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Grau en
Enginyeria
Química

Treball Final de Grau

Ammonia recovery using a gas-permeable membrane under different operational conditions.

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Hi ha una força motriu més poderosa que el vapor,
l'electricitat i l'energia atòmica: la voluntat.

Albert Einstein

Molta gent m'ha ajudat durant aquest temps en el qual he fet el treball final de grau.

Primer de tot, vull agrair al meu tutor, el doctor Joan Dosta, per tota l'ajuda que m'ha aportat durant aquests mesos d'investigació, així per haver-me proposat un tema el qual he trobat molt interessant. També, li agraeixo totes les correccions fetes a la memòria.

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CONTENTS

SUMMARY

Ammonia recovery from wastewaters is one of the best forms of ensuring the natural cycle of nitrogen, because it's low consume of energy compared to other technologies for ammonia production. In the last decades, membrane technology has emerged because is an effective way recovering nitrogen from urban wastewaters, piggery slurry or organic fraction of municipal solid waste. These effluents are rich on ammonia nitrogen, with a high content in range of 0.5 to 5 g N-NH_4^+/L. This specie is chemical compound that can be dangerous for human healthiness and environmental risks, such as eutrophication.

In this work, a laboratory scale study is conducted using a gas-permeable membrane, which is a membrane that allows gas species pass through it, but not aqueous compounds. Two different operational configurations were tested, applying vacuum inside the membrane and acidic trapping solution in closed loop circulation.

When vacuum application was performed in gas-permeable membrane, it did not result in a good efficiency, obtaining about 10% of ammonia removal in about 5 hours. However, the use of an acidic trapping solution achieved a TAN recovery >99% in 14 hours of experiment, and a mass transfer constant (K_m) of $(1.7 \pm 0.1) \cdot 10^{-7}$ [m/s]. This method was tested too in piggery wastewater, on a working pH of 9, resulting in a TAN recovery of >99% in 16 hours of experiment, and a K_m of $(8.8 \pm 0.5) \cdot 10^{-7}$ [m/s].

This research also studied the water passage through the GPM when the trapping solution achieved high ammonia concentrations, diluting the ammonium sulphate, which is not desirable for economic reasons. Tests in laboratory showed that the water passage is proportional to the N concentration in the trapping solution.

To sum up, the gas-permeable membrane technology has been proved to be highly efficient to ammonia removal and recovery from pig wastewater due its efficiency and low operational cost.

Keywords: Gas-permeable membrane, Nitrogen recovery, Piggery wastewater, Total Ammonia Nitrogen.

RESUM

La recuperació de nitrogen amoniacal en aigües residuals és una de les millors maneres de garantir el cicle natural del nitrogen, degut al baix consum d'energia que es necessita en comparació amb altres tecnologies per la producció d'amoníac. En les últimes dècades, les tecnologies basades en membranes han augmentat, ja que són una forma eficaç d'eliminar i recuperar el nitrogen d'aigües residuals urbanes, aigües contaminades amb purí o de la fracció orgànica dels residus sòlids urbans. Aquest efluents són rics en nitrogen amoniacal, amb un alt contingut del rang de 0.5 a 5 g $N\text{-}NH_4^+$/L. Aquesta espècie química pot ser perillosa per la salut humana i pot comportar riscos pel medi ambient, com la eutrofització.

En aquest treball, es realitza un estudi a escala de laboratori utilitzant una membrana permeable al gas, que és un tipus de membrana que permet el pas d'espècies en estat gas, però no compostos en estat aquós. Es van provar dues configuracions experimentals diferents, primer de tot aplicant el buit a l'interior de la membrana i després fent circular una solució àcida captadora a través de la membrana en un bucle tancat.

L'aplicació del buit en la membrana permeable al gas no va resultar en un procés eficient, obtenint aproximadament un 10% d'eliminació d'amoníac en 5 hores d'operació. D'altra banda, el bucle tancat de la solució àcida captadora va aconseguir una recuperació major al 99% en 14 hores d'experiment, amb una constant de transferència de massa (K_m) de $(1.7\pm0.1)\cdot10^{-7}$ [m/s]. Aquest mètode també va ser provat en aigües contaminades per puríns, amb una eficiència del 99% en 16 hores d'experiment i una K_m de $(8.8\pm0.5)\cdot10^{-7}$ [m/s].

En aquest treball també es va estudiar el pas de l'aigua a través de la GPM quan la solució captadora assolia una alta concentració d'amoníac, diluint el producte, fenomen no desitjat per raons econòmiques. Les proves realitzades van demostrar que el pas de l'aigua és proporcional a la concentració de sulfat d'amoni a la solució captadora.

En conclusió, la tecnologia de membranes permeables al gas és eficient per la recuperació de nitrogen d'aigües contaminades amb capacitat de ser tractada per recuperar-ne més nutrients.

Paraules clau: Membrana permeable al gas, Recuperació de nitrogen, Nitrogen amoniacal, Purí.

SUSTAINABLE DEVELOPMENT GOALS

Aquest treball final de grau incideix en diversos objectius de desenvolupament sostenible. Dintre dels grans àmbits, aquest estudi s'incideix en l'esfera de la persona i del planeta:

- ODS 2: Fam zero – Trobar nous mètodes per la producció de fertilitzants que requereixin un menor cost energètic, a través de nutrients presents en aigües residuals.
- ODS 6: Aigua Neta i Sanejament – Aquest treball es basa en l'eliminació de productes químics d'aigües residuals, nocius per la salut humana. La tecnologia estudiada es pot aplicar a depuradores i potabilitzadores per garantir l'aigua neta.
- ODS 9: Indústria, Innovació i Infraestructures – Un dels objectius d'aquest treball és la recuperació de nutrients d'aigües residuals i en el desenvolupament de tecnologies de tractament d'aigües residuals eficients i compatibles amb el medi ambient.
- ODS 12: Consum i Producció Responsables – Assegurar nous mètodes de producció neta i renovable de amoníac. També, incidir en el consum energètic responsable en els tractaments d'aigües residuals.
- ODS 13: Acció pel Clima – Adoptar noves mesures de producció de recursos essencials amb un menor impacte energètic , així com aprofitar tots els recursos presents en aigües residuals.
- ODS 15: Vida d'ecosistemes terrestres – Netejar, protegir i promoure la vida dels ecosistemes on arriba la contaminació per acció humana. L'eliminació del nitrogen en aigües residuals pot prevenir impactes negatius sobre els ecosistemes .

1. INTRODUCTION

Nitrogen (N) is an essential nutrient for life due to its integral role in cellular structures such as proteins or nucleic acids. Historically, N has always been a limited nutrient but in the last centuries, due to human intervention, the amount of fixed N has doubled (Galloway et al., 2013). However, most of this element exists as N_2, an unreactive gas, and the natural cycle of N is not enough to supply the whole population because of the slowness of the process. So, in the last decades, several ways of nitrogen production have been implemented to supply the vast demand for N.

At this stage ammonia nitrogen will be introduced as an essential chemical element present in nature, but also its toxicity and ecological impact in ecosystems. This specie can be removed and recovered from wastewater with a wide number of methods and can be a great option for its recyclability. Wastewater treatment using a gas-permeable membrane is one of the best methods to recover ammonia and obtain ammonium sulphate, which can be applied as fertilizer.

1.1. NITROGEN POLLUTION IN WASTEWATERS

The most predominant forms of nitrogen in wastewater are organic ammonia and nitrates. These are primarily waste products originated from human metabolism. About 60% of the nitrogen is in organic form as urea, and 40% is in ammonium form (Sedlak, 1991).

Though N is essential for life, high concentrations that exceed natural levels can directly affect ecosystems and even destroy them. Ammonia is an indispensable plant nutrient, used as fertilizer, which had a positive impact on human health increasing the volume and quality of food (Morrissy et al., 2021). However, elevated concentrations of NH_4^+, NO_2^- and NO_3^-, derived from human activities, are responsible of eutrophication, causing uncontrolled growth of harmful algae that can lead to toxicological effects on human health (Camargo & Alonso, 2006). It also can carry a reduction in the level of dissolved oxygen (DO) in the water. DO levels, pH variations in ecosystems and high quantities of N can cause diseases or death of aquatic animals or organisms.

Because of this, several countries have introduced policies and regulations to release N into the environment. Catalonia is one of the regions that has the highest livestock in Europe. About 39.9% of the land was declared in 2020 as a vulnerable zone due to contamination by nitrites generated by livestock (Fitxes de les zones vulnerables, 2022). In Catalonia, the limit value of ammonia concentration for wastewater effluents is 60 mg TAN/L (DOCG, No 3894, 29/05/2003). From 1990 to 2020, Spain increased ammonia emissions from 9.4 to 14 % of the total emissions of the European Union (European Union emissions inventory report, 2022). These emissions represent a notorious loss of ammonia affecting the chemical and fertilizer industry. Nowadays, the market value of ammonium sulphate is about 0.48-1.0 €/kg $(NH_4)_2SO_4$ (Menkveld & Broeders, 2018). Because of the high economical losses and the environmental problems, new methods of ammonia fixation from manure are being studied.

1.2. NITROGEN REMOVAL AND RECOVERY METHODS

With the increasing anthropogenic nitrogen sources, research on nutrient recovery involving nitrogen and phosphorus has begun in order, not only to prevent eutrophication but also to save energy and natural resources. In 1913 the Haber-Bosch process for ammonia production was implemented on an industrial scale, producing over 10 tons of ammonia each day. Nowadays this process is responsible for feeding 50% of the world’s population (Erisman et al., 2008). But as the Haber-Bosch process depletes around 35-50 MJ/(kg·N) of energy, representing 2% of the global energy (Yan et al., 2018), new methods of ammonia production and recovery are being studied to reduce the global impact of N sources and should allow a circular flow of the nitrogen cycle.

Nowadays, a lot of ammonia recovery processes are being studied and optimized. Table 1.1 describes a collection of methods studied with its ammonia removal and recovery efficiency tested, and the form of N recovered.

Table 1.1. Nitrogen recovery technique influent characteristics and results. (adapted from Beckinghausen et al., 2020) (Continues)

Technique	Substrate	N Removal [%]	N recovery [%]	Form of N recovered
Submersive Microbial Desalination Cell	Digestate	87.9	100	$(NH_4)_2SO_4$ Solution
Struvite Precipitation LSSA	Anaerobic Digestion	91.95	100	Struvite
GPM no aeration	Digested swine effluent	92 - 98	76 – 95	$(NH_4)_2SO_4$ Solution
GPM aeration	Digested swine effluent	97 - 99	96 – 98	$(NH_4)_2SO_4$ Solution
GPM	Supernatant from swine ww	93 - 97	92 – 93	$(NH_4)_2SO_4$ Solution
Electrodialysis with stripping	Filtered swine manure	59	6.2	Ammonia in HNO_3
Electrodialysis with vacuum stripping	Filtered swine manure	70	14.5	Ammonia in HNO_3
Reverse Osmosis	Filtered swine manure	75	66.6	Solution
GPM semicontinuous	Centrate from swine manure	56 - 79	90	$(NH_4)_2SO_4$ Solution
Microbial electrolysis cells	Urban reject water	72.2	100	Amm. Chloride
L-L Membrane Contactor	Zeolite regen. solution	85 - 98	95 – 98	$(NH_4)_2SO_4$ Solution
Bio-electrodialysis (BED)	Filtered cattle manure	94	100	Ammonia in Boric acid
Membrane Based PreConcentration Ion exchange	Raw sewatge after solid separation	74.4	37.5	Solution
MEC aeration	Landfill leachate	63.7	53.8	Amm. Bicarbonate
Microbial Recovery Cell - Anaerobic Osmotic Membrane BioReactor	Glucose based medium	28 - 45	100	Solution

Table 1.1. (Continuation) Nitrogen recovery technique influent characteristics and results. (adapted from Beckinghausen et al., 2020)

Recource Recovery Microbial Fuel Cell	Urine containing wastewater	98	42	Solution
BED without gas	Primary clarifier eff.	85	52	Ammonia in boric acid
Enlarged Microbial Nutrient Recovery Cell	Raw sewage after wastewater	80	62	Struvite
Capacitive mem. Stripping	Raw sewage after solids	62	100	$(NH_4)_2SO_4$ Solution
Struvite recycling	Swine wastewater	90	91	Struvite
VMD	And supernatant	85	100	Amm. Hydroxide solution
Forward osmosis	Synthetic side stream centrate	99.7	100	Struvite and Amm. Sulphate
TwoStep alkaline hydrolysis process	Sludge from secondary settler	7.78	41.98	Struvite
Sludge Fermentation	Centrate from fermented sludge	73	75.7	Struvite
Electrochemical Cell Stripping	Domestic urine	87.1	-	$(NH_4)_2SO_4$ Solution
Microbial Fuel Cells	Domestic urine	<1	<1	$(NH_4)_2SO_4$ Solution
TransMem. Chemisorption (TMCS)	Urine	63	56	$(NH_4)_2SO_4$ Solution
MEC – TMCS	Urine	47	100	$(NH_4)_2SO_4$ Solution
Hydrogen Recycling Electrochemical	Pretreated human urine	73	60	$(NH_4)_2SO_4$ Solution
Nutrient separation Microbial Electrolysis Cell	10x diluted urine	61	100	$(NH_4)_2SO_4$ Solution

Nitrogen removal from wastewaters has been studied and applied in full-scale plants implementing various techniques such as nitrification/denitrification, oxygen-limited autotrophic N/DN, Struvite ($Mg(NH_4)PO_4{\cdot}6H_2O$) or MAP precipitation or adsorption. The techniques of ammonia recovery can be categorized by the prevailing process involved for recovery as a chemical, physical, biological or hybrid process. In the following sections, these methods will be briefly presented.

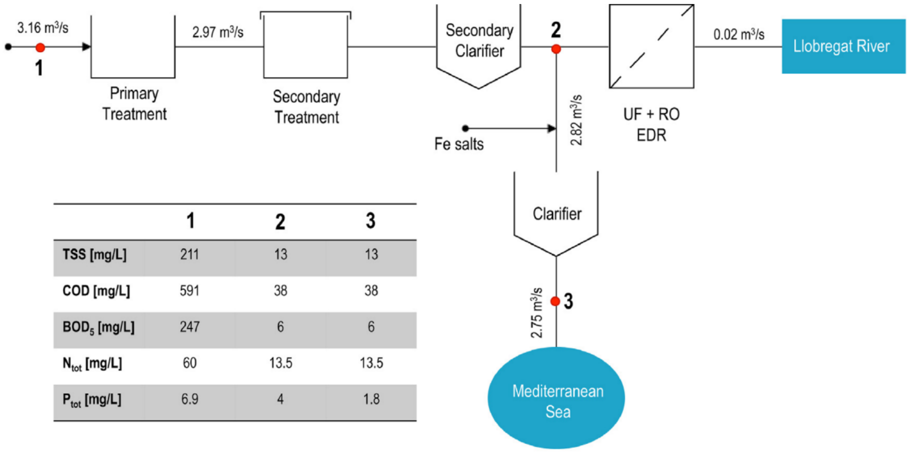
1.2.1. Chemical process for nitrogen recovery

The principles that determine chemical processes are the separation of N into another usable compound by means of a chemical reaction. The most common use of this type of process is the precipitation of struvite, a technique based on the formation of a solid that can be used as fertilizer. Other chemical processes are used for ammonia recovery, but in this section, the most used will be described.

<u>MAP Process</u>: The most used chemical technique used for nitrogen removal is the MAP process. Magnesium ammonium phosphate ($MgNH_4PO_4$) is a relatively insoluble crystalline precipitate that has the equimolar ratio of magnesium, ammonium, and phosphate ions. This method consists of the precipitation of this solid by the addition of phosphoric acid and magnesium oxide following the next reaction (Kabuba et al., 2022):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \qquad (1)$$

For this treatment it is necessary to control the working pH in a range between 8.5 to 10 to favour MAP precipitation, obtaining an ammonia removal of 92% at pH 9 (Yetilmezsoy et al., 2009). This method has been used for the treatment of various kinds of wastewater, such as municipal wastewater, piggery wastewater and landfill leachate, among many others. The process generates a solid called struvite, which has a low solubility of 0,169 g/L at 25 ºC, and can be effectively separated from the water phase. This struvite is utilized in horticulture to settle manure, garden soil or dried sewage sludge, but it needs to be dried first, because of the high crystal water content.



	1	2	3
TSS [mg/L]	211	13	13
COD [mg/L]	591	38	38
BOD_5 [mg/L]	247	6	6
N_{tot} [mg/L]	60	13.5	13.5
P_{tot} [mg/L]	6.9	4	1.8

Figure 1.1. MAP precipitation with Fe in a conventional WWTP (Xialei et al., 2018)

1.2.2. Physical process for nitrogen recovery

Physical processes explored for ammonia recovery include membrane processes, filtration, adsorption, and stripping. Osmotic-based systems have been studied for wastewater treatment but tend to focus more on producing clean water rather than recovering pure nutrients present in water. In this section, various methods of ammonia removal by physical process will be explained, excluding processes based on membranes, which will be described later.

Air stripping: In this technology, air is injected to release volatile compounds, such as free ammonia, which are carried away in gaseous form by air. To this purpose, the pH of the wastewater must be at 10 to convert NH_4^+ to NH_3, using $Ca(OH)_2$ as an alkali basis to raise the pH to optimal levels, reducing solids and heavy metals too. Alternatively, the temperature could be increased to promote a higher free ammonia production at moderately alkaline pH. An ammonia removal of 91% could be reached at 60 ºC and a working pH of 10 (Maghfiroh et al., 2022).

However, this process has numerous drawbacks, such as the generation of solid calcium carbonate ($CaCO_3$), floating into the surface of the wastewater and resulting in poor stripping performance. This also has additional costs, due to the elimination of this solid by flotation. Furthermore, if not properly recovered, the ammonia released into the atmosphere results in environmental pollution. However, adsorption techniques using H_2SO_4 can effectively solve this problem, but increasing the functional expense of the process.

Adsorption: Adsorption is a cost-effective technique by which the concentration of the absorbate from its wastewater sticks onto the surface of the pores of a solid. This method uses the activated sludge from the water, which is mainly bacterial cells and extracellular polymers with a negative surface charge, to benefit the adsorptive removal of NH_4^+, a positively charged ion. Physical adsorption happens if the attraction forces existing among adsorbate and adsorbent are Van Der Waal's forces (Kabuba et al., 2022).

Consequently, a good solid election is essential to this process as it offers a great adsorptive capacity as well as great kinetics. The main materials to adsorb ammonia are fly ash, zeolite, sepiolite, limestone, charcoal or activated carbon. The factors for deciding which is the most adequate adsorbent are dosage, particle size and porous structure, reaction time, the ammonia concentration in the wastewater, secondary treatments for the material or the effect of activation in adsorbents.

The adsorption process has been proven to be an efficient removal of both organic and inorganic solutes, reaching ammonia removal of 90% (You et al., n.d.), low cost, easy to apply, low sensitivity to pH and temperature and environmentally friendly.

1.2.3. Biological process for nitrogen removal

The biological process involves utilizing active microorganisms that catalyse reactions of nitrification/denitrification, deammonification such as anammox and combinations of this process. By employing these techniques reactive N is ultimately lost through its biological uptake and its conversion into gas, so the ammonia is not recovered for recycling purposes. These technologies are suitable to use when the objective of the treatment is to make the final effluent less contaminant to the environment and N recovery is not needed.

Biological nutrients removal (BNR): Nitrogen removal from wastewater by autotrophic microorganisms is one of the most notable procedures. Autotrophic Denitrification, Photoautotrophic Systems and Anaerobic Ammonium Oxidation (anammox) are the most BNR processes used. Among them, the anammox process in wastewater systems has resulted in higher rates of ammonia removal and lower cost and energy requirements. BNR processes consist in nitrification and denitrification reactions by which ammonium is converted to nitrite and nitrite is oxidized to nitrate. The nitrification is carried by ammonia-oxidizing bacteria (AOB) whereby the following reactions take place (Kabuba et al., 2022):

$$NH_4^+ + 3/2O_2 \overset{AOB}{\rightarrow} NO_2^- + H_2O + 2H^+ \qquad (2)$$

In the subsequent reaction, oxidation of nitrite to nitrate is possible due to nitrite-oxidizing microorganisms (NOB) by which reaction 3 takes place:

$$NO_2^- + H_2O + \overset{NOB}{\rightarrow} NO_3^- + 2H^+ + 2e^- \qquad (3)$$

The denitrification process is the microbial course of diminishing nitrate (NO_3^-) to gaseous forms of nitrogen, such as N_2. In the conventional denitrification process, the reaction is carried out by means of heterotrophic organisms under anoxic conditions, so it takes place in a total absence of dissolved O_2. This reaction steps when using acetic acid as biodegradable COD to carry out the process. During that process, the following reaction takes place:

$$8NO_3^- + 5C_2H_4O_2 \overset{Heterotrophs}{\rightarrow} 4N_2 + H_2O + 10CO_2 + 8OH^- \qquad (4)$$

The denitrification process can also be carried by microorganisms known as denitrifiers, specially Thiobacillus, Micrococcus, Serratia, Pseudomonas, and Achromobacter. During that process, the following reaction takes place:

$$2NO_3^- + 10e^- + 12H^+ \overset{Bacteria}{\rightarrow} N_2 + 6H_2O \qquad (5)$$

The principal factors of these reactions are alkalinity, pH, DO, temperature, inhibition, and mode of operation. In municipal wastewater has been proved that the removal rate of NO_3^--N and NH_4^+-N reached 95.8% and 92.8% respectively (Chen et al., 2021). The BNR process is considered to have numerous advantages regarding the removal of nitrogen due to the fact that utilized naturally occurring microorganisms and does not need expensive chemicals. Additionally, this process delivers less abundant sludge that needs slight handling, which has a lot of lower metals substances, usefully for agrarian lands.

Simultaneous nitrification and denitrification (SND): Simultaneous nitrification and denitrification are the mechanisms by which reactions (2-3) occur simultaneously in a single reactor.

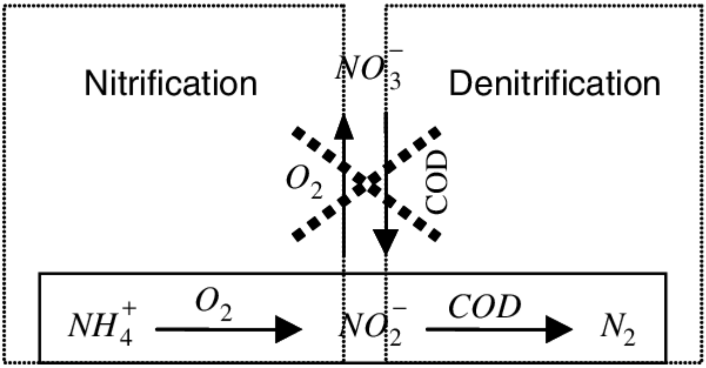


Figure 1.2. Schematic of mechanism of simultaneous nitrification and denitrification via nitrite pathway (Zeng et al., 2004)

This lowers the carbon consumption of biodegradable CODs by 20-40% and reduces sludge yield by 30%. The operational costs are also lower than the BNR process because sludge recycling is not necessary and requires easier operational procedures. The ammonia removal reported in the SND process is adobe 90% (Guerrero et al., 2016). To achieve the same performance as the Anammox technique, dissolved oxygen must be at optimal levels to let AOB and NOB microorganisms coexist.

1.2.4. Membrane technology for nitrogen recovery

Membrane systems are defined as a thin sheet, film, or layer which works as a selective barrier between two phases that can be liquid, gas, or vapour. The membrane itself can be a solid, a liquid, or a gel. It is considered a molecular sieve that could be constructed containing more than one layer with fine mesh or pores to enable the separation of tiny particles and molecules of this compound from the original mixture. The ability to differentiate among species is called selectivity (Saleh & Gupta, 2016).

A useful application of membrane technology is for concentrating and recovering nutrients in wastewater, previously treated to prevent operational issues. Nowadays, forward osmosis (FO), membrane distillation (MD), electrodialysis (ED), and gas-permeable membrane (GPM) are the main technologies used in wastewater treatment. In this research, gas-permeable membranes are the subject of study, so they will be discussed in detail in a separate section.

Forward Osmosis (FO): FO is a process based on a semi-permeable membrane that uses osmotic pressure gradient between the feed and the permeate solution as the driving force. A high concentration in the feed solution is used to induce a net flow of water through the membrane into the draw solution, concentrating the nutrient in the original solution.

Membrane distillation (MD): This process driving force is the vapour pressure gradient caused by the heating of the feed solution. In wastewater treatment, phosphate ions are concentrated in the feed solution and ammonium ions are accumulated in the permeate, normally H_2SO_4 or HCl, because of its higher volatility. According to the vapour collection, MD module is mainly categorized into the following types (Dong et al., 2023): Direct contact membrane distillation (DCMD), sweep gas membrane distillation (SGMD), and vacuum membrane distillation (VMD).

In this studio, VMD technology is tested using a gas-permeable membrane, introduced in a further section, for ammonia recovery. Compared with other MD types, VMD is characterized by high permeate flux because of the vacuum degree on the permeate side. However, due to its high permeate flux water flux is enhanced, driven by the vapour pressure difference, which is undesired for ammonia concentration.

Electrodialysis (ED): Electrodialysis process is a selective separation carried out in two chambers, anode and cathode. It transports salt ions from one solution to another by applying an electric potential gradient. To reduce energy consumption, electrochemical reactants are integrated into the process in order to profit from the bioelectricity generated from the oxidation of organic compounds.

1.3. GAS-PERMEABLE MEMBRANE

In this study, gas-permeable membrane (GPM) is studied for ammonia recovery. The GPM process for total ammonium nitrogen (TAN) recovery consists of the recirculation of nitrogen-rich effluent through one side of a selective hydrophobic membrane, while recirculating the trapping solution, usually diluted H_2SO_4 or HCl, on the other side of the membrane. NH_3 is a non-charged compound that can diffuse through the nano-perforated membrane, due to its selectivity, driven by the NH_3 concentration between the feed and trapping solution. On the other hand, when NH_3 is protonated to NH_4^+, it is unable to diffuse across the membrane (Vanotti et al., 2017).

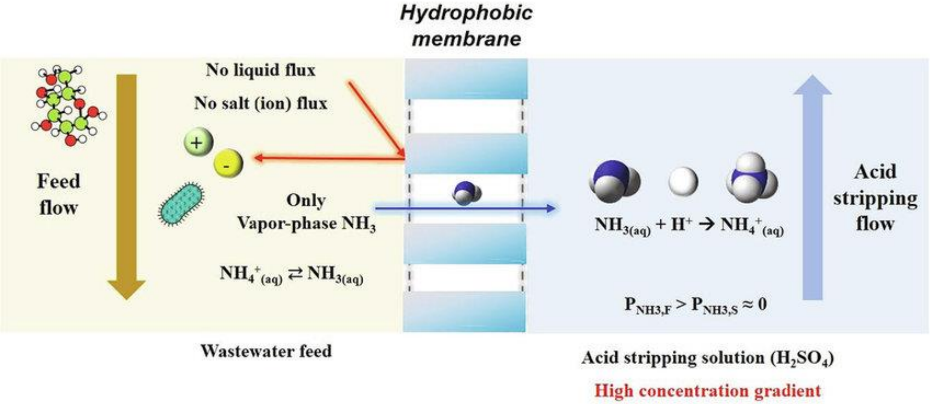


Figure 3.1. Gas-Permeable membrane technique. (Lee et al., 2021)

Several studies showed that GPM technology can fully recover total ammonia nitrogen (TAN) from a wide variety of residual effluents, such as municipal wastewaters, anaerobic digestion supernatant, human urine, and pig slurry. It has been reported that when applying GPM contactors in swine slurry or fermentation effluents (Serra-Toro et al., 2022, 2023), (Riaño et al., 2019), with an initial content ranging from 0.5 to 3 g N/L, the nitrogen content in the feed solution decreased to less than 1% of the TAN, obtaining a nitrogen recovery adobe the 99%.

On the other hand, despite all reports of successful results, some aspects of this technology require further research to characterize all aspects and optimize all the working parameters for its industrial application. The control of the pH in the feed solution is one of the essential parameters to optimise. Serra-Toro et.al.2022 reported that pH values between 8 and 11 showed the highest transfer rate of ammonia. He also concluded that pH 9 had a lower NaOH consumption per mole of TAN recovered.

In some studies, it has been observed that when the feed solution has a low TAN concentration, the volume of the feed solution decreases and water flows through the membrane from the feed to the trapping solution, diluting the nitrogen recovered.

In this study, the main objective is to evaluate the GPM technology to recover nitrogen recovery in synthetic wastewater and piggery slurry, as well as to assess the TAN recovery and investigate the water passage through the membrane.

2. OBJECTIVES

The main objective of this study is to evaluate the gas-permeable membrane under different operating conditions for nitrogen recovery of piggery wastewater. Another motivation for this research is to know the problematics of ammonia nitrogen in wastewater and learn various methods of removal and recovery of nitrogen.

To meet these objectives, the following goals were followed:

- To compare the ammonia removal and recovery with the gas-permeable membrane using an acidic trapping solution and by vacuum application.
- To characterize the GPM by evaluating its ammonia mass transfer constant (Km).
- To study the water passage through the membrane at different operational conditions.
- To test the process to recover ammonia nitrogen from a liquid fraction of pig slurry.

3. MATERIALS AND METHODS

3.1. SYNTHETIC FEED SOLUTION AND SWINE SLURRY COMPOSITION AND ORIGIN

Synthetic wastewater and liquid fraction of pig slurry were used as feed solutions in this study. In phase 1 experiments, synthetic wastewater was used to simulate piggery wastewater as a feed solution, using NH_4Cl (PanReac AppliChem NH_4Cl) as ammonia nitrogen for the removal and recovery. Table 3.1 summarizes the TAN concentrations of the feed solutions in the tests.

Table 3.1. Characteristics of synthetic wastewater used in phase 1.

Parameter	pH feed	pH trapping	Initial TAN trapping [g N/L]
1A	10	0.5 - 1.5	2.3
1B			2.3
1C			2.3
1D			2.3
1E	9	0.5 – 1.5	5

In the experiments used to characterize the water passage, the feed solution consisted of a 0.3 mol/L of $NaHCO_3$ (PanReac AppliChem $NaHCO_3$) solution to buffer the pH of the feed solution. As a trapping solution, a dissolution of ammonium sulphate (PanReac AppliChem $(NH_4)_2SO_4$) was used to recreate the trapping solution obtained in ammonia recovery experiments. Three different solutions were tested and summarized in Table 3.2.

Table 3.2. Characteristics of synthetic wastewater used in phase 2.

Parameter	pH feed	pH trapping	Initial TAN trapping [g N/L]	Buffer concentration [mol $NaHCO_3$/L]
2A	9	0.5-1.5	50	0.3
2B			30	
2C			10	

The swine slurry batch was collected at a swine farm in Lleida (Catalonia, Spain). The liquid fraction of the pig slurry was obtained after sieving, centrifugation (12000 x G, 15 min; Thermo scientific Sorvall ST8R centrifuge) and filtration (1,2 µ cellulose filters). It was kept in a refrigerator at 4ºC until use. Table 3.3 summarizes the main characterization of the swine slurry.

Table 3.3. Characteristics of swine slurry used in phase 3.

Parameter	pH	TAN
Units	-	g N/L
Value	9	2,6

3.2. EXPERIMENTAL SET-UP

Two different experimental setups using a gas-permeable membrane (GPM) as the core of the studied process were used in this work. The first device was devoted to study ammonia recovery in a GPM process using an acidic trapping solution and to analyse the water passage through the membrane due to a high osmotic pressure difference between the two sides of the membrane. The second device was similar to the first one but promoting the passage of ammonia through the membrane by means of a vacuum pump of an acidic trapping solution.

3.2.1. Gas-permeable membrane contactor using an acidic trapping solution.

Fig 3.1 shows the experimental set-up used in the GPM process using an acidic trapping solution. One 5 L jacketed glass tank was used as a chamber for the feed solution (synthetic water or piggery wastewater) and another 1 L glass tank was used for the acidic trapping solution. Both tanks were equipped with magnetic stirrers (IKA C-MAG HS7) and graduated to evaluate the volume of their content. The feed and trapping solutions were pumped using a peristaltic pump (Masterflex L/S models 7518-10 and 7518-12) in a closed loop to a gas-permeable membrane with a flow rate of 15 and 5 L/h respectively. The temperature of the feed tank was maintained at 35 ºC by means of a thermal reservoir (Thermo Scientific HAKE DC30) with an accuracy of ± 0.1 ºC. The trapping solution consisted of a sulphuric acid (0,1M) solution with pH less than 1.5. The pH of the trapping was monitored using a pH controller and regulated with additions of sulfuric acid (H_2SO_4 96%) to work at pH values below 1.5.

The membrane contactor used in the experiments was a microporous hollow-fibre made of polypropylene (3M Company) with a surface area of 0.5 m^2.

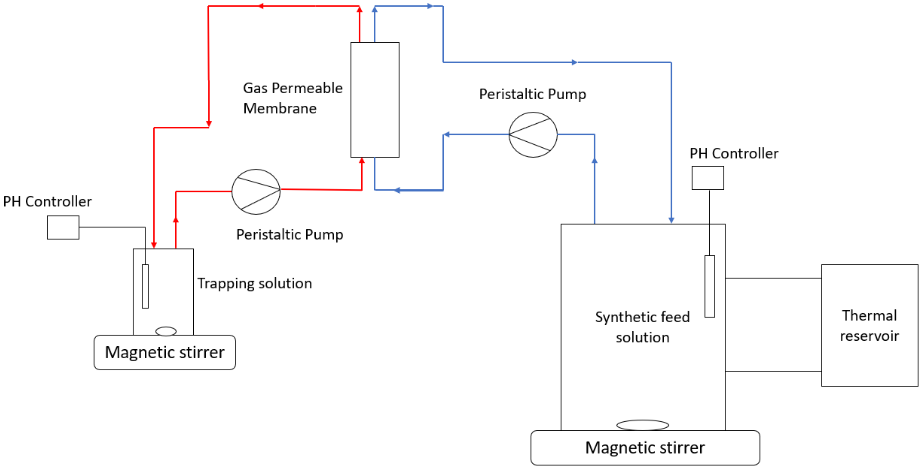


Figure 3.1. Experimental setup used in acidic trapping solution experiments.

3.2.2. Vacuum membrane distillation

Fig 3.2 shows the experimental set-up used in the vacuum membrane distillation. The same experimental set-up as the closed acidogenic loop was used, but instead of making the trapping solution go through the contactor, a depression was created inside the membrane to promote nitrogen recovery. The pressure inside the GPM was regulated using a vacuum pump

(VacuuBrand MD 1C Vario-SP CVC 3000) with an accuracy of ± 0,1 kPa and the permeate was collected in 0.5 L of the trapping solution (Initial concentration of 0.1 M).

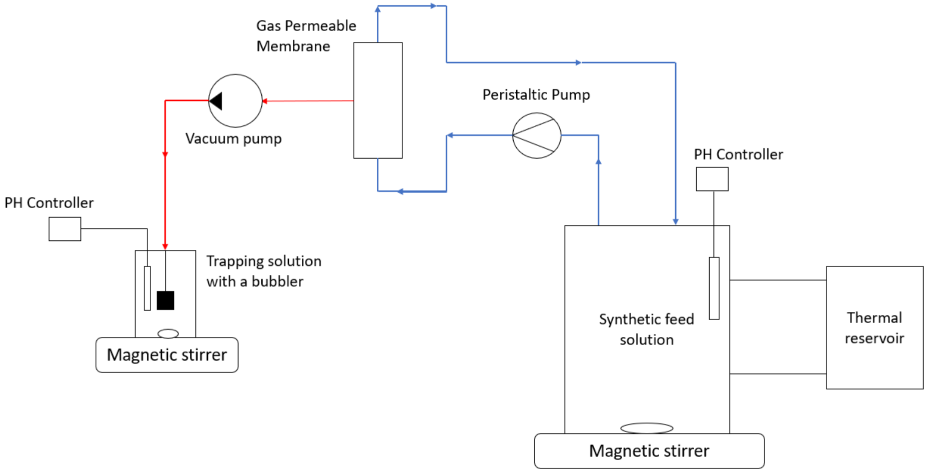


Figure 3.2. Experimental setup used in vacuum application experiments.

3.3. METHODOLOGY

According to objectives to be reached in this project, the study was divided in three experimental phases (see Table 3.3).

Table 3.3. Operational conditions of the experiments carried out in this study.

Feed solution	Test	Configuration	Temperature [ºC]	Duration [h]
Synthetic	1A	Vacuum application through the casing	35	5
	1B			
	1C	Vacuum application through the fiber		
	1D			
	1E	Acidic trapping		14
	2A			8
	2B			
	2C			

Piggery wastewater	3A		25	16

3.3.1. Phase 1: Comparison of ammonia recovery in a gas-permeable membrane using acidic trapping solution and vacuum application.

Experiments carried out in the first phase of the research aimed to compare the efficiency of the GPM process using two different configurations to capture ammonia: (i) using an acidic trapping solution (diluted H_2SO_4) and (ii) by vacuum application.

When the vacuum was applied (at different vacuum pressures of 10 and 120 mbar), experiments were planned to compare the impact of circulating the feed inside the hollow fiber membrane (experiments 1A and 1B) or through the GPM casing (experiments 1C and 1D). The feed and trapping solution volumes were 1.5 and 0.5 respectively. The initial pH of the trapping solution was 0.6 and the feed was set at 10 by dosing NaOH (PanReac AppliChem NaOH)(10M) when necessary. In the trapping solution, a bubbler was added, due to the fact that ammonia was removed from the feed solution as a gas, and it helped to reduce the contact area with the trapping solution. The duration of the experiments was 5 hours each, due to problems of overheating of the vacuum pump. To monitor these experiments, samples of the feed solution were taken every 30 minutes for the first 2 hours and every 60 minutes afterwards.

When an acidic trapping solution was used to capture ammonia, the feed only circulated through the casing of the membrane, as in the study of Serra-Toro et al. (2022). The feed pH was controlled at 9 by dosing NaOH (10M) when necessary and the trapping solution had a pH between 0.5 and 1.5 to avoid extremely low acidic pH values that could damage the membrane. When the pH of the trapping solution decreased below 1.5, more acid was added (H_2SO_4 (PanReac AppliChem) 96% w/w). The volumes of the feed and trapping solutions were 5 and 0.5 L respectively. The experiments were conducted in duplicate and run for 14 hours. To monitor the experiments, samples of feed were taken every 30 minutes for the first 2 hours and every 60 minutes afterwards. For the trapping solution, samples were taken every 2 extractions of the feed solution since the volume of this stream was lower.

3.3.2. Phase 2: Effect of the trapping salinity in the water flux period

Tests 2A, 2B and 2C aimed to determine the effect of the $(NH_4)_2SO_4$ concentration in the trapping solution on the water passage when the TAN concentration in the feed solution was completely depleted. These values were chosen based on the maximum trapping concentration of ammonium sulphate reached in the previous Phase. The pH was controlled to simulate the last period of the ammonia recovery experiments, keeping the feed pH over 9 with NaOH (10M) additions and sodium bicarbonate at a concentration of 0,3 mol/L to buffer the pH of the feed. Moreover, the pH of the acidic solution was set below 1.5 by dosing H_2SO_4 (96% w/w) when necessary. The experiments (done in duplicate) were run for 8 hours and during the process, only the volumes of each tank were monitored, to avoid changes in the working volume. Moreover, nitrogen content and conductivity were analysed at the beginning and the end of the experiment.

3.3.3. Phase 3: Ammonia recovery from piggery wastewater

Experiment 3A was performed with piggery wastewater. (TAN concentration of 2,6 g N/L) collected in a pig farm. More concisely, the wastewater was sieved, centrifuged, and filtered before the experiments, to prevent membrane fouling. The aim of this experiment was to compare the ammonia recovery between synthetic water and piggery manure wastewater. To maximize the nitrogen content reached in the trapping solution, the feed-to-trapping volume ratio selected was 1:15, using 6 L of pig slurry and 0.4 L of trapping solution. The pH during the run was controlled at 9 in the feed solution and at 0.5-1.5 in the trapping solution. To monitor these experiments, samples of the feed were taken every 30 minutes for the first 2 hours and every 60 minutes afterwards. For the trapping solution, samples were taken every 2 extractions of the feed solution.

3.4. ANALYTICAL METHODS

Total ammonium nitrogen was analysed following the Standard Methods for the Examination of Water and Wastewater (APHA, 2017), following the procedure 4500-NH3D. An ammonium electrode (Thermo Scientific 9512HPBNWP) was used to quantify the TAN concentration present in the feed and the trapping solution throughout the experiments. Samples were diluted before to obtain a lecture fitting to the calibration curve made using standard patrons of NH_4Cl (PanReac AppliChem NH_4Cl) with a known concentration (0 – 150 mg N/L). For each sample, the ammonia was determined by duplicate using two different dilutions. A conductivity probe and a pH probe (Hach Multimeter MM 41) were used to measure the conductivity and the pH of the samples.

3.5. CALCULATIONS

Ammonia recovery efficiency was calculated using equation (1), where $TAN_f(0)$ is the initial ammonia mass in the feed solution [g], $TAN_t(0)$ is the initial ammonia mass in the trapping solution [g], and $TAN_t(t)$ is the ammonia mass at a specific time [g]:

$$\%TAN\ recovery\ (t) = \frac{\mathrm{g}\,TAN_t(\mathrm{t}) - \mathrm{g}\,TAN_t(0)}{\mathrm{g}\,TAN_f(0)} \cdot 100 \tag{1}$$

NH_3 flux through the membrane was evaluated by calculating the mass transfer constant K_m. This constant represents the permeability of the ammonia, and it depends on the specific operational conditions for each experiment. To calculate the K_m, a physicochemical model is used, that considers: (i) the pH of the feed and trapping solution is constant, (ii) the membrane only permeates NH_3, (iii) NH_3 losses by volatilisation are negligible, and (iv) the volumes of the feed and trapping solution are constant.

The NH3 diffusion is described by Fick's law:

$$J_{NH3,f}(t) = -K_m \cdot (C_{NH3,t}(t) - C_{NH3,f}(t)) \tag{2}$$

Where $J_{NH3,f}(t)$ is the flux of ammonia [mol/m^{-2}/s^{-1}] from the feed to the trapping solution at a certain time. K_m is the NH_3 mass transfer constant (m/s), $C_{NH3,t}(t)$ is the NH_3 concentration in the trapping solution, and $C_{NH3,f}(t)$ is the NH_3 concentration in the feed solution.

By some simplifications, the K_m value form the experimental results was calculated assuming the NH_3/NH_4^+ equilibrium is fulfilled during the operation. Equation 3 determines the mass transfer constant depending on the initial TAN concentration $C_{NH3,f}(0)$ [g N/L], the TAN concentration at a certain time $C_{NH3,f}(t)$ [g N/L], the area of the membrane A [m^2], the volume of the feed solution [L], and the time t [s].

$$\frac{C_{NH3,f\,(t)}}{C_{NH3,f\,(t)}} = \exp\left(-\frac{K_m A}{V_f} t\right) \qquad (3)$$

This model was coded using Python using the curve fit function of the SciPy and the Levenberg-Marquardt algorithm to perform non-linear least squares estimates. The algorithm estimates Km and its standard deviation by fitting the TAN concentration in both solutions in the tanks. Finally, the NaOH and H_2SO_4 consumption was calculated in moles of reagent per mole of TAN recovered to compare all the tests. The total consumption didn't account for the reagent used to reach the initial pH value point.

In the ammonia recovery experiments in an acidic trapping solution, the ionic strength was evaluated in both feed and trapping solutions. The ionic strength was calculated using the concentration of all the ions present in both solutions. The [i] represents the molarity of each ion present in the solution [mol/L] and the z_i is its ionic charge.

$$I = \frac{1}{2}\sum_i [i] \cdot z_i^2 \qquad (4)$$

The water passage through the membrane was evaluated by the water mass transfer constant (K_w). By this constant, water permeation flux (J_w) [g·h^{-1}] across the membrane can be expressed with the water permeability constant (K_m) [L·h^{-1}] and the driving force for its passage, namely the osmotic pressure gradient between the feed and the trapping solution, which is proportional to the trapping TAN concentration (Youani & Tadeo, 2017).

$$J_w(t) = K_w \cdot Driving\ force\ ([TAN]_{trapping}(t)) \qquad (5)$$

The water permeation flowrate can be defined by macroscopic mass balance as equation 6.

$$J_w(t) = -\frac{dV_f}{dt} = \left[\frac{V_f(t-\Delta t) - V_f(t)}{\Delta t}\right] \qquad (6).$$

Where $V_f(t)$ is the volume of the feed solution at a certain time, $V_f(t-\Delta t)$ is the volume of the feed solution at previous time, and Δt is the interval of time between two measures.

4. RESULTS AND DISCUSSION

4.1. COMPARISON OF AMMONIA RECOVERY IN A GAS-PERMEABLE MEMBRANE USING ACIDIC TRAPPING SOLUTION AND VACUUM APPLICATION (PHASE 1)

The variation of TAN concentration in the feed solution of all the experimental configurations tested applying vacuum is illustrated in Figure 4.1. Table 4.1 summarizes the main results of these tests.

Table 4.1. TAN removal and recovery efficiencies, K_m values and reagent consumption in phase 1 experiments.

Test	**Test Configuration**	**Pressure [mbar]**	**TAN removal / recovery at test time [%]**	**K_m [m/s]**	**Total alkali consumption [NaOH/TAN recovered]**	**Total acid consumption [H_2SO_4/TAN recovered]**
1A	Vacuum application through the casing	10	16.23 / 5.93	$(2.6\pm0.1)\cdot10^{-8}$	6.15	2.15
1B		120	11.19 / 0.08	$(2.0\pm0.1)\cdot10^{-8}$	692	215
1C	Vacuum application through the fiber	10	18.71 / 4.89	$(1.7\pm0.2)\cdot10^{-8}$	7.90	2.77
1D		120	7.81 / 7.01	$(2.3\pm0.1)\cdot10^{-8}$	6.12	2.09
1E	Acidic trapping	Atm	99.97 / 99.97	$(1.7\pm0.1)\cdot10^{-7}$	1.11±0.04	0.64±0.09

The nitrogen transfer was very low in all scenarios tested by applying the vacuum. The ammonia removal was highly dependent on the vacuum pressure, comparing the experiments with the same experimental configuration in both cases, circulating the feed inside the fiber (1A and 1C) or through the GPM casing (1B and 1D), the highest ammonia removal efficiency obtained was recorded on the test working on a vacuum pressure of 10 mbar. For these experiments, 1A and 1C, the TAN concentration in the feed solution decreased about a 16 and 18% respectively in 5 hours of experiment., On the other hand, in tests working on a vacuum pressure of 120 mbar, 1B and 1D, the TAN removal achieved was lower, obtaining an 11 and 8% respectively.

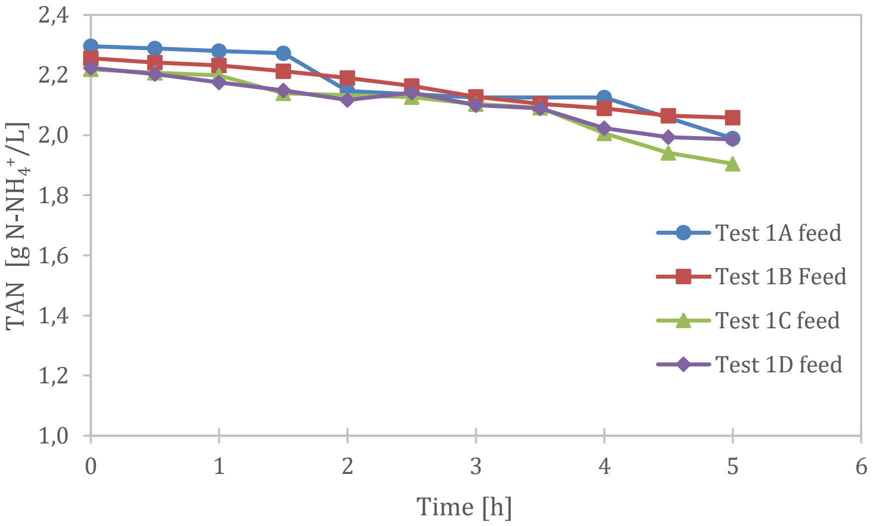


Figure 4.1 TAN concentration evolution of the feed solution of the experiments carried out applying vacuum in GPM.

This can be explained, because the pressure vacuum gradient between the feed and trapping solution is higher working on vacuum pressures of 10mbar, causing higher mass transfer of N (K_m) and a better diffusivity. Comparing the configuration, results showed that the biggest TAN elimination is obtained by circulating the feed solution through the membrane and making the void on the GPM casing. Otherwise, the biggest ammonia recovery doesn't get affected by the pressure operation, and it's more related to the operation configuration, obtaining the biggest TAN recovery in circulating the feed through the casing. However, the N recovery rates were very similar in all the tests performed.

Although nitrogen removal was more efficient on lower vacuum pressures, there were different problems in the experimental setup. First, the vacuum pump was suffering from excessive overheating. Because of this, experiments 1A and 1C were on semi-continuously, working at intervals of 30 minutes of circulation and another 30 minutes of letting the pump rest. Another problem of the vacuum application was the low ammonia recovery. That could be caused due to problems with the absorption of the ammonia into the acidic solution, driven by problems with the usage of a bubbler. Other studies applying the vacuum on gas-permeable membranes, showed the highest ammonia removal and recovery, reaching above 90% of recovery in some scenarios (Dow et al., 2022). This fact shows that this GPM technology must be studied and optimized to conclude if it's viable or not the ammonia recovery by just applying vacuum pressures.

To compare the vacuum application on the gas-permeable membrane, test 1E trapping solution circulation through the membrane, showed a notorious upgrade on the GPM using an acidic solution for ammonia removal and recovery. In both duplicates, over 99% of the TAN in the feed solution was eliminated in over 8 hours and recovered in the trapping solution. (See Figure 4.2)

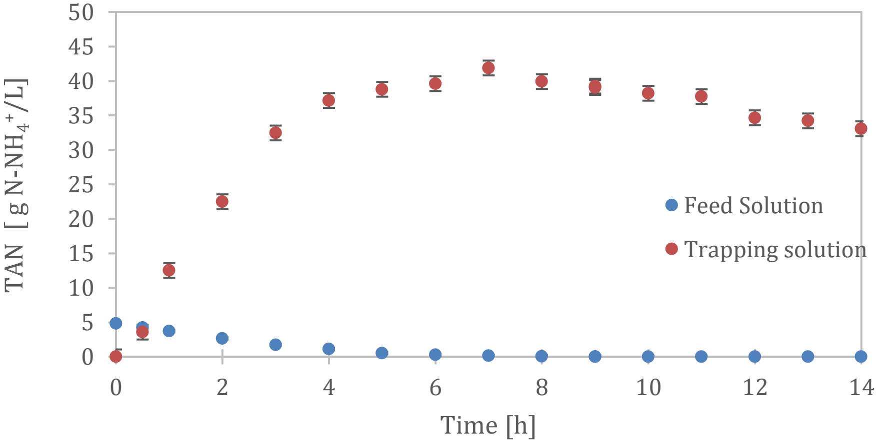


Figure 4.2. TAN concentration evolution of the feed and trapping solution of the experiments carried out in acidic trapping solution.

It could be observed that when the TAN in the feed solution was below 1% of the initial concentration, the trapping ammonium sulphate concentration decreases over time. This could be explained because the water in the feed solution starts passing through the membrane to the trapping solution, increasing the volume and diluting the salt. This phenomenon could be related to the difference of salinity between the feed and trapping solution which promoted the water molecules transfer through the membrane.

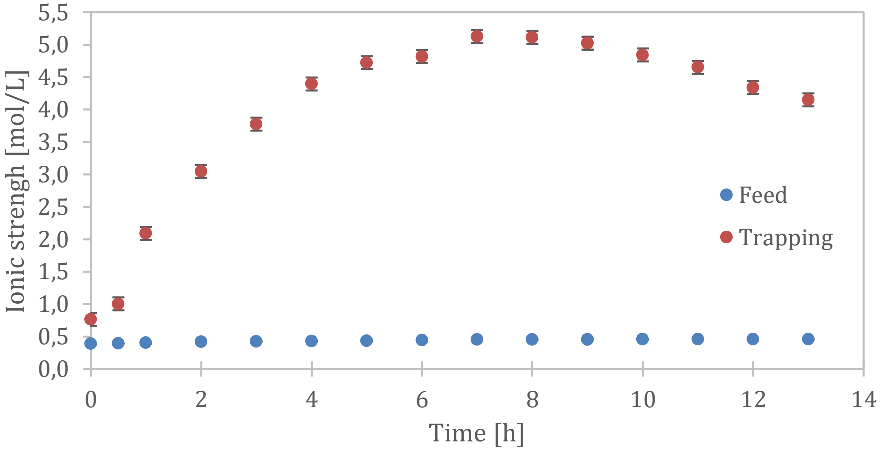


Figure 4.3. Comparison between feed and trapping ionic strength.

The total reagent consumption per mole of nitrogen recovered in all experiments of NaOH and H_2SO_4 in the vacuum application was higher than expected, according to the stochiometric ratio of 1:1 mole of NaOH consumed for each mole of NH_3 reacted. Otherwise, the sulphuric acid the stoichiometric ratio between NH_3 and H_2SO_4 is 0.5, so the value of the mole of acid for each mole of ammonia recovered should be around 0.5. Table 4.1 shows the total reagent consumption of all tests, where it can be observed that in the acidic trapping solution, the ratio consumption is close to the theoretical values in NaOH and H_2SO_4 consumption since these experiments were performed using a synthetic solution without extra alkalinity. But in the vacuum application, the ratio was higher than expected, because the ammonia recovery was low reaching higher consumption values.

The calculated ammonia transfer constant (K_m) in all experiments is shown in Table 4.1. From the experiment results and the K_m calculations, the acidic trapping solution operation mode was considered the best configuration for the TAN recovery process. Evaluating the K_m obtained in the tests, it could be concluded that the best configuration for vacuum application in GPM is applying vacuum inside the fiber and working at 10 mbar. But comprising all the configurations tested, the acidogenic trapping solution is by far the most efficient, among the strategies tested in this work.

4.2. EFFECT OF THE TRAPPING SALINITY IN WATER FLUX (PHASE 2)

Table 4.2. TAN concentrations, and feed and trapping initial and final volumes in phase 2 experiments.

Test	TAN concentration [g N/L]		Feed volume [L]		Trapping volume [L]	
	Initial	Final	Initial	Final	Initial	Final
2A	50	38	5	4.8	0.5	0.7
2B	30	25	5	4.9	0.5	0.6
2C	10	9.5	5	4.95	0.5	0.55

The results of the experiments are summarized in Table 4.2. The variation of the volume in the feed and trapping solution is illustrated in Figure 4.4 and Figure 4.5 respectively. The water transfer was highly dependent on the trapping solution salinity, given by the concentration of each ion present in both feed and trapping solution. For the experiments tested on 50 g N/L, test 2A, the volume decreased over 0.2 L in 8 hours, which represents 4% of the initial volume passing from the feed to the trapping solution. Evaluating the increase in the trapping solution, a 0.2 L of water passage to the trapping solution represented 40% of the initial volume. This caused the ammonium sulphate per cent in mass to go from 24 to 18%.

In the other tests a lower water mass transfer was observed, in test 2B the volume reduction in the feed was about 2%, going out from 5 to 4.9L, and reducing the ammonium sulphate per cent in mass from 14 to 11%. Finally, in test 1C a lower water transfer was appreciated, only reducing a 1% of the initial feed volume and a reduction of the ammonium sulphate percent in mass from 10 to 9%.

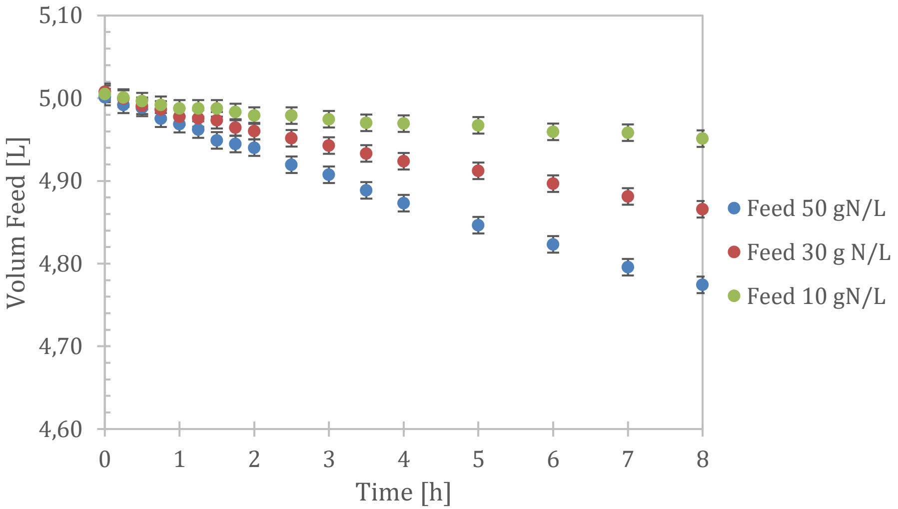


Figure 4.4. Feed volume evolution of the Tests 2A, 2B and 2C carried out in phase 2.

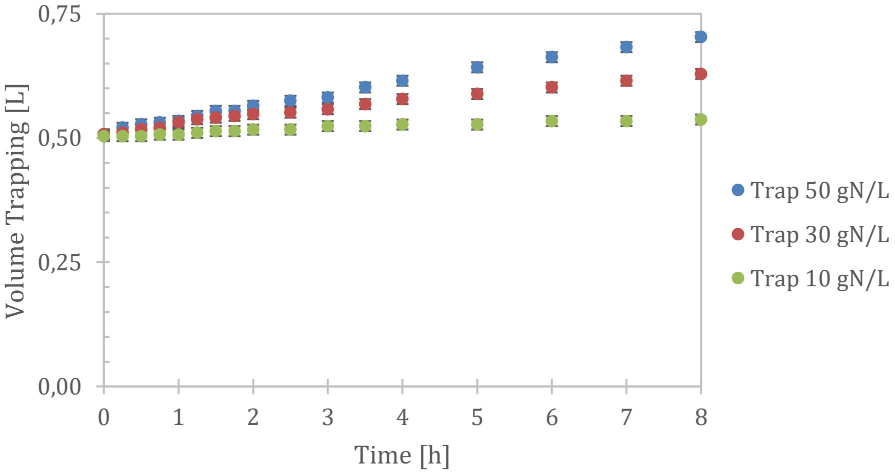


Figure 4.5. Trapping volume evolution of the Tests 2A, 2B and 2C carried out in phase 2.

This phenomenon can be explained due osmotic distillation, as the ionic strength that creates ammonium sulphate is much bigger than the one created by the sodium and bicarbonate ions. As this force depends on the concentration of each ion, the volume ratio between the feed and trapping is one of the causes of this problem. The total flowrate obtained, by applying equation 6, was proportional to the initial concentration, obtaining a water flux of 0.028 L·h^{-1} in the first test at a higher initial TAN concentration, 0.015 L·h^{-1} in the second test and 0.006 L·h^{-1} in the last test, working at lower values of TAN in the trapping solution.

Figure 4.6 shows the representation of the water flux in front of the trapping concentration, to evaluate the water flux passage through as a function that depends on the ammonium sulphate concentration in the feed solution such as equation 5, to obtain a water mass transfer constant.

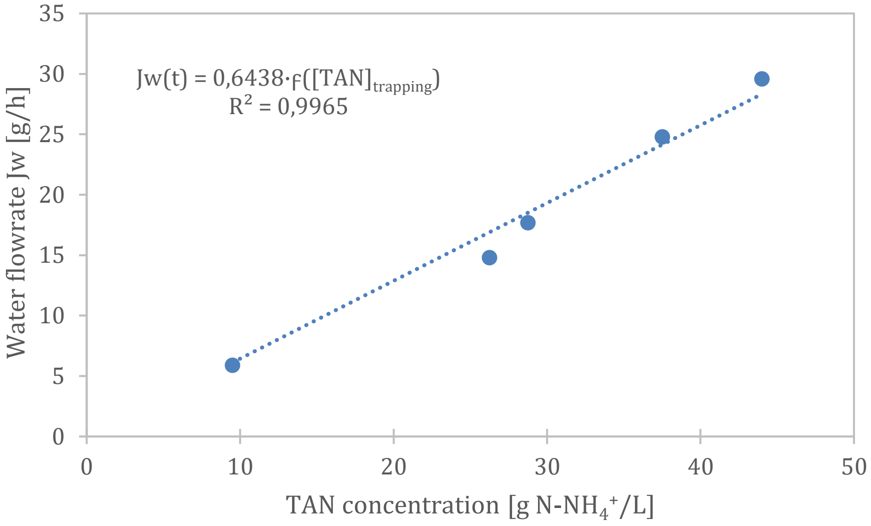


Figure 4.6. Evolution of the water flux though the membrane in function of the TAN in the trapping solution.

By adjusting the results obtained in the tests of the second phase to a regression line, it could be obtained the slope of the line, which is the constant K_w of the process at the working conditions of pH 9 and 35 ºC of temperature. The regression obtained is the representation of equation 5, where the 0.6438 value is the mass transfer constant K_w in [L·h^{-1}]. (Riaño et al., 2019) studied the osmotic distillation (OD) that may occur during the TAN removal process due to the difference of vapour pressure between both sides of the GPM. This can be caused because the salinity in the trapping solution is bigger than in the feed solution. This process could have a great impact on the economy of the process, as the market value of the ammonium sulphate is proportional to its concentration (Menkveld & Broeders, 2018). A possible strategy proposed in this studio was to heat the stripping solution and/or cool the feed solution, to counteract the OD.

Another possible strategy to avoid this problem could be replacing the trapping solution when the TAN concentration reaches the aimed value.

4.3. AMMONIA RECOVERY FROM PIGGERY WASTEWATER (PHASE 3)

Table 4.3. TAN removal and recovery efficiency, K_m value and reagent consumption in phase 3

Test	**Test Configuration**	**TAN removal / recovery at test time [%]**	**K_m [m/s]**	**Total alkali consumption [NaOH/TAN recovered]**	**Total acid consumption [H_2SO_4/TAN recovered]**
3A	Acidic trapping solution	99.21 / 99.13	$(8.8\pm02)\cdot10^{-7}$	1.02	0.64

Figure 4.7 shows the TAN concentration evolution of experiment 3A, carried out with piggery wastewater. Table 4.3 summarises their performance parameters. It can be observed that the operation time required for the swine slurry TAN recovery is higher than the time required for the synthetic wastewater. As Figure 4.8 represents, in about 11 hours of operational time, 95% of the nitrogen was removed from the feed solution and recovered in the trapping solution. An almost complete TAN recovery of 99% was achieved in the total operational time of 16 hours. The ammonia mass transfer constant obtained from the piggery wastewater was $(8.8\pm02)\cdot10^{-7}$ [m/s] Compared to the synthetic wastewater test, the value of the K_m obtained with the python adjust algorithm was lower. The higher operational time required in sine slurry can be attributed to the complexity of the feed solution, since there are more species in the piggery manure, it can cause fouling in the membrane.

It can be observed that when the trapping solution reaches the 35 g N/L, the TAN concentration starts decreasing, as the water mass transfer increases. During the operational time, the feed volume decreased from 6 to 5.8 Liters, increasing the trapping solution volume from 0.34 to 0.54, diluting the ammonium sulphate to 26 g N/L.

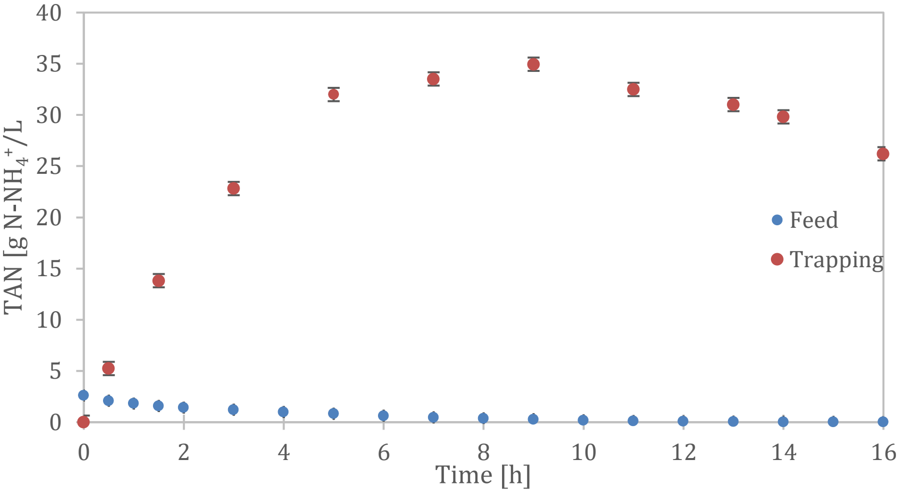


Figure 4.7. TAN concentration evolution of the feed and trapping solution of the experiment carried out with piggery wastewater.

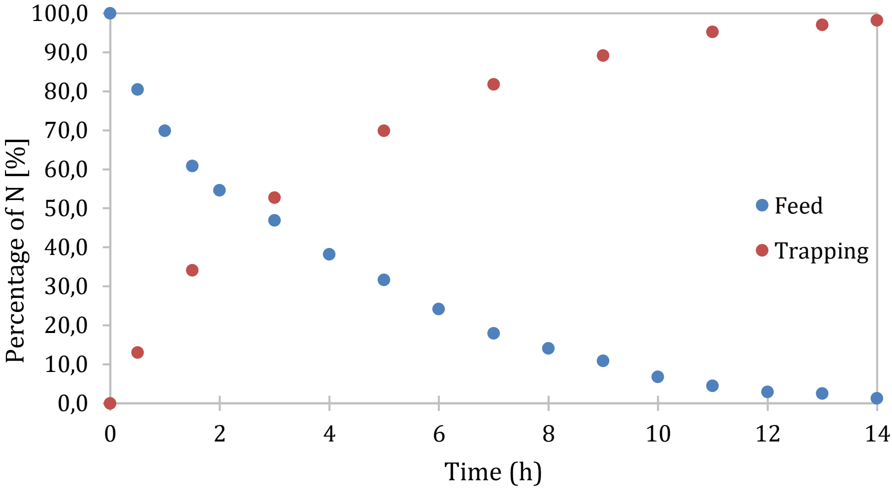


Figure 4.8 Percentage of N of the feed and trapping solution of the experiment carried out with piggery wastewater.

The total reagent consumption of the process values was the same as expected, obtaining a mole of NaOH consumption per mole of N recovered of 1.02 and a 0.64 in the acid consumption per mole of N. The values obtained in piggery slurry were almost the same as the synthetic wastewater. Comparing both consumption of NaOH the value was a bit lower. In the synthetic solution, the basis needed to raise the pH to 9 was lower than in piggery slurry, but during the experiment, the NaOH needed to control the pH was higher. This can be explained because probably in the synthetic wastewater an excess of basis was added when the ammonia was over in the feed solution. In the piggery wastewater, the high alkalinity of the feed solution could have acted as a buffer, making the pH of the solution harder to rise, but also making it easier to regulate the pH during the experiment. The total consumption of H_2SO_4 was almost the same too but its addition in pig slurry was lower. The values obtained in both tests were higher than the theoretical, probably caused by the excess of acid in the trapping solution.

The final TAN concentration in the feed solution was 21 mg $N\text{-}NH_4^+/L$. If we compare the nitrogen remaining in the feed solution with the limit value of TAN concentration in wastewaters effluents, established by the legislation in Catalonia (60 mg $N\text{-}NH_4^+/L$) (DOCG, No 3894, 29/05/2003), it can be concluded that the process is, not only effective for ammonia recovery, but also for applications in treatment plants of water as it generates a liquid fraction of wastewater ammonia free that can be used to recover some other nutrients, such as phosphorus, or to produce biogas.

5. CONCLUSIONS AND RECOMMENDATIONS

In this study, nitrogen recovery from wastewater was achieved by using a gas-permeable membrane in two different operational modes.

The usage of the GPM applying the vacuum did not result in an efficient process for nitrogen removal and recovery for wastewaters, obtaining mass transfer constants (K_m) lower than expected. This method also carried out some operational modes when applied at lab-scale. The overheating of the vacuum pump and the lower ammonia recovery of the process leads us to search for an alternative configuration to enhance nitrogen recovery efficiency, although other studies obtained promising results.

When using an acidic trapping solution in a closed loop, the ammonia removal and recovery were higher than the vacuum application, reaching about 99% of removal in 8 hours of operational time, and a Km of $(1.7\pm0.1)\cdot10^{-7}$ [m/s] when working at pH 9 on the feed solution.

Several tests were conducted with different initial nitrogen concentrations in the trapping solutions, to evaluate the water passage. It was appreciated that the waster diffusivity through the GPM was proportional to the TAN concentration in the acidic solution, with a constant mass transfer K_w of 0.6438 [$L\cdot h^{-1}$]. This phenomenon can be explained due the highest salinity difference between the trapping and feed solutions.

Finally, the acidic trapping solution in a closed-loop GPM configuration was tested for the treatment of piggery wastewater, to evaluate the TAN recovery and the water passage. Results showed a recovery adobe of 99% in 16 hours of operation, and a mass transfer constant of 8.8e-07±5.4e-08 [m/s].

Further studies could focus on other operational configurations for vacuum application in membranes for ammonia recovery, changing the vacuum pump or the trapping solution, to get better results as other references reached a high removal efficiency. In water passage experiments, more scenarios should be tested to fully characterize it and obtain mathematical modelling.

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