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Study of the nitrogen recovery from an internal stream of a municipal wastewater treatment plant using selective membranes.

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La mejor ciencia no se aprende en los libros; el sabio más grande y mejor maestro es la Naturaleza.

Galileo Galilei

Primer de tot m'agradaria agrair als meus tutors, en Joan Dosta i el Francesc Mas per la seva dedicació i ajuda que m'han ofert en tot moment durant aquests mesos.

També voldria agrair als meus familiars i amics, que m'han acompanyat durant tota l'etapa universitària.

CONTENTS

SUMMARY

This study is focused on the nitrogen removal and recovery from nitrogen rich wastewater streams using selective membranes. With this technology, nitrogen is removed from wastewater by means of the transfer of matter through the membrane and is subsequently recovered with an acid solution, in this case, sulfuric acid, since ammonium sulfate has fertilizing properties. A bibliographic research of the scientific literature has been made where the viability of this system has been evaluated and subsequently a proposal of a system to be implemented in a wastewater treatment plant has been presented. From the bibliographic research it can be concluded that the most used selective membranes are tubular permeable gas membranes made of e-PTFE. Removal and recovery percentages between 63% and 95% are reported. It is observed that optimum pH and temperature conditions are required to obtain higher yields. Both need to be increased, in case of pH increased to 10, and temperature increased to 30ºC. Subsequently, the nitrogen mass balances of a municipal wastewater treatment plant have been studied, and it has been identified the recirculation water after anaerobic digestion as the stream where the membrane recovery treatment could be easily implemented . A system with a tubular permeable gas membrane has been proposed with an expected 90% removal percentage, of which 95% recovery in the form of ammonia sulfate could be achieved. To obtain these yields, it would be necessary to increase the pH up to 10. By means of this nitrogen treatment, it has been possible to improve its function in the wastewater treatment plant, where the percentage of nitrogen released in the form of atmospheric nitrogen has been reduced from 58% to 52%, as well as the CO_2 emissions, the energy demand and the sludge production associated to this savings.

Keywords: Ammonia, Nitrogen Recovery, Selective Membranes, Reject water, Wastewater Treatment Plant

RESUM

La recuperació del nitrogen és una tecnologia que recentment estudiada. Aquest treball de fi de grau tracta sobre la recuperació del nitrogen mitjançant l'ús de membranes selectives. Amb aquesta tecnologia s'aconsegueix eliminar el nitrogen de l'aigua residual mitjançant la transferència de matèria a través de la membrana i posteriorment es recupera amb una solució àcida, en aquest cas, àcid sulfúric, ja que el sulfat d'amoni té un gran poder fertilitzant. En aquest estudi s'ha fet una recerca bibliogràfica de diferents articles on s'avalua la viabilitat d'aquest sistema i posteriorment s'ha presentat una proposta de sistema a implementar a una planta de tractament d'aigües residuals. De la recerca bibliogràfica es pot extreure que la membrana més usada és la membrana de gas permeable en forma tubular. Feta de e – PTFE. S'aconsegueixen percentatges de d'eliminació i de recuperació d'entre el 63% fins al 95%. S'observa que es necessita unes condicions òptimes de pH i de temperatura per obtenir uns rendiments més elevats. Posteriorment s'ha estudiar una planta de tractament d'aigües residuals, on a partir dels balanços de matèria s'ha determinat que la corrent on s'hauria d'implementar el tractament de recuperació amb membranes és l'aigua de recirculació després de la digestió anaeròbica. S'ha proposat un sistema amb una membrana de gas permeable en forma tubular on el seu percentatge d'eliminació és del 90%, dels quals es recupera un 95% en forma de sulfat d'amoni. Per obtenir aquests rendiments, s'ha necessitat augmentar el pH fins a 10 . Mitjançant aquest tractament del nitrogen s'ha pogut comprar la seva funció dins de la planta de tractament d'aigües residuals, on el percentatge de nitrogen alliberat en forma de nitrogen atmosfèric s'ha redit del 58% al 52%. D'aquesta manera es redueixen les emissions de CO_2, la demanda d'energia i la producció de fangs associats a aquests estalvis.

Paraules clau: Amoníac, Recuperació de Nitrogen, Membranes Selectives, Aigua Residual, Planta de Tractament d'aigües Residuals.

1. INTRODUCTION

1.1. IMPORTANCE OF AMMNONIA IN THE SOCIETY

The main use of ammonia is the fabrication of nitric acid and nitrogen fertilizers. Nitric acid is used to make fertilizer (90% of ammonia produced), for organic nitration, explosive products and in surface treatments (ChemicalSafetyFacts.org, 2021). Nitrogen fertilizers are very useful because plants cannot grab on nitrogen from the air. So, these fertilizers can help in growth plants and food production.

In industry ammonia is used as a refrigerant gas and for air-conditioning equipment for its benefits.

- Has a better heat transfer properties that other chemicals refrigerants because it can absorb large quantities of heat from surroundings, so it can be used in small equipment.
- Is environmentally friendly: is included in the group of “natural” refrigerant
- It is very efficient, because can reach very
- It has a better price than other refrigerants. In addition, ammonia has a low density in liquid phase, so for the same price (cost per kg) that other refrigerants it can be obtained a huge quantity.

Ammonia nowadays is mainly produced by the Haber – Bosch process, which is explained in the following section.

1.2. THE HABER – BOSCH PROCESS

The Haber – Bosch process is the reaction between nitrogen (N_2) and hydrogen (H_2), exempt of CO, CO_2, and other gases, forming ammonia (NH_3) from the following reaction:

$$N_2\,(g) + 3H_2\,(g) \rightleftarrows 2\,NH_3\,(g) \qquad (1.1)$$

The reaction below is very exothermic and with a total reduction in the number of moles. Hydrogen used is mainly obtained from fossil fuels. The reaction takes place at high pressure and at the lowest possible temperature due to the high reduction of the number of moles and the corrosivity of gases. It is catalysed by a solid catalyst, as a metallic oxide (Fe_3O_4 or Cr_2O_3). This process consumes around 2% of world's energy (Universitat de Barcelona, 2019).

The ammonia converter, where the reaction 1.1 takes place, has a very complex design. It is based on an intern heat exchanger and some catalyst beds with a heat exchanger in the entrance and exit of the reactor. Two examples of ammonia converter are the Kellogg ammonia and the Topsoe's ammonia converters.

The gases at the reactor outlet have a low percentage of ammonia, around 16%, because the conversion of the process is not very high, less than 40%. The gases pass through a heat exchanger where cold water condenses ammonia. The other gases, the ones that have not react (N_2 and H_2), the inert of non-condensed (NH_3), are recirculated (and purged) to the reactor and a higher conversion is obtained at the end of the process. To understand better the Haber – Bosch process, Figure 1.1. shows an example:

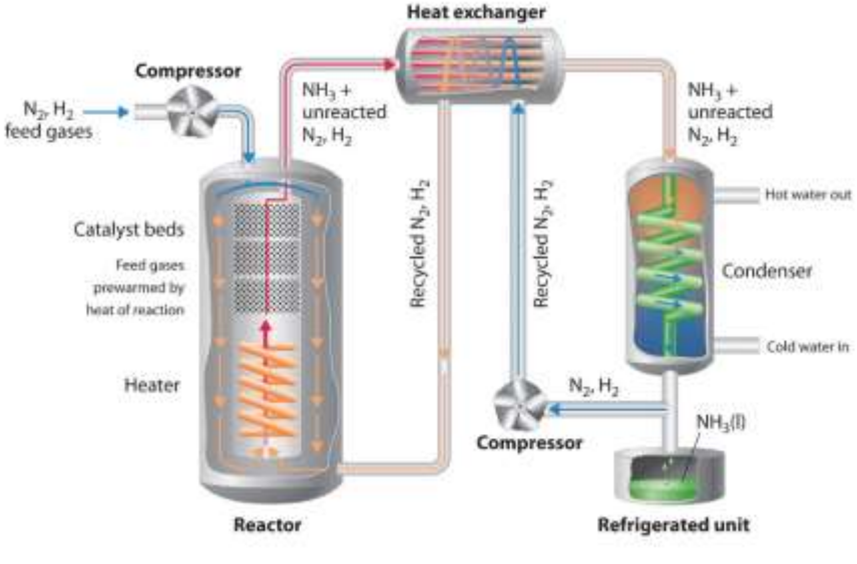

Figure 1.1: Example of the Haber – Bosch process (Saylor Academy, 2021)

1.3. PROBLEMS OF NH_4^+ - N PRESENT IN WASTEWATER

Nitrogen in wastewater is removed to avoids harmful effects of the water bodies, as eutrophication and toxicity problems. The toxicity of ammonia depends on the pH and temperature (California Water Resources Control Board, 2021). Ammonia is more toxic than ammonium, so as the pH increases more NH_3 is formed, and toxicity increases. The increase of temperature has the same effect in toxicity. In this section, these two main problems are explained in detail.

1.3.1. Eutrophication

Eutrophication is phenomenon that is formed in water when there is more availability of limiting growth factors needed for photosynthesis, such as carbon dioxide, nutrient fertilizers, and sunlight. Consequently, an excessive growth of plants and algal is found in water. Although eutrophication is a natural phenomenon, human activities have increased the process, especially the discharge of nutrient rich wastewater into water bodies.

The main problem related to eutrophication is the decrease of quality and clarity in water. Visually it can be observed turbidity and coloration of water. There is an abundance of organic and inorganic chemicals which could affect the odor and/or taste and form harmful substances in there. Also, the plants formed limit light penetration, reducing growth from other plants, and causing die-offs plants.

However, nutrient removal does not comply with the objectives of circular economy, which is based on recycling the elements which previously wanted to be disposed of. Waste can be recovered and included again in the production chain. Consequently, waste is converted in another product that has a lot of utilities in different sectors.

1.3.2. Nitrogen discharge limits in sensitive areas

The nitrogen discharge limit in EU concerning treated wastewater quality parameters is between 10 and 15 mg/L of total nitrogen (TN) in sensitive areas prone to the eutrophication (Preisner *et al.* ,2020). This parameter is for total nitrogen, but there is not a normalized parameter for different forms of nitrogen, such as amount of NH_4^+ or nitrogen atmospheric. If a system is implemented in wastewater treatment plants in order to remove part of nitrogen present in wastewater, total nitrogen concentration can be reduced and there are less problems of contamination when wastewater is discharged.

This parameter in some countries is smaller, so in a near future is going to decrease, making the limit more restrictive and avoiding contamination in sensitive areas.

1.4. TREATMENTS FOR NH_4^+- N REMOVAL AND RECOVERY IN WASTEWATER

In this section, some of the most common technologies applied to nitrogen removal and/or recovery are explained.

1.4.1. Biological nitrogen removal through conventional nitrification/denitrification

Nitrification is the aerobic biological oxidation of ammonia (NH_3) to nitrite (NO_2^-) and nitrate (NO_3^-). This reaction needs a bacteria to carry out the nitrogen conversion. In nitrification this microorganism is autotrophic. The following reactions corresponds to nitrification and denitrification.

Nitrification (Henze *et al*. 2006)

$$NH_4^+ (aq) + 3/2\ O_2 (g) \rightarrow NO_2^- (aq) + 2\ H^+(aq) + H_2O\ (l) \tag{1.2}$$

$$NO_2^- (aq) + ½\ O_2 (g) \rightarrow NO_3^- (aq) \tag{1.3}$$

Nitrification process takes place in two reactions. An aerobic conversion of NH_4^+ to NO_3^- is achieved. With this process, toxicity from NH_4^+ is removed from wastewater.

Denitrifcation is the anoxic biological reduction of nitrate to nitrite and molecular nitrogen (N_2). In this case the bacteria needed is heterotrophic.

$$4\ NO_3^- (aq) + C_2H_4O_2 (aq) \rightarrow 2\ CO_2 (g) + H_2O\ (l) \tag{1.4}$$

$$8\ NO_2^- (aq) + 3\ C_2H_4O_2 (aq) + H_2O\ (l) \rightarrow 4\ N_2 (g) + 8\ OH^- (aq) + 6\ CO_2 (g) \tag{1.5}$$

Denitrification in this case uses acetic acid as the organic carbon source. These processes consume a lot of energy because of aeration and agitation from reactors. As it can be seen in the equations of denitrification, CO_2 is produced. Also, it is important to mention that in denitrification, organic matter (COD, chemical oxygen demand) is removed.

Regarding nitrification/denitrification with swine manure, first there is a solid – liquid separation where most of organic nitrogen is removed, but there is a little fraction of total nitrogen and phosphorus that remains liquid in a soluble form. So, a nitrification/denitrification treatment is needed to treat the liquid fraction. Is considered the most efficient and relatively cost-efficient for nitrogen removal in wastewater.

1.4.2. Nitrogen recovery treatments

Nitrification/denitrification is the most common ammonium removal treatment but there are other treatments focused on ammonium recovery instead of removal, such as air or stream stripping combined with acid absorption, zeolite adsorption through ion exchange, struvite precipitation or selective membranes technology to recovery nitrogen (Capodaglio *et al.*, 2015). In the next sections, these nitrogen recovery process will be briefly described.

1.4.2.1. Nitrogen removal by steam - stripping or air - stripping

Stripping is used to separate the volatile fraction from wastewater. To achieve the separation, contact between gas/vapor phase and wastewater is provided. Some part the water, mainly impurities, are transferred to gas phase. After that, impurities are removed from the gas phase by stripping to reuse the gas again. Air - stripping is more common than steam - stripping because steam - stripping needs temperatures higher than 95 ºC, to work (Capodaglio *et al.*, 2015).

From this process, fertilizing agents, such as ammonium phosphate and ammonium sulphate, could be obtained while ammonium nitrogen is removed from the treated wastewater. Air – stripping process consists in two units. There is a reactor where struvite precipitates and a column for stripping and absorption. In this column, there is a contact between air and sulphuric acid solution. Ammonia is absorbed from the gas phase and ammonium sulphate is formed. Figure 1.2 shows this process described above.

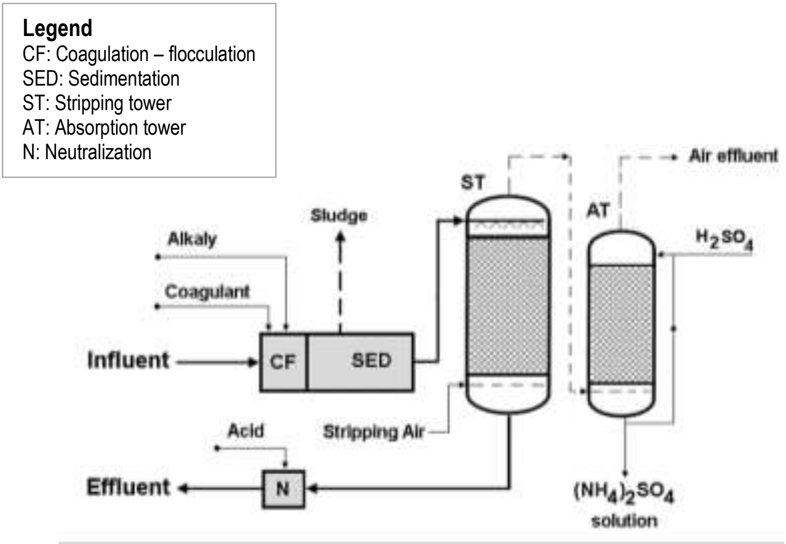

Figure 1.2: Typical flow diagrams of the air-stripping process for ammonia recovery (Capodaglio *et al.*,2015)

1.4.2.2. Nitrogen recovery using zeolite-based process.

The zeolite process is based on a simultaneous combination of an ion exchange and a separation of the zeolite regeneration fluid. Ellersdorfer *et al.*, 2020 designs a pilot plant to prove the nitrogen recovery with zeolites. In Figure 1.3 it can be seen the depicts of the plot plant. This consists in two columns with an ion exchange made of propylene and filled by zeolite. They can work in series (serial model) or separately (single model). There was also a stripper and scrubber for zeolite regeneration and ammonia extraction. NaOH is need for the regeneration of zeolite and sulphuric acid solution from the extraction of ammonia.

From this experiment the percentage of nitrogen removal achieved is between 85.8 and 90.3% depending on the model used.

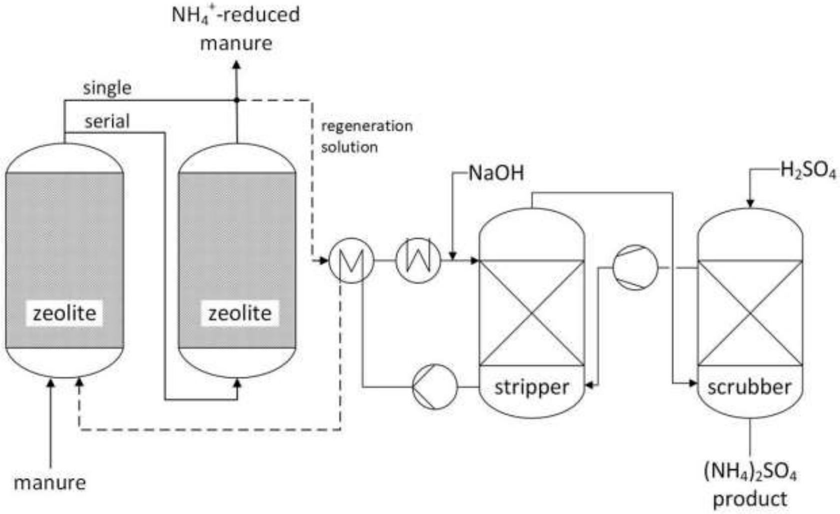

Figure 1.3: Principal flowchart of the ILS-pilot plant (treatment capacity: 500–1000 L/h) and the different operation modes of the ion exchanger columns (single/serial). (Ellersdorfer *et. al,* 2020).

1.4.2.3. Struvite precipitation

Struvite is composed of magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphate (PO_4^{3-}) in equal molar concentrations, and it crystallizes as a white orthorhombic crystalline structure. This precipitation happens when the concentration of its components exceeded the limit of solubilization. The reaction that takes place is the following:

$$Mg^{2+}(aq) + NH^{4+}(aq) + PO_4^{3-}(aq) + 6\,H_2O\,(l) \rightarrow MgNH_4PO_4 \cdot 6\,H_2O\,(s) \qquad (1.8)$$

Struvite precipitation is controlled by pH and temperature. pH needs to be the optimal because if it is very basic, ammonium is converted to ammonia, so struvite cannot precipitate. In contrary phosphate comes from an acid triprotic, so if the pH is very acid, phosphate is converted to phosphoric acid or one of their forms. Consequently, the pH optimal is around 8.5 for struvite precipitation. Struvite crystals precipitate, so a high percentage of phosphorus (90%) is removed from wastewater. In contrary this technology is not the best for total nitrogen removal because percentage of nitrogen present in struvite crystals is very low, because normally, phosphorus or magnesium are the limiting reagents. Figure 1.3 shows a pilot plant designed for the process of struvite precipitation with a fluidized reactor.

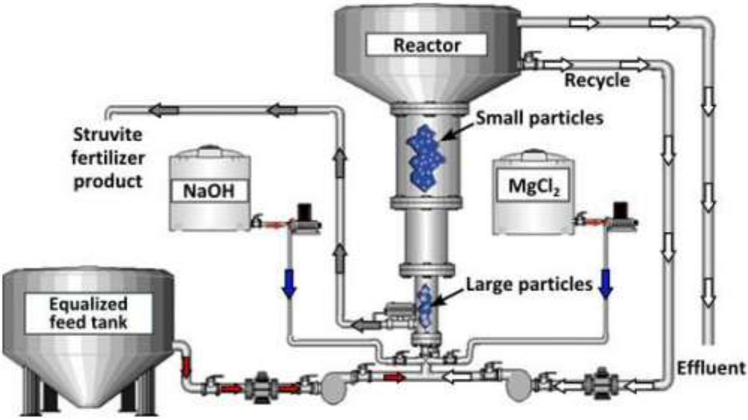

Figure 1.4: Diagram of the process for struvite precipitation and recovery (Capodaglio *et al.*, 2015))

1.4.2.4. Selective Membrane Technology

Nitrogen recovery from wastewater with selective membranes has several advantages such as:

- Selective membranes work at low pressure.
- When compared with air stripping towers or zeolite process, this process does not require clarification.
- When compares to struvite precipitation, in selective membranes there is no need to add Mg^{2+} or PO_4^{3-} to balance the stoichiometry of struvite precipitation.
- This process can be combined with others to obtain better results, such as anaerobic digestion.

For the abovementioned reasons, this study is focused on the study treatments with selective membranes because this technology has the advantage that can remove and recover total nitrogen in the form of a highly NH_4^+ concentrated solution with fertilizing value and with low energy demand, reduced CO_2 emissions.

2. OBJECTIVES

The general objective of this work is to study the possible recovery of nitrogen in a wastewater treatment plant to generate a fertilizer agent using a selective membrane system for NH_3.

To reach this general objective, the following specific goals were achieved:

- To perform a bibliographic research and critical discussion of scientific papers where this process was applied to treat ammonium rich wastes or wastewaters, and to evaluate the effect of several optional parameters (pH, temperature, type of membrane, among many others) on the process performance.
- To study the nitrogen mass balances of a municipal wastewater treatment plant and to identify the stream of the plant where a nitrogen recovery unit using selective membranes could be installed.
- To propose a selective membrane system based in all the information read in the references, highlighting nitrogen removal and recovery in optimal conditions.

3. NITROGEN RECOVERY FROM WASTES OR WASTEWATERS USING NH_3 SELECTIVE MEMBRANES

Table 3.1 and Table 3.2 summarize the main experimental conditions and results of recent studies related to the use of selective membranes for total ammonium nitrogen recovery from N – rich wastes or wastewater. From the analysis of these tables, it could be concluded the effect of different experimental set ups and operational conditions on the process performance, focusing on the nitrogen removal and the recovery rate:

3.1. TYPE OF MEMBRANE

The main function of the NH_3 selective membranes is the diffusion of ammonia across the membrane while other chemical components present in the treated waste or wastewater are rejected. The N mass transfer depends on the difference in NH_3 concentration between the substrate, located on one side of the membrane, and in the capture solution, located on the other side of the membrane. In this way, a certain amount of total ammoniacal nitrogen (TAN) per unit of time can be removed from the substrate, which corresponds to the removal percentage. Once removed, the TAN could be recovered using an extractor solution.

Figure 3.1. shows two tanks, one filled swine manure and the other with acid solution. In the tank with swine manure there was a gas – permeable membrane submerged. The two tanks were connected by a pump that impulses the acid solution. Acid solution passes through the gas – permeable membrane in continuous and captures ammonium. In both tanks, pH is controlled with a pH meter.

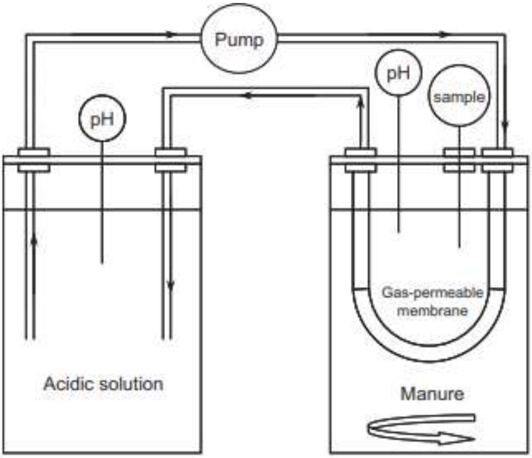

Figure 3.1: Experimental device for ammonia capture from manure using gas-permeable membrane (Garcia-González *et al.*, 2015)

Different types of membrane have been used depending on the experimental study performed. As it can be seen in Table 3.2, most of the reviewed papers used membranes made of (expanded polytetrafluoroethylene (e-PTFE). Mainly polymers are used in industry for gas separation process and, in particular, e-PTFE is resistant to acid, so corrosion could be avoided.

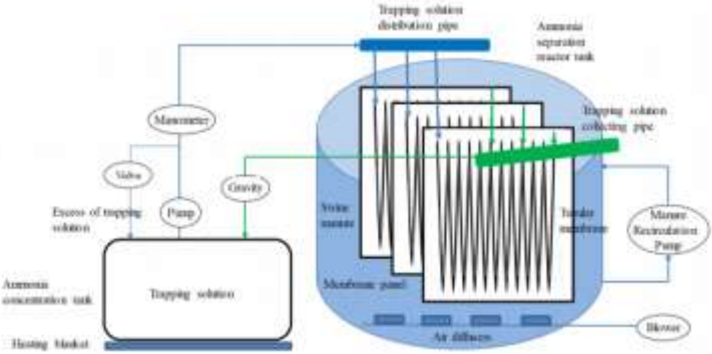

Figure 3.2: Experimental device for ammonia capture from manure using different panels submerged in the reactor (Molinuevo - Salces *et al.* (2020))

Although the membrane configuration is usually a tubular module (Molinuevo - Salces *et al.*, 2018), some researchers have used different panels submerged in the reactor, as in Figure 3.2 corresponding to the study of Molinuevo - Salces *et al.* (2020). The membrane surface is very varied depending on the experiment. When more membrane surface is used, more NH_3 can cross through it, so higher nitrogen recoveries are achieved.

If the percentage of nitrogen recovered with panels is compared with the percentage obtained with a tubular membrane, it can be seen in Table 3.2. that there is more efficient the recovery with tubular membrane. (85% or more with tubular membrane vs 63% with panels).

Another factor to consider is the relationship between area of membrane and volume of the treatment unit. It is important that this factor is high as it could be operated in this way without adding much energy to the system. Nagy *et al.* (2019) studied the effect of area/volume ratio in the range of 15 to 60. The highest percentage of TAN recovery (85%) was achieved with an area/volume ratio of 60, which was the maximum value tested.

Table 3.1: Substrate characteristics and operating conditions in studies working with NH_3 selective membranes

Reference	Substrate	Initial TAN concentration[mg/L]	Temperature [ºC]	Extractor solution (pH)	Substrate pH and control
Garcia-González *et al.* (2015)	Low Swine Manure (TS: 0.4 - 0.8 %)	(1070 ± 20) mg/L	25	H_2SO_4	NaOH (5 N), which was added as needed to endpoint pH 8.5–9.0 whenever the pH of the manure decreased below 7.7.
	Medium Swine Manure (TS: 0.8 - 1.7 %)	(1680 ± 30) mg/L			
	High Swine Manure (TS: 1.7 - 3.2 %)	(2290 ± 90) mg/L			
	Swine Manure	(1280 ± 0) mg/L	25	H_2SO_4	Not adjusted
Capodaglio *et al.* (2015)	Swine Manure	(2390 ± 160) mg N/L	25	H_2SO_4 1M	Aeration to increase pH
					8.5 adjusted with NaOH
					ot adjusted
Aymà et al. (2017)	Wastewater from dry anaerobic digestion.	2,000 mg N-NH_4^+/L	50	H_2SO_4 1M	7.35 increased to 12 with NaOH
Wang *et al.* (2017)	Low-strength wastewater (synthetic)	1.40 mmol NH_4^z/L	n.a.	SAC resina	n.a.
Molinuevo - Salces *et al.* (2018)	Swine Manure	3.36 g TAN/L	37 ± 1	Concentrated H_2SO_4 (96 - 98%) ($pH < 1$)	pH initial 7.6. It rapidly increased during the five first days of operation, being in the range of 8.4–8.6.
Nagy *et al.* (2019)	Wastewater	790 mg NH_4-N/L	25	H_2SO_4 1M (95 – 98%) (feed flow: 320 L/m^{2}h)	12 controlled with $Ca(OH)_2$

TS: total solids

Table 3.1 (continuation): Substrate characteristics and operating conditions in studies working with NH_3 selective membranes

Reference	Substrate	Initial TAN concentration[m	Temperature [ºC]	Extractor solution (pH)	Substrate pH and control
Zhang *et al.* (2020)	Landfill leachate	(2,000 ± 2) mg NH_4^+-N/L	n.a.	alkali solution	7.78–7.84
Gonzalez-Salgado *et al.* (2020)	High strength wastewater	4.9 g N/L	23 ± 2	H_2SO_4 0.5M	The pH of the effluent was increased by stripping carbon dioxide (CO_2) in a preaeration tank and by the addition of a base until reaching a pH value of 11.
Molinuevo-Salces *et al.* (2020)	Swine Manure	Between 2.30 and 3.05 g TAN/L	Up to 25	H_2SO_4 (96 - 98%) 1M	8.5. If pH decreases below 8.5 the air pump activated the aeration
Noriega-Heviaa *et al.* (2020)	Anaerobic digestion supernatant	Feed flow rates from 0.33 × 10−5 to 5.83 × 10-5 m3 /s	25	H_2SO_4 0.1M	9 controlled with NaOH
			30		
			35		
			25		10 controlled with NaOH
			30		
			35		

n.a.: data not available

Table 3.2: Membrane used and N removal and recovery in studies working with NH_3 selective membranes under certain operational conditions

Reference	Membrane	Operation mode	HRT/Operation time	% TAN removal	% TAN recovery as $(NH_4)_2SO_4$
Garcia-González *et al.* (2015)	Gas-permeable tubing made of ePTFE)(Phillips Scientific Inc., Rock Hill, SC)	Batch	20–44 days depending on the experiment	94,4% (concentration decreased to 60 ± 90 mg/L)	94,4% (1140 ± 180 mg NH_4^+/L recovered in H_2SO_4)
				89,9% (concentration decreased to 170 ± 60 mg/L)	89,9% (1760 ± 170 mg/ NH_4^+/L recovered in H_2SO_4)
				88,2% (concentration decreased to 270 ± 40 mg/L)	88,2% (2380 ± 150 mg NH_4^+/L recovered in H_2SO_4)
				57%	92% (recovery rate of 64 mg/L/day)
Capodaglio *et al. (*2015)	Gas-permeable tubing made of ePTFE)(Phillips Scientific Inc., Rock Hill, SC)	Batch	18 days	99%	99%
				85%	93%
				66%	99%
Aymà et al. (2017)	Liqui-Cel Extra-flow mini-module 3M contactor; Model G542; 1.7 x 5.5 MiniModule)	Batch	80 min	37%	34 g $(NH_4)_2SO_4$ (production 57 g/h)
Wang *et al.* (2017)	Electrode materials were covered with anion/cation exchange membrane (Grion 6172L/6322L, specific	Batch	n.a.	n.a	63%
Molinuevo - Salces *et al.* (2018)	Tubular gas-permeable membrane, made of e-PTFE(Zeus Industrial Products Inc., Orangeburg, SC, USA)	Semi - continuous	Period I: HRT of 7h during 30 days Period II: HRT of 5h during 20 days	68.6 %	Up to 90 % (19 g TAN/L in $(NH_4)_2SO_4$)

Table 3.2 (continuation): Membrane used and N removal and recovery in studies working with NH_3 selective membranes under certain operational conditions

Reference	Membrane	Operation mode	HRT/Operation time	% TAN removal	% TAN recovery as $(NH_4)_2SO_4$
Nagy *et al.* (2019)	Gas-permeable membrane tubes (Zeus Aeos™ ePTFE Extruded Special)	The two membranes are running in parallel	8 h	n.a	85%
Zhang *et al.* (2020)	Ion exchange membranes or bipolar membranes (Keka Polymer Materials Technology Co., Ltd)	Continuous reactor	3h	72,55%	86,17%
Gonzalez-Salgado *et al.* (2020)	TMCS module was formed by a microporous hydrophobic PTFE membrane (0.52 m^2 of surface) provided by POLYMEM	Combination of processes: screw press, dynamic cross flow nanofiltration with ceramic membranes and reverse osmosis	25 min	75%	n.a
Molinuevo-Salces *et al.* (2020)	Module of 16 membrane panels. The membrane was made of expanded polytetrafluoroethylene (e-PTFE) material (ZEUS, Orangeburg, South Carolina, USA)	Semi - continuous	7 - 20 days depending on the experiment	90 % (72 kg TAN/day)	62 % - 38.20 g TAN/(m^2·day) for 2.82 g TAN/L initial (3.2 % - 32.10 of N in $(NH_4)_2SO_4$)
Noriega-Heviaa *et al.* (2020)	X50 2.5 × 8 Liqui-Cel, Extra-flow of PP with a membrane surface of 1.4 m^2)	Two HFMC in series	15−80 min according to the operating conditions	Complete ammonium removal is achieved	36%
					44%
					53%
					85%
					89%
					92%

3.2. EXTRACTOR SOLUTION

Sulphuric acid is the mainly used extractor solution because it reacts with free ammonium to form $(NH_4)_2SO_4$, as it can be seen in Figure 3.3. H_2SO_4 is usually used because the solution of ammonium sulphate has several advantages as fertilizer, but it is possible to use another acid to recover free ammonium.

The concentration of sulphuric acid in water used to recover TAN depends on the experiment. Some researchers used a concentrated solution (96 – 98 %) but there are some with less concentration (see Table 3.1).

Normally the capture solution circulates constantly across the membrane. To keep the pH of the capture solution below 2, concentrated sulphuric acid is added so that even though $(NH_4)_2SO_4$. is formed it remains an acid solution.

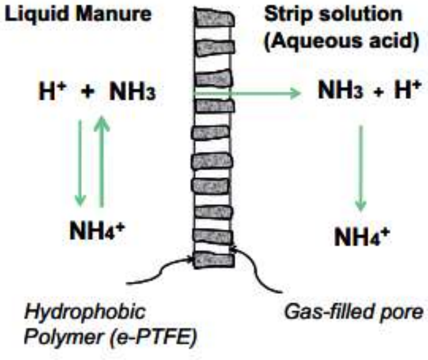

Figure 3.3: Cross section of a hydrophobic gas-permeable membrane (Garcia-(González *et al.*, 2015)

3.3. INFLUENCE OF THE SUBSTRATE PH

The initial pH of the substrate is usually between 7.5 – 8.0, which is considered too low to be able to eliminate the TAN through NH_3 selective membranes (Garcia-González *et al.,*2015, Aymà *et al.,* 2017, Molinuevo - Salces *et al.*, 2018, Zhang *et al.,* 2020). Therefore, the pH is increased with an alkaline solution, such as NaOH (mostly) or $Ca(OH)_2$. There are other techniques to increase pH, for instance a pre-aeration tank where carbon dioxide is stripped with the subsequent pH increase. When pH is higher, increased nitrogen recovery rates are recorded.

In Figure 3.4 it can be observed that as the pH increases there is more free ammonia available. In this Figure it also observed that the operating temperature also has an influence to select the working pH.

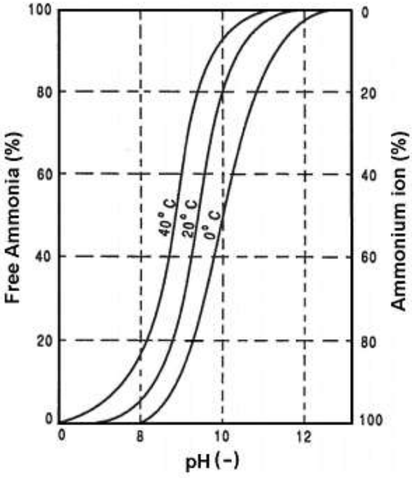

Figure 3.4: Free ammonia fraction as a function of temperature and pH (Capodaglio *et al.,* (2015)

Garcia-González *et al.* (2015) evaluated the efficiency of a selective membrane (Gas-permeable tubing made of expanded e–PTFE) when the pH of substrate was not adjusted, so the pH was lower than in other experiments. In this case, the TAN removal rate was only 57%, a very low value when compared with other experiments at controlled alkaline pH.

3.4. INFLUENCE OF THE SUBSTRATE AND TAN CONCENTRATION

The substrate to be treated could be very varied depending on the experiment. As can be seen in Table 3.1, several studies have been carried out with swine manure wastewater (from dry anaerobic digestion (Aymà *et al.,* 2017) or from wastewater treatment plant (Nagy *et al.,* 2019) or anaerobic digestion supernatant. It is important to mention that in some cases the substrate is synthetic, so it is prepared specifically to carry out the experiment and to study the impact of selected operational conditionals on the process performance.

Another aspect that should also be considered is the initial amount of TAN present in the substrate. Garcia-González *et al.* (2015) evaluated the effect of waste strength. Depending on the initial amount of TAN, more or less nitrogen would be removed and recovered: as the initial amount increased, more recovery rate was obtained. An average value of 2 g TAN/L could be considered a typical value from the different bibliographic sources consulted.

Apart from the concentration of TAN, some articles analyzed the impact on the process performance of other different components that the substrate could carry. In case that there are metal cations, such as Mg^{2+} and Ca^{2+}, it is necessary to remove them before the substrate passes through the membrane and thus avoid possible decreases in TAN recovery rate (Zhang *et al.,* 2020).

3.5. EFFECT OF TEMPERATURE

Temperature is another important parameter that influences the TAN recovery rate, and it is directly related to pH because, depending on the operating temperature, the pKa varies, modifying the ammonium – ammonia balance (see reactions 3.1 and 3.2).

$$NH_4^+ (aq) + H_2O (l) \rightleftarrows NH_3 (aq) + H_3O^+ (aq) \tag{3.1}$$

$$Ka = \frac{[NH_3]\cdot[H_3O^+]}{[NH_4^+]} \tag{3.2}$$

In case that Ka increases due to the working temperature, there is more free ammonia available so, there is more possibilities to recover it. In Figure 3.4, it can be seen the impact of temperature on the pKa value.

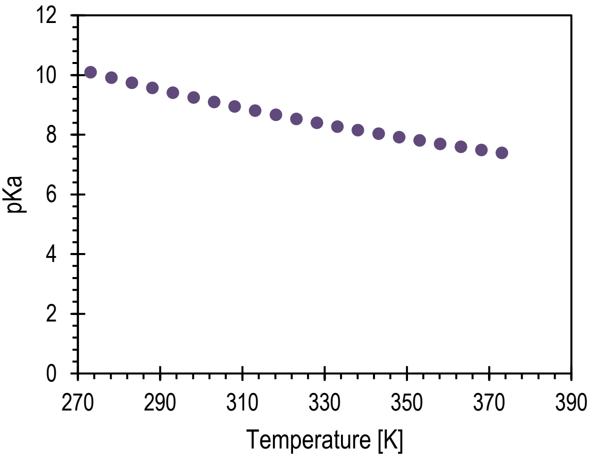

Figure 3.5: Variation of pKa of NH_4^+ - NH_3 equilibrium with temperature (Nallagounden, 1998)

As observed in Figure 3.4, a descending lineal dependence of pKa with temperature is observed and, consequently, when the temperature increases, pKa decreases and therefore is beneficial for nitrogen recovery (Bell *et al.* 2007). As stated in Table 3.1and 3.2, most of the experiments reviewed in literature are performed at room temperature or increased up to 37 ºC. Generally, as the temperature increases, the recovery rate is higher. However, this parameter has a lower effect than pH on TAN recovery rate. The effect of temperature and pH was evaluated in the study of Noriega-Hevia *et al.* (2020). In experiments where the temperature varied from 25 to 35 ºC and the pH was fixed at 10, the TAN recovery rate did not vary substantially (from 85 to 92 %) whereas in experiments where the temperature was fixed at 35 ºC and the pH varied from 9 to 10, the TAN recovery rate increased greatly (from 53 to 92%). Aymà *et al.* (2017) raised the substrate temperature to 50 ºC and this had a positive effect on the recovery of ammonium sulphate as improvements in the rate of ammonia transfer across the membrane were obtained, as well as preventing soiling. In contrast, operating costs increased by 52% compared to operating in environmental conditions.

3.6. OPERATION MODE AND OPERATION TIME

Depending on the operation mode, the reported operation time for NH_3 recovery in selective membranes units is very varied: it could be days, hours, or even minutes. In case that just a specific parameter needs to be determined, batch experiments are usually performed where operation time is relatively short.

However, when a pilot plants needs to be tested, the time increases greatly because there are many parameters that influence it. In addition, the N recovery performance must be guaranteed by operating for a test time before starting it up. In these cases, a period where the plant operates in continuous is experimented, to optimize the process. There, it can be observed different problems that may be solved to increase the yield of the operation. For example, in the experiment of Molinuevo-Salces *et al.* (2020), there is an initial period of 56 days working in continuous, where some technical problems are found and solved before the plant started to operate. This period has been done before the batch experiments in which different parameters, such as temperature or the concentration of ammonia solution obtained are done to view the effect that have on nitrogen removal and recover efficiencies. Later the pilot – scale demonstration plant was evaluated for 7 months.

3.7. CONFIGURATION OF NITROGEN RECOVERY DEVICE (SYSTEM)

Ammonia selective membranes could be configured both as single unit or multiple unit configuration. Multiple membrane units could be set up in series or in parallel as it can be seen in Table 3.2. Noriega-Hevia *et al.* (2020) studied the effect of membrane surface on nitrogen recovery rate. In this experiment two membranes were set up in series. The efficiency of each one was the same, so all the surface was used and, therefore, this paper concluded that the process was successful when using two membranes in series.

In contrast, Nagy *et al.* (2019) ran the experiment with two membranes in parallel. The percentage of TAN recovered in this experiment was 85% meanwhile the percentage obtained in the experiment where runs in series was 92%. Although the temperature of the two experiments was the same, these percentages of nitrogen recovery cannot be compared as each experiment had different conditions.

3.8. TAN REMOVAL EFFICIENCY VS RECOVERY EFFICIENCY

The TAN removal efficiency is defined as the decrease in TAN (or NH_4^+- N) concentration when compared to the initial concentration (considering that the volume of sample is maintained). Reported removal efficiencies from 57% to 94,4% could be found in specialized literature. Ideally, the removed nitrogen is recovered with an acidic solution. The TAN recovery efficiency is defined as the total amount of TAN (or NH_4^+- N) present in the extracting solution compared to the initial amount of NH_4^+ - N in the substrate. TAN recovery efficiencies from 36% to 94,4% are reported in literature and they are equal or lower values than TAN removal efficiencies.

3.9. TAN RECOVERY RATE

TAN recovery rate expresses the amount of nitrogen recovered per volume reactor and day, normally as a solution of $(NH_4)_2SO_4$, as mentioned above. This rate is called the observed recovery rate and it could also be expressed as the amount of nitrogen recovered as $(NH_4)_2SO_4$ per unit of membrane surface and day, which is called the specific recovery rate.

In the study Garcia-González *et al.* (2015) where a recovery percentage of 92% has been obtained, an observed TAN recovery rate was equal to 64 mg/(L·day). Molinuevo-Salces *et al.* (2020) recorded a specific recovery ratio of 38,20 g TAN/(m^2·day), corresponding to a 62% of TAN recovery efficiency.

4. STUDY OF A MUNICIPAL WASTEWATER TREATMENT PLANT

4.1. DEFINITION OF THE MUNICIPAL WASTEWATER TREATMENT PLANT

For this study, the municipal wastewater treatment plant (WWTP) of the work of Minini *et al.* 2015 was considered in order to study the nitrogen mass balances and to decide the stream where ammonia recovery through membranes technology could be applied.

Figure 4.1 shows the process flow diagram of the studied WWTP. As observed in this figure the influent of the plant is municipal wastewater previously pretreated prior to the primary treatment (high solids removal, sand removal, removal of fats oils and greases).

Firstly, there is a primary settling where primary sludge precipitates. In the primary settling process, part of the particulate fraction of the influent COD (slowly biodegradable and non – biodegradable) is removed. Consequently, the effluent resulting from primary sludge has a higher fraction of readily biodegradable substrate that is treated in the secondary treatment.

In secondary treatment, a biological COD and nutrient removal is performed, generating activated sludge is purged to the system, as secondary sludge. Part of the nitrogen entering to the secondary treatment is converted to atmospheric nitrogen and is discharged at low concentration with the treated liquid effluent.

The sludges from both, primary and secondary settling, are mixed and fed to the anaerobic digestion process, where biogas was produced and an anaerobically stabilized sludge is centrifuged generating, two streams. Dewatered sludge, that goes out of the system and the drains returns at the primary sludge line.

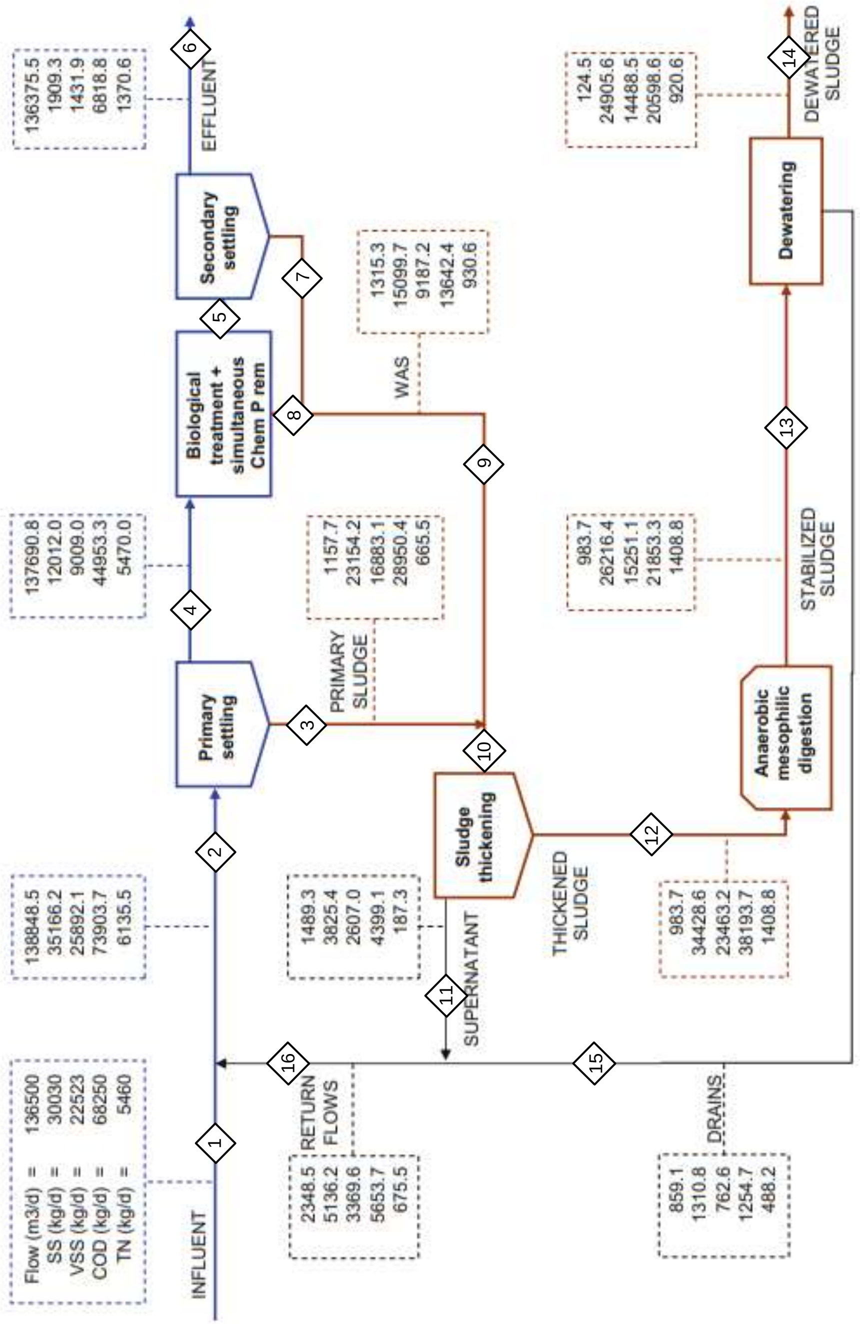

Figure 4.1: Scheme of a conventional municipal treatment plant where a mass balance is done (Minini *et al.*,2015)

The WWTP plant capacity considered is about 500.000 person equivalents (PE). As it can be seen in Figure 4.1 the influent is composed of suspended solids (SS), volatile suspended solids (VSS), chemical oxygen demand (COD) and total nitrogen (TN). Is also specified the flow rate of each stream. To determine the composition of each stream, mass balances are applied in every equipment.

For this study, it is important to focus on the total nitrogen composition of each stream. Nitrogen concentration needs to be controlled to be inside the limits of discharge. Depending on the concentration, different designs of the volumetric loading rate (VLR) for the biological tanks are assessed. The experiment that Mininni *et at.* (2015) have done demonstrated that a decrease of 26% of the VLR is needed to achieve the discharge limits proposed, in this case 10 mg N/L. So, the decrease of VLR leads to a decrease of nitrogen concentration.

It is also important to mention that in this process there is a return flow. The nitrogen percentage at the entrance and exit of the system has been compared with the return flow. If percentage of nitrogen have been done, it can be seen that in the entrance (stream 1) there is a very low percentage, 5%. There are two exits, one is the effluent, from the primary line, where the percentage is 14% and the other is the dewatered sludge, which has a very low percentage too, 2%. Compared with the return flow, stream 15, where there is a 16% of total nitrogen, the other percentage are substantially lower.

These percentage mentioned above are percentage of nitrogen present in relation of all components in stream. But for the study of advantages of implement a nitrogen removal and recovery system is important to determinate the percentage of nitrogen that goes out of the wastewater treatment plant in different ways. For the study of a wastewater treatment plant where there is no nitrogen system implemented, there are just two ways of nitrogen discharge, in form of gas as atmospheric nitrogen and in form of sludge (effluent and dewatered sludge in Figure 4.1.). So, in relation of the entrance of nitrogen, these percentage are calculated, and it can be reflected in Figure 4.2. Later the same study is going to be done for wastewater treatment plant with nitrogen removal and recovery system implemented.

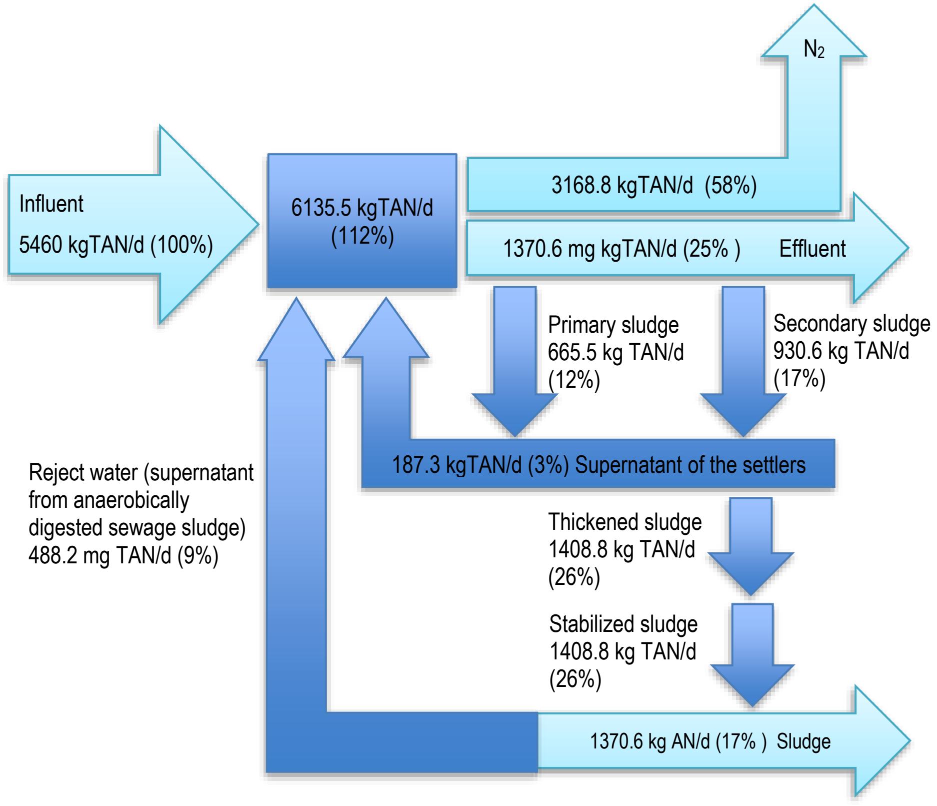

Figure 4.2: Nitrogen mass balance scheme for the municipal wastewater treatment plant (WWTP) calculated from Minini *et al.* (2015) results. The percentage of nitrogen in the influent and effluents of the process are shown.

4.1.1. Selection of the internal stream for nitrogen recovery through membranes

The nitrogen removal system with selective membranes could be implemented where the highest nitrogen concentration is present in the stream. The stream where there is the highest percentage of nitrogen, based in the diagram from Figure 4.1, is the streams 15 (Drains). At this stream, the percentage of nitrogen in the steam is 16%.

Nitrogen needs to be removed from wastewater. There are two principal reasons, explained in Chapter 1, eutrophication, and limits from nitrogen discharge. If total nitrogen is removed from the system, the primary sludge line has less nitrogen, these problems could be avoided.

This is the main objective to implement a nitrogen removal system but there are others:

- High temperature: temperature of the substrate needs to be high to move ammonium – ammonia balance and facilitate nitrogen removal. Anaerobic digestion is carried out at 30 ºC, so at this point after anaerobic digestion substrate has this temperature. A high temperature favors more nitrogen recovery.
- $NH_3/Co_3{}^{2-} = 1/1$: molar relation between ammonia (NH_3) and carbonate ($Co_3{}^{2-}$) needs to be 1/1 because, at this relation, alkalinity from carbonate remains the pH constant.
- COD eliminated: most of the COD is degraded in primary settling, so microorganisms cannot feed and therefore do not grow. If microorganisms grew up inside the membrane, the membrane became useless.

4.2. DESIGN OF NITROGEN REMOVAL AND RECOVERY SISTEM

Once the point, where nitrogen removal will take place, is found it is necessary to design the best configuration to carry out. At first place, it is important to consider that the substrate that is used is sludge from a wastewater treatment plant.

4.2.1. Pretreatment of the selected stream

For the pretreatment is considered that all the SS and VSS precipitates in the pretreatment with a rotary filter, therefore are eliminated before nitrogen removal. After the precipitation, SS and VSS goes to anaerobic digestion. As a consequence of the precipitation, the amount of COD and TN present in the substrate can be calculated. It is supposed that the composition of VSS is the same as the biomass activated approximately, so the mass relation between COD and VSS is 1.42 mg COD/mg VSS and the mass relation between TN and COD is 0.086 mg TN/COD. In Table 5.1 the composition of the stream before and after the pretreatment is shown. The flowrate is considered the same because all the COD present in the entrance of the treatment is the same and the concentration the concentration of nitrogen is low so, the grow of nitrifying biomass is insignificant.

Table 4.1: Characterization of wastewater stream before and after the pretreatment

	Before pretreatment	After pretreatment
Flowrate (m^3/d)	859.1	859.1
pH	8.3	10
Concentration in mg/L		
SS	1525.8	0
VSS	887.7	0
COD	1460.5	200
TN	568.3	442.7
TAN	442.7	437
PO_4^{3-}	30	0

After pretreatment, the stream is prepared to nitrogen removal and recovery. In this part, first part phosphate needs to be eliminated and pH and temperature conditions adjusted. As it can be seen in Table 5.1 in the stream there is no longer SS or VSS because they precipitate in pretreatment. Consequently, part of COD has also precipitated. The other part is considered that is non – biodegradable, so microorganisms cannot grow up inside the membrane and reduce its efficiency.

As it said before, this stream could have presence of phosphate and calcium or magnesium, so in order to prevent struvite or hydroxyapatite formation which could bring problems related to membrane clogging, causing the decrease of the membrane efficiency, it has also been chosen to implement a struvite precipitation system.

Struvite is composed of $NH_4MgPO_4 \cdot 6H_2O$, where it is observed that it also includes nitrogen, but its proportion is less than the total nitrogen present in the stream. Consequently, the initial concentration of total nitrogen considered is the same after the struvite precipitation system. Concentration of phosphate in the stream is considered 30 mg/L approximately, so if there is a relation 1/1 between PO_4^{3-} and NH_4^+, the concentration of NH_4^+ that precipitates is 5.7 mg NH_4^+/L. As it can be seen the concentration of NH_4^+ that precipitates is very low in comparation with the concentration of PO_4^{3-} . Struvite is obtained as a product, with fertilizing power. Temperature and pH need to be controlled in struvite precipitation. This process takes place in a stirred tank, which is the most common tanks used in industry for struvite precipitation due to its easiest set – up and operate.

As it is explained in Chapter 3, it is beneficial to increase the pH in the substrate to increase efficiency of the nitrogen removal. Substrate, in this case wastewater, normally has a pH between 7.5 to 8, so first, pH needs to be increased. To obtain a high percentage of nitrogen removal, it is chosen a pH value of 10. Experiment runs in continuous during 20 days. Consequently, as the substrate continues feeding the tank, pH decreases. It is necessary to implement a pH meter, to control pH. Whenever pH decreases, NaOH concentrated is added to the substate. Doing this, pH could remain constant, and a high percentage of nitrogen removal is obtained. In bibliographic research there is no information about the amount of NaOH needed to maintain pH at 10. So, laboratory experiments to determinate this parameter needs to be done.

Temperature does not need to be increased, because stream from anaerobic digestion it is at 30 ºC, so as it can be seen in Chapter 3, this temperature is enough to achieve a high percentage of nitrogen removal. Doing this, operation cost is chipper because, there is no need to implement a system to raise the temperature.

Figure 5.1 shows the steps before the selective membrane treatment where a pretreatment, which is explained before, is implemented.

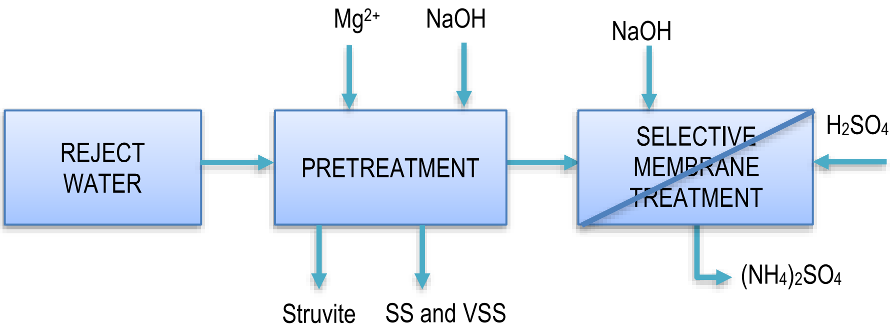

Figure 5.1. Block diagram of the proposed process for phosphorus and ammonia recovery

4.2.2. Selective membrane system

To remove total nitrogen a tubular gas – permeable membrane is chosen (Garcia-González *et al.,* 2015, Molinuevo - Salces *et al.,* 2018). Membrane is made of e – PTFE (expanded polytetrafluoroethylene). The e – PTFE material is chosen because this material avoids corrosion from the acid which passes through the membrane.

The experiment consists in two tanks. One of them it is filled with wastewater, which had the ammonia that is going to be captured. In the other tank, an acid solution is needed for nitrogen recovery. The nitrogen removed is recovered to take advantage of its properties. The capture solution chose is sulphuric acid because ammonium sulphate ($(NH_4)_2SO_4$) has a lot of advantages as fertilizer. Some of them are that nitrogen concentration is an easy spreadable solution and the reduction of transportation cost, N pollutions and NH_3 emissions. In both tanks a pH meter is included to control pH. As it was said before, a control of pH can increase the efficiency of nitrogen removal and recovery.

The system runs in continuous, so wastewater is feeding in the tank meanwhile nitrogen is removed and recovered. Acid solution needs to be a pH less than 2, because although ammonium sulphate is formed, the solution remains being acid. So, a concentrated solution of sulphuric acid (H_2SO_4) is introduced whenever pH solution decreases below 2.

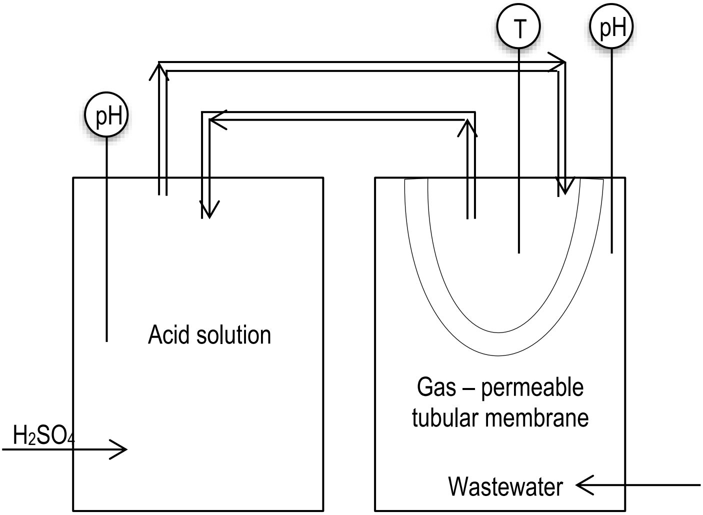

Figure 5.2. Scheme of selective membrane system proposed

Selective membrane system has a 90% of nitrogen removal, so the concentration of nitrogen to 437 mg TAN/L o 43.7 mg TAN/L. Later as it mentioned before, nitrogen is recovered as ammonium sulfate. There is a percentage of nitrogen recovery of 95%, therefore, the concentration of nitrogen recovered is 373.6 mg TAN/L. To accomplish these percentage a membrane surface of 50 cm^2 is needed. This surface is based in Garcia – Gonzalez *et al.* 2015 paper, considering the amount of nitrogen needed to remove and recovery in this study. A summary of the characteristics of selective membrane system are reflected in Table 4.1.

Table 4.1: Characterization of selective membrane treatment proposed

Substrate	Wastewater
Initial concentration of TAN [mg/L]	437 mg TAN/L
Temperature [ºC]	30
Extractor solution (pH)	H_2SO_4
Substrate pH and control	8.3 increased to 10 with NaOH
Membrane	Gas - permeable membrane in tubular shape made of e - PTFE
Operation mode	Continuous
HRT (Continuous operation)	20 days
% TAN removal	90%
% TAN recovery as $(NH_4)_2SO_4$	95%

4.3. NITROGEN BALANCE IN THE WWTP WITH AND WITHOUT SELECTIVE MEMBRANE TREATMENT

To see the result of the implementation of a selective membrane treatment the balances of nitrogen in the wastewater treatment plant have been repeated. In both systems, concentration of nitrogen in effluent is 10 mg TAN/L approximately, so it already accomplishes nitrogen discharge limits. In contrary percentage of nitrogen discharged as atmospheric nitrogen is reduced because as selective membrane system is implemented, the concentration of nitrogen in rejected water decreases.

Figure 5.2 shows the same depicts as wastewater treatment plant but with a selective membrane treatment implemented.

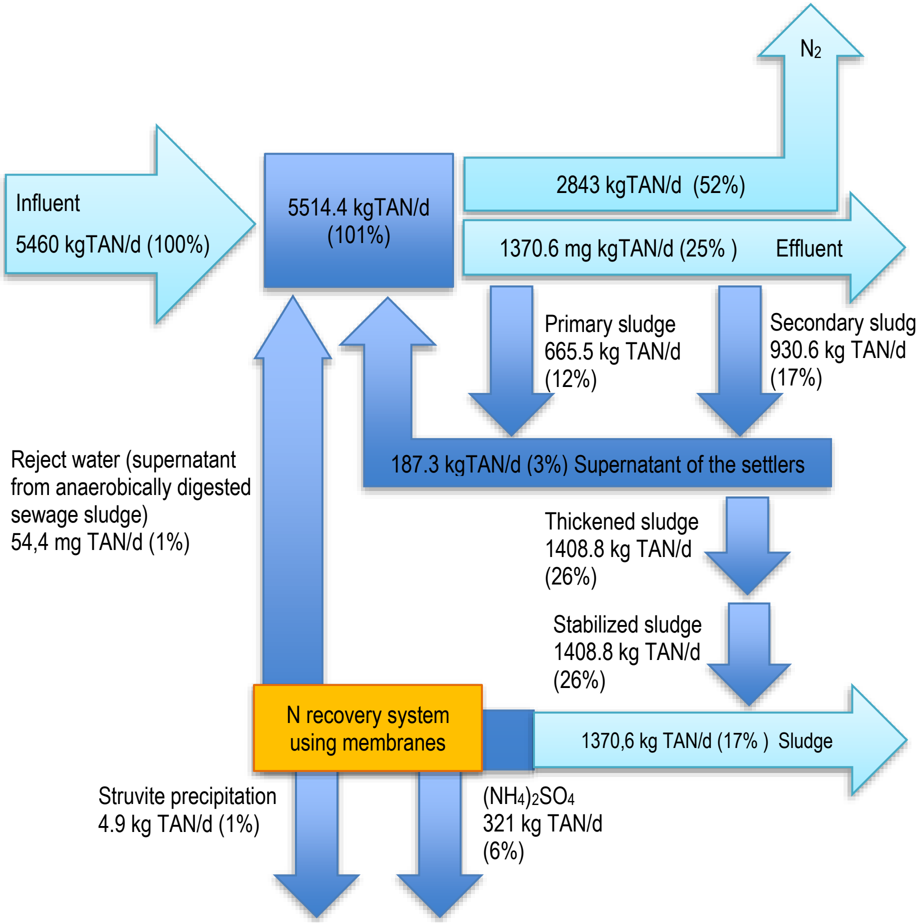

Figure 5.2: Percentage of nitrogen in all streams for wastewater treatment plant when a selective membrane treatment is implemented to treat reject water for nitrogen recovery calculated from Minini *et al.* (2015) results and considering the recovery yield proposed in this study.

When the results of nitrogen mass balance using selective membranes (Figure 5.2) are compared to the results of the conventional wastewater treatment plant (Figure 4.2) all streams have the same percentage of nitrogen without and with selective membrane treatment, but the percentage of nitrogen discharged in form of atmospheric nitrogen with a selective membrane treatment is implemented is lower than without it. As a consequence, the wastewater treatment plant can complete with discharge limits of sensitive areas, and eutrophication can be avoided, because the concentration of nitrogen is reduced.

This treatment could be implemented to reduce carbon footprint from wastewater treatment plant, the energy demand and the sludge production associated to this savings. However, nitrogen removal and recovery with selective membranes is a very new technology that needs to be continued studied in depth. In this study cost operation of this experiment is not calculated. Also, laboratory experiments for determinate some parameters are not included in the objective of the study. These could be the objectives for a future study.

5. CONCLUSIONS

In this work, a possible implementation of ammonia selective membrane treatment in a municipal wastewater treatment plant (WWTP) has been studied yielding promising results that could be further studied at lab scale. To accomplish with the cannons of circular economy, this nitrogen is recovered as a solution used as a fertilized due to its beneficial properties.

More concisely, the main conclusions of this study are the following:

- From bibliographic research a high percentage of nitrogen removal and recovery could be achieved (between 63 to 95%) by using a selective membrane contactor. Most of the experiments used a gas – permeable tubular membrane made of e – PTFE, where it is observed that there are some optimal conditions where the percentage of nitrogen removal and recovery are higher, such as the increase of pH and temperature.
- From the study of the nitrogen mass balance in a municipal wastewater treatment plant, the stream where selective membrane treatment for nitrogen removal and recovery could be implemented is found. This stream is the reject water from anaerobically digested sewage sludge characterized by a high percentage of nitrogen present, pH around 8 and a molar ratio of 1 between ammonia and carbonate and mesophilic temperature.
- A selective membrane treatment is proposed based in all the information read in the references. A percentage of nitrogen removal of 90%, of which 95% recovery in the form of ammonia sulfate are stablished with 50 cm^2 of surface membrane. These yields are achieved with a continuous experiment of 20 days. With selective membrane treatment proposed, nitrogen could be recovered as ammonium sulphate and the conversion of total ammoniacal nitrogen present in the influent to the municipal wastewater to nitrogen gas could be reduced from 58% to 52%. In addition, the wastewater treatment could accomplish more easily the strict nitrogen discharge limits in sensitive areas, since the recovery of ammonia in reject water decreases the nitrogen load in the secondary treatment of the wastewater line of the plant.

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ACRONYMS

AT: Absorption tower

CF: Coagulation – flocculation

COD: chemical oxygen demand

e-PTFE : expanded polytetrafluoroethylene

HFMC: hollow fibre membrane contactors

HRT: hydraulic retention time

N: Neutralization

PE: Person equivalents = 273 L/d of wastewater with 220 mg/L of suspended solids (SS), 500 mg/L of COD, 40 mg/L of total nitrogen (TN) and 5.5 mg/L of total phosphorus (TP)

SED: Sedimentation

SS: suspended solids

ST: Stripping tower

TAN: total ammoniacal nitrogen

TMCS: transmembrane chemisorption

TN: total nitrogen

TS: total solids

VLR: volumetric loading rate

VSS: volatile suspended solid