



UNIVERSITAT DE
BARCELONA

MASTER FINAL PROJECT
MASTER OF ENVIRONMENTAL ENGINEERING

Study of a gas-permeable membrane contactor for ammonia recovery from manure

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June 2022

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IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS

The Sustainable Development Goals (SDGs) related to this final Master project are represented below.



PEOPLE. Goal 6: Ensure access to water and sanitation for all.

This study aligns with the 6.3 objective because the main propose is to reduce pollution by recycling wastewaters such as liquid fraction of pig manure.

6.3 By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally.

The pig manure treatment proposed in the current study using Gas Permeable Membrane (GPM) contactors to reduce nitrogen contamination from livestock discharges to the environment pretends to encourage the adoption of clean and environmentally sound technologies, as mentioned in 9.4.

PROSPERITY. Goal 9: Build resilient infrastructure, promote sustainable industrialization and foster innovation.

9.4 By 2030, upgrade infrastructure and retrofit industries to make them sustainable, with increased resource-use efficiency and greater adoption of clean and environmentally sound technologies and industrial processes, with all countries taking action in accordance with their respective capabilities.

The reduction of waste generation through recycling and the ammonia recovery present in pig manure to reuse it as a fertilizer (instead of dumping it as waste), aligns with goals 11.4, 12.4 and 12.5.

PLANET. Goal 11: Make cities inclusive, safe, resilient and sustainable.

11.4 Strengthen efforts to protect and safeguard the world's cultural and natural heritage.

Goal 12: Ensure sustainable consumption and production patterns.

12.4 By 2030, achieve the environmentally sound management of chemicals and all wastes throughout their life cycle, in accordance with agreed international frameworks, and significantly reduce their release to air, water and soil in order to minimize their adverse impacts on human health and the environment.

12.5 By 2030, substantially reduce waste generation through prevention, reduction, recycling and reuse.

ABSTRACT

Ammoniacal nitrogen present in livestock manure represents a valuable resource that can be recovered to generate fertilizers by using gas-permeable hydrophobic membranes, which have gained increasing interest for their efficiency and low cost. In this study, the use of an ammonia-permeable hollow fibre membrane (active surface area of 0.50 m²) to recover the nitrogen present in a synthetic solution and filtered manure was analysed. Its principle of operation is based on the ammonia (NH₃) mass transfer from the feed to an acid extract solution or trapping solution (in this study, using diluted H₂SO₄ 75%) due to the difference in concentrations of ammonia, enhanced by the control of pH. For experiments with 2L of synthetic feed at pH values above 9, more than 98% of ammonia (1.8 g N/L) was recovered in 8 hours at 25°C (equal volumes of feed and trapping solution). The manure experiments were performed after pre-treating the manure by centrifugating and filtrating it in order to determine the nitrogen recovery under different conditions. The pH set for the manure experiments was determined from the synthetic feed experiments where duplicates were executed testing a pH range value for the feed from 6 to 12. Volume ratios of 1:1 and 1:10 were analysed and recoveries of more than 99% were obtained with a trapping volume 10 times lower than the feed solution (pre-treated manure) under the conditions mentioned above. From the current project, the use of a lab-scale hollow-fiber ammonia gas permeable membrane contactor has been proved to be highly efficient to recover ammonia from a high loaded nitrogen wastewater such as pre-treated manure.

TABLE OF CONTENTS

1. INTRODUCTION	5
2. OBJECTIVES	10
3. MATERIALS AND METHODS	11
3.1 Influent characteristics	11
3.2 Experimental set-up	12
3.3 Methodology	13
3.4 Analytical methods	15
3.5 Ammonia transfer calculations	15
4. RESULTS AND DISCUSSION	18
4.1 Effect of the pH in a synthetic feed solution at 25°C	18
4.2 Efficiency evaluation from the manure experiments based on volume ratio	21
4.3 Efficiency evaluation from the manure experiments regarding pH control strategies ..	23
5. CONCLUSIONS	26
6. REFERENCES	28

1. INTRODUCTION

Total ammonia nitrogen (TAN) is a parameter that should be treated in wastewaters to meet the quality standards required before its discharge in a receiving media. However, TAN, which includes both free ammonia nitrogen ($\text{NH}_3\text{-N}$) and ionic ammonium nitrogen ($\text{NH}_4^+\text{-N}$), is a valuable resource, essential for human population growth. Nevertheless, when it is not properly managed, this nutrient is responsible for eutrophication in many cases and it is toxic to various aquatic organisms.

TAN could be transformed into nitrogen gas using microbial methods by wasting ammonia resources. In order to remove nitrogen, mainly present as TAN, from municipal wastewaters, a biological nitrogen removal (BNR) process is usually applied. BNR consists of ammonia oxidation to nitrate (nitrification) and nitrate reduction into dinitrogen gas (denitrification). However, this process presents limitations related to sustainability, cost and operational stability. Converting a valuable resource such as ammonia into a lacking value substance (nitrogen gas) after investing large amounts of energy, supposes a significant waste of ammonia resources. To overcome the limitations of the BNR processes and recovery of ammonia, extensive research has studied alternative processes such as struvite precipitation, ion exchange and ammonia stripping, although they also present their own limitations. Anaerobic ammonium oxidation (Anammox) has been also highly studied, where the Anammox bacteria converts ammonium to nitrogen gas using nitrite as electron acceptors (*Darestani et al., 2017*).

Nowadays, commercial ammonia or nitrogenous fertilizer are mainly produced by the Haber-Bosh process from atmospheric nitrogen (N_2) and natural gas (*Flotats, 2021*), which is a high demanding process. The ammonia present in wastewaters may compensate 20-30% of the Haber-Bosch produced ammonia (*Tarpeh and Chen, 2021*).

Nutrients recovery from waste streams has gained interest in recent years regarding economic, environmental and energy considerations (*Sareer et al., 2015*). Struvite precipitation has been investigated as a promising approach to recover both phosphorous and ammonia from wastewaters by producing struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) which is a highly valuable fertilizer. However, this process is

significantly dependant on phosphorous concentration in treated wastewaters. As wastewaters present low concentration of phosphorous (8 mg P/L as the average value for domestic wastewaters), the ammonia recovery in form of struvite is shown to be demanding large amounts of magnesium and phosphate salts (*He et al., 2020*). A significant TAN removal has been performed by air stripping, but this process has a high energy consumption due to the stripping tower, risk of severe corrosion and scaling (*Renou et al., 2008*).

Hydrophobic membrane contactors (MCs) could be a feasible option for recycling ammonia from wastewaters as they are simple to use and produce a fertilizer product such as ammonium sulphate (*Darestani et al., 2017*). The membrane contactors are selective to ammonia gas removal present in low concentrations and are able to operate with low energy demand. In order to enhance the removal of ammonia, temperature of the feed solution is elevated to increase ammonia volatilisation raising the concentration of ammonia gas. The use of MCs combined with the variation of temperatures is called membrane distillation (MD). MD processes can be performed in different configurations such as direct contact MD, vacuum MD and sweep-gas MD, which have proved up to 99% ammonia dissolved recovery for a vast feed concentration range (50 - 5000 mg NH₃-N/L) regardless of the dilution of the ammonium salt solution due to a transmembrane water vapour flow (*Dutta et al., 2022*). The MC processes have also shown similar ammonia recoveries from different feed streams (50 - 25 000 mg NH₃-N/L) (*Dutta et al., 2022*). Serra-Toro et al. (2022) study analysed the recovery of ammoniacal nitrogen from a synthetic and a biowaste fermentation broth using a GPM contactor under different working pH (from 6 to 11) and temperatures (35 and 55°C). The results determined that GPM separates efficiently ammoniacal nitrogen from fermentation broths. Also, a higher operating temperatures and pH increased the rate of NH₃ mass transfer, specially at alkaline pH (from 9 to 11). However, the optimum pH was 10 due to a higher ammonia mass transfer constant (K_m) was achieved employing less reagents to maintain the set pH.

For MC and MD processes, the significant concentrations of foulants and dissolved solids in wastewaters are responsible of membrane fouling. For MD processes, severe fouling of the hydrophobic membrane was caused by organic foulants leading to a lower ammonia transfer (*Zarebska et al., 2015*). The presence of volatile organic

compounds represent a relevant issue for MD as they can potentially traverse the hydrophobic membrane (Xie *et al.*, 2016).

The gas-permeable membrane (GPM) process has become the foremost wastewater treatment due to its high efficiency and low cost. Many studies on TAN recovery have revealed that GPMs are highly effective in ammonia recovery from the effluent of a primary treatment in a municipal wastewater treatment plant (Lee *et al.*, 2021), and pig slurry (Riaño *et al.*, 2019), among many others. The process consists of recirculating a strong acid solution (i.e. H₂SO₄) through a GPM that receives a high pH wastewater feed to treat. The feed solution is introduced to one side of the hydrophobic membrane allowing only gas-phase molecules (ammonia) to cross. On the other side of the membrane, an acidic liquid flow is applied to extract the ammonia gas from the feed side. This arrangement provides a driving force for ammonia mass transfer, which is the partial pressure difference between the feed solution and the acid trapping solution (Lee *et al.*, 2021). The principle of ammonia recovery with a GPM relies on adjusting the feed pH at alkaline values (typically higher than 9) to ensure that TAN is mainly presented as ammonia, the unionized form, and maximize its transfer across the membrane. The ammonia extracted from the feed accumulates in the acidic solution as NH₄⁺ while the treated wastewater is returned and constantly recirculated to the membrane. The pH increases in the acidic solution and decreases in the treated wastewater, so the pH condition control and adjusting the solutions when needed becomes essential in this process. This method also requires a pre-treatment such as wastewater filtration to protect the membranes fibers from damage. It has been demonstrated that recirculating the feed in the shell side of the membrane has a significant effect on the efficiency of the process (Hasanoğlu *et al.*, 2010). Therefore, this arrangement permits higher yields of ammonia removal. The hydrophobic hollow fibre separates both recirculating solutions and an air gap fills the micropores, that remains not wetted by the solutions. The membrane wetting does not occur due the capillary effect caused by the hydrophobic nature of the membrane and the small pores (Boehler *et al.*, 2015). The ammonia diffuses from the feed on the shell side to the feed-membrane interface where it volatizes crossing the air filled pores. Then, this ammonia reacts with sulfuric acid on the lumen side trapping solution.

The flow geometry in the membrane modules as well as the membrane permeation (Teoh *et al.*, 2008) are determining for ammonia flux and transfer. Temperature polarization can be enhanced if the turbulence among fibers is not adequate, which diminishes the driving force through the membrane. For MC processes, heat from the feed solution is transferred to the permeate side. Due to water vaporisation and heat conduction at the membrane feed side the membrane temperature at the surface will be below the feed solution temperature. Also, the temperature at the membrane surface at the permeate side will be higher than the acidic solution. This phenomenon generates a lower temperature and vapor pressure driving forces, which leads to a lower flux across the membrane. Teoh *et al.* (2008) determined that for unaltered original hollow fibre membrane modules, higher feed temperatures achieved a greater flux improvement. In addition, many studies (Boehler *et al.*, 2015; Rongwong and Goh, 2020) have analysed the impact of pH and temperature on the performance of GPM contactors and have determined that specially these operational conditions have a significant effect on $\text{NH}_4^+/\text{NH}_3$ equilibrium.

The purpose of this study is to contribute to manure treatment using GPMs in order to reduce contamination on affected areas. For instance, Catalonia has approximately 7.9 million pigs, 637 000 cattle heads and 44.6 million birds (DARP, 2020) that produce about 9.4 million tons of manure and 2.8 million tons of faeces and hens each year. Another issue to be addressed is the fact that excessive application of livestock to the soil over the years has resulted in the accumulation of nitrate in the underground waters and phosphorous in the soil. According to the European Directive on nitrates (91/676/EEC), a 33.8% of the area of Catalonia is declared vulnerable to contamination by livestock originated nitrates affecting 422 municipalities, which represent the 45% of all Catalan municipalities (ACA, 2020). However, according to the Catalan Climate Change Office, the agriculture and livestock sectors contribute to the greenhouse effect gases emitted in Catalonia by a 12%. And it is estimated that 47% of these emissions is produced during the management of livestock discharge. The agricultural sector is also responsible for 92% of ammonia atmospheric emissions causing acidification, eutrophication of ecosystems and affecting as well the health of animals themselves while representing a loss of ammonia in form of valuable nutrient by agriculture. Therefore, it is fundamental to develop processes for manure treatment that enable the recovery of nutrients as organic fertilizers eliminating elements that

may compromise their quality (heavy metals, antibiotic residues, pathogenic microorganisms, etc.) and minimizing emissions related with these processes (*Boldú et al., 2020*).

2. OBJECTIVES

Considering a previous study conducted by Serra-Toro et al. (2022) for the treatment of biowaste fermentation liquids at 35 and 55°C, the general aim of this study is to investigate NH₃ recovery from wastewaters using a gas-permeable membrane contactor at 25°C and to test its effectiveness to recover nitrogen from piggery wastewater. To reach this general objective, the following goals were planned:

- To assess the short-term effect of different working pH (from 6 to 12) at 25 °C to recover ammonia from a highly loaded nitrogen wastewater (synthetic feed) using the same volume of trapping and feed solution. The main parameter used to analyse the process performance is the conditional permeability of the membrane (k_m).
- For a prefixed volume ratio between the feed and trapping solution (1:10) and a working pH of 9.0, to evaluate the nitrogen recovery efficiency to treat piggery wastewater using a gas-permeable contactor at a selected in a single or multiple (10) stage configuration.
- Considering the results of the previous objective, to test the performance of the membrane recovery process from piggery wastewater under several pH control strategies.

3. MATERIALS AND METHODS

3.1 Influent characteristics

Two highly nitrogen loaded streams were treated in this study: synthetic and piggery wastewater. The synthetic wastewater was prepared by diluting 7 g NH₄Cl/L (PanReac AppliChem) and 6 g/l of acetic acid (J.T. Baker) in deionized water producing a solution. Pig manure was collected in a pig farm of Catalonia. Once collected, a pre-treatment consisting of a centrifugation (14000 rpm, 8 min; Sigma 1-14 microcentrifuge) and filtering (1.2 µm cellulose filters) was applied to separate its liquid fraction, generating a piggery wastewater suitable to be treated in the gas-permeable membrane contactor. Once pre-treated, the piggery wastewater was stored in a refrigerator at 4°C until its use. *Table 3.1* summarises the main characteristics of the piggery wastewater used in this study. Two loads (P1 and P2) of manure were used for the experiments.

Table 3.1. Piggery wastewater characteristics. P1 and P2 refer to period 1 and 2.

Parameter	Units	P1 values	P2 values
pH	-	8.1 ± 0.2	8.4 ± 0.1
TS	g/kg	-	13.2 ± 0.5
VS	g/kg	-	6.1 ± 0.4
COD	g/L	18.7 ± 1.1	11.9 ± 0.1
Soluble COD	g/L	14.20 ± 2.1	5.5 ± 0.2
Alkalinity	g CaCO ₃ /L	12.8 ± 0.3	10.0 ± 0.2
TAN	g N/L	2.8 ± 0.1	2.1 ± 0.3

TS: Total Solids; VS: Volatile Solids; COD: Chemical Oxygen Demand

The trapping solution was prepared adding H₂SO₄ 75% (PanReac AppliChem) to deionized water in order to obtain a pH lower than 2.

To control the pH in the feed stream, a sodium hydroxide (NaOH) solution (5 or 10M) was prepared by dissolving sodium hydroxide pellets (Scharlau) in deionized water, while the control of pH in the trapping solution was performed by adding, when necessary, H₂SO₄ 75%.

3.2 Experimental set-up

As shown in *Fig. 3.1*, the experimental set-up of this study consisted of two sealed glass reactors, a 2-L glass reactor used for the trapping solution and a 5-L jacketed glass tank for the feed solution, connected to a gas permeable membrane module. In this study, a microporous hollow-fibre polypropylene (PP) MC (manufactured by 3M Company and Liqui-Cel) with an active surface area of 0.50 m² was used. Both the feed and the trapping solutions were pumped in a closed-loop through the membrane module using two gear pumps (easy-load, models 7518-12 and 7518-10). A flowrate of 15 L/h and 5 L/h were used for the feed stream and the trapping solution,

respectively, according to the manufacturer recommendations. The feed solution velocity was higher in order to decrease the thickness of liquid boundary layer (LBL) resistance and to increase the ammonia flux (*Sethunga et al., 2019*). This effect is negligible for the draw side LBL (*Tan et al., 2006*). The feed was recirculated through the hollow-fibre membrane shell side to facilitate the cleaning process of the membrane. Therefore, the trapping solution was recirculated internally (lumen side).

The tanks were equipped with magnetic stirrers (IKA C-MAG HS7 and Thermo Scientific RT) in order to keep the solutions well mixed. The feed tank was kept at a desired temperature of 25°C by using a water bath heater (Thermo Scientific HAAKE DC30). The pH of both solutions was controlled using two pH-meters (Crison 53 35 electrodes connected to Crison pH 28 controllers) in order to add H₂SO₄ 75% to the trapping solution or an alkaline solution (5 or 10M NaOH) to the feed.

In the very first tests a NaOH peristaltic pump (Ismatec, Type ISM827) was used to add automatically alkali solution to the feed as the pH dropped from the pH initially established for the test. However, due to its malfunctioning as it leaked some solution, it was replaced and the alkali solution was added manually.

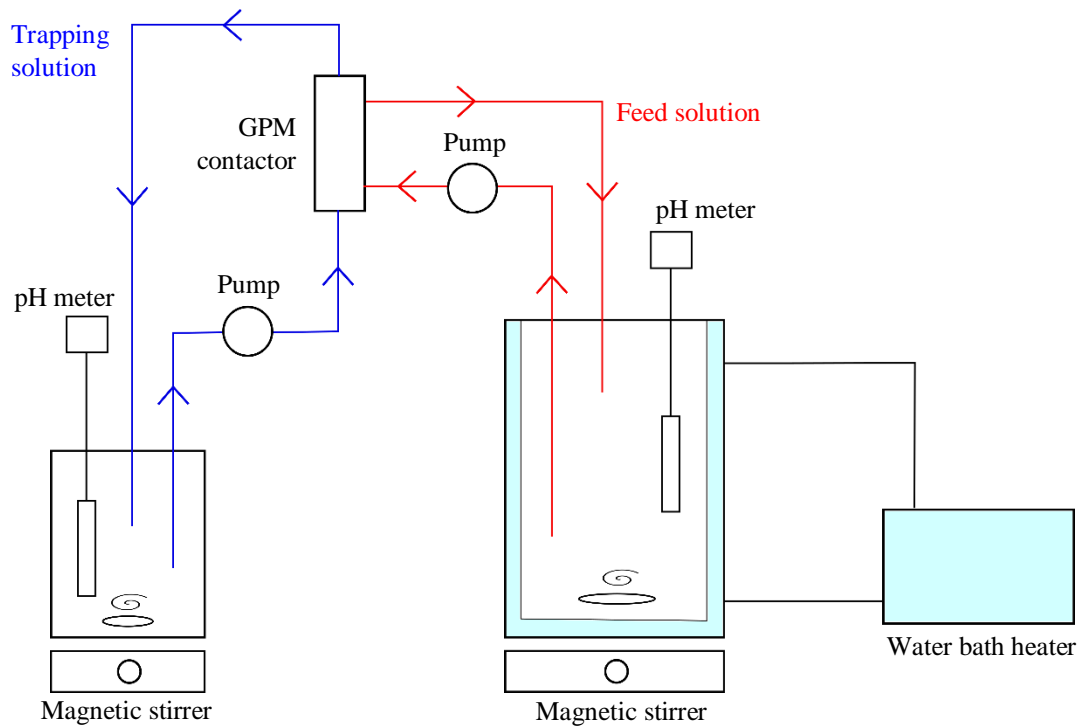


Figure 3.1 - Experimental set-up employed for the tests.

3.3 Methodology

The experiments were set in three phases, according to the specific objectives to be fulfilled. *Table 3.2* summarizes the operational conditions for each phase of this study.

The synthetic feed experiments (Phase 1) were conducted in duplicate and run for 8 hours, testing different feed pH from 6 to 12 by keeping the draw solution at a pH lower than 2. The feed tank was set to be at 25 °C and the ratio volume between feed and draw solution was 1, preparing 2 L of each. In all tests, the trapping solution initially contained 2.5 ml of H₂SO₄ 75%, added to the 2-L trapping solution.

The second phase aimed to evaluate the effect of a single or multiple stage configuration on the efficiency of the process for a prefixed total volume of the trapping and feed solution of 10:1 and a working pH in the feed chamber of 9. In this phase, the first experiment consisted of 10 stages where the volume ratio (feed volume/trapping volume) between solutions was 1 using 0.5 L of both pre-treated manure and trapping solution. The trapping solution was reused for the 10

experiments conducted with fresh feed. The second experiment of this phase consisted of a single-stage process with a volume ratio of 10, using 5 L of manure and 0.5 L of trapping.

Table 3.2 – Operational conditions for synthetic feed and pre-treated manure experiments.

Phase	1	2		3	
Wastewater	Synthetic	Piggery	Piggery	Piggery	Piggery
pH of feed chamber	6-12	9	9	8.4-8.5	10
Temperature of the feed solution (°C)	25	25	25	25	25
Number of stages	1	10	1	2	1
Trapping: Feed volume ratio in each stage	1:1	1:1	1:10	1:5	1:5
Volume of trapping and feed in each stage (L-L)	2-2	0.5-0.5	0.5-5.0	0.5-2.5	0.5-2.5
Hours per experiment	8	4	26	34-11	12

The P1 load raw manure was treated using a Sigma 1-14 microcentrifuge and filters in order to obtain the feed solution used. The trapping solution was prepared adding 50 mL of H₂SO₄ 75% to 450 mL of deionized water in the 10 stages experiment, which was reused for the 10 experiments. On the other hand, the trapping employed for the 1:10 volume ratio experiment using pre-treated manure, was prepared from 0.5 L of deionized water and 2.5 mL of H₂SO₄ 75% initially in order to ensure a pH below 2. As the test progressed, H₂SO₄ solution was added as the trapping pH level raised. The total amount of acidic solution added for this test was 44 mL. For the phase 3, two tests were conducted following the operational conditions mentioned in *Table 3.2*. The P2 load manure was used for this last phase. In the first test lasted for 45 hours in total. No control pH was established during the first 34 hours in order to

evaluate the ammonia transference testing the membrane at a manure set pH. Afterwards, a pH control was set at 8.5 to compare the both stages. The second test consisted of adding the required alkali solution to maintain a pH feed of 9 at the beginning of the experiment. Consequently, the pH control becomes undemanding.

To monitor the experiments, samples of both the feed and the trapping solutions were extracted from both tanks every 30 minutes during the first 1.5 hours and every 60 minutes after in order to analyse the required parameters.

3.4 Analytical methods

An ammonium electrode (Thermo Scientific Orion High Performance Ammonia Electrode, 9512HPBNWP) was used to determine the concentration of total ammonium nitrogen present in the samples of feed and trapping solution following the procedure 4500-NH₃D. The samples were diluted before to obtain a lecture fitting to the calibration curve. For each sample, the ammonia was determined in duplicated. Average deviation values of the measurements obtained for each experiment are represented in figures by error bars. As a result, the TAN concentration was established for both solutions.

In order to characterise the manure used, COD and soluble COD content was determined by the Standard Method 5220C (APHA, 2017). Total solids (TS) and volatile solids (VS) were also determined according to Standard Method 2540G (APHA, 2017). The soluble fraction was obtained from the pre-treated manure, which was centrifuged using a Sigma 1-14 microcentrifuge for 8 minutes and filtrated after using 1.2 µm cellulose filters. Alkalinity was defined according to the Standard Method 2320B, by using an automated titrator (Crison pH Burette 24) set at 4.30 endpoint pH and 0.1M HCl.

3.5 Ammonia transfer calculations

Ammonia transfer across the membrane occurs due to the ammonia concentration gradient between the feed and the trapping solutions, where the ammonia can pass through the membrane pores due to gaseous diffusion. When the acid dissociation

constant of ammonium expressed as pK_a is equal to the solution pH, the 50% of the TAN is NH_4^+ and the other 50% is NH_3 :



$$pH = pK_a \rightarrow pH = -\log [H^+] = -\log k_a = pK_a \quad [2]$$

$$k_a = [NH_3][H^+] / [NH_4^+] \rightarrow k_a = [H^+] \quad [3]$$

By keeping the feed solution at a pH higher than the pK_a (9.45 at 25°C), the presence of NH_3 rises promoting the ammonia transfer. On the other hand, the trapping solution promotes the presence of NH_4^+ maintaining a much lower pH, which is fixed in the trapping as ammonium sulphate, $(NH_4)_2SO_4$ (see Fig. 3.2). As a result, NH_3 contained in the trapping solution is negligible and its partial pressure in the membrane interface is also negligible. This generates a partial pressure difference promoting the feed-to-draw transfer. It is important also to consider that the pK_a value decreases as temperature increases (Anthonisen et al., 1976).

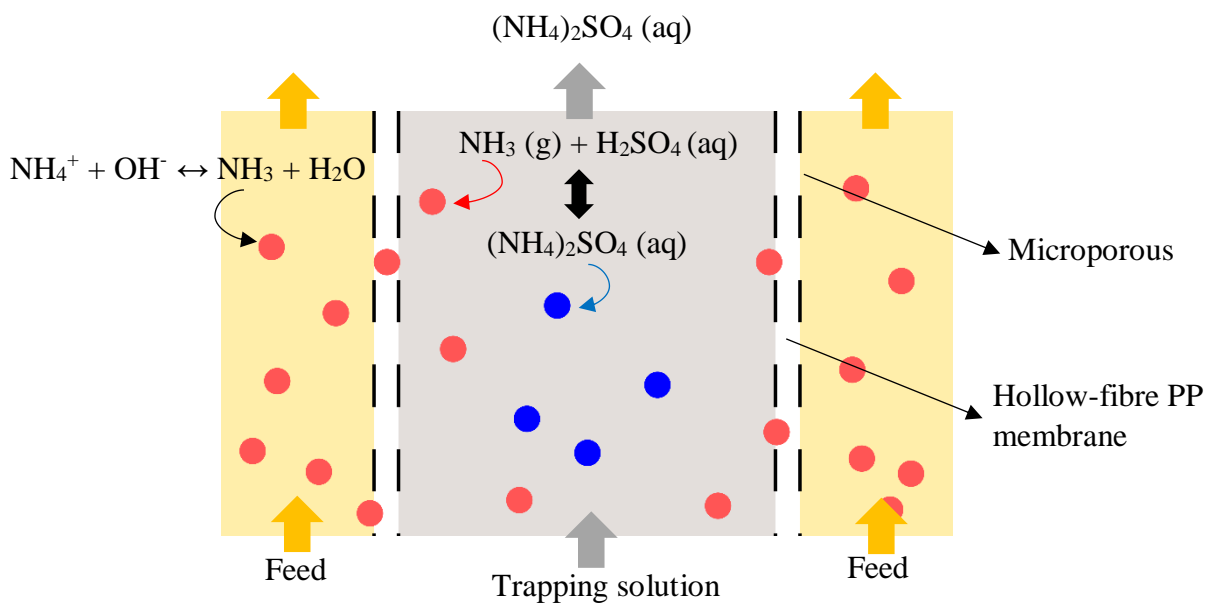


Figure 3.2 - Diagram of ammonia mass transfer through the hollow fibre PP membrane.

The model used to determine the TAN concentration is represented in [3]. This model contemplates that the membrane is only permeable to NH₃, the pH and volume set for the solutions remain constant, the NH₃ loss by volatilization is negligible and the acid-base equilibrium is preserved.

$$\frac{C_{TAN,f}(t)}{C_{TAN,f}(0)} = \exp\left(-\frac{K_m A}{V_f} t\right) \quad [3]$$

Where $C_{TAN,f}$ is the TAN concentration in the feed (g NH₄⁺/L), V_f is the feed volume (L), A is the area of the membrane (m²) and K_m is the ammonia mass transfer constant or conditional permeability (m/s) defined in [4]. The K_m determines the nitrogen transfer under certain conditions (*Reig et al. 2021*).

$$K_m = \frac{D_{NH_3}}{\Delta x} \quad [4]$$

Where D_{NH_3} is the diffusion coefficient of NH₃ (m²/s) and Δx is the thickness of the membrane (m). The K_m was estimated for each working pH aligning the TAN concentration of the feed and trapping over time by Python using a curve fit function of the SciPy.

It is important to differentiate the membrane permeability, P_{NH_3} (m/s) and K_m , which is obtained out of the flux of NH₃ (g/m²s) from the feed to the trapping and the variation of NH₃ concentration as ΔC_{NH_3} (g/m³). The membrane permeability [5] depends on the characteristics of each membrane and remains constant even changing the operational conditions.

$$J_{NH_3,feed} = P_{NH_3} \cdot \Delta C_{NH_3} \quad [5]$$

4. RESULTS AND DISCUSSION

The experiments mentioned referred to the synthetic feed (phase 1) and the pre-treated manure (phase 2 and 3) were conducted. The effect of the pH in the synthetic feed experiments will be discussed first followed by the phase 2 experiments performed at the selected pH determined previously. The phase 3 experiments were executed to verify and establish the optimal working pH when treating manure using the hollow-fibre membrane contactor under certain pH control strategies.

4.1 Effect of the pH in a synthetic feed solution at 25°C

The variation of TAN expressed as $\text{g NH}_4^+\text{-N/L}$ of these experiments is illustrated in *Fig. 4.1*, where it is observed that the nitrogen removed in the synthetic feed was accumulated in the trapping solution (same volumes of feed and trapping solutions). The initial feed solution contained $1.83 \text{ g NH}_4^+\text{-N/L}$, which decreased considerably during the first 2 h for pH 10, 11 and 12. A complete TAN recovery was achieved for these highly alkaline pH values (from 10 to 12) after 6 hours, due to the high presence of free NH_3 in the synthetic feed.

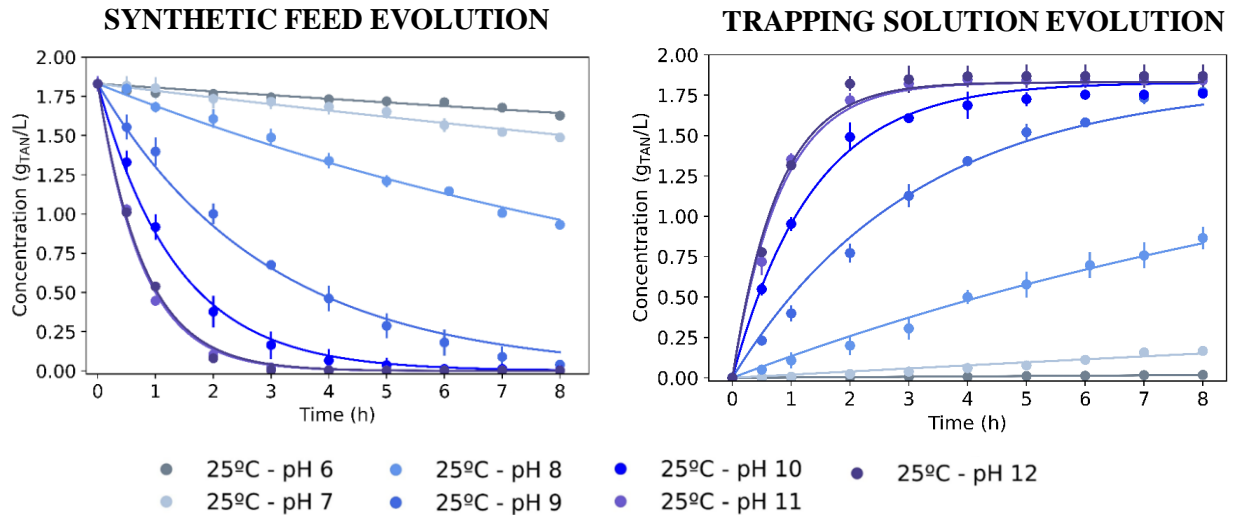


Figure 4.1. - Ammonia recovery evolution using synthetic feed for different working pH (from 6 to 12) applying the TAN model for the synthetic feed and the trapping solution. The dots represent the experimental results and the solid lines refer to the TAN concentration evolution by considering the adjusted K_m over time considering different synthetic feed pH. Standard deviation is represented by error bars.

The conditional permeability obtained for the membrane used is shown in *Table 4.1* and represented in *Fig. 4.2*. The values estimated for K_m show a significant increase from pH 9 to 11, where it seems to stabilize at $1.40 \cdot 10^{-6}$ m/s. This value is has a similar order of magnitude compared to the K_m estimated by Serra-Toro et al. (2022). In order to select the optimum working pH to recover ammonia from wastewaters, it is important to consider the generation of inorganic fouling on the membrane. According to Lee et al. (2021), operating under a moderately alkaline pH values close to 9 could be favourable to prevent this type of fouling. The results show that K_m regarding pH 9 and 10 resemble as the values have the same order of magnitude compared to the other K_m evaluated. On account of this, the suitable working pH would be 9 despite a better performance occurs at a higher pH.

Table 4.1 – Conditional permeability (K_m) estimated for the membrane used at different working pH from 6 to 12 (average values \pm standard deviation).

pH	K_m (m/s)		
	Synthetic feed	Trapping	Average
6	$1.49 \cdot 10^{-8} \pm 9.52 \cdot 10^{-10}$	$1.34 \cdot 10^{-9} \pm 3.84 \cdot 10^{-11}$	$8.14 \cdot 10^{-9} \pm 9.62 \cdot 10^{-9}$
7	$2.72 \cdot 10^{-8} \pm 9.38 \cdot 10^{-4}$	$1.20 \cdot 10^{-8} \pm 7.27 \cdot 10^{-10}$	$1.96 \cdot 10^{-8} \pm 1.08 \cdot 10^{-8}$
8	$8.92 \cdot 10^{-8} \pm 2.28 \cdot 10^{-9}$	$8.44 \cdot 10^{-8} \pm 2.34 \cdot 10^{-9}$	$8.68 \cdot 10^{-8} \pm 3.41 \cdot 10^{-9}$
9	$3.80 \cdot 10^{-7} \pm 1.51 \cdot 10^{-8}$	$3.58 \cdot 10^{-7} \pm 1.55 \cdot 10^{-8}$	$3.69 \cdot 10^{-7} \pm 1.56 \cdot 10^{-8}$
10	$8.17 \cdot 10^{-7} \pm 2.35 \cdot 10^{-8}$	$8.18 \cdot 10^{-7} \pm 3.68 \cdot 10^{-8}$	$8.17 \cdot 10^{-7} \pm 1.09 \cdot 10^{-9}$
11	$1.45 \cdot 10^{-6} \pm 4.84 \cdot 10^{-8}$	$1.35 \cdot 10^{-6} \pm 6.87 \cdot 10^{-8}$	$1.40 \cdot 10^{-6} \pm 6.51 \cdot 10^{-8}$
12	$1.40 \cdot 10^{-6} \pm 4.08 \cdot 10^{-8}$	$1.43 \cdot 10^{-6} \pm 9.32 \cdot 10^{-8}$	$1.41 \cdot 10^{-6} \pm 2.14 \cdot 10^{-8}$

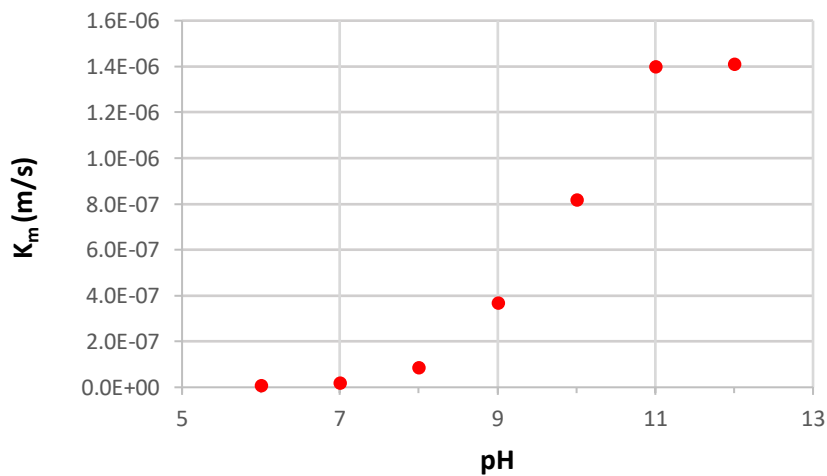


Figure 4.2 - Conditional average permeability estimated for the membrane for pH 6 to 12.

The K_m obtained by Serra-Toro et al. (2022) for pH 9 was $3.2 \cdot 10^{-7}$ m/s at 35°C and $5.9 \cdot 10^{-7}$ m/s at 55°C. Compared to the K_m for pH 9 at 25 °C ($3.69 \cdot 10^{-7}$ m/s), there is not much difference. For this reason, working at a lower temperature (i.e 25°C) should not affect the membrane performance.

As seen in *Table 4.2* recoveries up to 97% have been determined for pH above 8 operating at 8 hours. For pH 6 and 7 seems to be a considerable amount of ammonia loss that does not transfer to the trapping solution. On the other hand, for pH 9 and above there is no ammonia loss as the elimination equals to the recovery. The higher recovery is performed at pH 12, although there is almost no considerable difference in ammonia recovery between pH 11 and 12. These results show that working at pH 9, the ammonia recovery and elimination from the feed are high enough contemplating the use of reagents in order to keep the feed solution at the fixed pH.

A lower working pH seems to generate a higher efficiency of TAN loss as reflected in *Table 4.2*. This may be caused due to the volatilization of ammonia enhanced by a lower transfer rate.

Table 4.2 – Average removal and recovery of TAN expressed in % for different working pH (from 6 to 12) (average values \pm standard deviation).

pH	% removal	% recovery
6	11.96 \pm 0.00	1.10 \pm 0.00
7	20.64 \pm 4.84	11.32 \pm 0.74
8	49.09 \pm 5.86	48.02 \pm 7.89
9	97.76 \pm 1.33	97.73 \pm 1.34
10	99.66 \pm 0.26	99.65 \pm 0.26
11	99.81 \pm 0.02	99.81 \pm 0.03
12	99.85 \pm 0.02	99.85 \pm 0.02

The reagents consumption for the experiments is shown in *Table 4.2*. The total alkali consumption increases as the pH rises, especially above pH 9. On the other hand, the total acid consumption seems to remain similar from pH 9 to 12. However, the total acid used does not vary excessively from pH 6 to 8 following a similar trend and presenting higher values compared to greater pH values.

Table 4.3 – Alkali (NaOH 5 and 10M solution) and acid (H₂SO₄ 75% solution) consumption of the synthetic feed experiments (average values ± standard deviation).

Units	mol NaOH/mol N recovered		mol H ₂ SO ₄ /mol N recovered	
pH	Total alkali consumption	Alkali consumption to maintain the feed pH	Total acid consumption	Acid consumption to maintain the trapping pH
6	1043.34 ± 0.00	0.90 ± 0.00	316.00 ± 0.00	0.00
7	1055.76 ± 638.92	0.86 ± 0.44	345.90 ± 212.36	0.00
8	1011.50 ± 488.61	0.61 ± 0.27	289.92 ± 63.20	0.40 ± 0.13
9	1015.57 ± 247.82	0.75 ± 0.24	253.95 ± 78.22	0.54 ± 0.07
10	1206.75 ± 0.55	0.37 ± 0.07	199.82 ± 88.81	0.62 ± 0.06
11	2489.10 ± 182.18	0.03 ± 0.03	214.80 ± 42.98	0.60 ± 0.04
12	3161.84 ± 508.71	0.00	294.90 ± 19.81	0.57 ± 0.03

From this results, it can be seen that without considering the reagents required to reach the selected pH the process is more efficient at higher feed solution pH due to a lower reagent consumption.

4.2 Efficiency evaluation from the manure experiments based on volume ratio

Fig. 4.3 illustrates ammonia recovery from the 10 stage pre-treated manure experiment. Regarding to the results obtained from the synthetic feed tests, the manure was decided to be treated at a pH of 9. As mentioned, the trapping solution was reused showing an ammonium accumulation through the 10 stages performed. The experiments lasted for 4 hours each due to the ratio volume used (1:1), where the ammonia transfer was rapidly completed. The initial NH₄⁺ content present in the pre-treated manure was 2.77 g/L. At the end of the experiment, the trapping solution contained 19.54 g/L of NH₄⁺-N.

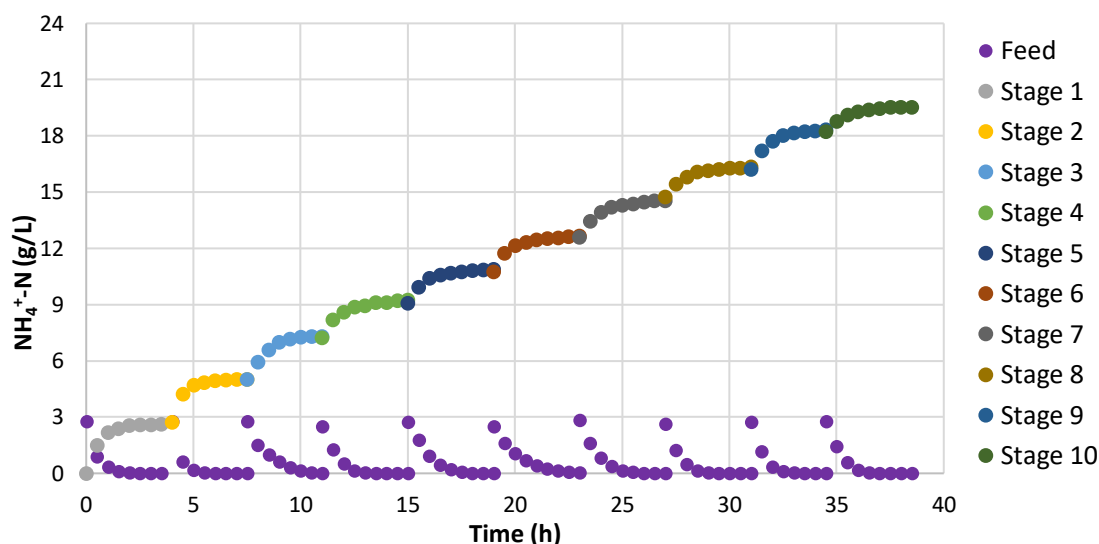


Figure 4.3 - Ammonia recovery using pre-treated manure as feed solution (1:1 volume ratio). The stages refer to the concentration of the trapping solution as it is reused during the entire experiment. The dots correspond to experimental results determined with the ammonium electrode.

The reagents consumption was 0.79 mol NaOH/mol TAN recovered to maintain the set pH at the pre-treated manure feed and 212 mol NaOH/mol TAN recovered was the total consumption including the reagent required to reach the set feed pH. Regarding the acid solution, as the trapping solution was prepared with 50 mL of H₂SO₄ 75% the pH value never surpassed a value of 2. In this case, the removal and recovery efficiencies were 99.84 % and 99.98 % respectively.

On the other hand, the ammonia recovery from the 26 hours experiment is represented in *Fig. 4.4*. The trapping solution achieves a higher concentration more rapidly compared to the 10 stage experiment. The final concentration accumulated is 28.70 g/L of NH₄⁺-N, which is considerably higher as well regarding the 10 stage experiment. This result show that the membrane performance using a bigger feed volume has been proved to be more efficient as the trapping/feed volume ratio was 1:10 in this case.

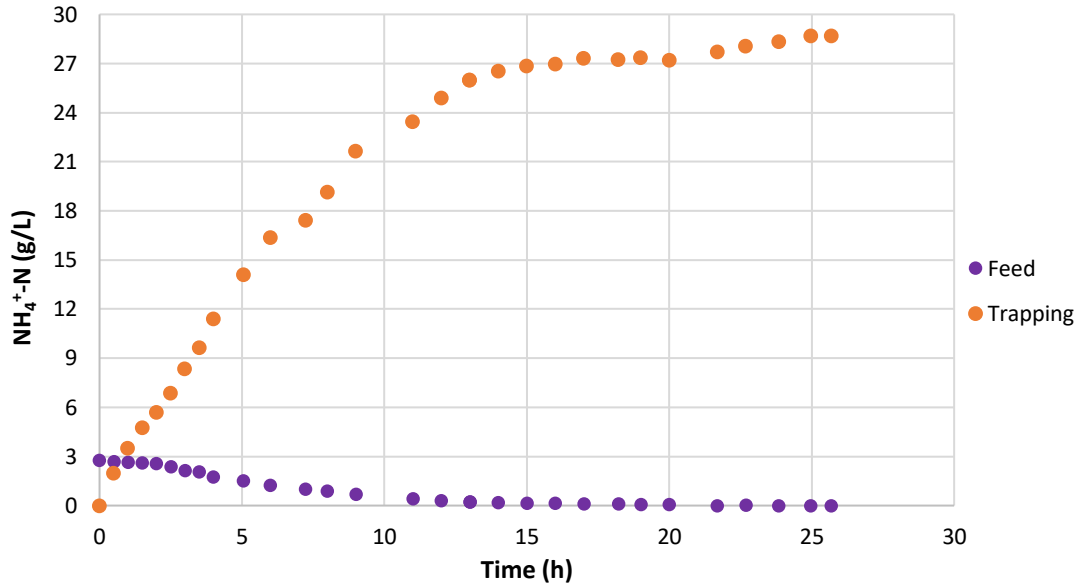


Figure 4.4 – Ammonia recovery using pre-treated manure as feed solution (1:10 volume ratio). The dots represent experimental results obtained from analysing samples using the ammonium electrode.

In addition, the reagents consumption was 0.93 mol NaOH/mol TAN recovered and 0.64 mol H₂SO₄/mol TAN recovered to keep the set pH. The total consumption considering the reagents to adjust the pH of both solutions was 515 mol NaOH/mol TAN recovered and 872 mol H₂SO₄/mol TAN recovered. In this case, the removal and recovery efficiencies were 99.24 % and 99.17 % respectively.

4.3 Efficiency evaluation from the manure experiments regarding pH control strategies

Phase 3 consisted of two tests runned as well at 25°C by using 2.5 L of pre-treated manure and 0.5 L of trapping solution. Fig. 4.5 represents the test where no pH control was established during the first 34 hours. The initial feed pH of 8.42 dropped to 7.80 during this phase, where the ammonia recovery seemed to decelerate around 6 g/L. The ammonia transfer slows down considerably compared to the test realised by Allou (2022), where the working conditions were the same except a set pH control at 9. From this point onwards, a pH control was established at 8.50 and the ammonia transfer was almost concluded after 45 hours. The trapping solution reached a TAN concentration of 7.82 g/L and the N present in the pre-treated manure lowered to 0.21

g/L (containing approximately 2 g/L of $\text{NH}_4^+\text{-N}$ initially). As a result, this experiment proves that maintaining a pH under 8.50 diminishes the efficiency of the process.

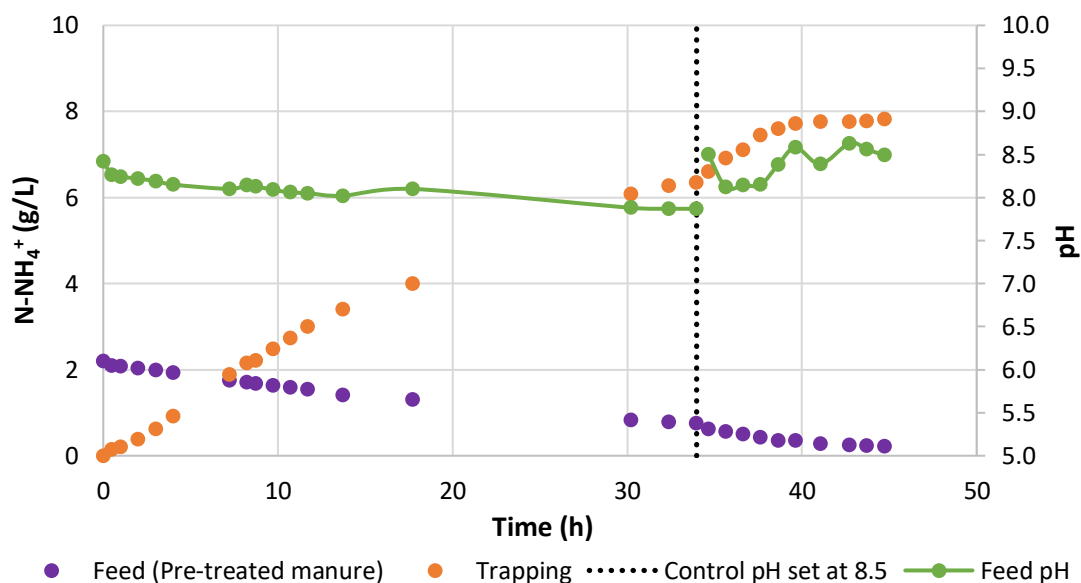


Figure 4.5 - Ammonia recovery performed first without pH control and setting a pH control at 8.5 after 34 hours until the end of the experiment. The dots represent experimental results.

The removal and recovery efficiencies were 92.51 % and 91.14 % in this case, respectively. The reagents consumption was 0.27 mol NaOH/mol TAN recovered and 1.74 mol H_2SO_4 /mol TAN recovered to keep the set pH. The total consumption considering the reagents to adjust the pH of both solutions was 0.28 mol NaOH/mol TAN recovered and 2560 mol H_2SO_4 /mol TAN recovered.

The second test is illustrated in *Fig. 4.6*, and consists of adding the required amount of alkali solution before running the experiment. The amount added to 2.5 L of pre-treated manure was 36.7 mL of NaOH 10M solution, according to the experiment performed at pH 9 and maintaining the same conditions by Allou (2022). The initial pH rose to 10 after adding the basic solution and decreased to 9 until the ammonia transfer was completed. The final concentrations found in the solutions were 8.59 g/L of $\text{NH}_4^+\text{-N}$ for the trapping and 0.04 for the pre-treated manure. As expected, the ammonia transfer resembles to the pH 9 test realised by Allou (2022).

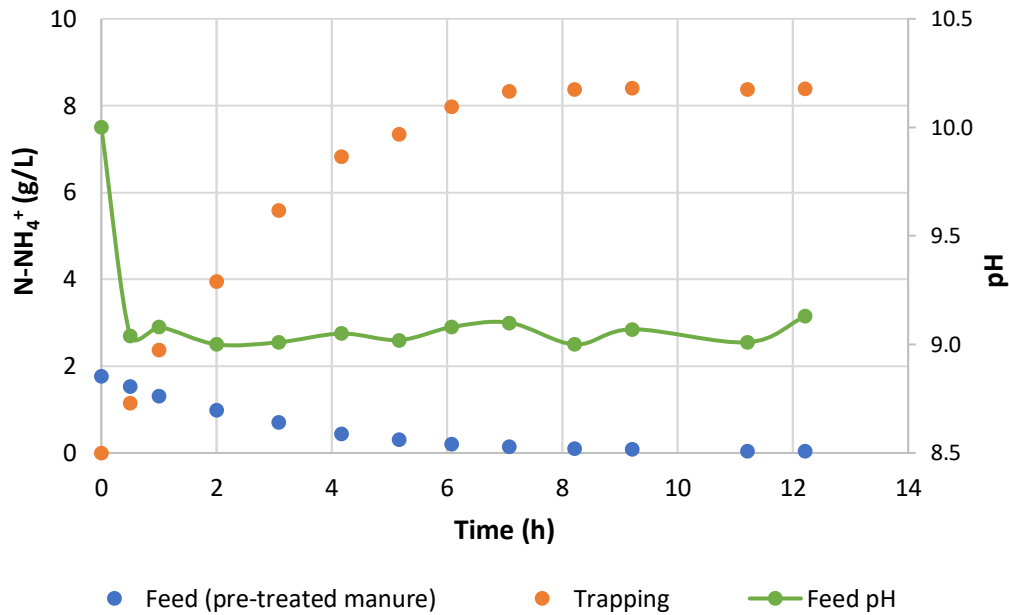


Figure 4.6 - Ammonia recovery performed without pH control and adding at the beginning the NaOH 10M needed to maintain a working pH of 9. The dots represent experimental results.

The removal and recovery efficiencies were 97.97 % and 98.03 % in this case, respectively. The reagents consumption was 0.00 mol NaOH/mol TAN recovered and 0.44 mol H₂SO₄/mol TAN recovered to keep the set pH. The total consumption considering the reagents to adjust the pH of the trapping solution was 1944 mol H₂SO₄/mol TAN recovered.

Another aspect to consider is the formation of precipitates that could cause the fouling of the membrane. For this reason, the solids of the used pre-treated manure regarding this last experiment were tested showing a solids generation of 0.20 g/L by using the 1,2 μm cellulose filters. Allow (2022) performed another test using the gas permeable membrane under the same operational conditions but analysing the effect of maintaining a pH of 10. The precipitates generated as solids were 0.54 g/L in this case, as the use of reagents was much higher.

5. CONCLUSIONS

In this study, the recovery of ammoniacal nitrogen from piggery wastewater was successfully performed using a lab-scale hollow-fiber ammonia gas permeable membrane contactor (0.5 m² active area). More specifically, the main conclusions obtained in this project are:

- Nitrogen recoveries over 98% were obtained with synthetic feed (1.83 g NH₄⁺-N/L) in 8 hours at 25°C and pH or above, 1:1 trapping/feed volume ratio (2 L each).
- The value of the conditional permeability (K_m) at short term conditions increased considerably from pH 9 to 12 when using synthetic wastewater.
- The synthetic feed experiments determined that working at pH 9 the process was effective enough to recover almost 98% of ammonia in 8 hours under the aforementioned conditions (K_m of $3.69 \cdot 10^{-7}$ m/s).
- Working at a higher pH than 9 with pre-treated manure could lead to the formation of precipitates promoting the fouling of the membrane.
- When the N recovery was performed in 1:10 volume ratio with pre-treated manure, the recovery exceeded the 99% as a concentration of 28.7 g NH₄⁺-N/L were reached in the trapping solution.
- When the N recovery was performed in 10 stages with pre-treated manure in 1:1 volume ratio, the recovery efficiency did not show any decrease during the first 3 stages and the trapping solution obtained contained approximately 3 times the initial TAN concentration of the manure. As the experiment continued, the recovery showed a withdraw due to the lower N concentration recovered compared to the 1:10 volume ratio experiment. Moreover, the overall nitrogen recovery rate was lower using 10 stages when compared with 1 stage.
- The pH control strategies showed that maintaining a pH under 8.50 diminishes the efficiency of the process. In addition, considering that the ammonia transfer occurs with not much difference setting a pH control at 9 (using 36.7 ml of NaOH 10M) and adding the 36.7 ml of alkali solution to the feed first with no pH

regulation after, there seems to be no difference between maintaining a regular feed pH value and adding the entire alkali volume at the beginning of the experiment.

Regarding to the future, there has still work to be done in order to recuperate the $(\text{NH}_4)_2\text{SO}_4$ from the trapping solution as it has to be highly concentrated to precipitate.

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