Ammoniacal nitrogen recovery from pig slurry using a novel hydrophobic/hydrophilic selective membrane

Andreu Serra-Toro [a], Sergi Astals [a], Sergio Madurga [b], Joan Mata-Álvarez [a], Francesc Mas [b,*], Joan Dosta [a,*]

[a] *Chemical Engineering and Analytical Chemistry Department & Water Research Institute, University of Barcelona, Barcelona, Catalonia, Spain*
[b] *Materials Science and Physical Chemistry Department & Research Institute of Theoretical and Computational Chemistry (IQTCUB), University of Barcelona, Barcelona, Catalonia, Spain*

ABSTRACT

The implementation of the circular economy paradigm in intensive pig farming requires technologies able to recover ammoniacal nitrogen from pig slurries. This research explores the feasibility of a novel hydrophobic/hydrophilic non-porous membrane to recover ammoniacal nitrogen from pig slurry at ambient temperature and using a H_2SO_4 solution as trapping agent. The influence of (i) the pH of the feed solution, (ii) the volume ratio between feed and trapping solution, and (iii) the trapping solution concentration on nitrogen recovery and flux were evaluated using a synthetic solution and pig slurry. The best performance was achieved when the pH of the feed solution was controlled at 9.0, where average fluxes of 145 and 116 g N/(m²·day) were achieved for the synthetic solution and pig slurry after 24 h, respectively. Decreasing the feed-to-trapping volume ratio improved the recovery efficiency after 24 h from 62% to 74% for the synthetic solution and from 32% to 46% for pig slurry. However, renewing the H_2SO_4 concentration of the trapping solution only led to minor improvements despite the higher reagent consumption. The diffusion coefficients of NH_3 and NH_4^+ through the membrane at pH 9.0 were $(7.3 \pm 0.2) \cdot 10^{-11}$ and $(2.1 \pm 0.1) \cdot 10^{-11}$ m²/s for the synthetic solution and $(2.7 \pm 0.1) \cdot 10^{-11}$ and $(1.0 \pm 0.1) \cdot 10^{-11}$ m²/s for the pig slurry, respectively. The capacity of ions to diffuse through the membrane is a distinctive feature of this membrane and allowed recovering 33% of potassium and 21% of phosphate in pig slurry after 24 h.

1. Introduction

Nitrogen is an essential element for all living organisms due to its role in genetic molecules and proteins that play vital functions in plant and animal cells. The exponential population growth during the 20th century is primarily attributed to the increased synthesis of NH_3 by the Haber-Bosch process which allowed producing nitrogen fertilisers for food production [1]. However, the Haber-Bosch process is energy-intensive and environmentally unfriendly since it represents 1% of the world's energy consumption and 2% of carbon dioxide global emissions [2–4].

Large amounts of the synthesised NH_3 are excreted by livestock in urea, faeces, undigested protein and ammoniacal nitrogen [5]. The ammoniacal nitrogen contained in animal slurries should be removed or recovered since its discharge to the environment can cause contamination. Most of this contamination is caused by nitrates that leach from the soil to groundwaters and end up in rivers, lakes, and estuaries. High nitrate concentrations in surface waters lead to eutrophication while high concentrations in drinking water have been related to a variety of human health problems [6–8].

The implementation of circular economy schemes in the agro-industrial sector requires implementing technologies that allow recovering ammoniacal nitrogen rather than removing it. Additionally, traditional biological ammoniacal nitrogen removal processes (e.g., nitrification/denitrification) where nitrogen is converted to nitrogen gas are characterised by greenhouse gas N_2O emissions and high energy consumptions [5,9,10]. Accordingly, new technologies must be developed to recover ammoniacal nitrogen from animal slurries to replace biological nitrogen removal processes [11,12]. NH_3 selective membranes stand as an emerging technology to recover ammoniacal nitrogen due to its capacity to operate at ambient temperature and pressure, and not requiring intensive aeration nor reagents [13,14].

Table 1
Characterization of the sieved pig slurry (average ± standard deviation).

Parameter	Units	Average
pH	–	8.1 ± 0.1
TSS	g/L	9.7 ± 0.4
VSS	g/L	8.6 ± 0.6
COD	g/L	18.7 ± 1.1
Alkalinity	g CaCO$_3$/L	12.8 ± 0.3
TAN	g N/L	2.6 ± 0.1
PO$_4^{3-}$-P	mg P/L	62 ± 8
SO$_4^{2-}$-S	mg S/L	14 ± 3
Na$^+$	g/L	4.8 ± 0.6
K$^+$	g/L	2.4 ± 0.3
Ca^{2+}	g/L	0.19 ± 0.03
Mg^{2+}	g/L	0.10 ± 0.02
Cl$^-$	g/L	1.5 ± 0.2
Zinc (Zn)	mg/L	6.96 ± 0.03
Arsenic (As)	mg/L	0.02 ± 0.01
Cadmium (Cd)	mg/L	< 0.01
Iron (Fe)	mg/L	19.11 ± 0.39
Mercury (Hg)	mg/L	0.01 ± 0.01
Lead (Pb)	mg/L	0.02 ± 0.01
Copper (Cu)	mg/L	2.79 ± 0.02
Manganese (Mn)	mg/L	3.67 ± 0.06

TSS: Total Suspended Solids, VSS: Volatile Suspended Solids, COD: Chemical Oxygen Demand, TAN: Total Ammoniacal Nitrogen.

Membrane systems consist of a selective barrier that allows only some molecules diffusing through it, which makes possible to separate these compounds from the original mixture [15]. Gas-permeable membranes (GPM) have shown promising results to recover ammoniacal nitrogen from animal slurry [16]. These are nano-perforated membranes designed to facilitate the diffusion of unionised free NH$_3$ and other neutral species while limiting the diffusion of charged species, including NH$_4^+$ ion. In contrast to hydrophobic/hydrophilic membrane systems, GPM are more likely to suffer clogging even when the feed has low suspended solids (pig slurry must be thoroughly pre-treated to remove suspended solids before entering the membrane system) [17]. Another disadvantage of GPM is that it has to operate at a feed solution pH above pKa of the NH$_4^+$/NH$_3$ equilibrium [18]. The novel hydrophobic/hydrophilic membrane used in this study allows the diffusion of neutral molecules (acting like a GPM) as well as the diffusion of some ions at lower fluxes, mainly monovalent ions. This nonporous membrane aims to preserve the operational advantages of GPM while increasing nitrogen transfer rates and reducing capital cost.

Recovering ammoniacal nitrogen using GPM requires increasing the pH of the slurry to values at or above 9.0 to displace this acid-base equilibrium of the ammoniacal nitrogen towards free NH$_3$ [4]. This pH regulation is essential to maintain the driving force between the feed and the trapping solution and can be performed either by adding an alkali reagent or by aeration. The capacity of NH$_4^+$ ion to diffuse through the hydrophobic/hydrophilic membrane may allow working under less alkaline conditions (pH 8.0–9.0), which could represent a competitive advantage due to the lower operation cost. An acidic solution (usually H$_2$SO$_4$ at pH ≤ 2) on the other side of the membrane traps the NH$_3$ in the form of NH$_4^+$ (i.e., ammonium sulphate) [19], which can be valorised as fertiliser.

The goal of this research was to study the feasibility of a novel hydrophobic/hydrophilic selective membrane to recover ammoniacal nitrogen from pig slurry. The influence of several factors on process performance (i.e., nitrogen recovery and nitrogen flux) were studied, including the pH of the feed solution, the volume ratio between feed and trapping solution, and the impact of the trapping solution concentration. All experiments were carried out at room temperature (ca. 22 °C) using both a synthetic solution and pig slurry. To gain further insight, the experimental results were evaluated using a physicochemical model.

2. Materials and methods

2.1. Synthetic solution, pig slurry and reagents

A synthetic solution mimicking the pig slurry composition was used during the first experiments. The synthetic pig slurry was prepared diluting in deionised water 6.0 g/L of NH$_4$Cl, 0.08 g/L of CaCl$_2$, 0.80 g/L of NaCl, 0.20 g/L of K$_2$HPO$_4$ and 0.40 g/L of MgSO$_4$ [19]. All chemicals were reagent grade chemicals (Panreac, S.A., Spain). The pH of the synthetic solution was adjusted throughout the experiment since the pH of the feed solution was one of the parameters studied in this research. Pig slurry was collected from a fattening pig farm located in La Noguera (Lleida, Catalonia, NE Spain), where most of the solid particles were removed before flushing the floor. After collection, the pig slurry was sieved through a 100 μm mesh to further remove solid particles to minimise membrane clogging and organic matter degradation. The sieved pig slurry was stored in a refrigerator at 4 °C until use. Table 1 summarises the main characteristics of the sieved pig slurry. The pig slurry total ammoniacal nitrogen (TAN = NH$_4^+$ + NH$_3$) concentration was 2.7 g N/L, which aligns with concentration reported from pig farms using flushing systems in Catalonia [20,21].
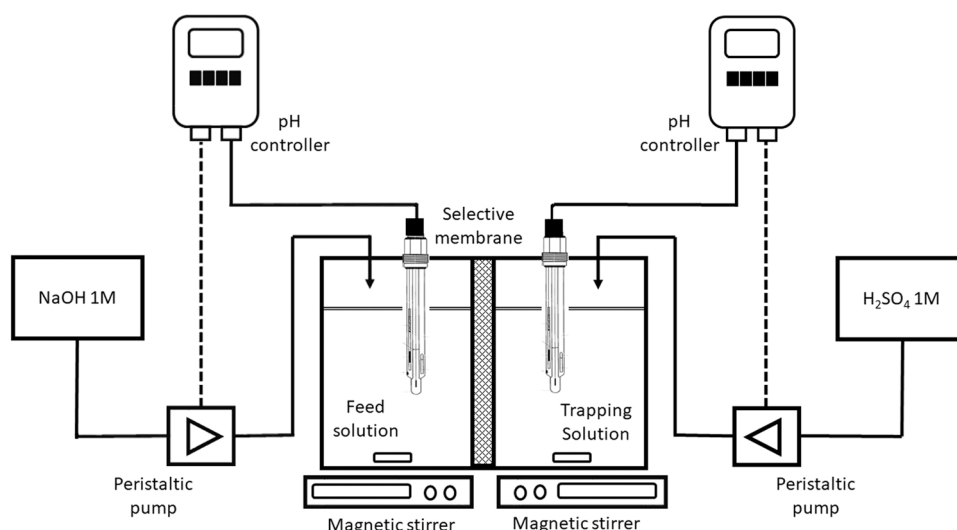

Fig. 1. Schematic representation of the lab-scale membrane contactor device.

Table 2

Experimental conditions of the experiments carried out in this study to assess the effect of pH of feed solution, volume ratio (ω), and number of stages.

	Exp. Test	Feed solution pH (-)	Trapping solution pH (-)	Operation time (h)	ω (V$_f$/V$_t$)	Number of stages	Feed solution (g TAN/L)
Effect of pH	1A	9.0–9.5	1.0–1.5	24	1	1	Synthetic (1.7 g N/L)
	1B	8.0–8.5	1.0–1.5	24			
	1C	6.0–6.5	1.0–1.5	24			
	1D	5.0–5.5	1.0–1.5	24			
	1E	3.0–3.5	1.0–1.5	24			
Effect of volume ratio	2 A	9.0–9.5	1.0–1.5	24	1	1	Synthetic (1.7 g N/L)
	2B	9.0–9.5	1.0–1.5	48			
	2C	9.0–9.5	1.0–1.5	24	2/3		
	2D	9.0–9.5	1.0–1.5	48			
	2 F	9.0–9.5	1.0–1.5	24	1	1	Pig slurry (2.7 g N/L)
	2G	9.0–9.5	1.0–1.5	48			
	2H	9.0–9.5	1.0–1.5	24	2/3		
	2I	9.0–9.5	1.0–1.5	48			
Effect of number of stages	3A	9.0–9.5	1.0–1.5	3 x 8 h	2/3	3	Synthetic (1.7 g N/L)
	3B	9.0–9.5	1.0–1.5	3 x 8 h	2/3	3	Pig slurry (2.7 g N/L)

2.2. Experimental device and methodology

The hydrophobic/hydrophilic selective membrane used in this research was a selective membrane for neutral molecules (e.g., water and ammonia) and for some monovalent ions (e.g., NH_4^+, Na^+, K^+ and Cl^-). This semi-permeable membrane uses the concentration gradient between the feed solution (synthetic solution or pig slurry) and the acid trapping solution as driving force. Water diffusion through the membrane was considered negligible since the initial and final volume of both solutions remained constant during the experiments.

Experiments were carried out in a lab-scale experimental device (Fig. 1). The device is divided in two 1-L chambers by a completely submerged selective membrane (membrane area of 0.005 m^2). One chamber contained the feed solution, and the other chamber contained an H_2SO_4 solution (0.1 M) that acted as a trapping solution. Each chamber was equipped with a magnetic stirrer (agitation velocity of 180 rpm) and a pH control system. The pH control system consisted of a pH electrode (Crison, code 53 35), a pH controller (pH 28, Crison), a peristaltic pump (Ismatec, Type ISM827), and a tank containing either an acidic or a basic concentrated solution (H_2SO_4 1 M and NaOH 1 M, respectively). The pH controller switched on the peristaltic pump (Ismatec, Type ISM827) connected to the tank to control the pH within a predefined pH setpoint. To minimise free NH_3 losses by volatilisation, both chambers were completely sealed using a lid and parafilm. Experiments were carried out at room temperature (20 – 25 °C).

To monitor the process, several samples were withdrawn from the feed and trapping solution during the experiments. During the first 2 h samples were withdrawn every 30 min; afterwards, samples were withdrawn every hour. Experiments running overnight were sampled after 12 h. In each sampling event 4 mL were withdrawn for both solutions. For the feed solution, 0.1 mL of sulfuric acid (1 M) was immediately added to decrease the pH and prevent TAN losses by volatilisation. All samples were stored at 4 °C prior analysis. The volume of samples withdrawn to monitor the process were recorded and considered to correct the calculations. In all experiments, the withdrawn volume represented less than 7% of the total volume.

The TAN removal and recovery efficiency were determined using Eqs. (1) and (2), respectively. The difference between TAN removal and recovery is associated with TAN losses by volatilisation.

$$\% \ TAN \ removal \ (t) = \frac{gTAN_{feed,0} - gTAN_{feed}(t)}{gTAN_{feed,0}} \cdot 100 \quad (1)$$

$$\% \ TAN \ recovery \ (t) = \frac{gTAN_{trapping}(t) - gTAN_{trapping,0}}{gTAN_{feed,0}} \cdot 100 \quad (2)$$

Where $TAN_{feed,0}$ is the initial TAN mass in the feed solution, $TAN_{feed}(t)$ is the TAN mass at a specific time, $TAN_{trapping,0}$ is the initial TAN mass in the trapping solution, and $TAN_{trapping}(t)$ is the TAN mass at a specific time.

2.3. Experimental conditions

Table 2 summarises experiments carried out in this study to analyse the potential and limitations of the hydrophobic/hydrophilic NH_4^+/NH_3 selective membrane. Process performance was assessed by quantifying (i) the rate and percentage of ammoniacal nitrogen recovery, (ii) the diffusion values obtained from the model (see Section 2.5), and (iii) the consumption of alkali (NaOH) and acid (H_2SO_4) to keep the pH of each solution constant.

Experiments 1A–1E aimed to understand the behaviour of the membrane at different pH since the NH_3 concentration gradient has been identified as a critical factor on TAN recovery rate when using GPM [17]. The pH of the trapping solution was set at 1.0–1.5 (most common pH in the literature) while several pH for the synthetic feed solution were tested, i.e., pH 9.0, 8.0, 6.0, 5.0 and 3.0.

Experiments 2A–2I were performed to determine the TAN removal and recovery efficiency and the TAN transfer rate under different volume ratios between the feed and the trapping solution ($ω = V_{feed}/V_{trapping}$). Two technical replicates were carried out for each condition where the second replicate was operated for a longer time (48 h instead of 24 h) to assess the ultimate recovery efficiency. The pH of the feed solution (synthetic solution or pig slurry) and the trapping solution were set at 9.0–9.5 and 1.0–1.5, respectively.

Experiments 3A and 3B assessed the impact of the TAN concentration in the trapping solution on process performance using both synthetic solution and pig slurry. The experiments were divided in three stages of about 8 h each. At the beginning of each stage, the trapping solution was renewed for an acidic solution without TAN. The pH of the feed solution and the trapping solution were set at 1.0–1.5 and 9.0–9.5, respectively.

2.4. Analytical methods

All the analyses were performed according to the Standard Methods for the Examination of Water and Wastewater [22]. TAN concentration was determined using a Thermo Fisher Scientific selective electrode (Orion 9512HPBNWP) following the procedure 4500-NH3D. Chemical oxygen demand (COD) was determined according to the Standard Method 5220 C [22]. Total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to Standard Method 2540 G [22]. Cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, SO_4^{2-}) were analysed using an 863 Advanced Compact IC Metrohm ionic
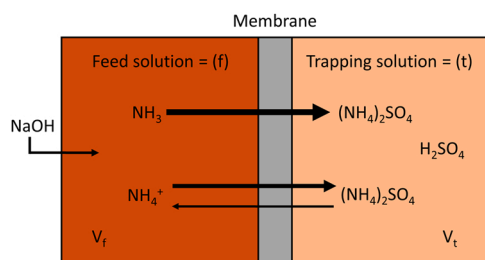
Fig. 2. Diagram of the model species and nomenclature (V_f: feed solution volume, V_t: trapping solution volume).

chromatographer using Metrosep columns (Metrosep C 4–150/4.0 and Metrosep A Supp 17–250/4.0, respectively). Alkalinity was determined following the Standard Method 2320B procedure using an automated titrator (Crison pH Burette 24) with a 0.1 M HCl solution and a pH endpoint of 4.30. Heavy metals concentration in the sieved pig slurry were determined using an ICP-MS spectrophotometer (Perkin Elmer Nexion 350D). Before analysis the pig slurry was digested (1 mL sample + 3 mL HNO$_3$ + 1 mL H$_2$O$_2$) in a closed Teflon reactor at 90 °C for 24 h.

2.5. Physicochemical model

A physicochemical model was developed to evaluate and compare the TAN diffusion across the membrane for the different experimental conditions [23]. Fig. 2 aims to clarify the model structure and nomenclature. Eq. (3) represents the acid-base equilibrium between NH$_3$ and NH$_4^+$ that mainly depends on the pH, the temperature, and the ionic strength of the solution [24].

$$NH_4^+(aq) \xrightleftharpoons[k_b]{k_a} NH_3(aq) + H^+(aq) \qquad (3)$$
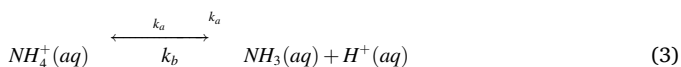
The hypothesis and assumptions considered in the model are the following [23]:

1. Both NH$_3$(aq) and NH$_4^+$(aq) diffuse through the membrane independently (first Fick law).
2. The feed and the trapping solution are considered as very diluted solutions. Therefore, the activity coefficients are equal to 1 and the crossed coefficients negligible.
3. The acid-base kinetics, on each side of the membrane, is considered to take place very quickly (high kinetic constants are used). According to the law of mass action, $K_a = k_a/(k_b \cdot c°)$, where K_a is the thermodynamic acidic equilibrium constant and $c°$ is 1 M. The pka value was 9.245 [25] and it was referred to 25 °C.
4. The pH of each solution is kept constant during the experiment and equal to the controller setpoint.
5. The loss of NH$_3$ by volatilisation is negligible due to the high solubility of NH$_3$ in water and the sealing of the solutions.

The equation system used to solve is based on NH$_3$ (x) and NH$_4^+$ (y) moles in relation to the initial TAN moles value (Eqs. (4) and (5), respectively) at both sides of the membrane (i represents f = feed or t = trapping), where mol$_{TAN,0}$ is the total amount of TAN in the system, which will be constant during the experiment. $z_i(t)$ represents the moles fraction of TAN on both sides of the membrane (Eqs. (6) and (7)).

$$x_i(t) = \frac{mol_{NH_3,i,(t)}}{mol_{TAN,0}} \qquad (4)$$

$$y_i(t) = \frac{mol_{NH_4^+,i}(t)}{mol_{TAN,0}} \qquad (5)$$

$$z_i(t) = \frac{mol_{TAN,i}(t)}{mol_{TAN,0}} \qquad (6)$$

$$z_i(t) = x_i(t) + y_i(t) \qquad (7)$$

$$z_f(t) + z_t(t) = 1 \qquad (8)$$

The equation system comprises four linearly dependent ODEs, which can be reduced to 2 linearly independents ODEs considering that (i) only 3 ODEs are linearly independents (the sum of the fractions is equal to 1, Eqs. (8) and (9)) and that (ii) the fraction of NH$_3$ in the trapping solution is assumed to be negligible due the acidic pH.

$$\frac{dx_f(t)}{dt} + \frac{dy_f(t)}{dt} + \frac{dx_t(t)}{dt} + \frac{dy_t(t)}{dt} = 0 \qquad (9)$$

Finally, considering high values for the kinetic constants ($k_a > 1$ h^{-1}), a non-linear equation for the TAN fraction, $z_f(t)$, can be obtained (Eq. (10)) [23].

$$z_f(t) = x_f(t) + y_f(t) = (1+\mu) \left(c_1 \cdot exp(r_1 t) + \frac{c}{b} \right) \qquad (10)$$

Where:

$$c_1 = \frac{1}{1+\mu} - \frac{c}{b} \qquad (11)$$

$$\frac{c}{b} = \frac{\omega \cdot \alpha_y}{\alpha_x + \omega' \cdot \alpha_y} \qquad (12)$$

$$r_1 = -\left(\frac{\alpha_x + \omega' \cdot \alpha_y}{1+\mu} \right) \qquad (13)$$

$$\omega' = \omega + (1+\omega) \cdot \mu \qquad (14)$$

$$\mu = 10^{pK_a - pH_f} \qquad (15)$$

$$\alpha_j = \frac{P_j \cdot A}{V_{feed}} \qquad (16)$$

$$P_j = \frac{D_j}{\Delta x} \qquad (17)$$

α_j is the time gradient referred to the moles fraction of each specie [h^{-1}]; P_j is the permeability of the membrane [m/s]; D_j is the diffusion coefficient of the membrane [m^2/s]; ω is the feed-to-trapping volume ratio; Δx is the thickness of the membrane (1.8·10^{-5} m); and A is the surface of the membrane (0.005 m^2). Subindex j refers to either NH$_3$ or NH$_4^+$.

The model has only two parameters, α_x and α_y, which can be fitted to the experimental data. The model was coded in Python using the curve fit function of the scipy.optimize sub-module which uses the Levenberg-Marquardt algorithm to perform non-linear least squares to fit the TAN concentration in the trapping solution chamber. The input experimental data was the TAN concentration and pH of both solutions at each sampling event. The model calculated the diffusion coefficients, D_{NH3} and, D_{NH4^+}, quantifying the easiness of the NH$_3$ and NH$_4^+$ ion to diffuse through the membrane under each experimental condition. The model also allows quantifying the initial recovery rate of TAN moles fraction of the feed solution. This parameter is quantified from the time derivative of $z_f(t)$ at $t = 0$ (Eq. (18)).

$$z_f'(0) = \lim_{t \to 0} z_f'(t) = -\frac{\alpha_x + \mu \cdot \alpha_y}{1+\mu} < 0 \qquad (18)$$

This magnitude is expressed in h^{-1}, and it can be expressed as initial TAN recovery rate (g TAN/(L·h)) by multiplying it by the TAN concentration at $t = 0$.

Table 3

Results of experiments carried out with synthetic solution to assess the impact of the feed solution pH after 24 h of operation.

Substrate	Synthetic (1.7 g TAN/L)				
Test	1A	1B	1C	1D	1E
pH	9.0	8.0	6.0	5.0	3.0
Average TAN removal (%)	65	62	51	45	39
Average TAN recovery (%)	62	59	49	43	36
TAN flux at 8 h (g TAN/(m^2·day))	231	201	175	156	140
TAN flux at 24 h (g TAN/(m^2·day))	145	129	113	97	87
NaOH consumption (mol$_{NaOH}$/mol$_{TAN,recovered}$)	2.9	2.8	3.2	3.3	0.5
H$_2$SO$_4$ consumption (mol$_{H_2SO_4}$ /mol$_{TAN,recovered}$)	2.0	2.1	2.5	2.6	0.0

3. Results and discussion

3.1. Effect of the feed solution pH on membrane performance

As shown in Table 3, the TAN recovery and flux through the membrane increased as the pH of the synthetic feed solution increased from 3.0 to 9.0. Specifically, the TAN recovery increased from 36% to 62% as the pH increased from 3.0 to 9.0 after 24 h. The higher TAN recoveries at higher pH values were expected because of the higher diffusion coefficient of NH$_3$ in comparison to NH$_4^+$ and the higher fraction of NH$_3$ in the feed solution. Interestingly, the percentage of TAN recovery increased linearly with pH (see Fig. S1 in supplementary material). TAN removal values were slightly higher than TAN recovery values because of NH$_3$ losses by volatilisation. Nonetheless, TAN losses were minimal since they were estimated at 3.4% and 2.9% for pH 9.0 and 8.0, respectively. Fig. 3 shows the exponential negative trend of the TAN concentration in the feed solution, where TAN fluxes decrease over time. For the trapping solution, the same behaviour with the inverse sign was observed. As the developed model shows, this behaviour can be explained by the Fick's law of diffusion where diffusive flow is controlled by the concentration gradient. Experiments carried out without pH control showed that the feed and trapping solutions reached the same TAN concentration and pH (data not shown). This result showed that the maximum TAN recovery without pH control is 50% and, therefore, indicating that pH control is needed to create a concentration gradient and higher TAN diffusion rates.

The reagent consumption normalised by the amount of TAN recovered showed the most suitable feed solution pH were 9.0 and 8.0 (Table 3). At pH 9.0 and 8.0, alkali consumption was 2.9 and 2.8 mol NaOH/mol TAN recovered, respectively, and the acid consumption was 2.0 and 2.1 mol H$_2$SO$_4$/mol TAN recovered, respectively. Overall, a pH of 9.0 for feed solution was selected as the most suitable option due to (i) the higher TAN flux and (ii) the similar reagent consumption when compared to pH 8.0. The superior performance of GPM membranes at

pH 9.0 agree with those results reported by Garcia-González and Vanotti [26], who observed that TAN recovery triples when adjusting the pig slurry pH from 7.5 to 9.0 using a GPM.

3.2. Impact of feed/trapping volume ratio and retention time

Table 4 summarises the results obtained in experiments where the effect of volume ratio (ω) between the feed solution and the trapping solution was evaluated. Reducing this ratio by 1/3 (ω of 2/3) improved the TAN removal and recovery yields without affecting the NH$_3$ and NH$_4^+$ diffusion coefficient (Table 4). Accordingly, the higher TAN recoveries can be explained by the higher TAN flux across the membrane (145 vs 118 g TAN/(m^2·day) for synthetic solution). Fig. 4 shows the TAN concentration over time of the feed and the trapping solution for the experiments carried out with synthetic solution and pig slurry at volume ratio of ω = 1 and 2/3. The TAN fluxes when the membrane system was operated at ω of 2/3 (Fig. 4B and D) were higher than those at ω of 1 (Fig. 4A and C). The different ω had also an effect on the initial TAN recovery rate with lower ω values leading to higher TAN recovery rates. The initial TAN recovery rate parameter was − 109 g TAN/(L·h) for ω of 1 and − 156 g TAN/(L·h) for ω of 2/3 operating with synthetic solution. This can be explained by the greater driving force (concentration gradient between both sides of the membrane) since the TAN concentration in the trapping solution increased more slowly. The ω could be further reduced to increase the TAN flux and decrease the operation time, however, this would imply a higher reagent consumption and a less concentrated (NH$_4$)$_2$SO$_4$ solution. The plateau observed for synthetic solution experiments was reached after around 35 h, when

Table 4

Results of experiments carried out at pH = 9.0 with synthetic solution and pig slurry under different feed and trapping volume ratios (ω), retention times and number of stages.

| Substrate	Synthetic (1.7 g TAN/L)				Pig slurry (2.7 g TAN/L)			
Test	2A	2B	2C	2D	2F	2G	2H	2I
Volume's relation (ω)	1		2/3		1		2/3	
TAN flux at 8 h (g TAN/ (m^2·day))	231		192		205		144	
Diffusion coef. for NH$_3$ (10^{-11} m^2/s)	7.4 ± 0.2		7.2 ± 0.2		2.79 ± 0.20		2.57 ± 0.13	
Diffusion coef. for NH$_4^+$ (10^{-11} m^2/s)	2.2 ± 0.2		1.9 ± 0.1		1.10 ± 0.14		0.99 ± 0.11	
Initial TAN recovery rate (g TAN/(L·h))	−(109 ± 7)		−(156 ± 8)		−(70 ± 7)		−(96 ± 8)	
Total operation time (h)	24	48	24	48	24	48	24	48
Average TAN removal (%)	65	75	77	84	34	46	51	63
Average TAN recovery (%)	62	73	74	76	32	45	46	59
TAN flux (g TAN/ (m^2·day))	145	119	118	83	116	91	90	58
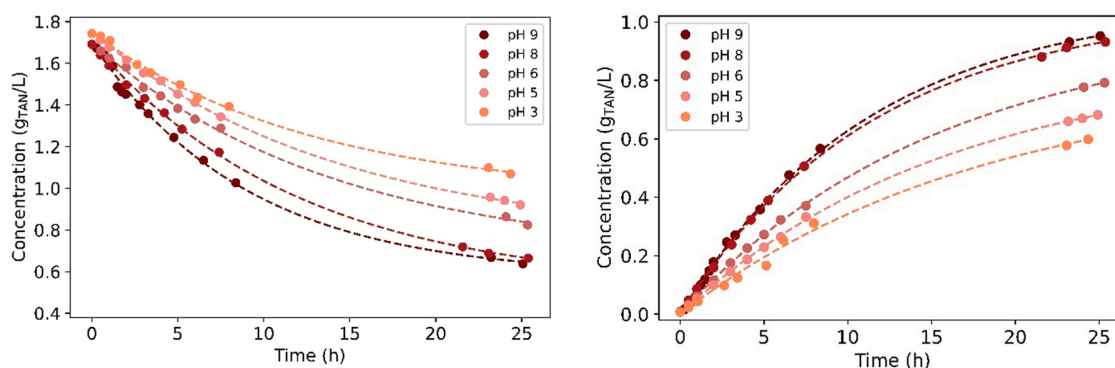
Fig. 3. Experimental results of the experiments assessing the impact of the feed solution pH on membrane performance. (Left) TAN concentration in the feed solution (Right) TAN concentration in the trapping solution. Dots represent the experimental data; dashed lines indicate the TAN concentration pattern.
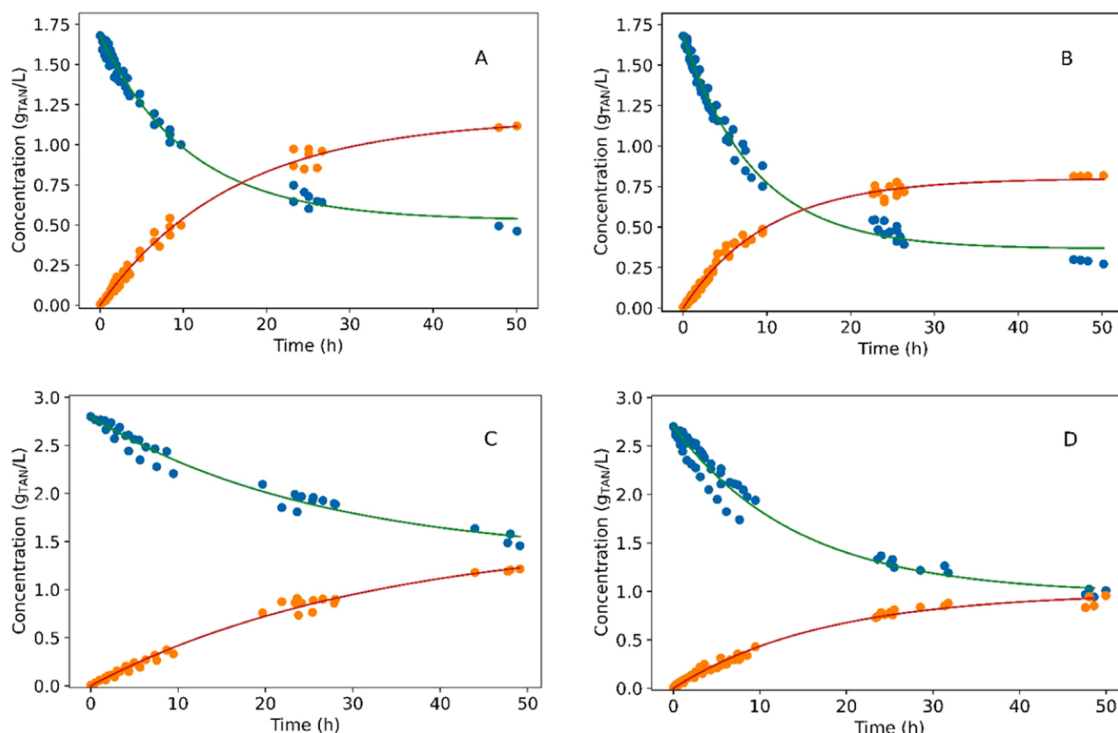
Fig. 4. Experimental and model results of the TAN concentration for experiments carried out at pH = 9.0 with (A) synthetic solution and ω of 1, (B) synthetic solution and ω of 2/3, (C) pig slurry and ω of 1, (D) pig slurry and ω of 2/3. Dots represent the experimental data and solid lines represent the model best fit.

TAN recovery was above 73% and 76% operating at ω of 1 and 2/3, respectively. For pig slurry, the plateau was reached at a TAN recovery of 50% and 62% operating at ω of 1 and 2/3, respectively.

Experiments carried out with pig slurry (Table 4) showed a slightly lower TAN flux than the synthetic solution experiments. For a ω of 1, the TAN fluxes after 24 h were 116 and 145 g TAN/(m^2·day) for pig slurry and synthetic solution, respectively. For ω of 2/3, the TAN flux after 24 h were 90 and 118 g TAN/(m^2·day); note that the lower flux is due to the lower feed solution volume used in this scenario (0.5 L for ω of 2/3 instead of 0.75 L for ω of 1). The TAN fluxes achieved in this study are higher than those achieved by Molinuevo-Salces et al. [13] who reported TAN flows between 12 and 38 g TAN/(m^2·day) when treating pig slurry at room temperatures using an e-PTFE membrane.

The physicochemical model was used to calculate the diffusion co-efficients for both species, which remained constant with different volumes ratio. The calculated values of the different parameters of the model and the standard deviation of the fitting (χ^2_{red}) are shown in Table S1 of supplementary material. χ^2_{red} gives an estimation of the goodness of the model.

The average values for the diffusion coefficient of NH$_3$ and NH$_4^+$ through the membrane at pH 9.0 were $(7.3 \pm 0.2) \cdot 10^{-11}$ and $(2.1 \pm 0.1) \cdot 10^{-11}$ m^2/s for the synthetic solution experiments and $(2.7 \pm 0.1) \cdot 10^{-11}$

and $(1.0 \pm 0.1) \cdot 10^{-11}$ m^2/s for the pig slurry experiments, respectively. These results suggest that the diffusion coefficients are dependent mainly on the species and feed solution matrix. The diffusion co-efficients from the pig slurry experiments were stable along the mem-branes usage, indicating that no membrane fouling occurred during these experiments (~150 h of operation and a pig manure of 10 g TSS/L). However, long-term experiments are required to determine the membrane resistance to fouling. For those experiments carried out at pH below 9.0 (Section 3.1), the model could not accurately estimate the diffusion coefficients because of the low fraction of NH$_3$ in the feed solution.

For synthetic solution, the NH$_3$ diffusion coefficient was 3.5 times higher than the NH$_4^+$ diffusion coefficient because of NH$_4^+$ charge. A charge implies a bigger radius due to water molecules gained by the species (hydrated radius), which hinders NH$_4^+$ diffusion through the membrane [27]. For the pig slurry experiments, NH$_3$ diffusion coeffi-cient was 2.5 times higher than NH$_4^+$ diffusion coefficient. The higher diffusion of both species for synthetic solution was attributed to higher ionic strength of the pig slurry since the model assumes ideal solution for both scenarios (Fick law considers diluted solutions). The ratio between diffusion coefficients is a useful parameter to estimate the final con-centration that both solutions can achieve.

Table 5
Concentration of charged species and proportion that crossed the membrane at specified times (tests 2A, 2B and 2F, 2G).

	Synthetic feed (ω = 1) Tests 2A, 2B			Pig slurry (ω = 1) Tests 2F, 2G		
	Initial concentration (mg/L)	Recovery at 24 h (%) Test 2A	Recovery at 48 h (%) Test 2B	Initial concentration (mg/L)	Recovery at 24 h (%) Test 2F	Recovery at 48 h (%) Test 2G
TAN	2024	56.0	64.7	2675	42.1	55.5
Na$^+$	315	25.7	30.6	4818	17.5	21.3
K$^+$	90	32.9	43.6	2392	32.9	41.9
Ca^{2+}	29	< 1	< 1	187	6.7	13.8
Mg^{2+}	79	6.4	12.2	101	5.9	10.7
Cl$^-$	4516	20.1	26.0	1541	12.9	19.0
PO$_4^{3-}$-P	109	19.5	31.6	62	21.1	33.7

Table 6
Results of experiments carried out at pH = 9.0 with synthetic solution and pig slurry operating with 3 stages where each one means a new trapping solution that did not contain any TAN.

Substrate	Synthetic (1.7 g TAN/L)			Pig slurry (2.7 g TAN/L)		
Test	3A			3B		
Volume's relation (ω)	2/3			2/3		
Total operation time (h)	3 × 8			3 × 8		
Average TAN removal (%)	78			54		
Average TAN recovery (%)	73			50		
TAN flux at 24 h (g TAN/(m²·day))	153			143		
	Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3
TAN flux of 8 h (g TAN/(m²·day))	194	135	82	148	102	61
ΔTAN recovered (g TAN)	0.33	0.11	0.007	0.28	0.19	0.13

Table 5 shows the percentage of charged species that crossed the membrane from the feed to the trapping solution. As expected, the diffusion of monovalent cations (Na^+, K^+, NH_4^+) was higher than the diffusion of divalent cations (Ca^{2+}, Mg^{2+}). This is directly related to the species charge since a higher charge implies a bigger hydrated radius [27]. To calculate Na^+ diffusion in Table 5, the sodium added to adjust the pH was subtracted to only consider the Na^+ added as NaCl. Cl^- and PO_4^{3-} anions were also able to diffuse through the membrane with a recovery percentage of 26% and 32% after 48 h, respectively. The diffusion of PO_4^{3-} was relatively high because of its equilibrium between HPO_4^{2-} and $H_2PO_4^-$ (HPO_4^{2-} is the main species at pH 9.0). The proportion of charged species that crossed the membrane from the feed to the trapping solution when working with pig slurry was similar to the recorded when using the synthetic solution (Table 5). The diffusion of ions, in addition to NH_3, is a distinctive feature of this membrane under study compared to GPM. This feature allows recovering other valuable nutrients (K^+ and PO_4^{3-}) from pig slurry. H^+ and OH^- also diffuse through the membrane since they are monovalent ions, contributing to the reagent consumption. To minimise the diffusion of H^+ and reagent consumptions, a higher trapping solution pH could be tested. A trapping solution with pH 4.0 may be low enough since this pH value is much lower than the pKa and, therefore, almost all the TAN exists as NH_4^+. Nonetheless, the main NaOH and H_2SO_4 consumption was caused by the diffusion of NH_3 across the membrane and to reach both solution pH setpoints. Finally, it is worth highlighting that analysed heavy metals (Mn, Fe, Cu, Zn, Cd, Hg and Pb) did not diffuse through the membrane since the metals concentration remained constant in the pig slurry and

the heavy metals in the trapping solution were below the detection limit (< 0.01 mg/L).

3.3. Impact of TAN concentration in the trapping solution

In experiments 3A and 3B, the TAN recovery process was split in three stages. At each stage the trapping solution was renewed to increase the concentration gradient between both sides of the membrane to achieve a higher TAN recovery efficiency. For the synthetic solution, the TAN removal using 3 stages was 78% (at 24 h), a similar value to the one obtained when working with a single stage at 24 h (Table 6). The closeness of using 1 or 3 stages can also be observed in the overall TAN flux, which was 153 and 143 g TAN/(m²·day), respectively. These results indicate concentration gradient did not lead to a significantly higher TAN recovery improvement. Similar results were obtained when using pig slurry since the difference on TAN recovery between 1 and 3 stages was 4% (50% vs. 46%). Besides the similar performance, the main drawback of the 3 stages strategy is the higher consumption of reagents. The NaOH spent to control pH of feed solution operating with 3 stages was 25% higher and the H_2SO_4 spent to control the pH of the trapping solution was doubled. Considering these results, it is hypothesised that a new configuration where each step had a longer duration will yield higher recovery efficiencies (e.g., 24 instead of 8 h). Despite these limitations, using different stages is particularly useful when high TAN recoveries from pig slurry are needed.

Experiments 3A and 3B were modelled using the parameters obtained in Section 3.2 (i.e., 2C and 2H, respectively) since stages of 8 h are not long enough to reliably estimate the diffusion coefficients. It is likely that during this period α_x and α_y are correlated, i.e., both are mathematically related by a function where changes in the value of one variable are balanced by changes in the other variable. The goodness of fittings between the experimental and model results in Fig. 5 indicate that operating at 1 or 3 stages did not noticeably affect the species diffusivity and proves the robustness of the model.

4. Conclusions

The performance of a new hydrophobic/hydrophilic selective membrane to recover ammoniacal nitrogen from pig slurry was analysed. The higher nitrogen fluxes were achieved when the pH of the feed solution was controlled at 9.0. At pH 9.0, the average nitrogen flux after 24 h was 145 and 116 g N/(m²·day) for the synthetic solution and pig slurry experiments, respectively. A physicochemical model able to adapt to different operation conditions was developed to calculate the diffusion coefficients of NH_3 and NH_4^+. The diffusion coefficients of NH_3 and NH_4^+ through the membrane at pH 9.0 were $(7.3 \pm 0.2) \cdot 10^{-11}$ and $(2.1 \pm 0.1) \cdot 10^{-11}$ m²/s for the synthetic solution and $(2.7 \pm 0.1) \cdot 10^{-11}$ and $(1.0 \pm 0.1) \cdot 10^{-11}$ m²/s for the pig slurry, respectively. Experiments
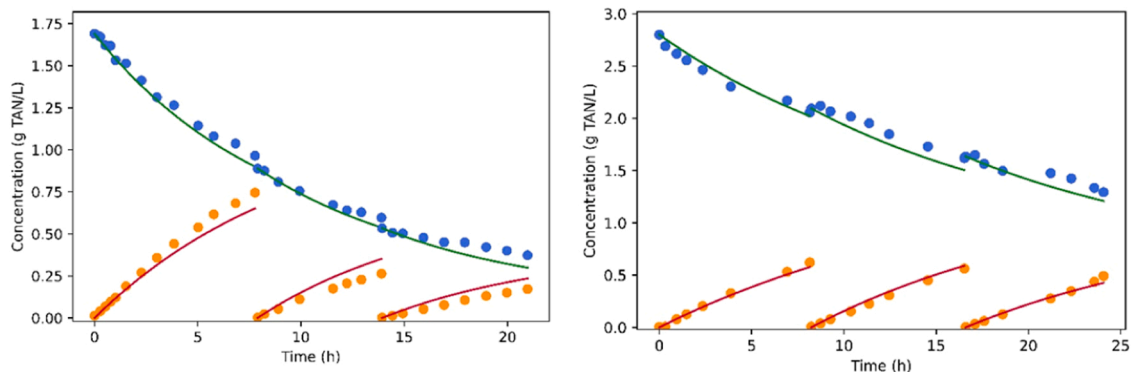

Fig. 5. TAN concentration evolution of the feed solution for (A) (Left) synthetic solution and (B) (Right)pig slurry experiments when 3 stages in series are applied. Dots represent the experimental data and solid lines represent the model best fit.

carried out with 3 stages did not offer a noticeable performance improvement but increased the alkaline and acid reagent consumption by 25% and 100%, respectively. Charged species such as K^+, Na^+, Cl^-, Ca^{2+}, Mg^{2+} or HPO_4^{2-} were able to diffuse through the membrane. The capacity of ions to diffuse through the membrane is a distinctive feature of this membrane compared to GPM and allows recovering 33% of PO_4^{3-} and 21% of K^+ in pig slurry after 24 h. The diffusion of heavy metals across the membrane was negligible (< 0.1%).

CRediT authorship contribution statement

A. Serra-Toro: Methodology, Investigation, Formal analysis, Writing – original draft, Visualization. **S. Astals:** Conceptualization, Writing – review & editing, Supervision, Visualization. **S. Madurga:** Formal analysis, Writing – review & editing, Visualization. **J. Mata-Àlvarez:** Writing – review & editing, Funding acquisition. **F. Mas:** Conceptualization, Methodology, Formal analysis, Writing – review & editing, Supervision, Visualization, Funding acquisition. **J. Dosta:** Conceptualization, Methodology, Investigation, Writing – review & editing, Supervision, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.108434.

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