

# Recovery of ammonia from wastewater by liquid–liquid membrane contactor: A review

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**Abstract.** Liquid–liquid membrane contactor (LLMC), a device that exchanges dissolved gas molecules between the two sides of a hydrophobic membrane through membrane pores, can be employed to extract ammoniacal nitrogen from a feed solution, which is transported across the membrane and accumulated in a stripping solution. This LLMC process offers the promise of improving the sustainability of the global nitrogen cycle by cost-effectively recovering ammonia from wastewater. Despite recent technological advances in LLMC processes, a comprehensive review of their feasibility for ammonia recovery is rarely found in the literature. Our paper aims to close this knowledge gap, and in addition to analyze the challenges and provide potential solutions for improvement. We begin with discussions on the operational principles of the LLMC process for ammonia recovery and membrane types and membrane configurations commonly used in the process. We then assess the performance of the process by reviewing publications that demonstrate its practical application. Challenges involved in the implementation of the LLMC process, such as membrane fouling, membrane wetting, and chemical requirements, are presented, along with discussions on potential strategies to address each. These strategies, including membrane modification, hybrid process design, and process optimization based on cost–benefit analysis, guide the reader to identify key areas of future research and development.

**Keywords:** ammonia recovery; ammonia removal; liquid–liquid membrane contactor; wastewater treatment

## 1. Introduction

Ammonia is an essential resource that can be used in various agricultural and industrial activities. About 85% of the world's total ammonia production is consumed as fertilizer, while 15% is used in other industries, such as plastic, explosives, chemical raw materials, semiconductor, and electronic components manufacturing (Vecino *et al.* 2019). Typically, more than 90% of the world's ammonia production employs the Haber–Bosch process, which consumes 1–2% of the annual global energy supply (Qin *et al.* 2017). Wastewater is one of the major routes via which nitrogen products consumed by humans are disposed. Recovery of ammonia from wastewater can be a promising approach to supplying ammonia to different demand sectors, as well as avoiding energy-intensive processes. The process could eventually contribute to sustainable wastewater management, one of whose goals is to recover valuable resources from wastewater.

While being a potential resource that can be recovered and purified to substitute for the Haber–Bosch produced ammonia, ammoniacal nitrogen in wastewater is often one of the principal targets for treatment. Release of ammoniacal

nitrogen through wastewater can cause severe environmental concerns in receiving waters, such as eutrophication and toxicity to aquatic organisms (Kwak *et al.* 2020). Ammoniacal nitrogen pollution has been estimated to result in monetary loss that is equivalent to 0.3–3% of the world's gross domestic product (GDP) (Bodirsky *et al.* 2014). For these reasons, ammoniacal nitrogen removal from wastewaters needs to be carried out to ensure environmental conservation and sustainable development.

Biological nitrogen removal (BNR) processes, which remove reactive nitrogen species from wastewater through their conversion to nitrogen gas, have been widely adopted in wastewater treatment plants (Sum *et al.* 2010). This method that uses naturally occurring bacteria can achieve relatively inexpensive processing costs (Crab *et al.* 2007). However, BNR processes have shown operational instability and inefficiency due to the slow biological conversion of ammonia nitrogen to nitrate nitrogen (Ashrafizadeh *et al.* 2010). In addition, the BNR process has the limitation of using a considerable amount of energy and money to convert a valuable resource, ammoniacal nitrogen, into a substance with negligible market value, which is dinitrogen gas. To date, in wastewater treatment, the removal of ammoniacal nitrogen through nitrification and denitrification has protected human health and the aquatic ecosystem. However, it is evident that this wastewater nitrogen management strategy does not conform to our current mission of moving towards a circular economy to improve the sustainability of our society through resource recycling.

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So far, several processes to recover ammoniacal nitrogen from waste streams have been developed; these processes include ammonia stripping, struvite precipitation, ion exchange, and membrane processes, each of which has its own challenges (Cruz *et al.* 2019). Ammonia stripping can recover ammonia at high purity, but it demands a large amount of chemicals to control the feed water pH, and the frequent occurrence of fouling at the stripping tower inhibits the process efficiency (Yuan *et al.* 2016, Burton *et al.* 2018). Struvite precipitation simultaneously recovers nitrogen and phosphorus in a short time, and has the advantage of producing a slow-releasing fertilizer as the precipitate (Yan *et al.* 2016). However, when ammonia is the major substance to be recovered, struvite precipitation is by nature not effective. Struvite contains only 5.7% nitrogen on a weight basis, and because of the formation of other crystals, such as calcium and magnesium phosphates, the nitrogen content in the precipitates of the actual process can be even lower (Cruz *et al.* 2019, Shaddel *et al.* 2020). Ion exchange can be applied in a wide range of ammonia concentrations and temperature, and the adsorbent for ammonia recovery can be regenerated by a chemical reagent (Huang *et al.* 2010, Tarpeh *et al.* 2017). The chemical reagent regeneration, which requires significant capital cost, contains a considerable amount of cations other than ionic ammonia (Crittenden *et al.* 2012). Moreover, when the influent ammonia concentration is low, the equilibrium shift may result in reversible chemical reactions going backwards (i.e., ammonium release from the exchange resin) during the process (Wang *et al.* 2006).

Recently, liquid–liquid membrane contactor (LLMC) – which enables extraction of gaseous molecules from a liquid solution to another – has emerged to become an efficient device for ammonia recovery from waste streams. By this device, ammonia present in the liquid feed is captured on the stripping liquid through a microporous hydrophobic membrane due to a concentration (or partial pressure) gradient across the membrane (Xie *et al.* 2016). In general, this technology holds advantages over other alternatives, such as: (1) low areal/volumetric footprint and diverse scalability of the treatment unit, due to the inherent nature of membrane devices, that is, compactness and modularity, respectively; (2) low energy consumption, because the substance transfer across the membrane is driven by diffusion, not by mechanical pressure; (3) applicability to wastewater with various strengths, because the removal/recovery rate is independent of the concentration of the target compound; (4) flexible operation allowed by the separate velocity control of the feed and stripping flows, which alleviates the problems of emulsion, flooding, and foaming; and (5) high purity of the recovered product due to the excellent selectivity from a feed solution with complex composition, which results in high market value of the product (Gabelman *et al.* 1999, Li *et al.* 2005, Hasanoğlu *et al.* 2010, Siagian *et al.* 2019, Xu *et al.* 2019, Brennan *et al.* 2021, Pandey *et al.* 2021).

With these unique advantages, the LLMC technique offers the promise of advancing the wastewater nitrogen management practices by enabling both cost-effective nitrogen removal from wastewater and conversion of the removed nitrogen into valuable products. To date, several review articles covering the application of LLMC for

ammonia recovery from different wastewater have been published. The review by Brennan *et al.* (2021) focused on the use of LLMC for the recovery of ammonia from high-strength waste streams, such as agricultural slaughterhouse wastewater. Darestani *et al.* (2017) provided a more comprehensive review, introducing case studies of ammonia recovery from various types of wastewater, while limiting their discussion with respect to membrane configuration as hollow fiber membranes. Unlike these previous reviews, this paper encompassed LLMC applications using different membrane configurations (i.e., flat sheet, tubular, spiral wound, hollow fiber) for ammonia recovery from various wastewater sources. Each wastewater source was specifically discussed regarding the opportunity for improved ammonia treatment using LLMC. We discussed challenges and proposed future research directions involved in chemical requirements and economic assessment of LLMC operation, which were not addressed in the previous reviews (Darestani *et al.* 2017, Rongwong and Goh 2020). Most recent progresses and applications of this fast-growing technique were updated in this review. We focused on the device that provides liquid–liquid contact with a membrane in between, i.e., LLMC, which among the three types of operations in membrane contactors (MCs), of gas–liquid, liquid–gas, and liquid–liquid (Rongwong and Goh 2020), is most widely used in wastewater treatment applications. We also concentrate on the contactors using membranes with gas-filled pores, and thus membrane gas separation devices that employ thin dense membranes as a selective barrier between the feed phase and permeate phase are not discussed. We start by describing the key operation principles and the mass transfer mechanisms involved in the LLMC process. We then categorize the hydrophobic membrane materials and configuration used for LLMC utilizing mass transfer through gas-filled membrane pores. Next, we provide an overview of the ammonia removal/recovery by employing LLMC from low-intensity wastewater to high-intensity wastewater with respect to ammonia content. In addition, we address the challenges that hinder the operation of the LLMC, such as membrane fouling and membrane wetting, and propose some candidate technologies to overcome these problems. We also investigate the economy of the process, and describe potential strategies to improve the cost-effectiveness of the membrane process. By addressing these discussions, we demonstrate that the LLMC, if operated under near-ideal operational conditions, could be an attractive candidate to replace existing ammonia recovery processes from wastewater.

## 2. Operating principles of the liquid–liquid membrane contactor process

### 2.1 Fundamental operating principles

The LLMC employing a hydrophobic microporous membrane can separate or extract volatile species, such as ammonia (Rezakazemi *et al.* 2012), carbon dioxide (Rahim *et al.* 2015), methane (Henares *et al.* 2018), and cyanide (Han *et al.* 2005) from a liquid solution, transferring the species through gas-filled membrane pores to another

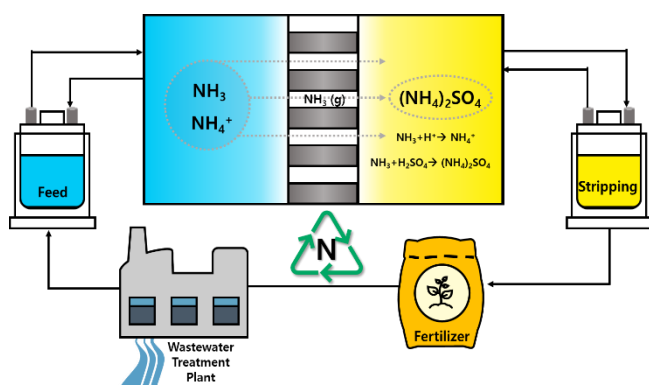


Fig. 1 Schematic of the operating principle of the liquid–liquid membrane contactor for ammonia recovery from wastewater

solution that is placed on the other side of the membrane. To accentuate the substance that is transported across the membrane (i.e., gaseous molecules), processes employing a membrane contactor (MC) are alternatively termed a gas-permeable membrane process (Vanotti *et al.* 2017), gas extraction process (Shen *et al.* 2012), gas absorption process (Mansourizadeh *et al.* 2012), or TransMeMbrane ChemiSorption process (Laknera *et al.* 2020). As the membrane pores are filled with gas, the membrane can prevent passage of any non-volatile constituents in the liquid solutions filled on the two sides of the membrane. It is critical that the wetting of membrane pores with the liquid phase should be prevented, so that the gas–liquid interface at the pore inlet can be maintained; failure to do so may lead to low mass transfer resistance (Dindore *et al.* 2004). When the membrane pores become completely filled by the liquid, the membrane no longer functions as a barrier of non-volatile constituents in the liquid solutions, and the LLMC thus loses its selectivity of separation (Deshmukh *et al.* 2018).

To facilitate the gas–molecule transfer across the hydrophobic membrane, several studies examined the effects of membrane structure (membrane pore size and porosity) and operational conditions (solution concentration, flow rates, pH, and temperature) on the transfer rates (Zhao *et al.* 2016). Ashrafizadeh *et al.* (2010) investigated the effect of the initial concentrations of the ammonia and sulfuric acid solutions, the feed pH, the feed flow velocity, and the presence of excess ions in the ammonia feed solution on the ammonia mass transfer rate. The results showed that the initial concentration of feed solution and stripping solution had negligible effect on the ammonia mass transfer rate. In contrast, increasing the ammonia feed velocity and feed pH value up to 10 significantly increased the rate. Noteworthy is that when the pH feed value is higher than 11, the ammonia mass transfer rate is only slightly increased. Ding *et al.* (2006) also investigated the factors that might affect the mass transfer coefficient and selectivity for ammonia. The mass transfer coefficient and selectivity were directly proportional to both feed pH and temperature, whereas no observable effect of feed flow velocity on the process performance could be found.

In LLMC for ammonia recovery from an aqueous

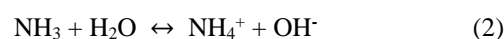
solution, the driving force for ammonia mass transfer across the membrane is the concentration gradient of the molecular form of ammonia (i.e., free ammonia) between the two sides of the membrane (Hou *et al.* 2019). It is generally believed that, mechanistically, three steps are required for the ammonia recovery to occur in a LLMC (Fig. 1). First, ammonia diffuses from the bulk feed solution to the boundary layer at the membrane pore. Then the ammonia volatilizes to the gas side of the feed solution–gas interface, moves through the gas-filled pore driven by the partial pressure gradient, and reaches the gas–stripping solution interface. Finally, the gas-phase ammonia is absorbed at the boundary layer of the stripping solution, is immediately converted to a nonvolatile form after dissolution, and diffuses into the bulk of the stripping solution, so that it can be recovered as a valuable resource (Li *et al.* 2005).

## 2.2 Ammonia mass transfer rate

Among the two forms of ammoniacal nitrogen, that is, free ammonia ( $\text{NH}_3$ ) and ionic ammonia ( $\text{NH}_4^+$ ; ammonium ion), only free ammonia can move through the gas-filled membrane pores via gaseous diffusion. Thus, the rate of ammoniacal nitrogen mass transfer across the membrane is described as (Zhu *et al.* 2005, Tun *et al.* 2016):

$$\frac{d[\text{TAN}]_f}{dt} = -k_o \frac{A_m}{V_f} [\text{NH}_3]_f \quad (1)$$

where,  $[\text{TAN}]_f$  and  $[\text{NH}_3]_f$  are the total ammoniacal nitrogen (TAN, sum of free ammonia and ionic ammonia) and free ammonia concentrations in the feed solution, respectively,  $V_f$  is the feed solution volume, and  $A_m$  is the membrane surface area. The dissociation equilibrium of the two ammoniacal nitrogen species is described as:



with the acid dissociation constant  $K_a$  defined as follows:

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \quad (3)$$

The molar fraction of free ammonia relative to the sum of the free and ionic ammonia is primarily determined by the solution pH and the  $\text{p}K_a$  of the ammonium–ammonia system (Fig. 2). The concentration gradient of free ammonia, which is the driving force for ammonia mass transfer, is maintained by the control of the pH difference between the feed solution and the stripping solution. Ammoniacal nitrogen is readily absorbed at the stripping side by keeping the stripping solution pH sufficiently lower than the  $\text{p}K_a$ , such that nearly zero free ammonia concentration is maintained at the bulk, as well as at the boundary layer of the solution (Lee *et al.* 2021). When the feed solution pH is above the ammonium  $\text{p}K_a$ , the fraction of free ammonia is greater than that of ionic ammonia, favoring the extraction of ammoniacal nitrogen from the feed solution. More specifically, by rearranging Eq. (3) and using the mass balance of  $[\text{TAN}]_f = [\text{NH}_3]_f + [\text{NH}_4^+]_f$ , where  $[\text{NH}_4^+]_f$  is the ionic ammonia concentration in the feed solution, the fraction of free ammonia in the feed

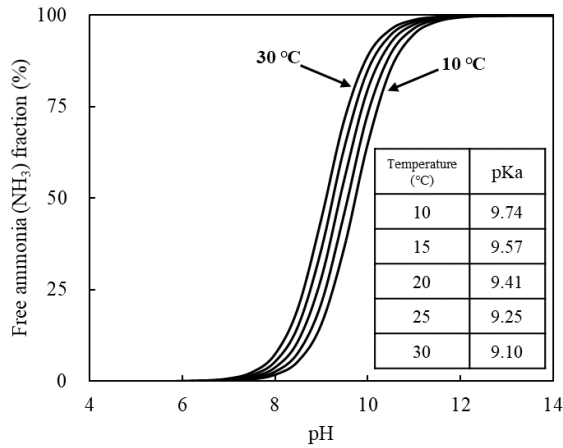


Fig. 2 Free ammonia fraction by the total ammoniacal nitrogen (TAN) as a function of pH at five different temperatures from 10 to 30°C with 5°C intervals

solution is written as:

$$\frac{[\text{NH}_3]_f}{[\text{TAN}]_f} = \frac{1}{1 + 10^{\text{pK}_a - \text{pH}}} \quad (4)$$

Eqs. (1) and (4), in combination, explain why experimental works showed that the ammonia mass transfer rate was sensitive to the feed pH at pH range close to ammonia  $\text{pK}_a$ , but was not so at the range sufficiently higher than ammonia  $\text{pK}_a$  (e.g.,  $\text{pH} > 11$ ). (e.g.,  $\text{pH} > 11$ ).

The overall mass transfer coefficient can be obtained by conducting an experiment to monitor the free ammonia concentration at the feed solution over time (Zhu *et al.* 2005). Obtaining the slope of the linear regression curve of  $\ln([\text{NH}_3]_{f,0}/[\text{NH}_3]_{f,t})$  versus  $t$ , where  $[\text{NH}_3]_{f,0}$  and  $[\text{NH}_3]_{f,t}$  are the free ammonia concentration in the feed solution at time 0 and  $t$  ( $>0$ ), respectively, allows experimental determination of the overall mass transfer coefficient  $K$  according to the following equation:

$$\ln \frac{[\text{NH}_3]_{f,0}}{[\text{NH}_3]_{f,t}} = \frac{A_m}{V_f} \cdot K \cdot t \quad (5)$$

Note that Eq. (5) is obtained by rearranging Eq. (1) after substituting the left hand side of the equation with  $d[\text{NH}_3]_f/dt$ . This suggests that for Eq. (5) to be theoretically valid, the change of feed solution TAN concentration should be equivalent to the change of feed solution free ammonia concentration. Fig. 2 and Eq. (4) tell that this premise holds when the feed solution pH is maintained sufficiently higher than the ammonium  $\text{pK}_a$  throughout the experiment. In the LLMC operation, the mass transfer between the two sides of the membrane can be described by the resistance-in-series model (Rongwong *et al.* 2019).

$$\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_s} \quad (6)$$

Eq. (6) illustrates that the overall mass transfer resistance ( $1/K$ ) can be expressed as the combination of the resistance of the diffusion boundary layer of the feed liquid side ( $1/K_f$ ), the resistance of the diffusion through the membrane ( $1/K_m$ ), and the resistance of the boundary layer of the stripping liquid side ( $1/K_s$ ). The equation also

explains why the feed flow velocity is observed to play a significant role in the overall mass transfer rate in one set of experiments whereas it is not in another set; when the overall mass transfer resistance is almost solely controlled by the resistance of the gaseous diffusion through the membrane, the overall rate would not be a function of the feed flow velocity.

### 3. Membrane material and configuration

#### 3.1 Membrane material

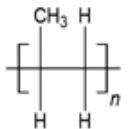
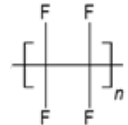

Hydrophobic microporous membranes used in LLMCs have been fabricated from many different polymers that include polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) (Li *et al.* 2019) (Table 1). Among these materials, PP membrane is commercially well developed and is inexpensive, but it is less hydrophobic than fluorine-containing membrane such as PTFE and PVDF, and thus more prone to wetting (Wang *et al.* 2018). PTFE is a commonly used material on hydrophobic membrane, due to its excellent hydrophobicity, thermal stability, and chemical resistance (Khaisri *et al.* 2009, Wang *et al.* 2021). However, the large-scale application of PTFE is challenged by its limited solubility to common solvents, which disfavors mass production via the phase inversion process (Huang and Arning 2019). PVDF is also widely utilized for LLMCs, as they are cheaper and easier to fabricate than with PTFE, while exhibiting fairly low surface energy and good stability (Liu *et al.* 2011). For the selection and development of membrane materials, it is important to consider the capital and operational cost of the process in which the membrane is to be used, as well as the physical and chemical characteristics of the materials that are associated with thermal stability, chemical resistance, robustness, and longevity.

Membrane fabrication or modification techniques have been extensively studied using various recipes of polymer blending and additives, polymer concentration, coagulant types, and post treatment methods to improve the membrane functionality. For example, novel hydrophobic membranes, such as PVDF-hexafluoropropylene (HFP)/ $\text{SiO}_2$  (Toh *et al.* 2020), PVDF-HFP/ortho-phosphoric acid (Hosseini *et al.* 2017), PVDF/lithium chloride (Mansourizadeh *et al.* 2010), and PVDF/montmorillonite (DashtArzhandi *et al.* 2015), have been demonstrated to exhibit enhanced gas flux, owing to their greater hydrophobicity compared to conventional polymeric membranes. However, to the best of our knowledge, only limited study of these novel membrane materials for their use in LLMCs has been conducted, few studies for carbon dioxide stripping but none for ammonia recovery. Thus, future efforts are necessary to develop membrane fabrication or modification techniques, and demonstrate the prepared membranes for the purpose of their application to the LLMC system for ammonia recovery.

#### 3.2 Membrane configuration

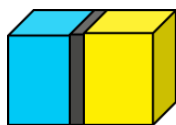

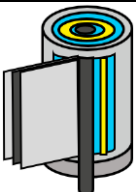
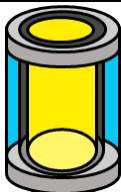
In addition to membrane material, the membrane

Table 1 Properties of polymer materials generally used for the hydrophobic membrane

Polymer material	Chemical structure	Thermal stability	Chemical stability	Contact angle	Cost (\$/m)
PP		Moderate	Good	100 <sup>1</sup>	0.01 <sup>2</sup>
PTFE		Excellent	Excellent	123 <sup>1</sup>	11.50 <sup>2</sup>
PVDF		Good	Moderate	111 <sup>1</sup>	0.36 <sup>2</sup>

<sup>1</sup> Onsekizoglu *et al.* 2012, <sup>2</sup> Khaisri *et al.* 2009

Table 2 Schematics and properties of module types generally used for membrane application

	Flat-sheet	Hollow fiber	Spiral wound	Tubular
Schematic				
Surface area (m <sup>2</sup> /m <sup>3</sup> )	50 – 100 <sup>1</sup>	6,000 – 8,000 <sup>1</sup>	600 – 800 <sup>1</sup>	50 – 70 <sup>1</sup>
Packing density (m <sup>2</sup> /m <sup>3</sup> )	100 – 400 <sup>2</sup>	< 10,000 <sup>3</sup>	200 – 1,000 <sup>3</sup>	400 – 800 <sup>4</sup>
Ease of fabrication	Easy	Moderate	Difficult	Easy
Fouling control	Easy	Moderate	Difficult	Very easy
Energy usage	Low–moderate	Low	Moderate	High
Manufacturing cost (\$/m <sup>2</sup> )	50 – 200 <sup>5</sup>	2 – 10 <sup>5</sup>	5 – 50 <sup>5</sup>	50 – 200 <sup>5</sup>

<sup>1</sup> Martin *et al.* 2016, <sup>2</sup> Kalla *et al.* 2019, <sup>3</sup> Chen *et al.* 2015, <sup>4</sup> Urper *et al.* 2017, <sup>5</sup> Baker *et al.* 2000

module design plays a crucial role in determining the ammonia recovery performance of a LLMC. Significant design features of a membrane module include membrane module type (e.g., flat sheet, hollow fiber, spiral wound, and tubular), spatial arrangement of fibers, and flow direction (e.g., longitudinal flow and cross flow) (Warsinger *et al.* 2018) (Table 2). A flat sheet (alternatively termed a plate sheet or frame) module has much lower membrane area and practical packing density than a hollow fiber module. However, compared to others, this module type allows easy membrane fabrication and assembly (Chen *et al.* 2018). The hollow fiber module has been widely used for ammonia recovery, because it presents advantages of high packing density and surface area per volume, which lead to high throughput per module volume. The circulation configuration of the hollow fiber membrane has two major options. One is the feed solution in the lumen side and stripping solution on the shell side, while the flow is configured exactly the opposite for the other. Placing the feed solution in the shell side and acid in the lumen offers advantages in terms of reduced flow resistance of the liquid and large specific surface area (Bazhenov *et al.* 2018). It is usually preferred to flow the feed solution on the shell side, since the relatively wide flow path can reduce the potential

of fouling formation (Darestani *et al.* 2017). In spiral wound modules, several flat sheet membrane envelopes combined with a spacer are spirally wrapped around a central permeate collecting tube. By taking advantage of its high packing density and specific surface area, this module can overcome the limitations of flat sheet and tubular modules (Sarp *et al.* 2018). However, because of the relative vulnerability of this module to particulate fouling as compared to other configurations, effective anti-fouling strategies, such as pretreatment or cleaning, should be conducted to maintain the process efficiency and to prolong the membrane lifetime (Warsinger *et al.* 2018). Tubular modules are easy to manufacture and control fouling, but are limited by their large energy demands (Obotey Ezugbe *et al.* 2020).

## 4. Applications of LLMC to ammoniacal nitrogen recovery from wastewaters

### 4.1 Laboratory research

Investigations have been made to determine the

Table 3 Literature studies reporting laboratory-scale experimental results for ammonia removal and recovery using LLMC

Feed solution type	Stripping solution	Membrane configuration	Feed concentration (mg/L)	Feed pH	Ammonia removal efficiency (%)	Ammonia recovery efficiency (%)	Mass transfer coefficient (m/h)	Reference
Anaerobic reactor digestate	0.025 M Sulfuric acid	Hollow fiber PP	(3,000 – 3,500) as NH <sub>3</sub>	8.60 – 10.0	80.0 – 98.5	-	(1.24 – 3.70) × 10 <sup>-2</sup>	Wäeger-Baumann and Fuchs (2012)
Anaerobic reactor digestate	0.120 M Sulfuric acid	Hollow fiber PP	(6,000 – 7,400) as NH <sub>4</sub> <sup>+</sup> -N	8.00 – 8.20	44.0 – 90.0	-	(1.70 – 10.1) × 10 <sup>-3</sup>	Lauterböck <i>et al.</i> (2012)
Swine manure	0.500 M Sulfuric acid	Tubular ePTFE	(2,270 – 2,620) as NH <sub>4</sub> <sup>+</sup> -N	7.50 – 9.00	66.0 – 99.0	93.0 – 99.0	(1.20 – 6.52) × 10 <sup>-4</sup>	Garcia-González <i>et al.</i> (2015)
Swine manure	0.500 M Sulfuric acid	Tubular ePTFE	(1,070 – 2,290) as NH <sub>3</sub>	7.70 – 9.0	88.0 – 94.0	87.0 – 91.0	(1.85 – 2.64) × 10 <sup>-4</sup>	Garcia-González and Vanotti (2015)
Swine manure	0.500 M Sulfuric acid	Tubular ePTFE	(1,465 – 2,097) as NH <sub>4</sub> <sup>+</sup> -N	7.99 – 9.26	92 – 99	76 – 98	(3.07 – 54.4) × 10 <sup>-4</sup>	Dube <i>et al.</i> (2016)
Swine manure	0.500 M Sulfuric acid	Tubular ePTFE	2,350 as NH <sub>4</sub> <sup>+</sup> -N	8.36	93.1 – 97.1	92.0 – 93.4	(1.77 – 2.34) × 10 <sup>-3</sup>	Vanotti <i>et al.</i> (2017)
Human urine	0.500 M Sulfuric acid	Hollow fiber PP	0.336 as TAN <sup>1</sup>	10 – 12	62.1 – 80.1	-	(1.75 – 6.00) × 10 <sup>-7</sup>	Zhang <i>et al.</i> (2020)
Human urine	(1.0 – 4.0) M Phosphoric acid	Hollow fiber PP	(5,097.5 – 5,831.3) as TAN	12	-	88.5 – 90.9	(1.95 – 2.28) × 10 <sup>-6</sup>	Zhang <i>et al.</i> (2021)
Human urine	(0.005 – 0.5) M sulfuric acid, phosphoric acid, nitric acid, DI water	hollow fiber PVDF	6,100 as TN <sup>2</sup>	9.7	-	-	-	Damtie <i>et al.</i> (2021)
Radioactive wastewater	sulfuric acid	hollow fiber PVDF	(2,211 – 23,898) as NH <sub>3</sub>	12	94.1 – 95.0	-	(5.3 – 8.9) × 10 <sup>-6</sup>	Liu and Wang (2015)
Landfill leachate	(0.1 – 0.4) M sulfuric acid	hollow fiber PP	881 as TAN	8 – 11.5	98.6 – 99.9	79.1 – 88.6	(3.33 – 5.83) × 10 <sup>-6</sup>	Amara <i>et al.</i> (2016)
Electrolysis solution	0.018 M sulfuric acid	hollow fiber PP	(5 – 15) as NH <sub>4</sub> <sup>+</sup> -N	7.3 – 10.4	< 95	-	3.5 × 10 <sup>-2</sup>	Licon <i>et al.</i> (2016)
Electrolysis solution	0.02 M sulfuric acid	hollow fiber PVDF	(5 – 25) as NH <sub>4</sub> <sup>+</sup> -N	8 – 11	> 78	-	1.66	Licon <i>et al.</i> (2015)
Domestic wastewater	0.05 M sulfuric acid	flat-sheet PVDF	35 as TAN	9.2 - 11	79 – 99	-	(6.60 – 7.68) × 10 <sup>-2</sup>	Lee <i>et al.</i> (2021)

<sup>1</sup> Total ammoniacal nitrogen, <sup>2</sup> Total nitrogen

performance of the LLMC systems for recovering ammonia from wastewater, including industrial wastewater, animal manure, urine, and domestic wastewater. Table 3 summarizes the literature for demonstration of LLMC for ammonia removal/recovery by performing laboratory-scale experiments.

#### 4.1.1 Anaerobic reactor digestate

Laboratory-scale research by Wäeger-Baumann and Fuchs (2012) and Lauterböck *et al.* (2012) demonstrated that ammoniacal nitrogen could be removed using PP

hollow fiber LLMC that is submerged into the digestate of an anaerobic reactor. The submerged LLMC technique offered promising results in that the ammonia could be directly removed from the high suspended solids content liquor. At a feed pH of 10, Wäeger-Baumann and Fuchs (2012) showed sufficient ammonia removal efficiencies of 80 – 98.5% in the particle-rich solutions with high ammonia concentrations of 3,000 – 3,500 mg/L. The study also identified the challenge of very low ammonia mass transfer rate when no base was added and the digestate pH was let to stay at approximately 8.6. A large amount of sodium hydroxide was consumed to elevate the feed solution pH to

10, since the anaerobic digestate had a high buffer capacity due to the  $\text{NH}_3/\text{NH}_4^+$  and  $\text{HCO}_3^-/\text{CO}_3^{2-}$  buffer systems. Lauterböck *et al.* (2012), with the results of their 351-day experiment, provided several implications for long-term operation of the LLMC-anaerobic digester system. During the long-term operation, they observed sulfuric acid leakage into the digester or *vice versa* transport of potassium ions and sodium ions into the stripping side of the LLMC. The paper also suggested that the highly viscous media could be a restricting factor in mass transfer. However, the continuous removal of ammonia enhanced the substrate conversion rates and increased biogas yield in the anaerobic digester.

#### 4.1.2 Animal manure wastewater

García-González *et al.* (2015) investigated the factors including ammonia content, pH, and aeration rate for enhancing ammonia recovery using the submerged tubular PTFE membrane in swine manure. The results showed that aeration, which split bicarbonate ion into carbon dioxide and hydroxide ion to increase the feed pH to above 8.5, can replace the alkali chemical. This strategy of using the low-rate aeration for ammonia recovery both reduced the operational costs by 57% relative to the alkali addition, and achieved high recovery efficiency of 98%. García-González and Vanotti (2015) evaluated the influence of feed pH on ammonia recovery, adjusting manure pH with sodium hydroxide whenever pH decreased below 7.7. The effect of manure strength was also investigated using three different ammonia concentrations from 1,070 to 2,290 mg/L of swine manure. They observed that both pH adjustment and high manure strength can contribute to raising the ammonia recovery rate. Specifically, ammonia recovery efficiency achieved 81% when adjusting feed pH to 9, which showed 26% higher than without pH adjustment. Dube *et al.* (2016) employed low-rate aeration (120 mL air/(L · min)) instead of alkali chemicals to increase pH. In addition, they added a nitrification inhibitor to prevent alkalinity consumption via nitrogen oxidation, and thus to improve the efficiency of the aeration to increase the pH. Compared to the system without aeration, the membrane system with low-rate aeration reduced costs by 70% and removed ammonia about five times faster. Vanotti *et al.* (2017) proposed a combined process of nitrogen recovery using an ammonia LLMC with low-rate aeration and phosphorus recovery via magnesium dichloride precipitation for treating anaerobically digested swine wastewater containing 2,300 mg  $\text{NH}_4^+\text{-N/L}$  and 450 mg P/L. The increase in wastewater pH by the aeration improved the ammonia recovery rate at the LLMC, which not only had the benefit of increasing the nitrogen recovery efficiency, but also obtained a precipitate with higher phosphorus content in the phosphorus recovery step.

#### 4.1.3 Human urine

Zhang *et al.* (2020) investigated the performance of ammonia recovery at various feed velocity and pH values by employing an open-loop PP hollow fiber LLMC from synthetic hydrolyzed human urine. They found that the ammonia capture efficiency was improved by lowering the velocity of feed, or increasing the pH value of the feed side.

The LLMC used by Zhang *et al.* (2020) both enabled the highest ammonia capture efficiency of 80.13% at the feed velocity of  $2.61 \times 10^{-5}$  m/s and feed initial pH of 12, and showed excellent ion rejection, with more than 99.44% of phosphate ion and potassium ion remaining on the feed side. The same group carried out follow-up research by changing the stripping solution from sulfuric acid to phosphoric acid to obtain liquid nitrogen–phosphorus fertilizer products from human urine (Zhang *et al.* 2021). The liquid fertilizer, which is a mixture of diammonium hydrogen phosphate and ammonium phosphate, has been shown through economic analysis to make a profit of \$7.089/L. Damtie *et al.* (2021) employed various stripping solutions for ammonia recovery from a simulated hydrolyzed human urine using a hollow fiber PVDF membrane LLMC. By analyzing the influence of the acid type (nitric, sulfuric, or phosphoric acid) and acid concentration on the ammonia recovery efficiency, they showed that there is a unique relationship between the acid concentration and the recovery efficiency for each acid type. This observation can at least partially be attributed to the different number of exchangeable protons and acid dissociation constants among the tested acids (Damtie *et al.* 2021). Although the studies in the current literature demonstrate the potential of LLMC to produce liquid nitrogen fertilizers from human urine, it is clear that future studies are necessary to further validate the feasibility of this process in practical applications. Of utmost significance in this context is to demonstrate long-term performance under the influence of membrane fouling caused by human urine constituents. In particular, as devices treating, transporting, or storing urine are highly prone to scale formation (Yan *et al.* 2021), studies are necessary to improve understanding of the scale development and growth mechanisms at hydrophobic membrane surfaces by urine constituents, and to develop cost-effective solutions for scale prevention.

#### 4.1.4 Radioactive wastewater

Liu and Wang (2015) used PVDF hollow fiber membranes to treat radioactive wastewater containing a high concentration of ammonia (up to 23,898 mg/L), and studied the impact of the operating parameters, including wastewater composition, feed velocity, and initial ammonia concentration, on ammonia separation. These results demonstrated that neither the coexisting substances, such as  $^{238}\text{U}$ , nitrate species, urea, and tetrahydrofurfuryl alcohol (THFA), nor the initial ammonia concentration, at 2,211 – 23,898 mg/L range, influence the ammonia mass transfer coefficient. An increase in feed velocity could accelerate the ammonia removal efficiency from 75.5 to 90.4% by promoting the turbulence of feed solutions, and thus decreasing the feed-side diffusional boundary layer thickness. This study exemplifies the potential of LLMC to treat wastewater with extremely high ammonia concentrations.

#### 4.1.5 Landfill leachate

Amaral *et al.* (2016) evaluated the capability of PP hollow fiber LLMC to remove and recover ammonia from landfill leachate containing a high ammonia concentration

of 1,300 mg/L. This study examined the influence of pH of feed solution, concentration of sulfuric acid used as stripping solution, and the flow rate of liquid phases on the performance of LLMC for ammonia removal and recovery. Increasing the concentration of sulfuric acid and flow rate improved process efficiency while achieving up to 99.9% ammonia removal, which corresponded to 79.1% ammonia recovery. Amaral *et al.* (2016) assumed that the difference between the value of ammonia removal and the recovery efficiency was caused by ammonia gas leaks during the pH adjustment of feed solution or during the LLMC operation. Despite the ever-growing demand for landfill leachate treatment and the limitations of the current technology (e.g., biological nitrogen removal) to deal with changes in leachate composition over the life cycle of landfill operation (Mandal *et al.* 2017, Peng *et al.* 2017), only a very few research efforts have addressed landfill leachate treatment by LLMC. As one of the most attractive candidates to treat high-strength wastewater and produce valuable nitrogen products, we expect LLMC to be more extensively studied for landfill leachate treatment in the near future.

#### 4.1.6 Electrolysis solution

LLMC can be applied to treating highly concentrated ammonia wastewater, and also water containing a low level of ammonia to produce purified water for particular uses. The latter case has been demonstrated by studies that investigated the feasibility of using LLMC to remove ammonia as water impurities that may interfere with water electrolysis operations. Licon *et al.* (2015) evaluated the performance of a PP hollow fiber LLMC for the removal of aqueous ammonia in the concentration range 5–25 mg/L. They reported a relatively low ammonia removal efficiency of 78% or greater, but a high ammonia mass transfer coefficient of 1.66 m/h, the highest value among those reported in the literature. With the employment of an open loop system, a system in which the feed solution passes through the LLMC and is not recirculated, the results of the study showed that increasing the feed flow velocity reduced the ammonia removal efficiency. The same research group later reported a follow-up study employing a closed loop system, a system in which the effluent at the feed side is directed back to the inlet for recirculation (Licon *et al.* 2016). The results showed that the ammonia removal efficiency could be enhanced by increasing the pH or the feed flow rate at the same operation time and feed volume. By employing a closed loop instead of an open loop system, the 15 mg/L ammonia feed solution could be treated down to 1 mg/L, which is set in the study as a benchmark value to achieve the conductivity requirement for water electrolysis.

#### 4.1.7 Domestic wastewater

The LLMC process have rarely been studied for ammonia recovery from domestic wastewater, which features complex composition and relatively low ammonia concentration. One of the earliest works to demonstrate the feasibility of LLMC for ammonia recovery from domestic wastewater, by Sancho *et al.* (2017), employed LLMC as a sidestream process. In their work, zeolite column was used to remove ammonia from domestic wastewater effluent.

The exhausted zeolite was regenerated by a concentrated sodium hydroxide solution. A PP hollow fiber LLMC system was used to reclaim this alkaline solution after use for regeneration. The LLMC system treated the ammonium-concentrated regeneration solution to achieve a high ammonia recovery efficiency of > 98%, while also producing a liquid fertilizer that reached up to 2–5 wt.% as total nitrogen. Lee *et al.* (2021) demonstrated for the first time the feasibility of the direct usage of a LLMC to recover ammonia from domestic wastewater. They used a flat-sheet PVDF membrane to treat real domestic wastewater, and applied a moderately alkaline feed pH of 9.2. Lee *et al.* (2021) argued that, although the ammonia mass transfer coefficient at a feed pH of 9.2 was 1.53-fold smaller than that at a feed pH of 11, the ammonia recovery rate at the former case was sufficient for the application of the LLMC as a mainstream process for treating wastewater with low levels of ammonia (35.2 mg NH<sub>3</sub>-N/L). They demonstrated that operating a LLMC at moderately alkaline feed pH had the advantages of substantially reducing the chemical cost, and preventing inorganic fouling of membrane.

#### 4.2 Pilot-and full-scale implementation

Various pilot-scale and full-scale trials have been attempted to demonstrate the feasibility of the LLMC for ammonia removal and recovery from different types of wastewater. Table 4 summarizes the application of LLMC for ammonia removal/recovery at pilot and full-scale.

The first full-scale ammonia LLMC system was installed in Wuppertal, Germany in 2004 following a pilot-scale demonstration (Ulbricht *et al.* 2013). Two cylindrical hollow fiber LLMCs of 35.6 cm diameter and 71.1 cm length were connected serially to treat an inflow of 5–10 m<sup>3</sup>/h. Industrial wastewater with a high ammonia concentration of 500–2,000 mg/L was fed to the LLMC after pretreatment using a 10 μm polypropylene cartridge filter. Ulbricht *et al.* (2013) reported up to 95% ammonia removal efficiency after two years of system operation. They also reported that the ammonia was recovered as a concentrated ammonium sulfate solution with a final concentration of 30 wt.%, which was sold as fertilizer.

Boehler *et al.* (2015) conducted a pilot-scale test that employed hollow fiber LLMC to recover ammoniacal nitrogen from sludge water at a wastewater treatment plant. Up to 99% ammonium could be captured from the sludge water samples containing 700–3,400 mg N/L under various conditions of flow rate, pH, temperature, and ammonia concentration. Approximately 90% of the ammonia was removed with a feed flow rate of 4.2 L/(m<sup>2</sup>·h). When the flow rate was increased to 8.5 L/(m<sup>2</sup>·h), the ammonia removal efficiency was substantially reduced. This observation contrasts with the implication of the resistances-in-series model (Eq. (6)) that increase in the feed flow rate (and thus the feed flow velocity) should reduce the overall resistance of ammonia mass transfer across a LLMC membrane by reducing the feed-side diffusional boundary layer thickness (Liu and Wang, 2015). However, Boehler *et al.* (2015) did not discuss possible reasons for the decrease



Table 4 Literature studies reporting the results of pilot- and full-scale operations for ammonia removal and recovery using LLMC

Feed solution type	Stripping solution	Membrane configuration	Feed concentration (mg/L)	Feed pH	Ammonia removal efficiency (%)	Mass transfer coefficient (m/h)	Reference
Rendering facility condensate wastewater	Sulfuric acid	Spiral wound PP, PTFE	800 – 1,600 as TN <sup>1</sup>	8.0 – 9.0	> 64	2.02	Brennan <i>et al.</i> (2020)
Sludge water at the wastewater treatment plant	Sulfuric acid	Hollow fiber	700 – 3,400 as NH <sub>4</sub> <sup>+</sup> –N	9.3 – 10.2	79 – 99	-	Boehler <i>et al.</i> (2015)
Ammonia leaks in water treatment plants	Sulfuric acid	Hollow fiber PP	11,000 as NH <sub>3</sub>	-	< 99.9	(2.0 – 3.0) × 10 <sup>-3</sup>	Jiahui <i>et al.</i> (2008)
Industrial wastewater	Sulfuric acid	Hollow fiber	500 – 2,000 as NH <sub>3</sub>	< 9.0	95	-	Ulbricht <i>et al.</i> (2013)
Mesophilic digester	Sulfuric acid	Tubular ePTFE	882 – 1,250 as TAN <sup>2</sup>	7.5 – 8.0	< 90	-	
Biogas plant reject	Sulfuric acid	Tubular ePTFE	2,900 – 4,700 as TAN	8.2 – 8.8	-	3.60 × 10 <sup>-3</sup>	Kaljunen <i>et al.</i> (2021)
Urine	Sulfuric acid	Tubular ePTFE	3,000 – 3,100 as TAN	-	< 70	3.60 × 10 <sup>-7</sup>	
Landfill leachate	Sulfuric acid	Tubular ePTFE	990 – 1,000 as TAN	7.9 – 8.0	< 85	-	

<sup>1</sup> Total nitrogen, <sup>2</sup> Total ammoniacal nitrogen

in the removal efficiency by increase in the flow rate.

Brennan *et al.* (2020) described their pilot-scale application of LLMC for the recovery of ammonia from the rendering operation of a meat processing plant. The rendering condensate wastewater was pretreated for heating and filtering before it was fed to the LLMC. Spiral wound membrane modules with two different membrane materials, PTFE and PP, were used. The PTFE membrane LLMC achieved a reasonably high ammonia removal efficiency of up to 65% from the wastewater. However, the use of the PP membrane was determined to be not suitable, because of its susceptibility to contamination by the feed solution, which led to membrane wetting after only 15 minutes of contact with the wastewater. These results demonstrate that the compatibility to the wastewater for treatment should be taken into account when selecting hydrophobic membrane material for LLMC. Brennan *et al.* (2020) also conducted a cost-benefit analysis based on the pilot-scale experience. They concluded that the costs to remove ammonia using the LLMC were more expensive than currently available ammonia treatment methods, mainly due to the consumption of the chemicals (i.e., base and acid), and operation of the heaters and filters for wastewater pretreatment. However, when compensation of the operation cost by selling the product (i.e., concentrated ammonium sulfate solution) as a liquid fertilizer was taken into account, the LLMC was estimated to cost less than the currently available methods.

Kaljunen *et al.* (2021) conducted a pilot-scale study to test a novel process that enables simultaneous recovery of nitrogen and phosphorus from real wastewater. The process described in the study consisted of a pretreatment step for chemical (base, coagulant, and ballasting agent) addition, mixing, and settling, and a nitrogen recovery step where LLMC with PTFE membrane was employed to treat the

supernatant from the pretreatment step. Four wastewaters, sludge digestate liquid, biogas plant reject, landfill leachate, and urine, were fed to the pilot plant. The feed flow rate was adjusted differently according to the wastewater type, wastewaters with high suspended solids (SS) content were subject to lower flow rate to reduce the rate of fouling development over time. Despite this effort, for the biogas plant reject that exhibited the highest initial SS content of 1,800 – 7,200 mg/L, the ammonia recovery by the LLMC was not consistently observed over time. The ammonia recovery rates for the other three wastewaters showed a descending order of toilet urine, landfill leachate, and sludge digestate liquid with numerical values of 366, 210, and 95 mg/(L · h), respectively. This order of ammonia recovery rates aligned with the ascending order of SS content in the wastewater. Unfortunately, it was not possible to quantitatively determine how much difference in the ammonia recovery rates was caused by the differential SS contents in the wastewater, because different feed flow rates, ranging widely from 40 L/h for the sludge digestate liquid to 133.3 L/h for the toilet urine, were applied. However, Kaljunen *et al.* (2021) did demonstrate that for ammonia recovery using LLMC, in a practical sense, low-SS wastewater was much more preferable than high-SS wastewater. Lower SS content in wastewater resulted in smaller retardation in ammonia mass transfer due to the presence of particulates in the feed water and less accumulation of solids on the membrane. In addition, the low SS content allowed application of relatively high feed flow rates, which may reduce the ammonia mass transfer resistance. The paper also reported the analysis results of potential pollutants, such as microorganisms, heavy metals, and pharmaceuticals, in the concentrated ammonium sulfate solution obtained from the LLMC. The solution contained none of the ten pathogenic indicators measured, and was

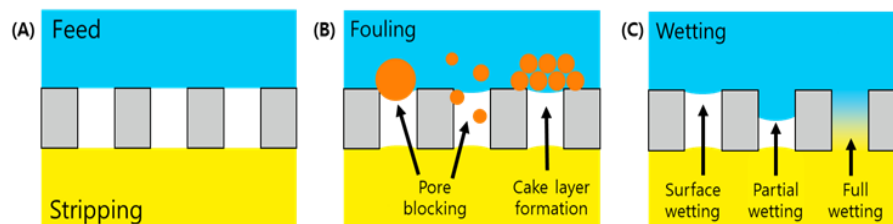


Fig. 3 Schematics of the fouling and wetting behavior on the surface of the membrane used for LLMC. (A) Surface of the pristine membrane, (B) mechanisms of membrane fouling: pore blocking and cake layer formation, (C) mechanisms of membrane wetting: surface wetting, partial wetting, and full wetting

also much lower in heavy metal and pharmaceutical contents compared to the legislative limit. This result demonstrated the potential of the LLMC to produce a high-quality liquid fertilizer.

## 5. Challenges and their potential solutions

Despite the successful demonstration of the feasibility of the LLMC-enabled ammonia recovery process for various types of waste streams, there are still significant technological challenges that should be addressed for wide application of the process in the field. Occurrence of membrane fouling and wetting may substantially impair the long-term performance of the process, or in some instances, make the process not practically viable. Relatively high requirement of chemical consumption, including that being incurred while raising the feed pH, is also a significant concern, as chemical cost is likely to constitute the major portion of the total cost involved. Because the process has only been proposed relatively recently, high uncertainties remain in quantifying each cost component and also the benefit of recovering nitrogen products, limiting the currently ability to assess the economic feasibility of the process and to develop strategies for its improvement. Recognizing these challenges, some of the recent efforts on the process have been devoted to developing technological solutions to overcome the challenges and to close the knowledge gaps of understanding the economy of the process. In the following, each of the challenges involved in practical application of the LLMC-enabled ammonia recovery process is described in detail, along with an extensive review on recent studies to address the challenge.

### 5.1 Membrane fouling

Fouling is one of the major issues for almost all membrane-based systems involving the treatment of water with impurities. Membrane fouling refers to the accumulation of undesirable materials on the surface of the membrane or inside the pores of the membrane, which may deteriorate the overall membrane performance (Figs. 3A and 3B). If fouling is not treated appropriately, it could decrease the mass transfer rate, induce membrane wetting, and substantially increase the operational expenditures for cleaning, replacement, and energy (Gryta *et al.* 2008). The occurrence of fouling is affected by different factors that include membrane properties and configuration, solution

properties, and operational conditions (Tang *et al.* 2011).

It is likely that LLMC suffers relatively less from membrane fouling compared to membrane filtration processes such as ultrafiltration and reverse osmosis (RO), as well as to membrane distillation (MD). Li *et al.* (2020) compared the occurrence of fouling in a methane-extracting LLMC and a direct-contact MD. A 24 h run using a feed of 100 mg/L humic acid solution showed negligible foulant deposition at the membrane surface when the LLMC was operated isothermally, that is, with no temperature gradient between the feed and the stripping sides. On the other hand, when the same membrane assembly was used for MD with the application of a 25°C temperature difference across the membrane, severe fouling occurrence was visibly observable, and after 24 h, the water flux was declined by 50%. The resistance to fouling observed in the isothermal liquid-liquid contact type operation was attributed to the negligible water vapor flux across the membrane. Polarization of foulant concentration and hydrodynamic drag, which are significant inducers of membrane fouling, do not occur in the absence of water vapor flux. Because of this low fouling propensity, in many isothermal LLMC operations, simple pretreatment and/or membrane rinsing may suffice for the maintenance of the membrane performance over the long-term.

Wastewaters fed to the LLMC consist of mixed constituents that include inorganics, organics, particulates, and microorganisms. Achieving a feed solution composition that is conducive to membrane fouling control is an effective way to improve the membrane performance. Hence, wastewater pretreatment should be one of the key strategies for mitigating the extent of fouling in the LLMC process. Membrane filtration and coagulation/precipitation are commonly used to protect gas-permeable membranes used in MC or MD from fouling. Microfiltration or ultrafiltration could be viable options of pretreatment for the ammonia LLMC process, considering the relatively high SS concentration of wastewaters that are typically subject to the process. In fact, few LLMC ammonia recovery studies that employed membrane filtration for wastewater pretreatment prior to the ammonia recovery process used microfiltration (Amaral *et al.* 2016, Ulbricht *et al.* 2013) or ultrafiltration (Wäeger-Baumann and Fuchs 2012) membranes. A liquid-vacuum MC study also implemented either microfiltration or ultrafiltration for the wastewater pretreatment (Zarebska *et al.* 2015). These studies showed that the ammonia mass transfer rate could be enhanced by factors of 1.5 – 4 by the membrane filtration pretreatment

(Wäeger-Baumann and Fuchs 2012, Zarebska *et al.* 2015). To the best of our knowledge, the LLMC ammonia recovery process has not been employed in conjunction with coagulation/precipitation pretreatment. However, MD, a thermally driven technology that bears similarity to LLMC in terms of its reliance on the gas-phase flux through the pores of a hydrophobic membrane, has been demonstrated to benefit from the coagulation/precipitation pretreatments. Zhiqing *et al.* (2013) investigated the effect of coagulation using different chemicals that included polyaluminum chloride (PACl), ferric chloride ( $\text{FeCl}_3$ ), and polyacrylamide (PAM) in the treatment of RO-concentrated wastewater from a steel plant by vacuum MD. They reported flux enhancement by 30% and lowered fouling tendency by the pretreatments. Qu *et al.* (2009) studied the performance of a direct-contact membrane distillation (DCMD) module combined with accelerated precipitation softening (APS) for high water recovery desalination of RO concentrate. The APS method was implemented as a pretreatment for the DCMD by adjusting the feed pH using sodium hydroxide, along with calcite seeding and subsequent microfiltration. The results showed that the APS pretreatment removed 92% of calcium from the RO concentrate, resulting in the reduction of potential for scaling by  $\text{CaCO}_3$  and  $\text{CaSO}_4$  at the DCMD module membrane, and in turn, maintenance of the permeate flux at 80% of the initial value after 300 h of operation. From these MD studies, it can be inferred that coagulation/precipitation is one of the potential alternatives to control the fouling of LLMC membranes.

Despite the significance of periodic cleaning on the fouling control of membrane-based processes, cleaning procedures have yet to be studied extensively for the LLMC ammonia recovery process. As described above, it is expected that a gentle membrane rinsing procedure would successfully control membrane fouling for an ammonia LLMC. For example, Zarebska *et al.* (2015) investigated rapid flushing with deionized water, sodium hydroxide/citric acid, and commercial cleaning agents (product names Ro Dan 97 and Ro Dan Acid, Novadan APS, Denmark) as cleaning strategies in a liquid–vacuum MC for ammonia removal from animal slurry. This flushing step was effective for removing organic foulants from fouled membranes, which showed up to 94% ammonia flux recovery after alkaline/acidic rinsing. Kaljunen *et al.* (2021) used 0.1 M HCl to remove accumulated foulants in ammonia recovery LLMC pilot plants. The reasonable LLMC performance observed after the chemical rinsing suggests that the rinsing procedure was effective, although no systematic investigation on the fouling control was conducted in this pilot-scale study.

Another approach to deal with the problem of fouling is to modify the surface of the membrane to develop superhydrophobicity or omniphobicity (i.e., being both hydrophobic and lipophobic). Developing Janus membranes, a type of membrane that exhibits contrasting wettability on each side (Söz *et al.* 2020), has also been suggested as a strategy to effectively address fouling. These membrane modification methods have been extensively studied for the application of the modified membrane for MD. The

membrane surface modification techniques should address both fouling and wetting for their application to MD or MC operations. Reviews of previous works to develop superhydrophobic, omniphobic, or Janus membrane surface properties are discussed in detail in the next section.

Many fouling control strategies are available for practical application to membrane processes, if we include those developed under relatively mature membrane technologies, such as membrane filtration and MD. As described above, membranes in isothermal LLMCs are likely to suffer less from fouling compared to those in membrane filtration and MD processes. However, the remaining task of tuning the currently available fouling control techniques or developing simple techniques to accomplish cost-effective fouling control in the ammonia LLMC process is still not trivial. Fouling is affected by various factors that include membrane properties and configuration, feed solution properties, and operational conditions of a membrane process. Wastewaters that are considered for the ammonia LLMC treatment (e.g., those discussed in section 4.1) may exhibit different characteristics compared to typical influents of membrane filtration and MD. Thus, it is necessary to elucidate the fouling mechanisms and their resistance to fouling control measures for common foulants of the ammonia LLMC. The impact of the LLMC operational conditions (e.g., wastewater flow velocity and loading) on the fouling occurrence should be better known, and so should the impact of the variables of the clean-in-place (CIP) procedure (e.g., type and concentration of cleaning agent, cleaning solution velocity, temperature, cleaning frequency). The investigation of the CIP procedure should address robustness and longevity concerns of the membrane, which is critical when the membrane is surface-modified for improved fouling resistance. Finally, the fouling control strategies should be critically assessed for their economic feasibility. The cost incurred by the application of an anti-fouling technology, such as increased membrane manufacturing, energy, and chemical cost, should be compared with the cost savings or benefits involved in better fouling control, such as enhanced ammonia recovery rate, reduced frequency of membrane replacement, and reduced risk of process failure. Only with detailed analysis on the process performance and costs involved in membrane fouling will it become clear whether a given anti-fouling technology is viable for the ammonia LLMC (Ang *et al.* 2017).

## 5.2 Membrane wetting

Membrane wetting is another significant concern for operations that utilize gas molecule transfer across hydrophobic membranes. Wetting refers to partial or complete occupation of liquids inside the pores of the membrane (Fig. 3C). Wetting occurs when the trans-membrane pressure exceeds the liquid entry pressure (LEP) of microporous membrane. The LEP of membrane depends on its pore structure, surface energy of the membrane material, and surface tension of the feed solution (Lu *et al.* 2008). For example, low surface tension liquid constituents,

Table 5 Post super-hydrophobic modification for improving the wetting resistance of gas-permeable membranes

Substrate membrane material	Post modification method description		Wetting resistance indicator		
	Roughness modification method	Surface energy modification material	Water contact angle (Degree)	LEP (bar)	Reference
PVDF	TiO <sub>2</sub> NP grafting	1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane	163	1.9	Razmjou <i>et al.</i> (2012)
PP	SiO <sub>2</sub> NP grafting	1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane	150	N.A.	Shao <i>et al.</i> (2019)
Ball clay	TiO <sub>2</sub> NP grafting	1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane	156	N.A.	Aziz <i>et al.</i> (2020)
Glass fiber	SiO <sub>2</sub> NP grafting	1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane	140	N.A.	Lin <i>et al.</i> (2014)
PVDF	Solvent-thermal induced roughening	1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane	> 150	2.2	Qing <i>et al.</i> (2020)
PVDF	Chemical induced roughening	1H, 1H, 2H, 2H-perfluorodecyltrimethoxysilane	157	0.8	Zhu <i>et al.</i> (2020)
PVA	Carbon nanotube coating	1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane	157	N.A.	Pornea <i>et al.</i> (2020)
PVDF-HFP	SiO <sub>2</sub> NP grafting	Fluoro-silane (Un-specified)	157	N.A.	Huang <i>et al.</i> (2017)

\*Abbreviations: N.A., Not available, NP, nanoparticles, HFP, hexafluoropropylene, PTFE, polytetrafluoroethylene, PP, polypropylene, PVA, polyvinyl alcohol, PVDF, polyvinylidene fluoride

such as oil, fatty acids, surfactants, and alcohol, may readily wet the membrane, leading to water penetration. The occurrence of wetting can be enhanced if foulants such as organic matter or mineral scale originating from wastewater accumulate inside the membrane pore and build the hydrophilic route for water infiltration (Warsinger *et al.* 2015). Wetting is a serious problem that increases the mass transfer resistance and reduces selectivity for the ammonia LLMC processes.

There are two common approaches to prevent membrane wetting: 1) developing membrane with higher LEP by applying superior base material and/or post-modification technique and 2) retarding the occurrence of wetting by membrane fouling controls. Since the latter has been addressed in the previous section, here we limit the discussion to developing membrane base materials and post-modification methods for better resistance against membrane wetting. Because the anti-wetting concept has been largely studied for various hydrophobic membrane-based processes, such as MD, oil/water separation, and MC, we extend the discussion to the wetting resistance of general gas-permeable microporous membranes.

The advent of superior membrane base materials and texture has improved the wetting resistance of hydrophobic membranes (Ray *et al.* 2020). Fabrication of membrane using newly designed polymer dope with low surface energy enhances the hydrophobicity of membrane, while applying novel fabrication techniques, such as electrospinning, increases the roughness of membrane, which makes liquid permeation through the membrane pore thermodynamically unfavorable (Qing *et al.* 2017). Ju *et al.* (2020) designed a novel dope solution by incorporating 8 vinyl-grafted polyhedral oligosilicone into PTFE emulsion for an electrospinning fabrication process, and the resultant membrane showed up to 151° of water contact angle. Niknejad *et al.* (2021) designed polymethyl methacrylate-based dope solution, and fabricated nanofibrous super-

hydrophobic membrane with 164° of water contact angle and 2.3 bar of LEP, accompanied by remarkable water repellency. Pang *et al.* (2021) developed a novel electrospinning-sintering fabrication method, and adopted a mixture of pullulan and PTFE emulsion as dope solution, which confirmed that the subsequent sintering step enhanced membrane roughness. Lv *et al.* (2017) fabricated porous PDMS membrane with high roughness using 3D printing technique, which showed excellent mechanical strength and wetting resistance.

Meanwhile, post super-hydrophobic modification methods have been developed to maximize the wetting resistance of substrate membrane (Table 5). Post physico-chemical modification gives the substrate membrane outstanding wetting resistance, which can hardly be imparted by a single fabrication step (Xu *et al.* 2019, Lee *et al.* 2022). The general post modification strategy to fabricate a superhydrophobic membrane is to graft re-entrant nano-structure on the substrate membrane surface, followed by coating with low surface energy material, such as fluoro-silane or alkyl-silane. Typically, hierarchically patterned inorganic nanoparticles including silica oxide (Shao *et al.* 2019), aluminum oxide (Ahmad *et al.* 2013), titanium dioxide (Razmjou *et al.* 2012), and zinc oxide (Chakradhar *et al.* 2011) have been adopted to increase the surface roughness, raising the energy barrier to liquid penetration. Further chemical coating of re-entrant structure with low surface energy material, such as fluoro-silane and alkyl-silane, including perfluorododecyltrichlorosilane (Razmjou *et al.* 2012), perfluorooctyltriethoxysilane (Chen *et al.* 2009), and trimethoxysilane (Dong *et al.* 2015), allows superior wetting resistance to be achieved (Table 5).

Recently, Janus membrane is also gaining attention as an alternative to providing simultaneous resistance to fouling and wetting. The Janus membrane exhibits asymmetric surface wetting properties on either side of the membrane, such as inner hydrophobic-outer hydrophilic

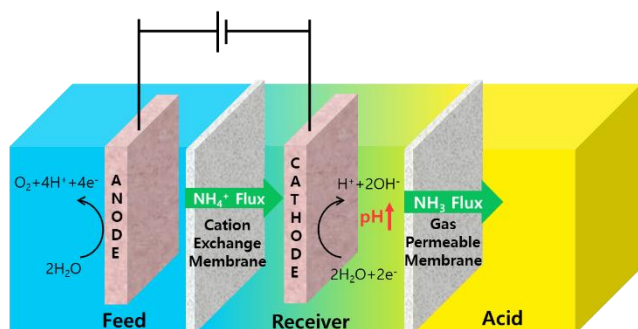


Fig. 4 Schematic of an exemplary hybrid process, where a LLMC is coupled with an electrochemical unit for ammonia recovery

pair, which suppress the adsorption of hydrophobic organic fouling, while preventing liquid penetration (Pornea *et al.* 2020). Huang *et al.* (2017) developed a Janus membrane by grafting hydrophilic chitosan layer onto super-hydrophobic PVDF–HFP membrane, which demonstrated resistance to both oil fouling and wetting. Zhao *et al.* (2021) fabricated a Janus membrane possessing a super-hydrophilic top layer and a hydrophobic bottom layer by a layer-by-layer multi coating approach using catechol and polyethylenimine, and the resultant membrane showed excellent performance for recovering water from oily saline wastewater. Chew *et al.* (2019) developed a polydopamine and silver nanoparticle coated Janus membrane, which successfully separated water from oily wastewater containing Tween 20 surfactant and crude oil without fouling or wetting. Super-hydrophobic or Janus membrane that is properly designed to address feed characteristics can simultaneously resist fouling and wetting, consequently allowing stable long-term MC operation.

### 5.3 Chemical requirement

Typically, LLMC studies for ammonia recovery have been conducted at relatively high feed pH conditions to achieve high mass transfer rate, and thus high efficiency of ammonia recovery. Appreciation of Eqs. (1) and (4) tells that to achieve as much driving force for ammonia mass transfer as possible at a given total ammoniacal nitrogen concentration, it is necessary to maintain the feed pH sufficiently above the ammonia  $pK_a$ . However, the higher the feed pH, the more chemical requirements, and in turn, the greater the chemical cost. The cost of chemicals to raise the feed pH is likely to comprise the major operational cost of the ammonia LLMC. Pandey and Chen (2021) analyzed the operational costs of the LLMC process for nitrogen recovery from animal manure, and concluded that the chemical cost was two orders of magnitude greater than the energy cost, and that the total operational cost strongly depended on the type of chemical used for pH adjustment. Lee *et al.* (2021) estimated the cost of base to adjust the domestic wastewater pH suitable as a feed solution for ammonia LLMC to be 0.016 USD per  $m^3$  wastewater treated. Although, other operational costs involved in the LLMC operation were not estimated in that study,

comparison of the chemical cost with the energy cost for microfiltration of secondary effluent of 0.004 – 0.007 USD per  $m^3$  wastewater treated suggested the predominance of the chemical cost among the overall operational cost. The results imply that there is a strong research need to effectively reduce the chemical consumption, while achieving reasonable process performance.

Recent developments have shown promise of enabling ammonia recovery with low chemical consumption by integrating an electrochemical process into a LLMC. Tarpeh *et al.* (2018) employed a three-chamber system by coupling an electrochemical unit for hydroxide production and a LLMC for ammonia recovery (Fig. 4). In this system, hydroxide ions are electrochemically generated at the cathode. When ionic ammonia in wastewater in the anode chamber diffuses through the cation exchange membrane, the high pH in the cathode chamber achieved by the production of hydroxide ions promotes immediate conversion of the ionic ammonia to free ammonia. Then, the free ammonia can be easily extracted by an acidic stripping solution through gas diffusion membrane, in other words, by the working principle of LLMC. Continuous-flow experiments using source-separated urine as a feed solution showed a nitrogen flux across the gas-permeable membrane of 1,010 g N/( $m^2 \cdot d$ ) with an energy input of 30.6 MJ/kg N. The energy consumption for nitrogen recovery was superior to that of other electrochemical nitrogen recovery units reported in the literature. Hou *et al.* (2018) developed a membrane cathode composed of a PP support layer, a PVDF/multi-walled carbon nanotube (MWCNT) composite layer, and a thin nickel film, across which ammonia can be transported to be extracted from wastewater, and harvested in an acid stripping solution. Use of the membrane cathode in place of the separate cathode improved the ammonia recovery rate, current density, and energy efficiency. The superiority of the membrane cathode was attributed to the active harvesting of free ammonia at the membrane cathode surface, which alleviated the accumulation of free ammonia and thus reduced cathode overpotential. In contrast to the cathode reaction shown in Fig. 4, the electrons at the membrane cathode were thought to be used to directly deprotonate the electro-adsorbed ionic ammonia, which may also have contributed to the 40% enhancement in the ammonia recovery rate compared to the process configuration with separate cathode. Yan *et al.* (2018, 2020) presented a hybrid (LLMC + electrochemical) system that required neither base nor acid addition to recover ammonia in wastewater in the form of concentrated ammonium sulfate solution. The electrochemical unit consisted of a repeating unit of a bipolar membrane, an anion exchange membrane, and a cation exchange membrane. Water splitting at the bipolar membrane supplied hydroxide ion to the wastewater that flowed between the cation exchange membrane and the bipolar membrane, and supplied proton to the water that flowed between the anion exchange membrane and the bipolar membrane. The basified wastewater from the electrochemical unit was fed to the LLMC unit, which released ammonia to the concentrated acid solution generated from the electrochemical unit. By running the

hybrid system in a recirculation mode, an ammonia recovery ratio of  $> 99\%$  could be achieved with the production of a concentrated (139.1 g/L) ammonium sulfate solution with an energy consumption of 7.95 MJ/kg N (Yan *et al.* 2020).

The limitation of the integration of an electrochemical process to a LLMC for the *in situ* generation of hydroxide ion and proton is that it reduces the chemical cost at the expense of increased electricity cost. To address this concern, a few hybrid processes that utilize industrial byproducts or chemical energy of wastes have been proposed. One approach is to employ a bioelectrochemical process for the *in situ* generation of hydroxide ion. Hou *et al.* (2018) combined a microbial electrolysis cell with LLMC for their experiment to compare the performance of hybrid systems with a membrane cathode (PP + PVDF/MWCNT + nickel, as described above) and a separate cathode. Acetate was supplied as the carbon source in the anode compartment. The energy consumption was estimated to be 5.80 and 6.95 MJ/kg N for the membrane and separate cathode configurations, respectively, which showed superiority to other competing electrochemical processes. Chen *et al.* (2021) suggested utilizing a waste alkali solution as the receiver solution for a three-compartment cell, which resembles Fig. 4 but without the electrodes, and thus in the absence of the chemical reactions shown in the figure. It was expected that avoiding direct mixing of the wastewater feed with waste alkali solution would minimize detrimental impact on the wastewater quality and the concern with membrane fouling. The ammonia recovery efficiency of the three-compartment cell using red mud leachate as the receiver solution was reasonable, although the result was slightly inferior to the case when a sodium hydroxide solution was used instead.

In sum, hybrid systems, which have been employed in various configurations, show opportunities to resolve the concerns with chemical consumption in the ammonia LLMC process. However, to demonstrate the practical feasibility of the hybrid systems, it is clear that further investigations are necessary, particularly with respect to the long-term performance and robustness, and the system scalability. As the hybrid systems generally require complicated fabrication procedures, it is necessary to examine the viability of the industrialization of the procedures.

#### 5.4 Economic assessment

Literature regarding economic assessment of the ammonia LLMC is relatively scarce, because the technique is still in its infancy. The background data used in the scarcely found literature largely rely on the results of short-term operations and/or bench-scale laboratory studies. It is yet to be clearly understood how the results of an economic assessment conducted for a system with a specific LLMC and a specific type of wastewater would apply to another. The cost breakdowns, which would provide valuable information for improving the cost-effectiveness of the LLMC process, are also currently not well known. Therefore, in general, many more studies are required to

verify the economic feasibility and identify opportunities of improvement in the cost–benefit balance for the process, preferentially based on the data from long-term, full-scale operations.

As is common for the expenses of a business, the costs involved in the LLMC process for ammonia recovery can be divided into capital and operational expenditure (CAPEX and OPEX, respectively). CAPEX should include the design and construction cost, cost of the spare parts for equipment, and product inventories. OPEX must take into account values related to energy and reagent consumption, replacement, regeneration, maintenance, and load (Martin *et al.* 2020). Because it is generally expected that a saleable nitrogen-based product would be obtained through the application of the LLMC process to wastewater, the benefit involved in the product sale should also be taken into consideration in the economic assessment (Jafari *et al.* 2021).

A very recent work that is worth introducing is Kaljunen *et al.* (2021), which conducted cost–benefit analysis of an ammonia LLMC combined with coagulation/precipitation for simultaneous nitrogen and phosphorus recovery based on a pilot plant operation. The CAPEX and OPEX were calculated by evaluating each cost element, including the cost of the treatment unit, the cost of unit modification, design and construction cost, fixed operation cost, utilities cost, and consumables cost. The CAPEX for treating 2,500 m<sup>3</sup>/day of liquid digestate from a real wastewater treatment plant was estimated to be 7.6M €. The OPEX, calculated based on the volume of wastewater treated, was 5.16 €/m<sup>3</sup> for the liquid digestate. This OPEX value was comparable to that of industrial-scale ammonia strippers. The benefit was calculated as the cost savings that would otherwise be consumed for aeration and chemical dosage if the digestate were sent back to the mainstream wastewater treatment process, plus the direct monetary benefit of selling the produced ammonium sulfate assuming 80% recovery efficiency and 50% of market value. It was estimated that when the process was optimized to lower the OPEX to 1.25 €/m<sup>3</sup>, a 20-year payback period would be achieved. Although many of the cost component estimations conducted by Kaljunen *et al.* (2021) are based on crude assumptions, this exemplary study shows the importance of comprehensive economic analysis of the ammonia LLMC process to understand its current status, and its room for future improvement.

To date, there is no standard method to assess the economic cost and benefit of the LLMC process for ammonia recovery. General consensus on the requirements of the cost-benefit analysis method regarding both the “cost” and “benefit” components is necessary to improve the reliability of the economic assessment. Whereas the knowledge of the cost components may be borrowed from the experience with other processes that are similar to the ammonia LLMC process, the key benefit of the process, which is selling the nitrogen product recovered from the process, can hardly be deduced from other experiences. Through the ammonia LLMC process, a valuable nitrogen resource is produced, which may be used in various industrial sectors, including agricultural fertilizer

production, flame retardant compositions, food additives and preservation, and protein purification. For a realistic assessment of the market price of the nitrogen-based products, the chemical composition (e.g., purity, concentration, and anion counterpart), usage, and handling and transportation requirements need to be taken into account. Substitution of the Haber–Bosch produced ammonia with the ammonia recovered from wastewater via LLMC may not only produce market value, but also non-market values, such as environmental and resource-saving benefits. Therefore, methods that can comprehensively address the benefits involved in producing nitrogen products via the ammonia LLMC should be established to better demonstrate the economic feasibility of the process, and its economic competitiveness against other nitrogen treatment/recovery processes.

## 6. Conclusions

The LLMC process for ammonia recovery is an emerging technology that shows promise of improving the sustainability of the nitrogen cycle by replacing the conventional wastewater treatment process of nitrogen. In this review, we provided the process principles, possible varieties with regard to membrane material and configuration, recent progress, and challenges of the technology. The feasibility of ammonia recovery by LLMC is substantially improved thanks to recent efforts. However, much advancement is still needed to further improve its performance and stability to attain feasibility for long-term operation in the field. We have delineated major challenges of the LLMC process, which are membrane fouling, membrane wetting, chemical requirement, and uncertainties in the current knowledge in the process economy, along with potential strategies to address each of the challenges.

Because this technology has yet to be extensively studied and the performance reported in the literature shows large variation, we believe that optimizing the membrane material and configuration, and the operational conditions of the LLMC, could effectively reduce the mass transfer resistance and improve energy consumption. With regard to addressing fouling and wetting, much less effort has been made specifically for ammonia LLMC compared to that for other membrane devices such as those for water purification via membrane distillation. It may be wise to apply to the LLMC the accumulated knowledge on the occurrence and control measures of fouling and wetting in such relatively well-studied membrane devices. In this context, studies focused on understanding the key differences in the fouling and wetting characteristics between the ammonia LLMC and the reference membrane devices are necessary. Economic stress involved in the consumption of a considerable amount of base for pH adjustment, which presents a significant limitation in the ammonia LLMC operation, may be alleviated by integrating the contactor with units that offer chemical-free basification. Future studies should also pay attention to calibrating the operational feed pH to obtain the “pareto optimum” with respect to ammonia recovery efficiency and chemical

requirements. We expect that by addressing the remaining challenges by future efforts, the ammonia LLMC process will prove both its economic competitiveness and environmental friendliness, leading to it replacing the conventional nitrogen treatment processes in many wastewaters.

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