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# Selectivity of vacuum ammonia stripping using porous gas-permeable and dense pervaporation membranes under various hydraulic conditions and feed water compositions

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## ABSTRACT

Recovery of ammonia (NH<sub>3</sub>) from residual waters offers various reuse opportunities, such as the production of fertilisers and the generation of electricity and heat. However, simultaneous evaporation of water (H<sub>2</sub>O) during NH<sub>3</sub> stripping under vacuum results in diluted recovered NH<sub>3</sub> gas with high H<sub>2</sub>O contents. Whereas porous gas-permeable membranes are already used for vacuum NH<sub>3</sub> stripping, the use of non-porous silica-based pervaporation (PV) membranes showed promising results in recent literature, with respect to more selective transfer of NH<sub>3</sub> compared to H<sub>2</sub>O. In this study, we assessed the selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer ( $S_{\text{NH}_3/\text{H}_2\text{O}}$ ) for different types of membranes, under various hydraulic conditions and feed water compositions. The three following membranes were tested: a porous gas-permeable polytetrafluoroethylene (PTFE) membrane, a hydrophilic (Hybrid Silica PV) membrane and a hydrophobic polydimethylsiloxane PV (PDMS PV) membrane.

For the PTFE and the Hybrid Silica PV membrane,  $S_{\text{NH}_3/\text{H}_2\text{O}}$  ranged between 0.1 and 0.4, indicating that the transfer of NH<sub>3</sub> was consistently less preferred compared to the transfer of H<sub>2</sub>O. The preference for H<sub>2</sub>O over NH<sub>3</sub> transfer through the membranes at various hydraulic conditions and feed water compositions can be assigned to the similarity in polarity and kinetic diameter of NH<sub>3</sub> and H<sub>2</sub>O and the low relative concentration of NH<sub>3</sub> in the used feed waters (approximately 0.1–1.0 wt%). The PDMS PV membrane showed negligible NH<sub>3</sub> transfer and deteriorated rapidly during the NH<sub>3</sub> stripping experiments. The  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of both gas-permeable and PV membranes was higher for unsteady than for steady hydraulic conditions. Furthermore, the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of the both PTFE and the Hybrid Silica decreased when the ionic strength of the feed water increased from 0.0 to 0.8 mol·L<sup>-1</sup> and when the NH<sub>3</sub> feed water concentration increased from 1 to 10 g·L<sup>-1</sup>. According to the results, the used PV membranes did not show selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer. In fact, the used PV membranes consistently had a lower  $S_{\text{NH}_3/\text{H}_2\text{O}}$  than the PTFE membrane. Hence, the dense silica-based PV membranes did not allow for the recovery of gaseous NH<sub>3</sub> from water, with lower H<sub>2</sub>O content in the recovered gas, compared to porous PTFE membranes.

## 1. Introduction

### 1.1. Recovery and use of gaseous ammonia

In contrast to the application of conventional biochemical technologies to remove NH<sub>3</sub> from residual waters, recovery of NH<sub>3</sub> offers multiple opportunities for reuse [1]. Biochemical treatment for the removal of NH<sub>3</sub> from water, such as nitrification in combination with denitrification and/or partial nitrification in combination with anaerobic ammonium oxidation (anammox), relies on the biochemical conversion

of NH<sub>3</sub> to nitrogen gas (N<sub>2</sub>), which is an energy-consuming process, while strong greenhouse gases such as nitrous oxide (N<sub>2</sub>O) are emitted [2]. Ammonia (NH<sub>3</sub>) can be recovered from residual waters in the form of ammonium (NH<sub>4</sub><sup>+</sup>) salt solutions or solid crystals, which can be used as (a resource for the production of) fertilisers [1]. Furthermore, according to the review study of Deng et al. [1], NH<sub>3</sub> can also be recovered for the production of microbial proteins or for the generation of energy in combustion-based or fuel cell technologies, opening new opportunities for NH<sub>3</sub> recovery and treatment methods of residual waters that contain NH<sub>3</sub>.

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## 1.2. Evaporation of water during recovery of gaseous ammonia from water

During  $\text{NH}_3$  recovery by vacuum stripping processes, such as vacuum membrane stripping (VMS) using porous gas-permeable membranes, stripping of  $\text{NH}_3$  is accompanied by the evaporation of  $\text{H}_2\text{O}$ , which dilutes the obtained gaseous  $\text{NH}_3$  [3–5]. To obtain more concentrated  $\text{NH}_3$  gas, the concentration of  $\text{NH}_3$  in the feed water can be increased [5–7]. Moreover, according to our previous study, increasing the feed water temperature at an  $\text{NH}_3$  feed concentration of  $10 \text{ g}\cdot\text{L}^{-1}$  from 25 to 35 °C results in an increase in  $\text{NH}_3$  concentration in the permeate from 8 to 11 wt%. However, a further increase in the feed water temperature to 45 and 55 °C leads to dilution of  $\text{NH}_3$  in the gaseous permeate to 5 and 4 wt %, respectively [5]. To obtain more concentrated  $\text{NH}_3$  by VMS, the evaporation of  $\text{H}_2\text{O}$  must be minimised. To this end, a physical barrier for the transfer of  $\text{H}_2\text{O}$  that does not negatively affect the  $\text{NH}_3$  transfer may be introduced. Porous gas-permeable membranes are not considered to be effective barriers, because the pore size of about  $0.1 \mu\text{m}$  is at least two orders of magnitude larger than the kinetic diameter of transferred molecules such as  $\text{NH}_3$  and  $\text{H}_2\text{O}$  ( $<1 \text{ nm}$ ). To recover more concentrated  $\text{NH}_3$  by vacuum stripping processes, the use of dense pervaporation (PV) membranes to more selectively transfer  $\text{NH}_3$  through the membrane was initially proposed by Yang et al. [8].

## 1.3. Selectivity of ammonia transfer through PV membranes

For PV, selectivity ( $S$ ) is defined as the ratio of the permeances of the respective gases permeating through the membrane, whereas the permeance describes the normalised transfer rate: the mass flux normalised for the driving force [9]. Hence, selectivity ( $S_{i/j}$ ) describes the normalised transfer rate of gas ‘i’ with respect to another gas ‘j’. In this view, selective transfer of ‘i’ over ‘j’ is considered when  $S_{i/j} > 1$ . Selective permeation of  $\text{NH}_3$  over hydrogen ( $\text{H}_2$ ) and  $\text{N}_2$  by using PV membranes proved to be feasible for gas separation, for the recovery of  $\text{NH}_3$  from gas mixtures consisting of the respective gases [10,11]:  $S_{\text{NH}_3/\text{H}_2}$  and  $S_{\text{NH}_3/\text{N}_2} > 1$ . Camus et al. [10] showed that silica-based PV membranes had a seven and fourteen times higher  $\text{NH}_3$  permeance compared to the permeance of  $\text{H}_2$  and  $\text{N}_2$  when using mixtures of  $\text{NH}_3\text{--H}_2$  and  $\text{NH}_3\text{--N}_2$  gas as a feed at a temperature of 80 °C. Subsequently, Kanezashi, et al. [11] reported  $\text{H}_2$  permeances up to twenty times higher than the  $\text{NH}_3$  permeances for silica-based PV membranes when pure  $\text{H}_2$  and  $\text{NH}_3$  gas were used as the feed at a temperature of 50 °C. However, when mixtures of  $\text{NH}_3/\text{H}_2$  gas were used as feed at the same temperature, selective transfer of  $\text{NH}_3$  over  $\text{H}_2$  took place ( $S_{\text{NH}_3/\text{H}_2}$  of 29), in agreement with Camus et al. [10]. Both Camus et al. [10] and Kanezashi et al. [11] attributed the selective transfer of  $\text{NH}_3$  over  $\text{H}_2$  to the adsorption of  $\text{NH}_3$  to the membrane material, which contained silica groups. According to Kanezashi et al. [11],  $\text{NH}_3$  and  $\text{H}_2$  have a kinetic diameter of 0.33 and 0.26 nm, respectively. Hence, for pure gases, the transfer rate of  $\text{H}_2$  is higher than the transfer rate of  $\text{NH}_3$  based on the higher reported permeances, but when gaseous  $\text{NH}_3\text{--H}_2$  mixtures are present in the feed,  $\text{NH}_3$  adsorbs on the membrane interface and hinders the adsorption and permeation of  $\text{H}_2$ , resulting in selective transfer of  $\text{NH}_3$  over  $\text{H}_2$  [10,11].

## 1.4. Recovery of gaseous ammonia from feed waters using PV membranes

In addition to the application to obtain more enriched permeate streams from gas mixtures by gas separation, PV membranes can also be used to remove and/or recover gases from a liquid feed such as water. According to the review of Jyoti et al. [12], different types of PV membranes are used to allow for either selective transfer of water ( $\text{H}_2\text{O}$ ) or volatile organics from liquid  $\text{H}_2\text{O}$ -organics mixtures. For the selective transfer of  $\text{H}_2\text{O}$  from liquid  $\text{H}_2\text{O}$ -organics mixtures, hydrophilic PV membranes are used, whereas hydrophobic PV membranes are used for selective transfer of volatile organics, such as alcohols or volatile fatty acids.

Research of Yang et al. [8] focused on the recovery of gaseous  $\text{NH}_3$  from liquid feed water, using silica-based PV membranes that were hydrothermally-treated by addition of iron and cobalt in the membrane material. Yang et al. [8] did not report on the transfer selectivity of the PV membranes according to the proposed definition of Baker et al. [9], but did report concentration factors up to 63 for a PV membrane for an  $\text{NH}_3$  feed concentration of  $0.8 \text{ g}\cdot\text{L}^{-1}$  at feed temperatures ranging between 45 and 50 °C. Because the concentration factor represents the ratio of the  $\text{NH}_3$  concentration in the permeate and the feed, the relatively high concentration factors suggest high transfer rates of  $\text{NH}_3$  compared to  $\text{H}_2\text{O}$ . In a follow-up study, Yang, et al. [13] stripped  $\text{NH}_3$  from liquid water using a PV membrane that contained a combination of silica and organic groups for hydrothermal stability in the selective layer and was further referred to as hybrid-silica. For an  $\text{NH}_3$  feed concentration of  $50 \text{ mg}\cdot\text{L}^{-1}$  and at a feed temperature of 45 °C, the authors reported a concentration factor of 12 and an  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of 0.5, indicating selective transfer of  $\text{H}_2\text{O}$  over  $\text{NH}_3$  for the used PV membranes. Finally, Yang, et al. [14] assessed the effect of cobalt content in the selective layer of silica-based PV membranes on the transfer of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  and observed again selective transfer of  $\text{H}_2\text{O}$  over  $\text{NH}_3$  ( $S_{\text{NH}_3/\text{H}_2\text{O}} < 1$ ).

Hence, in currently available literature, there is no consensus on whether selective transfer of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  can be achieved by using silica-based PV membranes. The differences in transfer selectivity observed in previous studies may be explained by the differences in applied experimental conditions, as Yang et al. [8] and Yang et al. [14] used configurations in which the membranes were submerged in the feed water, whereas Yang et al. [13] used a cross-flow configuration. The mentioned studies did not describe the location of the selective layer on the membranes. The location of the selective layer of the membrane and the used configuration are key to control the hydraulic conditions, which affect polarisation effects at the membrane interface, which in their turn affect the mass transfer rates through the membrane [15]. Furthermore, the contradicting results on the transfer selectivity of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  also may be explained by differences in tested feed characteristics, such as feed temperature and  $\text{NH}_3$  feed concentration.

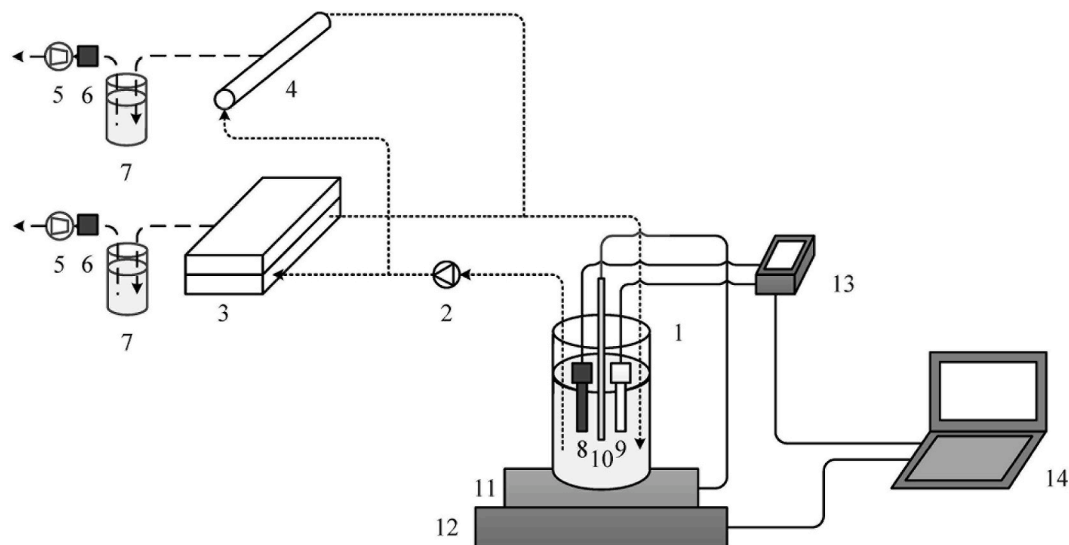
## 1.5. Research objective

Currently available literature showed that silica-based PV membranes allow for selective transfer of  $\text{NH}_3$  over  $\text{N}_2$  and  $\text{H}_2$  when treating gas mixtures, but it remains unclear whether also selective transfer of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  can be achieved when stripping  $\text{NH}_3$  from liquid water. Silica-based PV membranes are considered to be hydrophilic, indicating that these membranes allow for the transfer of  $\text{H}_2\text{O}$ . To our best knowledge, it is unknown whether hydrophobic silica-based PV membranes allow for selective transfer of  $\text{NH}_3$  when stripping  $\text{NH}_3$  from water. Furthermore, according to available literature, there is no clarity whether PV membranes have higher  $S_{\text{NH}_3/\text{H}_2\text{O}}$  compared to conventional porous gas-permeable membranes. Therefore, in this study, we assessed the mass transfer rates and  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of a porous gas-permeable membrane and dense hydrophilic and hydrophobic PV membranes while stripping  $\text{NH}_3$  from water. We assessed the effect of the hydraulic conditions and the feed composition, in terms of  $\text{NH}_3$  feed concentration and ionic strength, on the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  for the various membranes.

## 2. Materials and methods

### 2.1. Materials

For the porous gas-permeable membrane experiments, we used the same equipment and spacer-filled flat sheet membrane configuration as described in our previous study [16]. For the experiments with the PV membranes, again the same experimental set-up was used, except a stainless-steel membrane housing was used for the tubular PV membranes, including rubber rings at the ends of the PV membranes to ensure liquid and gas tightness. Fig. 1 presents the experimental set-up,



**Fig. 1.** Schematic representation of the used experimental set-up including feed water bottle (1), peristaltic pump (2), gas-permeable membrane housing including membrane (3), PV membrane housing including membrane (4), vacuum pump (5), pressure sensor (6), cooled permeate scrubber (7), EC-sensor (8), pH-sensor (9), temperature sensor (10), integrated heating and mixing plate (11), balance (12), multimeter (13) and laptop (14).

including the membrane housings for the porous gas-permeable and PV membranes. The porous gas-permeable membrane was a Sterlitech polytetrafluoroethylene membrane (hereafter PTFE membrane) and the PV membranes were a hydrophilic Pervatech Hybrid Silica (hereafter Hybrid Silica PV membrane) and a hydrophobic Pervatech polydimethylsiloxane membrane (hereafter PDMS PV membrane). Table 1 presents an overview of the specific characteristics and measured dimensions of the used membranes.

The feed waters were prepared by the addition of Acros Organics 25 wt% ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) stock solution, or Sigma Aldrich ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) salt and Merck 1 M sodium hydroxide ( $\text{NaOH}$ ) solution to demineralised water. The used  $\text{NH}_4\text{OH}$  solution,  $\text{NH}_4\text{HCO}_3$  salt and  $\text{NaOH}$  solution were all analytical grade. The prepared feed waters consisted of  $\text{NH}_4\text{HCO}_3$  because bicarbonate ( $\text{HCO}_3^-$ ) is often the main anion in nitrogen-rich residual streams, such as reject waters, urine and industrial condensates. All experimental runs were conducted in at least triplicate.

## 2.2. Performance indicators

For the assessment of the  $S_{\text{NH}_3/\text{H}_2\text{O}}$ , the overall mass transfer coefficient ( $K_o$ ) for  $\text{NH}_3$  and  $\text{H}_2\text{O}$  was determined. The  $K_o$  normalises the mass flux with respect to the respective driving force for the transfer of

gases, which for  $\text{NH}_3$  and  $\text{H}_2\text{O}$  is the vapour pressure difference between the liquid feed water and the gaseous permeate.  $K_o$  is usually described by a series-resistance model, consisting of three separate components: the mass transfer coefficients for the liquid feed water ( $K_f$ ), the membrane ( $K_m$ ) and the gaseous permeate ( $K_p$ ) as described in Eq. (1).

$$\frac{1}{K_o} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_p} \quad 1$$

Where,  $K_o$ ,  $K_f$ ,  $K_m$  and  $K_p$  = the overall, the liquid feed water, the membrane, and the gaseous permeate mass transfer coefficient (in  $\text{s}\cdot\text{m}^{-1}$ ), respectively.

$K_p$  is negligible for vacuum stripping applications due to the low absolute pressure of the gaseous permeate, according to the studies of Bandini et al. [18], Lawson, et al. [19] and Jyoti et al. [12].

$K_f$  can be determined as a function of the hydraulic conditions and the diffusion characteristics of the dissolved gases in the feed water [15, 20], but this is only applicable for uniform hydraulic conditions of the feed water. At the interface of the feed water and the membrane, the hydraulic conditions are different from those in the bulk phase, due to polarisation phenomena. For stripping of gases from water in vacuum configurations, three polarisation phenomena are relevant:

1. Temperature polarisation;

**Table 1**

Key characteristics of the membranes used for the  $\text{NH}_3$  stripping experiments.

	Unit	Porous gas-permeable (PTFE) membrane	Hydrophilic (Hybrid Silica) PV membrane	Hydrophobic (PDMS) PV membrane
Channel height	mm	2.3	–	–
Channel width	mm	39	–	–
Internal diameter	mm	–	7	7
Membrane thickness	mm	0.2	1.5	1.5
Membrane length	mm	87	250	250
Effective membrane area	$\text{cm}^2$	34	55	55
Pore size <sup>e</sup>	nm	100	0.5 [17]	–
Selective membrane layer	–	PTFE <sup>a</sup>	Hybrid Silica – AR <sup>c</sup>	PDMS <sup>d</sup>
Membrane material	–	PTFE – PP <sup>b</sup>	$\alpha\text{-Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$
Maximum temperature <sup>e</sup>	$^\circ\text{C}$	82	150	70

<sup>a</sup> PTFE = polytetrafluoroethylene.

<sup>b</sup> PP = polypropylene.

<sup>c</sup> Hybrid Silica – AR = organic (methyl and ethanol) groups and silica [13].

<sup>d</sup> PDMS = polydimethylsiloxane.

<sup>e</sup> According to the supplier.

2. Ion accumulation concentration polarisation;
3. Gas depletion concentration polarisation;

Firstly, temperature polarisation, which is the decrease in temperature of the feed water at the membrane interface as a result of heat transport due to the evaporation of H<sub>2</sub>O [19,21]. Secondly, accumulation concentration polarisation, describing the increase in concentration of non-volatile solutes such as ions at the membrane interface as a result of the evaporation of H<sub>2</sub>O [19,21]. Thirdly, gas depletion concentration polarisation, which is the decrease in concentration of volatile solutes such as dissolved gases at the membrane interface, caused by a higher transfer rate of the respective gas through the membrane than the transfer rate from bulk-phase of the feed liquid to the membrane interface [18,22].

Finally,  $K_m$  depends on the type of membrane. For porous gas-permeable membranes, the main mass transfer mechanism is Knudsen diffusion because the ratio of the kinetic diameter of the gas molecule and pore size is smaller than 0.05 [4,19,23], whereas PV membranes are dense membranes for which the main mass transfer mechanisms rely on sorption/dissolution and diffusion [12]. In general, for both types of membranes,  $K_m$  is a function of the specific membrane characteristics, such as thickness, and the temperature of the membranes [12,19]. However, due to temperature polarisation, the actual temperature of the membrane is different from the temperature of the bulk phase of the liquid feed.

The mentioned three polarisation phenomena occur simultaneously during vacuum stripping of gases such as NH<sub>3</sub> from water and do not only affect the mass transfer coefficients  $K_f$  and  $K_m$ . The polarisation phenomena also affect the driving force of NH<sub>3</sub> and H<sub>2</sub>O transfer, because the local accumulation of ions, the local depletion of dissolved NH<sub>3</sub> and the lower temperature at the membrane interface compared to the bulk feed water temperature affect the vapour pressures of NH<sub>3</sub> and H<sub>2</sub>O at the liquid side of the membrane. To our best knowledge, understanding the mass transfer in vacuum membrane stripping processes, including all three polarisation phenomena and their interdependency is lacking in current literature. Therefore, in this study, we did not investigate the respective contribution of  $K_f$  and  $K_m$  separately, but only  $K_o$ .

To calculate the  $K_o$  of NH<sub>3</sub> ( $K_{o,NH_3}$ ), various studies used the logarithmic decrease in NH<sub>3</sub> concentration over time, in combination with the initial feed volume [4,6]. However, this method of determining the  $K_o$  only applies to the transfer of the solute (NH<sub>3</sub>) and not to the solvent (H<sub>2</sub>O). Moreover, this method assumes a fixed feed volume, whereas the feed water volumes decrease due to the evaporation of H<sub>2</sub>O during the stripping process. Therefore, we determined the  $K_o$  for NH<sub>3</sub> and H<sub>2</sub>O using the measured fluxes and the calculated vapour pressure difference, in line with the study of [12]. The NH<sub>3</sub> (Eq. (2)) and H<sub>2</sub>O (Eq. (3)) fluxes were determined using the mass changes in the feed water over time. The vapour pressures of NH<sub>3</sub> and H<sub>2</sub>O in the liquid feed were obtained by simulations using chemical equilibrium simulation software named PHREEQC, whereas the vapour pressures of NH<sub>3</sub> (Eq. (4)) and H<sub>2</sub>O (Eq. (5)) in the gaseous permeate were calculated using the ratio of the fluxes and the absolute pressure of the permeate. More details on the determination of the fluxes can be found in our previous study [16]. Based on the NH<sub>3</sub> and H<sub>2</sub>O fluxes and vapour pressures, the  $K_{o,NH_3}$  and  $K_{o,H_2O}$  were determined using Eq. (6) and Eq. (7), respectively. Finally,  $S_{NH_3/H_2O}$  was determined using Eq. (6), as the ratio of  $K_{o,NH_3}$  and  $K_{o,H_2O}$ , in line with Camus et al. [10] and Baker et al. [9].

$$J_{NH_3} = \frac{-(m_{NH_3,i+1} - m_{NH_3,i})}{A_m \cdot (t_{i+1} - t_i)} \quad 2$$

$$J_{H_2O} = \frac{-(m_{H_2O,i+1} - m_{H_2O,i})}{A_m \cdot (t_{i+1} - t_i)} \quad 3$$

Where,  $J_{NH_3}$  and  $J_{H_2O}$  = NH<sub>3</sub> and H<sub>2</sub>O flux (in kg·m<sup>-2</sup>·s<sup>-1</sup>),  $m_{NH_3,i}$  and  $m_{H_2O,i}$  = NH<sub>3</sub> and H<sub>2</sub>O mass at time instant 'i', respectively (in kg),  $A_m$

= membrane area (in m<sup>2</sup>) and  $t_i$  = time instant 'i' (in s).

$$p_{p,NH_3} = \frac{J_{NH_3}}{J_{NH_3} + J_{H_2O}} p_p \quad 4$$

$$p_{p,H_2O} = \frac{J_{H_2O}}{J_{NH_3} + J_{H_2O}} p_p \quad 5$$

Where,  $p_{p,NH_3}$  and  $p_{p,H_2O}$  = vapour pressure of NH<sub>3</sub> and H<sub>2</sub>O in the gaseous permeate, respectively (in Pa = kg·m<sup>-2</sup>·s<sup>-1</sup>) and  $p_p$  = permeate pressure (in Pa = kg·m<sup>-2</sup>·s<sup>-1</sup>,  $p_p = 1,500$  Pa).

$$K_{o,NH_3} = \frac{J_{NH_3}}{p_{f,NH_3} - p_{p,NH_3}} \quad 6$$

$$K_{o,H_2O} = \frac{J_{H_2O}}{p_{f,H_2O} - p_{p,H_2O}} \quad 7$$

Where  $K_{o,NH_3}$  and  $K_{o,H_2O}$  = mass transfer coefficient of NH<sub>3</sub> and H<sub>2</sub>O, respectively (in s·m<sup>-1</sup>) and  $p_{f,NH_3}$  and  $p_{f,H_2O}$  = vapour pressure of NH<sub>3</sub> and H<sub>2</sub>O in the liquid feed water (in Pa = kg·m<sup>-2</sup>·s<sup>-1</sup>).

$$S_{NH_3/H_2O} = \frac{K_{NH_3}}{K_{H_2O}} \quad 8$$

Where  $S_{NH_3/H_2O}$  = selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer (no unit).

### 2.3. Experimental conditions

For all conducted experiments in this study, the vacuum pressure at the permeate side was fixed at 1,500 Pa by a vacuum pump, while unsteady hydraulic flow conditions were maintained unless stated otherwise. Moreover, the temperature of the feed water was 35 °C, unless stated differently, because according to our previous study, stripping NH<sub>3</sub> at 35 °C resulted in the most concentrated NH<sub>3</sub> in the vapour permeate [16]. Initially, we assessed the transfer of H<sub>2</sub>O through the various membranes at three different feed water temperatures: 25, 35 and 45 °C. Subsequently, unless stated differently, feed waters with a feed water concentration of 1 g·L<sup>-1</sup> of NH<sub>3</sub> as NH<sub>4</sub>OH were used to assess the  $S_{NH_3/H_2O}$  for the various membranes, similar to Yang et al. [8] and Yang et al. [13].

#### 2.3.1. Hydraulic conditions

We assessed the effect of the hydraulic conditions on the  $S_{NH_3/H_2O}$ , by using various Reynolds numbers, corresponding to steady (poorly mixed, or laminar) or unsteady (well-mixed, or transition/turbulent) hydraulic conditions. Unsteady flow conditions refer to the hydraulic flow conditions with good mixing properties. The unsteady flow conditions cover the range between laminar and turbulent hydraulic conditions. The Reynolds number is a function of the feed water properties, the cross-flow velocity and the hydraulic diameter of the flow channel (Eq. (9)). According to the study of Oliveira et al. [15], the hydraulic flow conditions are unsteady at a Reynolds number of 2,300 in tubular channels, whereas according to Mojab et al. [24] unsteady hydraulic conditions in spacer-filled channels correspond to a Reynolds number of 500. By taking the feed water properties into account, the Reynolds numbers were set by controlling the cross-flow velocity through the flow channels using the peristaltic pump.

$$Re = \frac{\rho_f \cdot u \cdot d_h}{\mu_f} \quad 9$$

Where  $\rho_f$  = feed water density (in kg·m<sup>-3</sup>),  $u$  = average cross-flow velocity (in m·s<sup>-1</sup>),  $d_h$  = hydraulic diameter (in m),  $\mu_w$  = dynamic viscosity of feed water (in kg·m<sup>-1</sup>·s<sup>-1</sup>).

The hydraulic diameter relates the surface tension and the shear stress of a liquid flowing through a channel. For circular open channels (for the tubular PV membranes), the hydraulic diameter is equal to the

diameter of the respective channel. For spacer-filled channels (for the flat-sheet PTFE membrane), the determination of the hydraulic diameter is more elaborate, as the liquid is in contact with both the spacer and the perimeter of the flow channel. To this end, Schock, et al. [25] proposed a general expression for the hydraulic diameter in spacer-filled channels (Eq. (8)), as a function of the void volume and the wetted surface area of the flow channel.

$$d_h = \frac{4 \cdot V_v}{A_w} \quad 10$$

Where,  $V_v$  = void volume (in  $\text{m}^3$ ) and  $A_w$  = wetted surface area (in  $\text{m}^2$ ).

The determination of the void volume and the wetted surface area of the flow channels as a function of the specific channel geometries are described in detail in the Supporting Information. The hydraulic diameters were 2.3 and 7.0 mm for the PTFE and PV membranes, respectively. For the PTFE membrane, the range of the cross-flow velocity was  $8\text{--}20 \text{ cm}\cdot\text{s}^{-1}$  and  $14\text{--}36 \text{ cm}\cdot\text{s}^{-1}$  for the PV membranes. The cross-flow velocities for the PTFE membrane to achieve unsteady hydraulic conditions are lower compared to the PV membranes, because the PTFE membrane is in contact with a spacer (to enhance mixing), while the PV membranes are open tubular channels.

### 2.3.2. Ammonia feed water concentration and ionic strength of the feed water

To the best of our knowledge, current literature mainly reports on the transfer of  $\text{NH}_3$  from feed water through membranes, in which the  $\text{NH}_3$  is only present as  $\text{NH}_4\text{OH}$ . Only the study of He et al. [6] and our previous study [16] did not use  $\text{NH}_4\text{OH}$  solutions as feed water, but used pre-treated biogas slurry and  $\text{NH}_4\text{HCO}_3$  solutions at a pH of 10, respectively. Whereas  $1 \text{ g}\cdot\text{L}^{-1}$  is a representative concentration of  $\text{NH}_3$  in residual waters,  $10 \text{ g}\cdot\text{L}^{-1}$  represents the concentration of  $\text{NH}_3$  in pre-concentrated streams [1]. Obtaining  $\text{NH}_3$  concentrations up to  $10 \text{ g}\cdot\text{L}^{-1}$  can be achieved by using electrodialysis to concentrate  $\text{NH}_4^+$  from 1.5 to  $10 \text{ g}\cdot\text{L}^{-1}$  [26], followed by the addition of chemicals to increase the solution pH, or by using bipolar membrane electrodialysis to directly obtain concentrated  $\text{NH}_3$  without chemical addition [27]. Because various nitrogen-rich residual waters, typically contain  $\text{NH}_4^+$  in combination with  $\text{HCO}_3^-$  as the main anion, the addition of NaOH to obtain concentrated  $\text{NH}_3$  from feed water with high  $\text{NH}_4^+$  concentrations results in a high ionic strength, as a result of the presence of  $\text{Na}^+$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . The presence of ions affects the vapour pressure of  $\text{NH}_3$  in two ways. On the one hand, when the ionic strength increases, the equilibrium between  $\text{NH}_4^+$  and  $\text{NH}_3$  shifts towards  $\text{NH}_4^+$ , according to chemical equilibrium simulations performed with PHREEQC software. On the other hand, the solubility of gases decreases when the ionic strength increases, which is called the salting-out effect, increasing the vapour pressure. According to Fig. 2, the vapour pressure of  $\text{NH}_3$  increases linearly when the ionic strength of the feed water increases, indicating that the salting-out effect is stronger than the effect of the ionic strength on the equilibrium between  $\text{NH}_3$  and  $\text{NH}_4^+$ . Furthermore, an increase in ionic strength results in a linear decrease in  $\text{H}_2\text{O}$  vapour pressure according to Raoult's Law. Hence, by increasing the ionic strength of the feed water, the  $\text{NH}_3$  vapour pressure increases, while the  $\text{H}_2\text{O}$  vapour pressure decreases. The effect of the ionic strength on the vapour pressure of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  is similar for feed waters with  $\text{NH}_3$  concentrations of 1 and  $10 \text{ g}\cdot\text{L}^{-1}$ . However, in addition to the effect of the ionic strength on the vapour pressures, the ionic strength also affects the resistance to mass transfer of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . Due to the evaporation of  $\text{H}_2\text{O}$ , ions accumulate at the membrane interface (ion accumulation concentration polarisation), which can hinder the transfer of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , particularly under steady hydraulic conditions.

We assessed the effect of ionic strength on  $S_{\text{NH}_3/\text{H}_2\text{O}}$ , because the presence of ions affects both the vapour pressure of dissolved gases (salting-out effect) and the mass transfer coefficient (ion accumulation concentration polarisation). To assess the effect of the  $\text{NH}_3$  feed

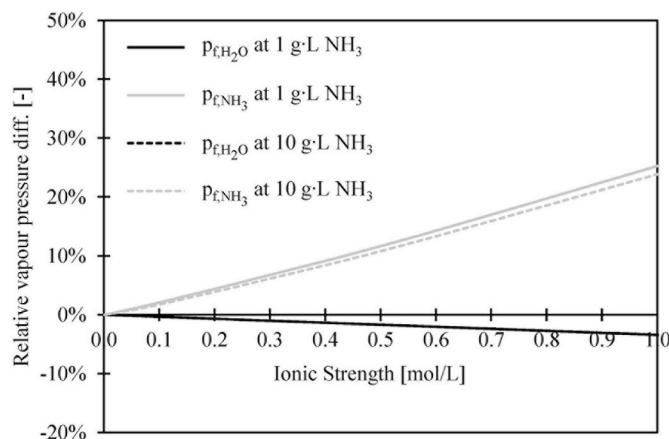


Fig. 2. The calculated vapour pressures of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in water with an  $\text{NH}_3$  feed water concentration of 1 and  $10 \text{ g}\cdot\text{L}^{-1}$ , as a function of the ionic strength of the feed water. The vapour pressures were calculated using PHREEQC simulation software, using the phreeqc.dat database.

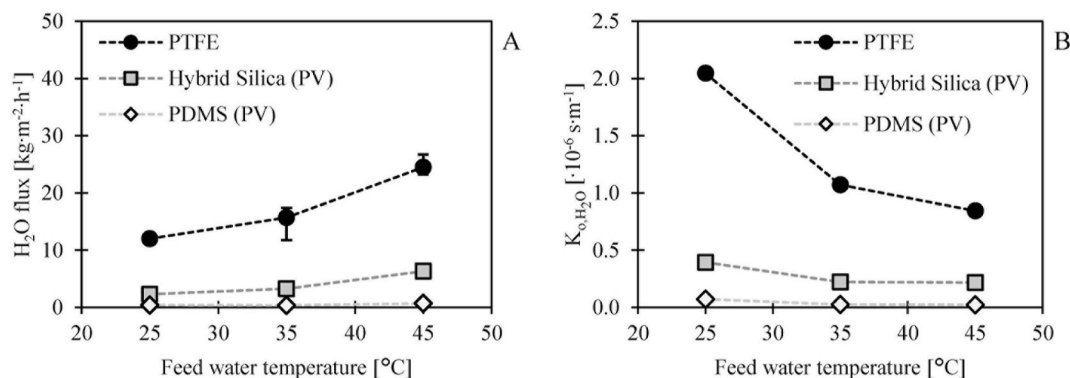
concentration and ionic strength on  $S_{\text{NH}_3/\text{H}_2\text{O}}$ , we prepared various feed waters containing dissolved  $\text{NH}_3$  with initial concentrations of 1 and  $10 \text{ g}\cdot\text{L}^{-1}$  as  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{HCO}_3$  (at a pH of 10 by addition of NaOH). According chemical equilibrium simulations, the ionic strength of feed water consisting of  $\text{NH}_4\text{OH}$  is negligible, whereas feed waters consisting of  $\text{NH}_4\text{HCO}_3$  at a pH of 10 have an ionic strength of 0.1 and  $0.8 \text{ mol}\cdot\text{L}^{-1}$  at  $\text{NH}_3$  feed water concentration of 1 and  $10 \text{ g}\cdot\text{L}^{-1}$ , respectively. For these calculations, the contribution of both  $\text{NH}_4\text{HCO}_3$  and NaOH to the ionic strength were taken into account.

## 3. Results and discussion

### 3.1. Water transfer through the various membranes as a function of the feed temperature

Initially, the transfer rate of  $\text{H}_2\text{O}$  as the  $\text{H}_2\text{O}$  flux and the  $K_{o,\text{H}_2\text{O}}$  through the membranes was assessed at various temperatures, using water as a feed without dissolved gaseous and ions, at unsteady hydraulic conditions. Fig. 3A presents the  $\text{H}_2\text{O}$  fluxes as a function of the feed water temperature for the PTFE, Hybrid Silica PV and PDMS PV membrane. The reported values represent averages of at least triplicate experimental runs. At a feed water temperature of  $25^\circ\text{C}$ , the  $\text{H}_2\text{O}$  flux for the PTFE membrane was  $12.0 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , compared to 2.3 and  $0.4 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for the Hybrid Silica PV and PDMS PV membrane, respectively. By increasing the feed water temperature to  $45^\circ\text{C}$ , the  $\text{H}_2\text{O}$  fluxes increased to 24.5, 6.3 and  $0.7 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for the PTFE, Hybrid Silica PV and PDMS PV membranes, respectively, because the vapour pressure of  $\text{H}_2\text{O}$  and thus the driving force increased as a function of temperature. The  $\text{H}_2\text{O}$  flux for the PTFE membrane was at least four times higher than the  $\text{H}_2\text{O}$  flux for the Hybrid Silica PV membrane, which in its turn was at least five times higher than the  $\text{H}_2\text{O}$  flux of the PDMS PV membrane.

Because the same feed water temperature range and same vacuum pressure were applied for the experiments, the higher  $\text{H}_2\text{O}$  fluxes of the PTFE membrane compared to the PV membranes are explained by the higher  $K_{o,\text{H}_2\text{O}}$  of the PTFE membrane (ranging between  $1\cdot 10^{-6}$  and  $2\cdot 10^{-6} \text{ s}\cdot\text{m}^{-1}$ ) compared to the  $K_{o,\text{H}_2\text{O}}$  of the Hybrid Silica PV (ranging between  $2\cdot 10^{-7}$  and  $4\cdot 10^{-7} \text{ s}\cdot\text{m}^{-1}$ ) and the PDMS PV membrane (ranging between  $7\cdot 10^{-8}$  and  $2\cdot 10^{-7} \text{ s}\cdot\text{m}^{-1}$ ), as presented in Fig. 3B. The difference in  $K_{o,\text{H}_2\text{O}}$  between the PTFE membrane and the PV membranes can be assigned to the differences in selective layers of the membranes. The PTFE membrane had pores of  $0.1 \mu\text{m}$ , whereas the Hybrid Silica PV and PDMS PV membranes were dense membranes, resulting in lower transfer rates of  $\text{H}_2\text{O}$  than compared to the porous PTFE membrane. The difference in  $K_{o,\text{H}_2\text{O}}$  between the Hybrid Silica PV



**Fig. 3.** (A) The H<sub>2</sub>O fluxes and (B) the K<sub>0,H<sub>2</sub>O</sub> of the gas permeable PTFE membrane and the hydrophilic Hybrid Silica PV and hydrophobic PV membrane as a function of the feed water temperature. The reported values and error bars represent average and the minimum and maximum measurements of at least three replicate experiments.

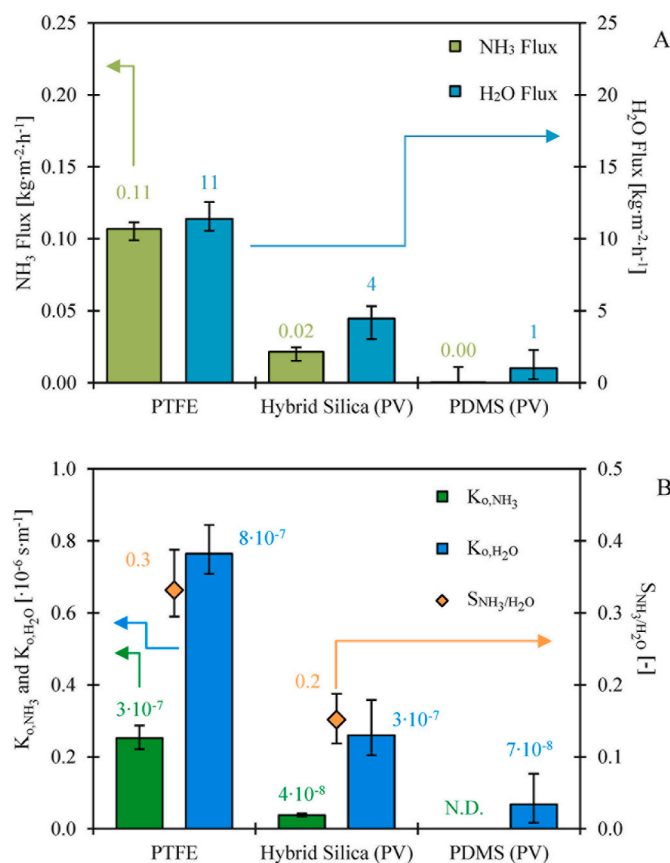
and the PDMS PV membrane can be explained by the functional groups present in the selective layers of the respective membranes. The selective layer of the Hybrid Silica PV membrane was hydrophilic and contained polar organosilica groups, allowing for the permeation of polar H<sub>2</sub>O molecules. On the contrary, the selective layer of the PDMS PV membrane was hydrophobic, which hindered the dissolution of H<sub>2</sub>O in the membrane and the subsequent diffusion of H<sub>2</sub>O through the membrane.

According to Fig. 3B, the K<sub>0,H<sub>2</sub>O</sub> of all three membranes decreased when the feed water temperature increased. The decrease of K<sub>0,H<sub>2</sub>O</sub> as a function of the increasing feed water temperature can be assigned to a stronger effect of temperature polarisation [21], as no ions or dissolved gases were present in the feed water. For the PTFE membrane, the decrease in K<sub>0,H<sub>2</sub>O</sub> as a function of the feed water temperature can be assigned to the decrease in K<sub>m</sub>, which decreases as a function of the temperature according to Knudsen diffusion. In addition, for the PV membranes, the mass transfer through the membranes can be described by sorption-diffusion models. When the temperature increases, diffusion increases, while sorption decreases. Therefore, the decrease in K<sub>0,H<sub>2</sub>O</sub> of the PV membranes as a function of the increasing feed water temperature may, besides temperature polarisation, also be caused by the effect of the feed water temperature on the sorption and diffusion mechanisms taking place during the transfer of H<sub>2</sub>O. However, because the temperature at the interface of the liquid feed water and the membranes was not determined, it remains unclear which component of the series resistance model for mass transfer (Eq. (1)) caused the decrease of the K<sub>0,H<sub>2</sub>O</sub> as a function of the increasing feed water temperature.

### 3.2. Selectivity of ammonia over water transfer of various membranes

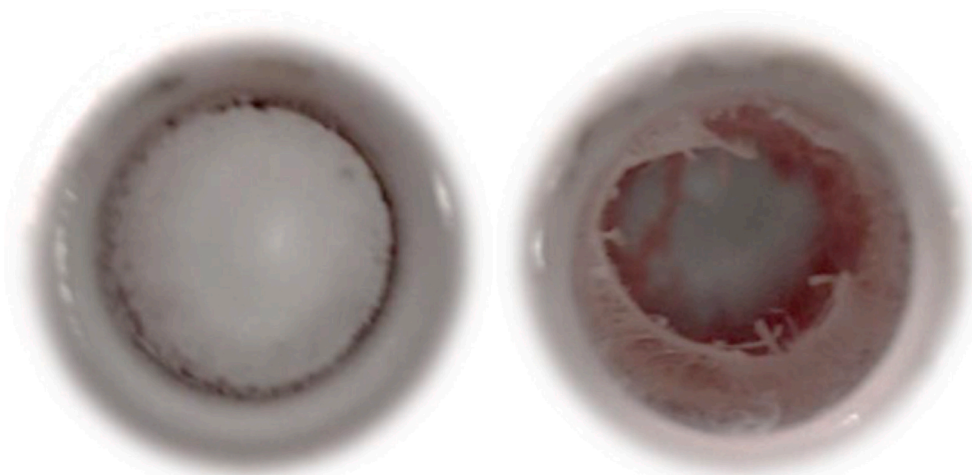
Fig. 4A presents the fluxes of both NH<sub>3</sub> and H<sub>2</sub>O for the various membranes. The H<sub>2</sub>O and NH<sub>3</sub> fluxes of the PTFE membrane were 11 and 0.11 kg·m<sup>-2</sup>·h<sup>-1</sup>, respectively. For the Hybrid Silica PV membrane, the H<sub>2</sub>O flux was 4 kg·m<sup>-2</sup>·h<sup>-1</sup> and the NH<sub>3</sub> flux was 0.02 kg·m<sup>-2</sup>·h<sup>-1</sup>. Furthermore, the H<sub>2</sub>O flux for the PDMS PV membrane was 1 kg·m<sup>-2</sup>·h<sup>-1</sup>, but the NH<sub>3</sub> flux was negligible. Moreover, the selective layer of the PDMS PV membrane deteriorated rapidly during the experiments (see Fig. 5), indicating that treating alkaline feed waters with an NH<sub>3</sub> concentration of 1 g·L<sup>-1</sup> was not possible for periods exceeding 3 h. Therefore, we did not further assess the applicability of the PDMS PV membrane.

The K<sub>0,H<sub>2</sub>O</sub> of the Hybrid Silica PV (3·10<sup>-8</sup> s·m<sup>-1</sup>) and PDMS PV (7·10<sup>-8</sup> s·m<sup>-1</sup>) membranes were again (also in 3.1) lower compared to the PTFE membrane K<sub>0,H<sub>2</sub>O</sub> (8·10<sup>-7</sup> s·m<sup>-1</sup>), caused by the lower resistance of H<sub>2</sub>O transfer through the PTFE membrane. The lower resistance of H<sub>2</sub>O transfer for the PTFE membrane compared to the Hybrid Silica PV membrane, which is expressed as higher H<sub>2</sub>O flux and higher K<sub>0,H<sub>2</sub>O</sub>,



**Fig. 4.** (A) The NH<sub>3</sub> and H<sub>2</sub>O fluxes and (B) the K<sub>0,NH<sub>3</sub></sub>, K<sub>0,H<sub>2</sub>O</sub> and S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> of the various membranes for stripping NH<sub>3</sub> from feed waters with an NH<sub>3</sub> feed concentration of 1 g·L<sup>-1</sup> (as NH<sub>4</sub>OH) at a feed water temperature of 35 °C at unsteady hydraulic conditions. The reported values and error bars represent average and the minimum and maximum measurements of at least three replicate experiments. N.D. = not determined (too low flux).

can mainly be assigned to the membrane characteristics. According to Table 1, the pore size of the PTFE membrane was orders of magnitude higher compared to the PV membranes, while also the membrane thickness of the PTFE membrane was lower compared to the PV membranes. Hence, both the higher pore size and the lower membrane thickness contributed to the higher H<sub>2</sub>O transfer rates through the PTFE membrane compared to the PV membranes. Furthermore, the K<sub>0,NH<sub>3</sub></sub> of the PTFE membrane (3·10<sup>-7</sup> s·m<sup>-1</sup>) was more than seven times higher than the Hybrid Silica PV (4·10<sup>-8</sup> s·m<sup>-1</sup>). The differences in NH<sub>3</sub> flux



**Fig. 5.** A new PDMS PV membrane (left) and a deteriorated PDMS PV membrane (right) after exposure to feed water of 35 °C with an  $\text{NH}_3$  concentration of 1 g  $\text{L}^{-1}$  for less than 6 h.

and  $K_{0,\text{NH}_3}$  between the PTFE membrane and Hybrid Silica PV membrane can again be assigned to the pore size and the thickness of the respective membranes. Due to the negligible  $\text{NH}_3$  flux, the  $K_{0,\text{NH}_3}$  of the PDMS PV membrane was not determined.

The PTFE membrane showed a preference to permeate  $\text{H}_2\text{O}$  over  $\text{NH}_3$  indicated by the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of 0.3. The  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of the PTFE membrane was higher than the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of the Hybrid Silica PV membrane (0.2). Hence, the Hybrid Silica PV did not show an increased preference to permeate  $\text{NH}_3$  compared to  $\text{H}_2\text{O}$ , in contrast to the findings of Yang et al. [8], but in line with the findings of Yang et al. [13]. The adsorption of  $\text{NH}_3$  on the silica groups of the PV membranes, leading to blocking of the  $\text{H}_2\text{O}$  transfer, as described by Yang et al. [8], was not present or not strong enough to promote selective  $\text{NH}_3$  permeation. This blocking mechanism was responsible for the selective transfer of  $\text{NH}_3$  over  $\text{H}_2$  in studies conducted by Camus et al. [10] and Kanezashi et al. [11]. However, in contrast to the non-polar  $\text{H}_2$ ,  $\text{NH}_3$  (dipole moment of 1.47 D) and  $\text{H}_2\text{O}$  (dipole moment of 1.85 D) are both polar molecules [28] and both bind with the polar silica groups at the selective layer of the Hybrid Silica PV membrane. In fact,  $\text{H}_2\text{O}$  is more polar than  $\text{NH}_3$  and probably bonded stronger with the selective layer of the Hybrid Silica PV membrane, contributing to the lower  $S_{\text{NH}_3/\text{H}_2\text{O}}$ . Furthermore,  $\text{H}_2\text{O}$  was more abundantly present in the bulk phase of the feed water than  $\text{NH}_3$  (>99 wt%), as the feed water  $\text{NH}_3$  concentration was 1 g  $\text{L}^{-1}$ , corresponding to 0.1 wt%. Therefore, also gas depletion concentration polarisation affected the transfer of  $\text{NH}_3$ , possibly explaining the

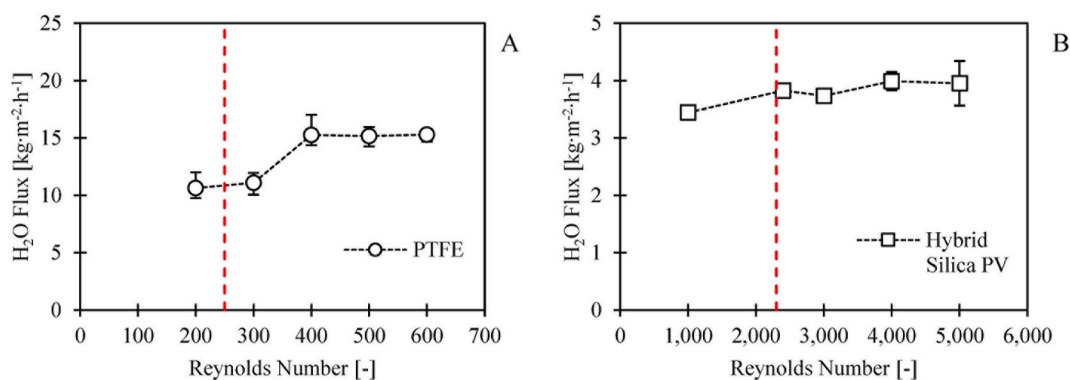
preference of  $\text{H}_2\text{O}$  over  $\text{NH}_3$  transfer.

### 3.3. Selectivity of ammonia over water under various hydraulic conditions

#### 3.3.1. Identification of hydraulic condition ranges

According to the studies of Oliveira et al. [15] and Mojab et al. [24], unsteady flow regions for tubular and spacer-filled channels start at a Reynolds number of 2,300 and 500, respectively. Fig. 6A and B presents the  $\text{H}_2\text{O}$  flux as a function of the Reynolds number for the PTFE and the Hybrid Silica PV membrane, respectively, when using demineralised water as feed water. For the PTFE membrane, the  $\text{H}_2\text{O}$  flux was 11  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  up to a Reynolds number of 300. The  $\text{H}_2\text{O}$  flux increased to 15  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  when the Reynolds number increased to 400 and remained stable when the Reynolds number further increased to 500 and 600. For the Hybrid Silica PV membrane, the  $\text{H}_2\text{O}$  flux increased from 3 to 4  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  when the Reynolds number increased from 1,000 to 2,400 and remained 4  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  when the Reynolds number further increased to 3,000, 4,000 and 5,000. Hence, the indicated Reynolds numbers for steady and unsteady hydraulic conditions were in line with the changes in  $\text{H}_2\text{O}$  flux for both spacer-filled rectangular and open tubular channels [15,24].

Because during the  $\text{H}_2\text{O}$  permeation experiments at various Reynolds numbers the driving force for  $\text{H}_2\text{O}$  transfer was equal, as the same feed water temperature and vacuum pressure were used, the increase in  $\text{H}_2\text{O}$



**Fig. 6.** (A) The  $\text{H}_2\text{O}$  flux of the PTFE membrane and (B) the Hybrid Silica PV membrane (PV) at a feed water temperature of 35 °C as a function of the Reynolds numbers. The dotted vertical lines represent the Reynolds numbers at which theoretically the hydraulic conditions become unsteady: 250 for spacer-filled rectangular flow channels and 2,300 for tubular flow channels. The reported values and error bars represent average and the minimum and maximum measurements of at least three replicate experiments.



flux due to the shift from steady to unsteady hydraulic conditions was caused by an increase in  $K_{o,H_2O}$ . By shifting from steady to unsteady hydraulic conditions, the effect of temperature polarisation was less apparent, resulting in a higher feed vapour pressure at the membrane interface and thus actual driving force for  $H_2O$  transfer. Moreover, as the membrane temperature was probably higher at higher Reynolds numbers due to the weaker effect of temperature polarisation, the  $K_m$  for the PTFE decreased, according to mass transfer described Knudsen diffusion. Apparently, the increase in actual  $H_2O$  driving force had a greater impact than the decrease in  $K_m$  on the  $H_2O$  flux. For the Hybrid Silica PV membrane, the increase in Reynolds number probably resulted into an increased actual  $H_2O$  driving force, as well as an increased  $K_m$ , due to the reduced effect of temperature polarisation, ultimately leading to an increase in  $H_2O$  flux.

### 3.3.2. Selectivity of ammonia over water under steady and unsteady hydraulic conditions

Subsequently,  $NH_3$  transfer was assessed under both steady and unsteady hydraulic conditions for the PTFE and the Hybrid Silica PV membranes. Based on results of  $H_2O$  transfer as a function of the Reynolds number experiments (see Section 3.3.1.), we used Reynolds numbers of 200 and 500 for the PTFE membrane and 1,000 and 2,400 for the Hybrid Silica PV membrane as representative values of steady and unsteady hydraulic conditions, respectively. In line with the findings in Section 3.2., the transfer rates of  $NH_3$  and  $H_2O$ , expressed as flux and  $K_o$  were consistently lower for the Hybrid Silica PV membrane, compared to the PTFE membrane, which can be explained by the membrane thickness and pore size of the respective membranes.

Fig. 7A shows that the  $NH_3$  flux for the PTFE membrane increased from 0.08 to 0.11  $kg \cdot m^{-2} \cdot h^{-1}$  when the hydraulic conditions shifted from steady to unsteady, whereas for the Hybrid Silica PV the  $NH_3$  flux increased from 0.01 to 0.02  $kg \cdot m^{-2} \cdot h^{-1}$ . The  $H_2O$  fluxes for the PTFE and Hybrid Silica PV membrane remained stable at 11 and 3  $kg \cdot m^{-2} \cdot h^{-1}$ , respectively, when the hydraulic conditions shifted from steady to unsteady. The rate of  $H_2O$  transfer during the experiments with demineralised water in Section 3.1 and Section 3.3.1. was consistently higher compared to the experiments using feed waters containing  $NH_4OH$ , indicating that the transfer of  $NH_3$  affected the transfer of  $H_2O$ . Furthermore, the shift from steady to unsteady hydraulic conditions had a greater impact on the  $K_{o,NH_3}$  than on the  $K_{o,H_2O}$ . The  $K_{o,NH_3}$  increased from  $1 \cdot 10^{-7}$  to  $3 \cdot 10^{-7} s \cdot m^{-1}$  and from  $2 \cdot 10^{-8}$  to  $3 \cdot 10^{-8} s \cdot m^{-1}$  for the PTFE and the Hybrid Silica PV membrane, respectively, whereas the  $K_{o,H_2O}$  remained at  $7 \cdot 10^{-7} - 8 \cdot 10^{-7} s \cdot m^{-1}$  and  $2 \cdot 10^{-7} s \cdot m^{-1}$ , respectively. The increase in  $NH_3$  fluxes and  $K_{o,NH_3}$  by shifting from steady to unsteady hydraulic conditions can be explained by a decrease in the effect of gas depletion concentration polarisation.

The  $S_{NH_3/H_2O}$  increased when the hydraulic conditions shifted from steady to unsteady conditions, in line with the findings of Ding et al. [3] and El-Bourawi et al. [4]. For the PTFE membrane,  $S_{NH_3/H_2O}$  increased from 0.2 to 0.3, while  $S_{NH_3/H_2O}$  for the Hybrid Silica PV membrane increased from 0.1 to 0.2, indicating that the PTFE membrane again had a higher selectivity for  $NH_3$  over  $H_2O$  transfer than the Hybrid Silica PV membrane, in line with the findings described in Section 3.2. The observed increase in  $S_{NH_3/H_2O}$  for the PTFE membrane contradicted to the observations of He et al. [6], who found that  $K_{o,H_2O}$  increased more than  $K_{o,NH_3}$  for higher cross-flow velocities. However, it was unclear whether these experiments were conducted in either steady or unsteady hydraulic conditions as the hydraulic diameter and geometry of the feed channel were not reported. Hence, our observations show that stripping  $NH_3$  at unsteady hydraulic conditions were preferred over operating at steady hydraulic conditions to maximise  $S_{NH_3/H_2O}$ , irrespective of the used type of membrane, also in line with the findings of Scheepers et al. [7].

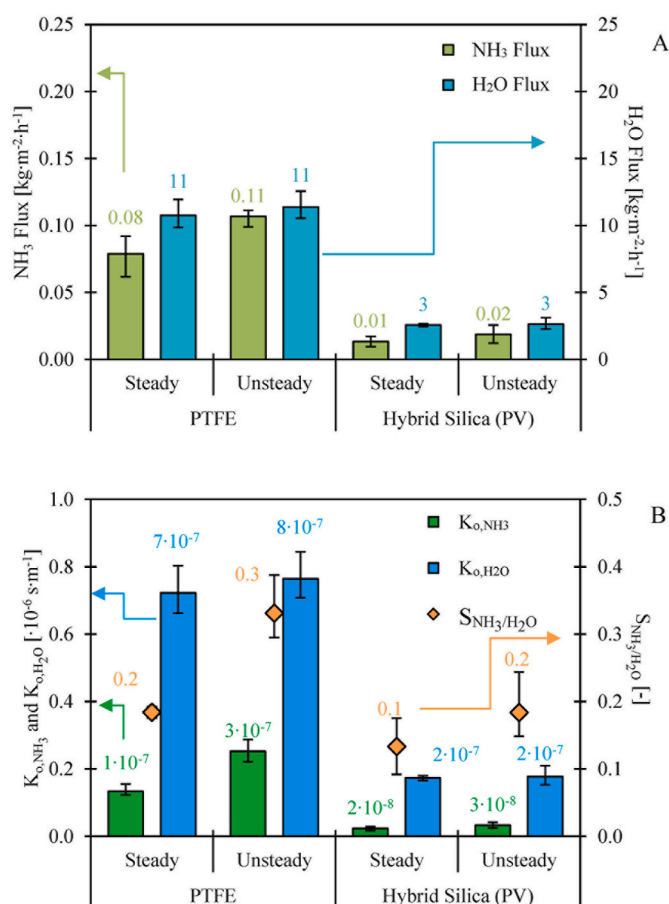
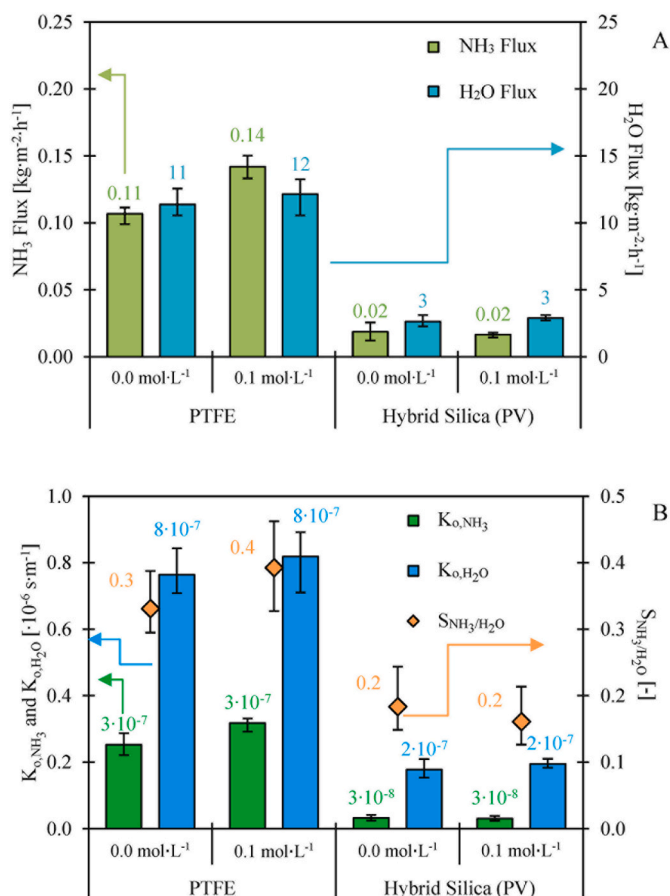


Fig. 7. (A) The  $NH_3$  and  $H_2O$  fluxes and (B) the  $K_{o,NH_3}$ ,  $K_{o,H_2O}$  and  $S_{NH_3/H_2O}$  of the PTFE and the hydrophilic Hybrid Silica PV membrane for stripping  $NH_3$  for steady and unsteady hydraulic conditions, from feed waters with an  $NH_3$  feed concentration of 1  $g \cdot L^{-1}$  (as  $NH_4OH$ ) at a feed water temperature of 35 °C at both steady and unsteady hydraulic conditions. The reported values and error bars represent average and the minimum and maximum measurements of at least three replicate experiments.

### 3.4. Selectivity of ammonia over water of various membranes for various feed water compositions

#### 3.4.1. Ammonia feed water concentration of 1 $g \cdot L^{-1}$ at various ionic strengths

Fig. 8A shows that the fluxes of  $NH_3$  for the PTFE membrane were 0.11 and 0.14  $kg \cdot m^{-2} \cdot h^{-1}$  when feed waters had a negligible ionic strength ( $NH_4OH$ ) and an ionic strength of 0.1  $mol \cdot L^{-1}$  ( $NH_4HCO_3$  at a pH of 10), respectively. The  $H_2O$  flux of the PTFE membrane ranged between 11 and 12  $kg \cdot m^{-2} \cdot h^{-1}$  for the feed waters with negligible and 0.1  $mol \cdot L^{-1}$  ionic strengths, respectively, while the  $K_{o,H_2O}$  was  $8 \cdot 10^{-7} s \cdot m^{-1}$  (see Fig. 8B). Based on the ratio of the  $NH_3$  and  $H_2O$  fluxes (0.01), the energy consumption can be derived, based on our previous study [5]. The energy consumption for stripping  $NH_3$  at an  $NH_3$  feed water concentration of 1  $g \cdot L^{-1}$  was approximately 100  $MJ \cdot kg \cdot N^{-1}$ . According to Fig. 8B, the  $K_{o,NH_3}$  was  $3 \cdot 10^{-7} s \cdot m^{-1}$  for both feed waters, indicating that the effect of the difference in ionic strength of 0.1  $mol \cdot L^{-1}$  was negligible on the  $NH_3$  transfer. The  $S_{NH_3/H_2O}$  for the PTFE membrane for these experiments ranged between 0.3 and 0.4, which indicates the transfer of  $H_2O$  was again preferential over  $NH_3$  (similar as in Section 3.2 and 3.3), independent of the difference in ionic strength. In addition, in line with the findings in Section 3.2. and Section 3.3., the transfer rates of  $NH_3$  and  $H_2O$ , expressed as flux and  $K_o$  were consistently lower for the Hybrid Silica PV membrane, compared to the PTFE membrane, which can be explained by the membrane thickness and pore size of the



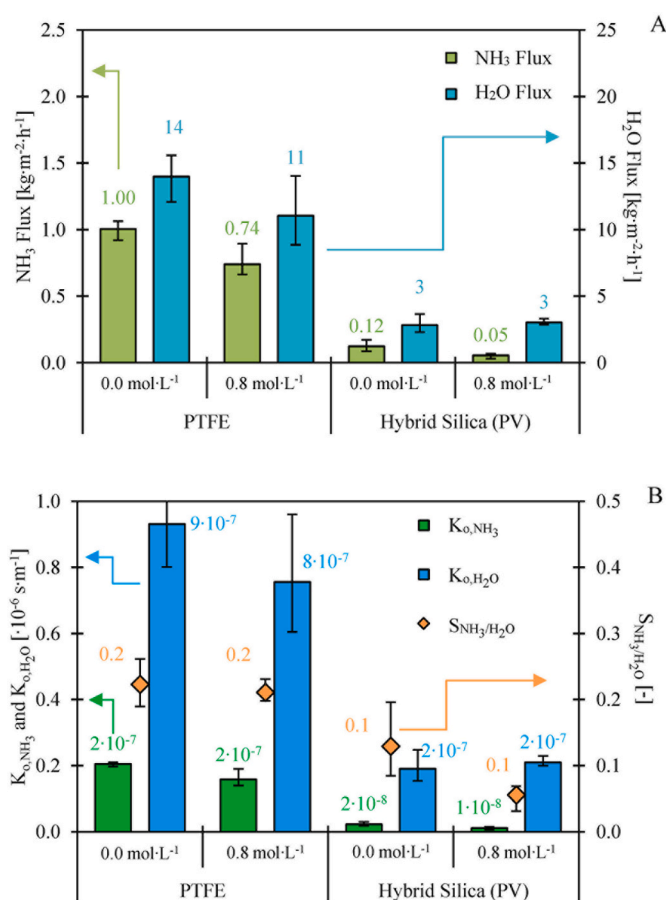
**Fig. 8.** (A) The NH<sub>3</sub> and H<sub>2</sub>O fluxes and (B) the K<sub>0,NH<sub>3</sub></sub>, K<sub>0,H<sub>2</sub>O</sub> and S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> of the PTFE and the Hybrid Silica PV membrane for stripping NH<sub>3</sub> from feed waters with an NH<sub>3</sub> feed concentration of 1 g·L<sup>-1</sup> having a negligible (as NH<sub>4</sub>OH) and 0.8 mol·L<sup>-1</sup> (as NH<sub>4</sub>HCO<sub>3</sub> at a pH of 10) ionic strength at a feed water temperature of 35 °C at unsteady hydraulic conditions. The reported values and error bars represent average and the minimum and maximum measurements of at least three replicate experiments.

respective membranes.

For the Hybrid Silica PV membrane, the NH<sub>3</sub> and H<sub>2</sub>O fluxes were 0.02 and 3 kg·m<sup>-2</sup>·h<sup>-1</sup>, respectively, when using feed water with a negligible and 0.1 mol·L<sup>-1</sup> ionic strength at an NH<sub>3</sub> feed concentration of 1 g·L<sup>-1</sup>. The K<sub>0,H<sub>2</sub>O</sub> of the Hybrid Silica PV membrane for the feed water with different ionic strengths was 2·10<sup>-7</sup> s·m<sup>-1</sup> and the K<sub>0,NH<sub>3</sub></sub> was 3·10<sup>-8</sup> s·m<sup>-1</sup>. The S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> of the Hybrid Silica PV membrane for both feed waters was 0.2, suggesting that the increase in ionic strength of 0.1 mol·L<sup>-1</sup> did not affect the selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer, which is in agreement with the findings for the PTFE membrane.

### 3.4.2. Ammonia feed water concentration of 10 g·L<sup>-1</sup> at various ionic strengths

At last, the S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> was assessed for the PTFE and Hybrid Silica PV membrane using feed waters with an NH<sub>3</sub> feed concentration of 10 g·L<sup>-1</sup> with a negligible ionic strength (NH<sub>4</sub>OH) and an ionic strength of 0.8 mol·L<sup>-1</sup> (NH<sub>4</sub>HCO<sub>3</sub> at a pH of 10). The NH<sub>3</sub> fluxes for the PTFE membrane were 1.00 and 0.74 kg·m<sup>-2</sup>·h<sup>-1</sup> for the feed waters with a negligible and 0.8 mol·L<sup>-1</sup> ionic strength, respectively, whereas the H<sub>2</sub>O fluxes were 14 and 11 kg·m<sup>-2</sup>·h<sup>-1</sup>, respectively (see Fig. 9A). Hence, the fluxes of both NH<sub>3</sub> and H<sub>2</sub>O decreased when the ionic strength of the feed water increased from 0.0 to 0.8 mol·L<sup>-1</sup>. With a ratio of the NH<sub>3</sub> flux and the total flux of 0.06, the electrical energy consumption for stripping NH<sub>3</sub> at an NH<sub>3</sub> feed water concentration of 10 g·L<sup>-1</sup> was approximately 10 MJ·kg<sup>-1</sup>, based on [5]. For the Hybrid Silica PV



**Fig. 9.** (A) The NH<sub>3</sub> and H<sub>2</sub>O fluxes and (B) the K<sub>0,NH<sub>3</sub></sub>, K<sub>0,H<sub>2</sub>O</sub> and S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> of the PTFE and the Hybrid Silica PV membrane for stripping NH<sub>3</sub> from feed waters with an NH<sub>3</sub> feed concentration of 10 g·L<sup>-1</sup> having a negligible (as NH<sub>4</sub>OH) and 0.8 mol·L<sup>-1</sup> (as NH<sub>4</sub>HCO<sub>3</sub> at a pH of 10) ionic strength at a feed water temperature of 35 °C at unsteady hydraulic conditions. The reported values and error bars represent average and the minimum and maximum measurements of at least three replicate experiments.

membrane, the NH<sub>3</sub> flux was 0.12 and 0.05 kg·m<sup>-2</sup>·h<sup>-1</sup> for feed waters with a negligible and 0.8 mol·L<sup>-1</sup> ionic strength, respectively, while the H<sub>2</sub>O flux was stable for both feed waters at 3 kg·m<sup>-2</sup>·h<sup>-1</sup>. In line with the findings on the PTFE membrane, the NH<sub>3</sub> flux also decreased for the Hybrid Silica PV membrane when the ionic strength increased from 0.0 to 0.8 mol·L<sup>-1</sup> for feed water with an NH<sub>3</sub> feed concentration of 10 g·L<sup>-1</sup>.

According to Fig. 9B, the K<sub>0,NH<sub>3</sub></sub> (2·10<sup>-7</sup> s·m<sup>-1</sup>) for the PTFE membrane did not change when the ionic strength increased from 0.0 to 0.8 mol·L<sup>-1</sup>, suggesting that the additional presence of ions did not affect the NH<sub>3</sub> transfer. In addition, the increase in ionic strength also did not affect the transfer of H<sub>2</sub>O for the PTFE membrane, as the K<sub>0,H<sub>2</sub>O</sub> (8·10<sup>-7</sup> - 9·10<sup>-7</sup> s·m<sup>-1</sup>) was similar for a negligible and 0.8 mol·L<sup>-1</sup> ionic strength. Eventually, the S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> was 0.2 for feed water with an NH<sub>3</sub> feed water concentration of 10 g·L<sup>-1</sup> with both a negligible and 0.8 mol·L<sup>-1</sup> ionic strength, indicating that the selectivity of NH<sub>3</sub> transfer was not affected by the increase in ionic strength for the PTFE membrane. For the Hybrid Silica PV membrane, the K<sub>0,NH<sub>3</sub></sub> decreased from 2·10<sup>-8</sup> to 1·10<sup>-8</sup> s·m<sup>-1</sup> when the ionic strength increased from 0.0 to 0.8 mol·L<sup>-1</sup>, while K<sub>0,H<sub>2</sub>O</sub> for the Hybrid Silica PV membrane was stable at 2·10<sup>-7</sup> s·m<sup>-1</sup>. Hence, the increase in ionic strength of 0.8 mol·L<sup>-1</sup> affected only the transfer of NH<sub>3</sub>, which can be assigned to the increased effect of gas depletion concentration polarisation. Eventually, the S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> for the Hybrid Silica was 0.1 for an NH<sub>3</sub> feed water concentration of 10 g·L<sup>-1</sup> with both a negligible and 0.8 g·L<sup>-1</sup> ionic strength.

By increasing the  $\text{NH}_3$  feed concentration from 1 to  $10 \text{ g}\cdot\text{L}^{-1}$ , the  $\text{NH}_3$  flux increased for the PTFE membrane from 0.08 to 0.11 to  $0.74\text{--}1.00 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , in line with the study of Scheepers et al. [7] However, the  $K_{o,\text{NH}_3}$  of the PTFE membrane decreased when increasing the  $\text{NH}_3$  feed water concentration, while the  $K_{o,\text{H}_2\text{O}}$  remained equal, resulting in a decrease in  $S_{\text{NH}_3/\text{H}_2\text{O}}$  from 0.3 to 0.4 to 0.2. In line with the findings for the PTFE membrane, also the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  for the Hybrid Silica decreased when the  $\text{NH}_3$  feed water concentration increased from 1 to  $10 \text{ g}\cdot\text{L}^{-1}$ , from 0.2 to 0.1, respectively. Hence, the increases in  $\text{NH}_3$  flux for both the PTFE and Hybrid Silica PV membrane when the  $\text{NH}_3$  feed water concentration increased from 1 to  $10 \text{ g}\cdot\text{L}^{-1}$  was caused by the higher driving force as a result of the higher  $\text{NH}_3$  vapour pressure in the feed water. Moreover, the selectivity of  $\text{NH}_3$  transfer over  $\text{H}_2\text{O}$  decreased further for both membranes when the  $\text{NH}_3$  feed water concentration increased. Apparently, even at a ten-fold higher  $\text{NH}_3$  feed concentration, the relative presence of  $\text{NH}_3$  was low (approximately 1 wt%) compared to  $\text{H}_2\text{O}$ , explaining partially the preferential transfer of  $\text{H}_2\text{O}$  over  $\text{NH}_3$  for both membranes, under all various feed water compositions.

### 3.5. Future outlook

The selected silica-based PV membranes did not allow for selective transfer of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  during the vacuum stripping of  $\text{NH}_3$  from various feed waters. In fact, the used PV membranes even did not have a higher  $S_{\text{NH}_3/\text{H}_2\text{O}}$  than the used porous PTFE membrane. A major restriction is the similarity between  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in terms of molecular weight (17 and  $18 \text{ g}\cdot\text{mol}^{-1}$ , respectively), kinetic diameter (0.33 and 0.26 nm, respectively) and polarity (dipole moment of 1.47 and 1.85 D, respectively). Furthermore, since  $\text{H}_2\text{O}$  was abundantly present (approximately 99 wt% in this study) in the used feed waters, it was not feasible to achieve preferential  $\text{NH}_3$  transfer with the used membranes and operational conditions. In contrast to previous literature, the hydrophilic PV membrane showed a preference for  $\text{H}_2\text{O}$ , while for the hydrophobic PV membrane the  $\text{NH}_3$  transfer was negligible and the selective layer rapidly deteriorated when being exposed to  $\text{NH}_3$  feed water. Hence, new membrane materials are needed to allow for selective permeation of  $\text{NH}_3$  over  $\text{H}_2\text{O}$ , for example as a selective layer of dense membranes. The materials of the selective layer of the membrane should either avoid the dissolution of  $\text{H}_2\text{O}$  and allow for solution and diffusion of  $\text{NH}_3$ , or allow for solution and diffusion of  $\text{NH}_3$  and strong binding of  $\text{H}_2\text{O}$  on the selective layer without blocking the transfer of  $\text{NH}_3$ . To develop new membrane materials that allow for more selective  $\text{NH}_3$  over  $\text{H}_2\text{O}$  transfer, advantage of the difference in acidity coefficients ( $\text{pK}_a$ ) between  $\text{NH}_3$  and  $\text{H}_2\text{O}$  can be made. By allowing for less strong bonding of  $\text{NH}_3$  than  $\text{H}_2\text{O}$  to the membrane material after sorption due to the differences in  $\text{pK}_a$ , potentially higher transfer rates of  $\text{NH}_3$  compared to  $\text{H}_2\text{O}$  can be established. To support the development of new membrane materials for more selective  $\text{NH}_3$  over  $\text{H}_2\text{O}$  transfer, we think more research on the surface affinity between  $\text{NH}_3$  and  $\text{H}_2\text{O}$  and membrane materials is needed. Finally, in contrast to the PDMS PV membrane, the respective selective layer must be resistant to alkaline aqueous conditions.

## 4. Conclusions

Based on the experiments to assess the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of various membranes while stripping  $\text{NH}_3$  from water under different hydraulic conditions and for various feed water compositions, we can conclude the following:

- The transfer rate of  $\text{H}_2\text{O}$  (as  $\text{H}_2\text{O}$  flux and  $K_{o,\text{H}_2\text{O}}$ ) through the used dense hydrophilic Hybrid Silica PV membrane is lower than the transfer rate of  $\text{H}_2\text{O}$  of the used porous gas-permeable PTFE membrane;

- The transfer rate of  $\text{H}_2\text{O}$  through the used dense hydrophobic PDMS PV membrane is lower than the transfer rate of  $\text{H}_2\text{O}$  of the Hybrid Silica PV and the PTFE membrane;
- The transfer of  $\text{NH}_3$  through the PDMS PV membrane is negligible and the membrane deteriorates rapidly when using feed waters containing  $\text{NH}_3$ ;
- The used PTFE membrane and Hybrid Silica PV membranes show selectivity for transfer of  $\text{H}_2\text{O}$  over  $\text{NH}_3$  for all tested hydraulic conditions and feed water compositions;
- The  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of the Hybrid Silica PV membrane (0.1–0.2) is consistently lower than the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of the used PTFE membrane (0.2–0.4);
- Unsteady hydraulic conditions result in a higher  $S_{\text{NH}_3/\text{H}_2\text{O}}$  compared to steady hydraulic conditions for both the PTFE and the Hybrid Silica PV membrane;
- An increase in ionic strength of the feed water from 0.0 to  $0.8 \text{ mol}\cdot\text{L}^{-1}$  decreases the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of both the PTFE and the Hybrid Silica PV membrane;
- An increase in  $\text{NH}_3$  feed concentration from 1 to  $10 \text{ g}\cdot\text{L}^{-1}$  leads to a decrease in  $S_{\text{NH}_3/\text{H}_2\text{O}}$  for both the PTFE and the Hybrid Silica PV membrane;

### CRedit authorship contribution statement

**Niels van Linden:** Investigation, Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Visualization. **Yundan Wang:** Investigation, Conceptualization, Methodology, Investigation. **Ernst Sudhölter:** Conceptualization, Validation, Writing – review & editing. **Henri Spanjers:** Funding acquisition, Supervision, Writing – review & editing. **Jules B. van Lier:** Funding acquisition, Supervision, Writing – review & editing.

### Declaration of competing interest

The authors declare no competing financial interest.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.memsci.2021.120005>.

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