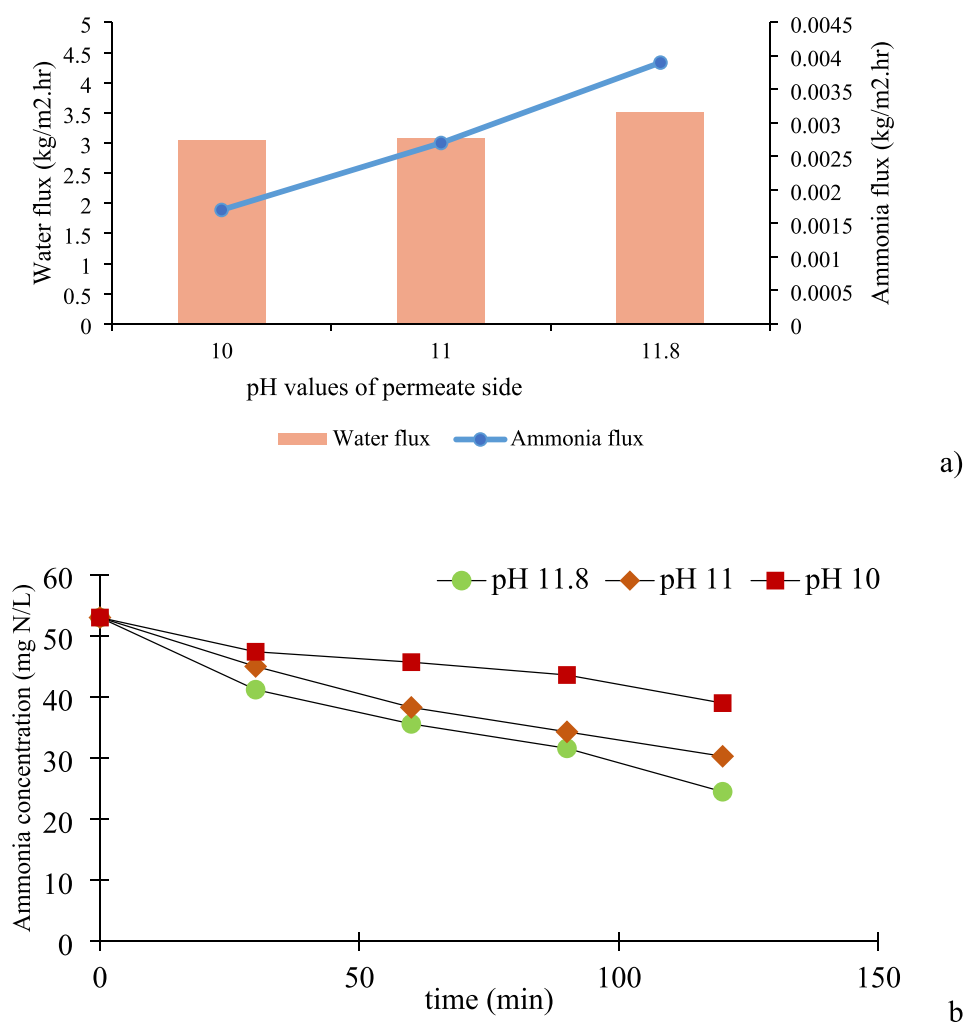
**3.2.2. Concentration of the Selected Permeate Solution.** From the previous experiment in Section 3.2.1, the H<sub>3</sub>PO<sub>4</sub> solution was found to be the most efficient permeate solution. Hence, a study on varying the H<sub>3</sub>PO<sub>4</sub> concentration as the suitable permeate solution was further performed to improve the ammonia recovery efficiency. The concentrations of 0.3, 0.4, and 0.5 M of H<sub>3</sub>PO<sub>4</sub> solution were investigated under the same operating systems (feed solution pH at 11.8). From the experimental results, the plotting of ln(C<sub>0</sub>/C<sub>t</sub>) and time is shown in Figure 5a. The transportation of ammonia from the feed side to the permeate side by partial pressure difference can lead to reaction with the phosphate ion, and then, the reaction will produce diammonium phosphate, as described by the following equation.



The mass transfer coefficient could be enhanced from 6.1 × 10<sup>-5</sup> to 7.7 × 10<sup>-5</sup> m/s when the H<sub>3</sub>PO<sub>4</sub> concentration was increased from 0.3 to 0.5 M, as shown in Figure 5b. The highest mass transfer coefficient could be achieved with the use of H<sub>3</sub>PO<sub>4</sub> at a concentration of 0.5 M after 120 min of operating time. The ammonia recovery in the permeate solution with different H<sub>3</sub>PO<sub>4</sub> concentrations had been illustrated in the mass balance as shown in Table 3.

The highest NH<sub>4</sub><sup>+</sup> recovery efficiency of 90.41% could be achieved with a H<sub>3</sub>PO<sub>4</sub> concentration of 0.5 M. Therefore, a higher H<sub>3</sub>PO<sub>4</sub> concentration could enhance more ammonia absorption and the formation of the ammonium phosphate compound. Some previous research works on the membrane contactor process reported that highly diluted and concentrated acid solution could reduce the ammonia capturing.<sup>23,25</sup> In the case of a strong acid, viscosity and concentration polarization were increased significantly, which then could reduce ammonia migration through the membrane contactor. However, in the case of the weak acid, the pH level significantly increased, and this phenomenon could cause the reduction of ammonia transfer by the pH gradient.

**3.3. Effect of Feed pH on Ammonia Recovery by the DCMD System Using H<sub>3</sub>PO<sub>4</sub> Permeate Solution.** From Section 3.2, the appropriate permeate solution for ammonia recovery by the DCMD system was found to be 0.5 M H<sub>3</sub>PO<sub>4</sub> solution. Then, H<sub>3</sub>PO<sub>4</sub> solution was used as the permeate phosphate solution for this investigation. Further investigation on the influence of feed pH on ammonia recovery by the negatively charged PTFE membrane in the DCMD system was



**Figure 6.** Influence of feed pH on the mass transfer coefficient,  $K_{ov}$ , and water flux: (a) water flux and ammonia flux at different feed pH; and (b) ammonia loss by time as a function of feed pH.

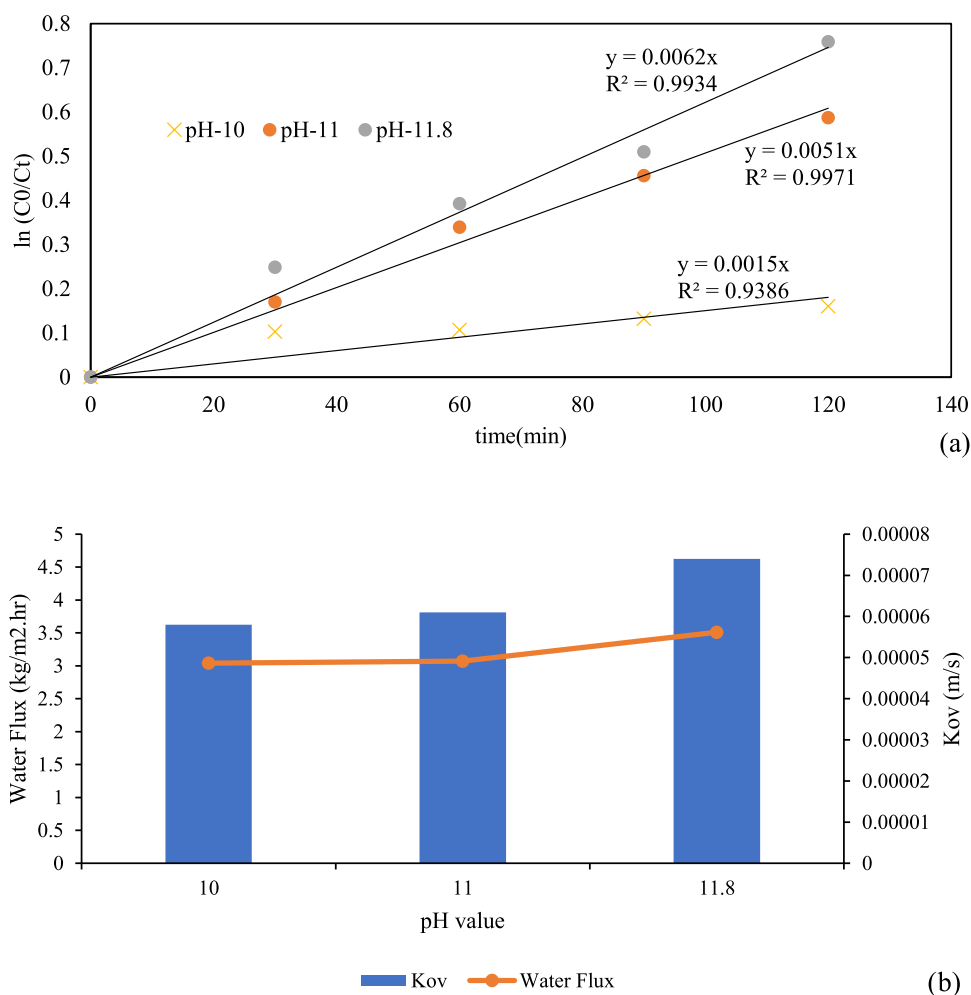
performed. Ammonia recovery in the permeate water increased with a higher feed pH. An increase in the feed pH tends to shift the chemical equilibrium in eq 1 to the left due to the greater formation of un-ionized  $\text{NH}_3$ . This phenomenon was investigated for the removal of ammonia in this DCMD process. NaOH reagent was used to raise the pH of the feed ammonium solution to pH 10, 11, and 11.8. The water flux was calculated by the accumulation of permeate from water vapor transportation through the membrane pore due to the vapor pressure difference, and then, it was condensed on the permeate side. For the obtained water fluxes of the DCMD system, they were 3.04, 3.07, and 3.51  $\text{kg/m}^2\cdot\text{h}$  with feed pH values of 10, 11, and 11.8, respectively, as shown in Figure 6a. Hence, a slightly higher water flux was found with the increase of feed pH from 10 to 11.8. The reason might be that an increase in the feed pH by NaOH could reduce the membrane fouling of the negatively charged PTFE membrane as well. Indeed, NaOH is a chemical that has been used to clean the PTFE to recover the membrane permeate flux.<sup>26</sup> The correlation between ammonia flux and pH of the feed side can also be seen in Figure 6a. An increased amount of ammonia transfer was found when the feed pH increased from 10 to 11.8. The ammonia vapor flux was in general very low (less than 0.004  $\text{kg/m}^2\cdot\text{h}$ ) in comparison with that of the water vapor ( $\sim 3.5$   $\text{kg/m}^2\cdot\text{h}$ ) at the same operating parameters. The

feed pH of 11.8 could achieve the highest reduction in ammonium concentration in the feed solution within the 120 min of operating time, as shown in Figure 6b.

As with the ammonia–ammonium equilibrium, the pH value can influence the formation of ammonium ions. The increased pH of the feed wastewater has a high tendency to convert ammonium ions to gaseous ammonia. As a result, the membrane phase resistance can be significantly reduced due to less interaction between the  $\text{NH}_4^+$  ion and the negative charge on the membrane surface. Therefore, when the pH increased to 11.8, more ammonium ( $\text{NH}_4^+$ ) ions were converted to ammonia gas ( $\text{NH}_3$ ), resulting in less adsorption between the  $\text{NH}_4^+$  ion and the negatively charged surface of the PTFE membrane. Ratanatamskul et al.<sup>27</sup> proposed the selectivity mechanism of ion transport through the negatively charged NF membrane. Some cations could be adsorbed on the negative charge membrane, resulting in membrane flux reduction in long-term operation.

From the experimental results, the plotting of  $\ln(C_0/C_t)$  and time is shown in Figure 7a. According to Figure 7b, the feed pH can influence the flux and mass transfer coefficient for ammonia removal by the DCMD process. The highest mass transfer coefficient of  $7.4 \times 10^{-5}$  m/s could be obtained with the feed pH of 11.8, while mass transfer coefficients of  $6.1 \times 10^{-5}$  and  $5.8 \times 10^{-5}$  were obtained with feed pHs of 11 and 10,





**Figure 7.** Influence of feed pH on the mass transfer coefficient,  $K_{ov}$ , and water flux: (a) relationships between  $\ln(C_0/C_t)$  and filtration time at different feed pHs, and (b) obtained value of  $K_{ov}$  and flux for different feed pHs.

**Table 4. Mass Balance of Ammonia Recovery at Different Feed pHs**

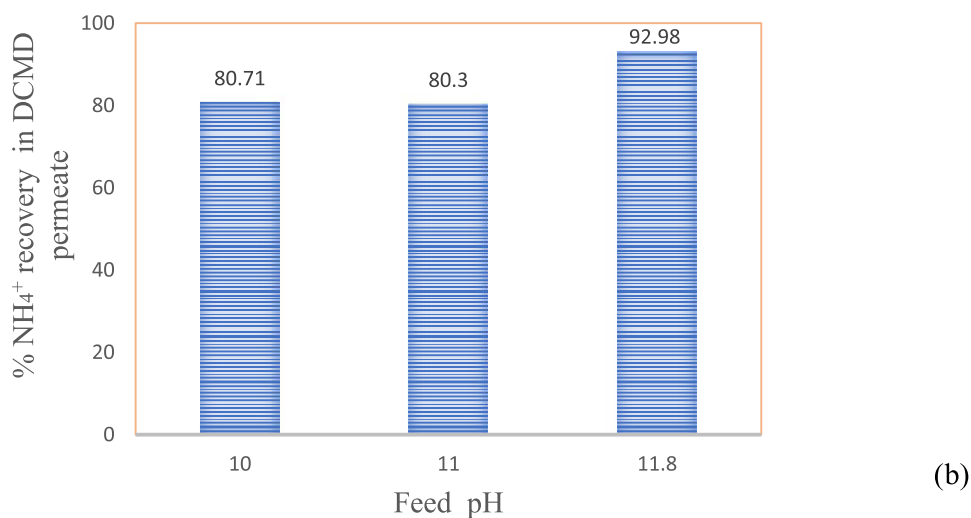
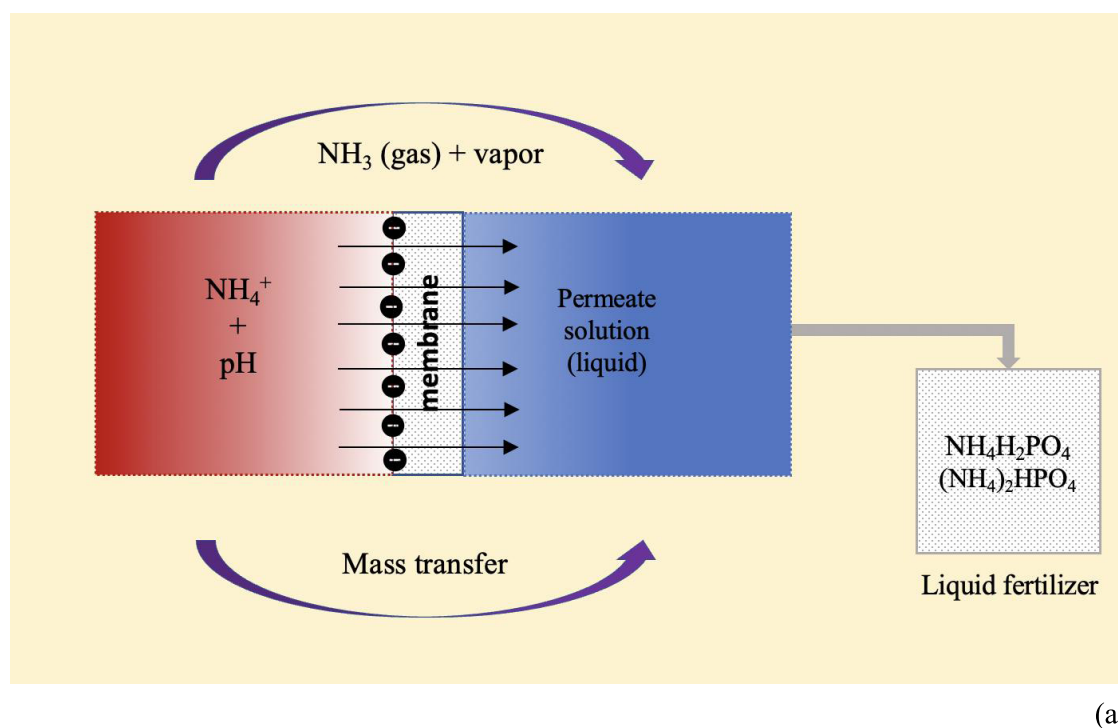
feed pH	initial $\text{NH}_4^+$ (mg/L)	remaining $\text{NH}_4^+$ after 120 min (mg/L)	$\text{NH}_4^+$ loss <sup>a</sup> (mg/L)	$\text{NH}_4^+$ recovered in permeate (mg/L)	$\text{NH}_4^+$ removal efficiency <sup>b</sup> (%)	$\text{NH}_4^+$ recovery efficiency <sup>c</sup> (%)	ammonia flux (kg/m <sup>2</sup> .h)
10	53	39	14	11.3	26.42	80.71	0.0017
11	53	30.3	22.7	18	42.83	79.30	0.0027
11.8	53	24.5	28.5	26.5	53.77	92.98	0.0039

<sup>a</sup> $\text{NH}_4^+$  loss = initial  $\text{NH}_4^+$  – remaining  $\text{NH}_4^+$  after 120 min. <sup>b</sup> $\text{NH}_4^+$  removal efficiency =  $(\text{NH}_4^+$  loss/initial  $\text{NH}_4^+$ )  $\times$  100. <sup>c</sup> $\text{NH}_4^+$  recovery efficiency =  $(\text{NH}_4^+$  recovered in the permeate solution/ $\text{NH}_4^+$  loss)  $\times$  100.

respectively. Ding et al.<sup>2</sup> reported that feed pH could also influence the  $K_{ov}$  value for SGMD and vacuum membrane distillation (VMD) systems. There was no remarkable increment  $K_{ov}$  value when the pH of the feed solution was over 11 in that research. However, Qu et al.<sup>12</sup> reported that an increased  $K_{ov}$  value could be obtained with feed pH values from 10 to 12.2. A previous study with biogas slurry reported no improvement in water flux under a higher feed pH solution. Bush et al.<sup>28</sup> studied the adjustment of pH to reduce the scaling in the DCMD membrane. They reported that a cleaning solution with a pH higher than 11 could enhance the DCMD flux due to the reduction of membrane fouling from silica dissolution. Moreover, the effect of pH on the water flux of nanofiltration was also studied by Mänttari et al.<sup>29</sup> They indicated that an increase of pH up to 11–12 might affect the opening of membrane pores. Higher water flux was obtained at

a higher pH. In this research, an increase in the feed pH up to 11.8 could slightly increase the water flux from 3.04 to 3.51 kg/m<sup>2</sup>.h since an increase in pH from the NaOH addition could yield the membrane self-cleaning mechanism for the case of the negatively charged PTFE membrane. The membrane self-cleaning mechanism could be assumed for the case of the negatively charged PTFE membrane.

The permeate ammonia that passed through the membrane pore can react with the receiving acid solution,  $\text{H}_3\text{PO}_4$ , in the permeate solution to form the nonvolatile ammonium ions. The lower pH of the permeate water could entrap more ammonium ions in the ammonia vapor. According to the results, phosphoric acid,  $\text{H}_3\text{PO}_4$ , could entrap ammonium ions more than normal DI water, as shown in Figure 4a. The reaction took place between the gaseous ammonia and phosphoric acid to produce the ammonium phosphate



**Figure 8.** (a) Diagram of ammonia mass transfer and liquid fertilizer production by the negatively charged PTFE membrane in direct contact membrane distillation. (b) Influence of feed pH on ammonia recovery in the DCMD permeate using 0.5 mM H<sub>3</sub>PO<sub>4</sub> solution as the permeate solution.

solution, as illustrated from eqs 9 to 12 in Section 2.6. The mass balance of ammonia recovery at different pH values is illustrated in Table 4. The ammonia could recover more than 80% of the NH<sub>4</sub><sup>+</sup> ion loss via ammonia gas by the negatively charged PTFE membrane in the DCMD system. The highest ammonia recovery could be achieved with pH 11.8 in this study. With the feed pH of 11.8 with the use of 0.5 mM H<sub>3</sub>PO<sub>4</sub> as the permeate solution of the DCMD system, a high amount of 92.98% ammonia recovery could be achieved with the DCMD system. Less ammonia recovery percentages of 80.3 and 80.71% were obtained when the feed pH values were 11 and 10, respectively.

### 3.4. Proposed Possible Ammonia and Water Recovery Mechanisms by the Negatively Charged PTFE

**Membrane in the DCMD System.** The gaseous ammonia transported through the membrane pore, after which it condensed and reacted with the permeate phosphate solution to form the compound ammonium phosphate solution. The driving force for this ammonia mass transfer is resulted from the temperature difference of two liquid phases on both sides of the MD membrane, together with the vapor pressure difference of the ammonia gas across the membrane. Moreover, the electrostatic force between the ammonium ion in the solution and the negatively charged surface of the membrane might help push the mass transfer of the ammonia molecule through the membrane surface faster than without the electrostatic force. Indeed, the effect of electrostatic force on the charged membrane due to the Donnan effect has also

been reported previously on a negatively charged nanofiltration membrane system.<sup>27</sup> The final ammonia vapor was captured by the permeate solution or receiving solution, as proposed in Figure 8a. The volatile ammonia that passed through the membrane pore was trapped in the receiving or permeate solution on the permeate side as the main mechanism for ammonia recovery by this direct contact membrane distillation. From our results, a slight increase in water flux was found on increasing the feed pH up to 11.8 due to the membrane self-cleaning with NaOH addition. On the permeate side, there is also the interaction between the ammonium ion and the phosphate ion in the reagent acid as the permeate solution. There are also different possible products that can be formed using phosphoric acid at different pHs, as shown in equations 9–12 of Section 2.6. Monoammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and diammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) can be formed in this range between pH 3.5 and 11.5. The high content of phosphorus and nitrogen of this compound can be used as a liquid fertilizer. From Figure 8b, when the feed pH was 11.8, a high amount of 92.98% ammonia recovery could be achieved with the DCMD using 0.5 mM  $\text{H}_3\text{PO}_4$  as the permeate solution, as illustrated in Figure 8b.

Hence, the optimal operating condition of the DCMD system in terms of feed pH and permeate solution type could promote ammonium resource recovery from wastewater up to 92.98% in this study. When the applied feed pH was lower at pH 11 and 10, lower ammonia recovery efficiencies of 80.3 and 80.71% were obtained. Therefore, the useful membrane distillation product may be one of the methods considered for ammonia recovery from wastewater without nitrate production. The products of this ammonia recovery with the use of 0.5 M phosphoric solution as the permeate solution will be ammonium phosphate compounds as valuable fertilizer products.

#### 4. CONCLUSIONS

The feasibility of ammonia recovery by the negatively charged PTFE membrane in direct contact membrane distillation was investigated in this study. The main concerning factors such as permeate solution type and feed pH could significantly enhance the ammonia recovery efficiency of the DCMD system. For the permeate solution, the  $\text{H}_3\text{PO}_4$  solution was found to be the suitable permeate solution among the three selected types. The strong relationship between pH and the mass transfer coefficient was illustrated in this research. The feed pH of 11.8 could give the highest ammonia recovery efficiency as well as water flux improvement. As for the influence of the concentration of the permeate phosphate solution, the higher phosphate molarity could give a higher mass transfer coefficient. Monoammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and diammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) can be produced from ammonia recovery by the DCMD system with the use of  $\text{H}_3\text{PO}_4$  solution as the permeate solution as the ammonium phosphate fertilizer.

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#### Notes

The authors declare no competing financial interest.

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