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Recovery of ammonia from anaerobic digester centrate to produce ammonium nitrate

Recuperació de l'amoni dels centrats de la digestió anaeròbia per a produir nitrat amònic

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No great discovery was ever made without a bold guess.

Isaac Newton

Agrair a tots els professors que he tingut, tant a la universitat com fora d'aquesta, per haver fomentat, encara que alguns més i altres menys, el desenvolupament de la meva curiositat. També agrair-los que m'hagin format com a professional i com a persona, realitzant una tasca que no es pot valorar mai suficient.

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SUMMARY

Ammonia runoff and subsequent accumulation in water sources leads to eutrophication, while on the other hand, NH_3 is a valuable chemical for use in agricultural fertilizers and in the chemical industry. Most of the practices for NH_3 production are energy intensive and contribute to global warming, therefore, developing new methods for removal and recovery of NH_3 it's an interesting line of research. Although most lines of research are working with Forward Osmosis (FO) processes, using gas-permeable hydrophobic membranes, there may be a better solution with not hydrophobic membranes.

In this project, an alternative process was studied. Instead of using a hydrophobic membrane, it was used a water-permeable membrane for the FO process. Instead of the acid solution, an ammonium nitrate high concentrated solution will be used. These type of solutions are typically used to fertilize crops. Farmers, instead of diluting the solution in water before using it, will get free ammonium nitrate and water to enlarge their quantity of fertilizer, and the Waste Water Treatment Plant (WWTP) will get rid of ammonia and an excess of Waste Water (WW). Beyond enhancing circular economy, ammonia concentration in WW will be significantly reduced, limiting the effects of eutrophication.

First, an exhaustive research of FO ammonia recovery's actual situation was carried out, showing that the majority of research lines are working with hydrophobic membranes.

Then, Reverse Osmosis (RO) simulated experiments were carried out with ROSA software to obtain the membrane parameters.

With the results obtained, FO simulated experiments were carried out with Visual MINTEQ (VM) and an own created mathematical model, which gave promising results about water and ammonia reduction in the feed solution.

Keywords: Ammonia, Forward Osmosis, Waste Water

RESUM

L'abocament d'amoníac i la seva conseqüent acumulació a les fonts d'aigua condueixen a la eutrofització, mentre que d'altra banda, l' NH_3 és un valuós producte químic que s'utilitza en fertilitzants agrícoles i en la indústria química. La majoria dels processos per generar l'amoníac tenen un alt cost energètic i contribueixen a l'escalfament global, i per tant, el desenvolupament de noves tècniques per recuperar-lo és una línia de recerca interessant. Encara que la majoria de les investigacions en aquesta direcció treballen amb processos d'Osmosi Directa, utilitzant membranes hidrofòbiques permeables al gas, una millor solució podria ser la utilització de membranes no hidrofòbiques.

En aquest projecte, s'ha estudiat un procés alternatiu. Enlloc d'utilitzar una membrana hidrofòbica, s'ha investigat la utilització d'una membrana no hidrofòbica en el procés d'Osmosi Directa. En comptes d'una solució àcida que absorbeix l'amoníac, s'ha utilitzat una solució concentrada de nitrat d'amoní. Aquest tipus de solucions són àmpliament utilitzades per fertilitzar conreus. Els agricultors, enlloc de diluir la solució en aigua abans d'utilitzar-la, podrien adquirir nitrat d'amoní i part de l'aigua de sortida de la planta de manera gratuïta. A més, la planta de tractament d'aigües residuals podria desfer-se de gran part de l'amoníac que emet a l'exterior, així com reduir la quantitat d'aigües residuals que genera. Més enllà de fomentar l'economia circular, la concentració d'amoníac a la sortida de la planta es veuria reduïda significativament, limitant els efectes de l'eutrofització.

Primer, s'ha realitzat una recerca bibliogràfica sobre la recuperació de l'amoníac mitjançant tècniques d'Osmosi Directa, mostrant que la majoria estan treballant amb membranes hidrofòbiques.

Després, s'ha realitzat la simulació d'experiments d'Osmosi Inversa utilitzant el software comercial ROSA per obtenir els paràmetres necessaris de la membrana que es volia utilitzar.

Amb els resultats obtinguts, s'ha realitzat la simulació d'experiments d'Osmosi directa utilitzant el software Visual Minteq (VM) i un model matemàtic de creació pròpia, que ha donat resultats prometedors sobre la reducció de l'amoníac i de l'aigua a la solució inicial.

Paraules clau: Amoníac, Osmosi directa, Aigües residuals

INTRODUCTION

Ammonia (NH_3) emissions to the atmosphere and water sources are an environmental quality problem because they can contribute to eutrophication of surface waters, nitrate contamination of ground waters, and deteriorate air quality.

Ammonia runoff and subsequent accumulation in water sources leads to eutrophication and destruction of marine habitats [1], while on the other hand, NH_3 is a valuable chemical for use in agricultural fertilizers and in the chemical industry. The majority of the practices for NH_3 production are energy intensive and contribute to global warming [2], therefore, developing new methods for removal and recovery of NH_3 from swine manure it's an interesting line of research, desirable for environmental and economic reasons.

Among technologies that focus on NH_3 emission capture and treatment, some are focused on the recovery of the nitrogen for further use. These technologies include:

- 1) Wet scrubber and stripping technologies (proposed for ammonia removal from swine manure WW) [3]; [4]; [5].
- 2) Struvite precipitation with phosphate and magnesium [6].
- 3) Reverse osmosis using osmotic pressure [7].
- 4) Ion exchange adsorption with zeolites [8]
- 5) A gas-permeable membrane process at low pressure [9].

This project is focused on gas-permeable membrane processes, which characteristics will be discussed along the document.

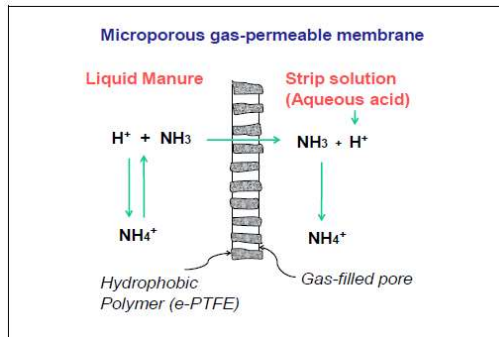


Figure 1 Basic process of gas permeable membrane ammonia recovery [10]

This section describes in detail what the eutrophication is and the problems it causes, as well as the current state of the natural N reserves. It also explains the process of anaerobic digestion from which the gas-membrane processes obtain the high strength ammonia WW that will be treated, as well as the fertilizing characteristics of ammonium nitrate. The last topic explained in this introduction will be the different osmosis processes that are available nowadays.

1.1. EUTROPHICATION

P (phosphorus) and N (nitrogen), mainly as phosphate and nitrate respectively, are considered responsible of eutrophication degradation. Eutrophication is an enrichment of water by nutrient salts that causes structural changes to the ecosystem such as: increased production of algae and aquatic plants, depletion of fish species, general deterioration of water quality and other effects that reduce and preclude use [10].

Natural eutrophication is a slow and irreversible process. Nevertheless, it is the anthropogenic causes that accelerate this process, despite in this case it can be reversible if the contribution of nutrients is stopped.

1.2. NATURAL SOURCES OF N

Nitrogen [30] is one of the primary nutrients critical for the survival of all living organisms. It is a necessary component of many biomolecules, including proteins, DNA, and chlorophyll. Although N is very abundant in the atmosphere as dinitrogen gas (N_2), it is largely inaccessible in this form to most organisms, making N a scarce resource and often limiting primary productivity in many ecosystems. Only when N is converted from dinitrogen gas into ammonia (NH_3) it becomes available to primary producers, such as plants.

In addition to N_2 and NH_3 , N exists in many different forms, including both inorganic (e.g., ammonia, nitrate) and organic (e.g., amino and nucleic acids) forms. Thus, N undergoes many different transformations in the ecosystem, changing from one form to another as organisms use it for growth and, in some cases, energy. The major transformations of N are fixation, nitrification, denitrification, anammox, and ammonification. The transformation of N into its many oxidation states is key to productivity in the biosphere and is highly dependent on the activities of a diverse assemblage of microorganisms, such as bacteria, archaea, and fungi.

1.3. AMMONIUM NITRATE

Ammonium nitrate (NH_4NO_3) is a white crystal solid and highly soluble in water, consisting of equimolar amounts of ammonium and nitrate. It is widely used in agriculture as a high-nitrogen fertilizer. It is also used to manufacture explosives as it acts as a strong oxidizing agent. In particular, ammonium nitrate is used to prepare an industrial explosive called ANFO (ammonium nitrate fuel oil), which is composed of 94% ammonium nitrate and 6% fuel oil. Ammonium nitrate forms according to the general reaction shown below:

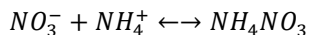


Table 1 Physical and Chemical properties of solid Ammonium nitrate [31], [32]:

Property	Value
CAS	6484-52-2
Physical state and appearance	Solid (white granular solid)
Molecular weight	80,05 g/mole
Decomposition temperature	210°C
Melting point	169,6°C
Specific gravity	1,725
Solubility in water (0°C)	119 g/100 mL
Thermal diffusivity	$1,8 \cdot 10^{-7}$ m ² /s

1.3.1. Ammonium nitrate as a fertilizer

Fertilizers are substances that increase the fertility of the land. Plants need to take from the soil the elements that, in the right proportions, are essential to achieve their normal development. The lack of these elements can be corrected by simple addition to the floor compounds that contain elements as N, P, K, S, Ca or Mg, which together with carbon and hydrogen, are elements that are in greatest proportion in vegetables.

Ammonium nitrate was the first solid N fertilizer produced at a large scale. Since plant roots do not directly absorb the urea form of N to a large extent, ammonium nitrate is an efficient and immediate source of plant nutrition. It provides half of the N in the nitrate form and half in the ammonium form. The nitrate form is mobile in the soil water and immediately available for plant uptake. The ammonium portion provides a delayed supply of N to the crop. It is often used for in season top-dressing of N according to crop demand. Because of its high density it can be evenly spread across wide distances.

1.4. ANAEROBIC DIGESTION

The water sources used for most of these ammonia recovery processes are digested liquid swine manures obtained from anaerobic digestion WW.

Anaerobic digestion is a series of biological processes that use a diverse population of bacteria to break down organic materials into biogas, primarily methane, and a combination of solid and liquid effluents, the digestate. It occurs in the absence of free oxygen. Sources of organic material for anaerobic digestion include dairy manure, food processing waste, plant residues, and other organic wastes such as municipal WW, food waste, fats, oils, and grease [16].

The end product biogas is composed of methane (CH_4 , typically 60-70% by volume) and carbon dioxide (CO_2 , typically 30-40% by volume) as well as small amounts of H_2S and other trace gases. Biogas can be combusted to generate electricity and heat or processed into renewable natural gas and transportation fuels.

Separated digested solids can be composted, utilized for dairy bedding, applied to croplands, or converted into other products. Digested liquid, which contains fewer pathogens and weed seeds and is rich in crop nutrients, can be directly used as agricultural fertilizer or by an osmosis process, be concentrated into a more effective fertilizer.

The process can be divided into four steps:

- 1) **Hydrolysis:** The first step, hydrolysis, occurs as extracellular enzymes produced by hydrolytic microorganisms (for example, cellulase, amylase, protease, and lipase) decompose complex organic polymers into simple, soluble, monomers.
- 2) **Acidogenesis:** The small molecules resulting from hydrolysis are converted by acidogens (fermentative bacteria) to a mixture of volatile fatty acids such as acetic, propionic, and butyric acids and other minor products such as hydrogen, carbon dioxide, and acetic acid.
- 3) **Acetogenesis:** In the third step, acetogenic bacteria further convert the volatile fatty acids to acetate, CO_2 , and/or hydrogen (H_2).
- 4) **Methanogenesis:** Step 3 provides substrates for methanogenesis, the last step in the anaerobic process for methane production.

1.5. OSMOSIS

Osmosis is a physical phenomenon that has been exploited by human beings since the early days of mankind [17] (ex. Use salt to preserve meat). There are three types of applications in the industry of this physical phenomenon.

However, FO has been developing rapidly in recent years and demonstrated its advantages in various applications [18].

1.5.1. Reverse osmosis

Reverse osmosis is the reverse process of osmosis. The driving force of the RO process is the hydraulic pressure that is used to oppose and overcome the osmotic pressure of an aqueous feed solution.

1.5.2. Pressure-retarded osmosis

Pressure-retarded osmosis can be viewed as an intermediate process between FO and RO, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient (similar to RO). However, the net water flux is still in the direction of the concentrated draw solution (similar to FO) [17].

1.5.3. Forward osmosis

FO has been developing rapidly in the last decade and demonstrated its advantages in various applications [18]. Basically, it is the transport of water from a solution of greater chemical potential of water to a solution of lower chemical potential of water separated by a selectively permeable membrane that allows the passage of water and rejects most molecules or ions of solute driven by a difference in osmotic pressure. The driving force in this case is the difference in osmotic pressure.

1.6. GAS-PERMEABLE MEMBRANES AMMONIA RECOVERY

The research started focusing on gas-permeable membranes, one of the most interesting techniques for recovery of ammonia. Gas-permeable membranes have been used in membrane oxygenator devices to imitate the function of the lungs in cardiopulmonary bypass, to add oxygen to, and to remove carbon dioxide from the blood (Gaylor, [23]). They have also been used to provide waterproof and breathable fabrics in sportswear and footwear (Gore-Tex® products). Brose and Van Eikeren [22] used gas-permeable membranes in a method for removal of toxic ammonia formed during the culturing of mammalian cells. Weiss et al. [24] used gas-permeable membranes to efficiently aerate surface waters by transferring oxygen without bubble formation.

The gas-permeable membrane process consists of the passage of gaseous NH_3 through a

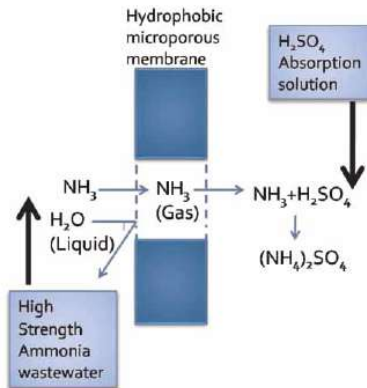


Figure 2 Principle of ammonia removal in gas permeable membrane contactor System [24]

microporous hydrophobic membrane and subsequent capture and concentration in an acidic stripping solution on the other side of the membrane. The membrane is submerged in the liquid manure and the NH_3 is removed from the liquid before it escapes into the air [9]; [10]. The NH_3 permeates through the membrane pores reaching the acidic solution located on the other side of the membrane. Once in the acidic solution, NH_3 combines with free protons to form non-volatile ammonium (NH_4^+) ions that are converted into a valuable NH_4^+ + salt fertilizer (usually sulphates). The process is responsive to increased pH through addition of alkali chemicals [12], as long as it deprotonates ammonium (NH_4^+), which leads to an increased release of NH_3 from the manure and capture by the membrane.

Gas-permeable membranes have been shown to effectively recover up to 98% of NH_4^+ from liquid swine manure [9]; [11]; [12]. Zarebska et al. [13] reviewed the pros and cons of six ammonia recovery methods including nanofiltration, RO, gas-permeable membrane process (membrane distillation), air stripping, zeolite ion exchange, and struvite chemical precipitation and indicated the energy consumption for the gas-permeable membrane process was among the lowest.

Furthermore, on the last 10 years, the prices of gas-permeable membranes have come down, so its use for recovering ammonia is now much more cost effective.

Several studies have been using tubular expanded polytetrafluoroethylene (ePTFE) membranes, due to its hydrophobic nature, only allowing ammonia permeate to the acidic solution on the other side of the membrane.

After exhaustive bibliographical research, these are the main parameters extracted for this processes:

1. Gas membranes are always hydrophobic, usually from polytetrafluoroethylene (ePTFE), although there are some alternatives as polypropylene (PP) and polyvinylidene fluoride (PVDF).
2. The alkaline solution consists of a low concentrated ammonium chloride solution, or swine manure with high ammonia concentration, at high pH (7-11, 5).
3. The acid solution normally consists of a low concentrated sulphuric acid solution, although hydrochloric acid can be used as well (to form ammonium chloride), at very low pH.

These main parameters are developed in the following table:

Table 2 Comparative table from different gas membrane processes

Article	Membrane	Alkaline solution	pH	Acid solution	pH	Experience	Maximum Ammonia removal
D(2006)_199_172-174 [26]	Polypropylene (PP)	Decarbonised ammonia solution	Best result → 11.5	H ₂ SO ₄ (1% w/w)		Experiment	
JEM(2010)_92_121-130 [27]	Microporous hydrophobic membrane	Ammonium chloride 0,01-0,12 M	Best result → 10.5	H ₂ SO ₄		Simulation	100%
JMS(2006)_271_59-68 [28]	Polyvinylidene fluoride (PVDF)	Ammonium chloride	8 – 12 Best result → 10	H ₂ SO ₄ 0,05 M		Experiment	80%
JEM(2015)_152_19-26 [12]	Polytetrafluoroethylene (ePTFE)	Swine manure (0,2 M)	7 – 9	H ₂ SO ₄ 1 M	<1	Experiment	67%
M(2017)_7(59)_1-13 [29]	Polytetrafluoroethylene (ePTFE)	Ammonium chloride different concentrations	7 – 8,9	H ₂ SO ₄ 0,001 M	2	Experiment	12,8%
WEF(2011)_NR&M_659-667 [10]	Polytetrafluoroethylene (ePTFE)	Ammonium chloride (0,02 M)	10	HCl 0,03 M	1,5	Experiment	50%
WM(2015)_38_455-461 [13]	Polytetrafluoroethylene (ePTFE)	Swine manure (0,12 – 0,16 M)	8,5 - 9	H ₂ SO ₄ 0,5 M		Experiment	55% without pH correction 92% with pH correction
WM(2016)_49_372-377 [15]	Polytetrafluoroethylene (ePTFE)	Swine manure (0,13 – 0,18 M)	8,5 - 9	H ₂ SO ₄ 0,5 M		Experiment	97%
WST(2011)_63_2944-2948 [25]	Polytetrafluoroethylene (ePTFE)	High Strength Ammonia WW (0,02 – 0,07 M)	11	H ₂ SO ₄ (10% w/w)		Experiment	80%

2. OBJECTIVES

The main aim of this Project is to study an alternative FO process for N recovery as a fertilizer (ammonium nitrate) from a synthetic WW anaerobic digestate.

After the previous research, an alternative process was studied. Instead of using a hydrophobic membrane, through which water does not permeate, use a water-permeable membrane for the FO process. Instead of the acid solution, an ammonium nitrate high concentrated solution will be used. These type of solutions are typically used by farmers to fertilize their crops.

Instead of diluting the solution in water before using it, farmers will get free ammonium nitrate and water to enlarge their quantity of fertilizer, and the WWP will get rid of ammonia and an excess of WW. Beyond enhancing circular economy, ammonia concentration in WW will be significantly reduced, and as explained before in chapter 1.1, limiting the effects of eutrophication.

To achieve this, there are different specific objectives:

- Study how to use the DuPont and Dow Reverse Osmosis System Analysis (ROSA) software [19] for getting membrane parameters.
- Find the ammonia permeability parameters and other characteristics from a sea water desalination RO membrane SW30HR-380.
- Study the viability of not hydrophobic membranes in FO processes.
- Study the effect of the parameters that influence ammonia's flux in a FO: pH and Osmotic pressure.

3. METHODS AND MATERIAL

3.1. SOFTWARE

The software used to simulate the experiments are ROSA, SMath and Minteq that are described in this section.

3.1.1. ROSA ver. 9.1

Reverse Osmosis System Analysis (ROSA) is a freeware model for the calculation of RO processes developed by DuPont, using The Dow Chemical Company's membranes [19]. It combines easy-to-use menus and options with a complex mathematical model which is hidden from the costumer, only showing the inflow and outflow characteristics, as a "black box" software. It is the most commonly used software by the RO industry around the world. This software was used for the computational simulation of ammonia RO processes.

3.1.2. SMath Studio ver. 0.99

SMath Studio [20] is a freeware mathematical program WYSIWYG editor and complete units of measurements support. This software was used for computational calculation of membrane parameters based on ROSA's feedback and FO simulation process.

3.1.3. Visual Minteq ver 3.1

Visual Minteq ver 3.1 (VM) is a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria, and other parameters for natural waters. It combines state-of-the-art descriptions of sorption and complexation reactions with easy-to-use menus and options for importing and exporting data from/to Excel [21]. This software was used for the computational simulation of FO processes.

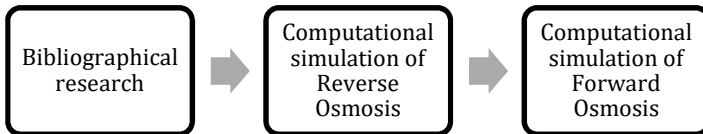
3.2. EXPERIMENTAL PROCEDURE

The main objective of the project is to study an alternative FO process for N recovery as a fertilizer (ammonium nitrate) from a synthetic WW anaerobic digestate.

First of all, an exhaustive bibliographical research was made about the current situation of FO processes in WW treatment.

Secondly, different simulated experiments were carried out to obtain the membrane parameters and other characteristics from a RO process. These experiments were carried out with ROSA and SMath Studio.

Thirdly, using the parameters obtained on the RO experiments, different FO simulated experiments were carried out to determinate the viability of not hydrophobic membranes, besides pH and osmotic pressure optimal conditions. These experiments were carried out with SMath Studio and VM.



3.3. GAS-PERMEABLE NOT HYDROPHOBIC MEMBRANES AMMONIA RECOVERY

3.3.1. Parameters of ammonia recovery

As in case of hydrophobic membranes, pH and osmotic pressure in both vessels will be the main parameters of ammonia recovery, in addition to the membrane parameters such as permeability (L_A , L_B).

3.3.1.1. pH

The solution pH is one of the most influential parameters for ammonia as it controls the $\text{NH}_3/\text{NH}_4^+$ equilibrium, and for instance, the ammonia concentration in each vessel. It will be stabilized by ammonium bicarbonate ($(\text{NH}_4)\text{HCO}_3$) in the alkaline solution and by nitric acid (HNO_3) in the acid solution.

In the alkaline solution the $\text{NH}_3/\text{NH}_4^+$ balance will be tilted towards the ammonia, whereas in the acid solution it will be tilted towards the ammonium. As explained later in this document, the difference of concentrations for both species will be the driving force in this process.

3.3.1.2. Osmotic pressure

Osmotic pressure is defined as the pressure that must be applied to the solution side to stop fluid movement when a semipermeable membrane separates a solution from pure water. The osmotic pressure for dilute ideal solutions obeys Van't Hoff's law:

$$\pi = n \cdot R \cdot T \cdot C_A \quad [Pa] \quad (1)$$

Where

n is the number of species

C_A is the salt concentration, mol/m^3

R is the gas constant, where $R = 8.314 \text{ J}/\text{mol}\cdot\text{K}$

T is the absolute temperature, K

Osmotic pressure's difference between vessels is the driving force in FO processes. In our case of study, osmotic pressure will be greater in the acid solution, which will enhance the water flux through the membrane from the alkaline solution.

3.3.1.3. Permeability

A membrane's species permeability is the facility which a molecule has to go through the membrane. Depending on the membrane and the solute, permeability may depend on solute size, solubility, properties, or chemistry. How the membrane is constructed to be selective will determine the permeability.

As will be explained in 4.1.2, our membrane's ammonia and water permeability will be estimated by ROSA simulations.

4. COMPUTATIONAL SIMULATION

After the exhaustive bibliographical research, and as explained in chapter 3.3, an alternative process was decided to be studied. A series of ROSA simulated experiments were carried out to obtain certain parameters of the membrane, and they were used to simulate FO processes.

ROSA's freeware is only able to simulate RO processes. As membrane parameters do not depend on the type of process, they were estimated and used later on to simulate FO processes with Smath Studio and VM.

4.1. WATER AND AMMONIA PERMEABILITY

As explained before in chapter 3.3.1.3, permeability is a very complex parameter which depends on several parameters and experimental conditions. However, as desalination membrane equations show below, it should not depend on pH:

$$N_B = L_B \cdot (\Delta P - \sigma \cdot \Delta \pi) \left[\frac{\text{mol } B}{\text{m}^2 \cdot \text{s}} \right] \quad (2)$$

$$N_A = L_A \cdot (C_{A1} - C_{A2}) + (1 - \sigma) \cdot N_B \cdot \frac{C_A}{C_B} \left[\frac{\text{mol } A}{\text{m}^2 \cdot \text{s}} \right] \quad (3)$$

Where:

- N_B is the water flux density through the membrane [$\text{mol}/\text{m}^2 \cdot \text{s}$]
- N_A is the ammonia flux density through the membrane [$\text{mol}/\text{m}^2 \cdot \text{s}$]
- L_B is the water permeability through the membrane [$\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{bar}$]
- L_A is the ammonia permeability through the membrane [$\text{m}^3/\text{m}^2 \cdot \text{s}$]
- C_A is the ammonia concentration [mol/m^3]
- C_B is the water concentration [mol/m^3]
- ΔP is the pressure difference between both sides of the membrane [bar]

σ is the polarization, which relates the solution's concentration with the concentration touching the membrane

ΔP is the osmotic pressure difference between both sides of the membrane [bar]

In this direction, the first series of ROSA simulated experiments were carried out to prove if water and ammonia permeability depend on pH conditions. ROSA simulation

4.1.1. ROSA simulation

As explained before, ROSA is a freeware model for the calculation of RO processes with an intuitive interface. The following figures show its interface for both the entry and the outlet of data:

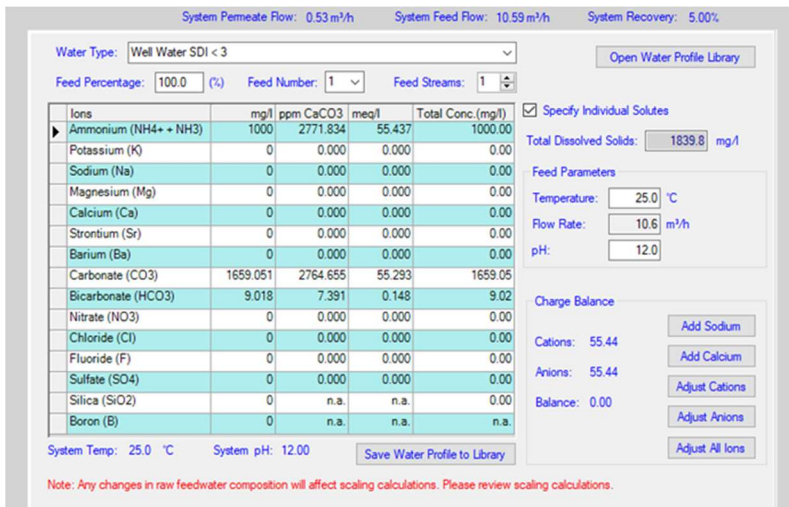


Figure 4 Feedwater data entry interface

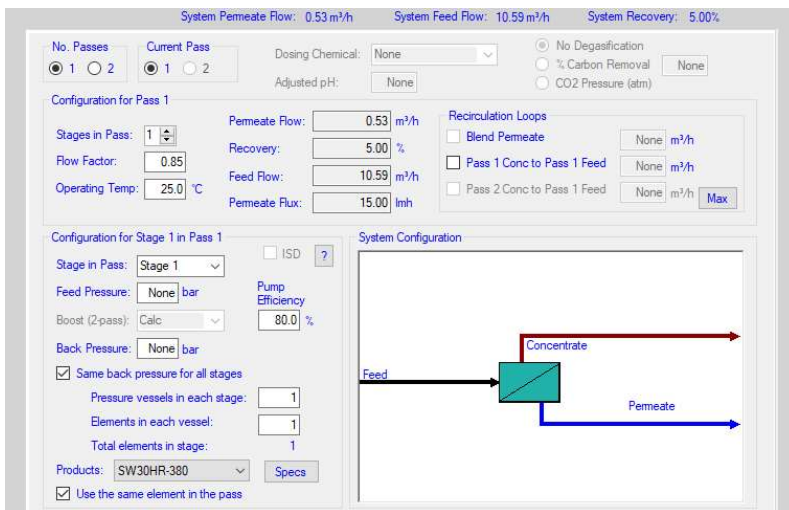


Figure 3 System configuration entry interface

System Details											
Feed Flow to Stage 1		Pass 1 Permeate Flow		Osmotic Pressure:		Feed					
Raw Water Flow to System	10.59 m ³ /h	Pass 1 Recovery	5.00 %	5.00 %	1.87 bar	Concentrate	1.87 bar				
Feed Pressure	15.52 bar	Feed Temperature	25.0 C	25.0 C	1.88 bar	Average	1.88 bar				
Flow Factor	0.85	Feed TDS	283.817 mg/l	283.817 mg/l	13.18 bar		13.18 bar				
Chem. Dose	None	Number of Elements	1	1	5.74 kW		5.74 kW				
Total Active Area	35.30 m ²	Average Pass 1 Flux	15.00 l/mh	15.00 l/mh	10.78 kWh/m ³		10.78 kWh/m ³				
Water Classification: Well Water SD1 < 3											

Stage	Element	#FV	#Ele	Feed Flow (m ³ /h)	Feed Press (bar)	Recirc Flow (m ³ /h)	Conc Flow (m ³ /h)	Conc Press (bar)	Perme Flow (m ³ /h)	Perme Press (bar)	Perme TDS (mg/l)	Pass Streams (mg/l as l/m)	
												Adjusted Feed	Concentrate
1	SI330HR-380	1	1	10.39	15.17	0.00	10.06	14.78	0.53	0.00	45.73	Stage 1	Total
	NH4+ + NH3			1.76		1000.00		2050.45	1006.24		1006.24		
	K			0.00		0.00		0.00	0.00		0.00		
	Na			0.00		0.10		0.10	0.00		0.00		
	Mg			0.00		0.00		0.00	0.00		0.00		
	Ca			0.00		0.00		0.00	0.00		0.00		
	Sr			0.00		0.00		0.00	0.00		0.00		
	Ba			0.00		0.00		0.00	0.00		0.00		
	CO3			1659.05		1659.05		1745.67	20.28		20.28		
	HCO3			9.02		9.02		8.79	6.16		6.16		
	NO3			0.00		0.00		0.00	0.00		0.00		
	Cl			0.00		0.00		0.00	0.00		0.00		
	F			0.00		0.00		0.00	0.00		0.00		
	SO4			0.00		0.00		0.00	0.00		0.00		
	SiO2			0.00		0.00		0.00	0.00		0.00		
	Boron			0.00		0.00		0.00	0.00		0.00		
	CO2			0.00		0.00		0.00	0.00		0.00		
	TDS			1839.83		2838.17		2985.02	45.73		45.73		
	pH			12.00		12.00		12.02	10.82		10.82		

Figure 5 Data outlet report

The different experiments at different pH conditions were carried out with several constant parameters, as:

1. DOW's seawater RO membrane SW30HR-380
2. Total N concentration: 1000 ppm
3. Temperature: 25°C
4. Permeate flux: 15 m³/h·m²
5. Same recovery values: 5-10-15%

The following results were obtained from the simulated experiments:

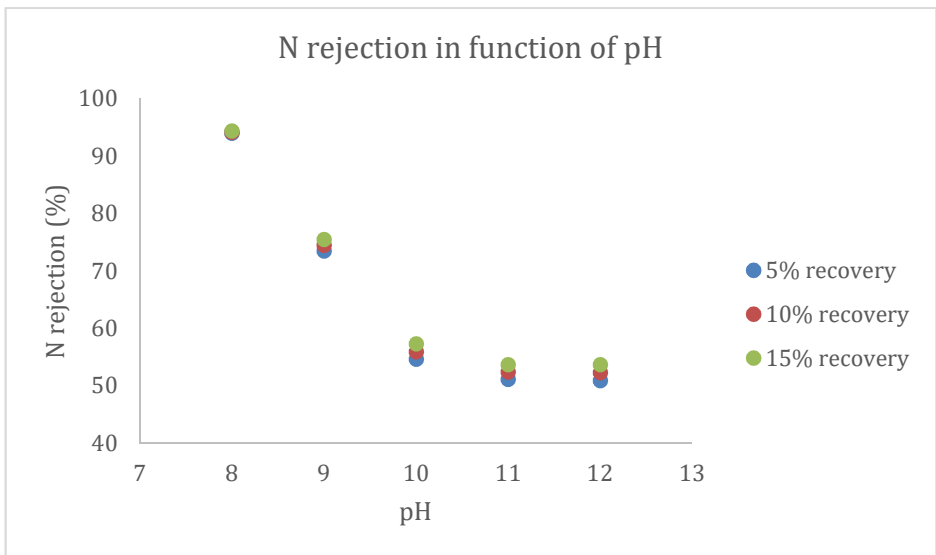


Figure 6 ROSA's simulated experiments results, rejection with pH variation, 5% N recovery

As the results reflect, high pH conditions, with the same N recovery, stand for lower N rejection. These results are directly related to the ammonia concentration in the feed flow.

As higher as pH gets, the NH₃/NH₄ equilibrium tilts to the ammonia. As the membrane is not able to reject the ammonia (it is a gas permeable membrane) the total N rejection decreases. The results also reflect that above pH=10, N rejection remains almost constant, because free NH₃ concentration is not significantly altered above pH=10.

All the results from ROSA's simulated experiments are on Appendix 1.

4.1.2. Membrane's parameters calculation

With the data obtained from the different simulated experiments, it was possible to calculate some parameters about the DOW's seawater RO membrane SW30HR-380. For this objective, SMath Studio freeware mathematical program was used.

As explained before in chapter 3.1.1 ROSA is a freeware with a complex mathematical model which is hidden from the customer, only showing the inflow and outflow characteristics, as a "black box" software. Because of this, a mathematical model developed with Smath Studio was created to obtain certain the required membrane parameters.

4.1.2.1. Mathematical model's inputs

The following parameters were introduced as inputs for the calculation of the membrane parameters:

1. pK_a : Acid dissociation constant of ammonia/ammonium equilibrium
2. M_{NH_3} : Molecular mass of ammonia [kg/mol]
3. S : Surface of membrane in contact with both solutions, provided by ROSA [m^2]
4. NDP : Difference between the feed pressure and the osmotic pressure, provided by ROSA [bar]
5. pH from both vessels, provided by ROSA
6. π : is the osmotic pressure in the feed solution, provided by ROSA [bar]
7. Total N concentration in both vessels, provided by ROSA [mg/L]
8. Permeated and rejected feeds, provided by ROSA [m^3/hr]
9. Free ammonia concentration, calculated from the total N concentration and both vessels pH [mol/m^3]

4.1.2.2. Mathematical model's equations

$$f = \left(\frac{N_B}{k_L} \right) = \left(\frac{N_B}{C \frac{m^{1-3 \cdot n}}{s^{1-n}} \cdot R^n} \right) \quad (4)$$

$$L_B = \left(\frac{N_B}{NDP + \pi \cdot (1 - f)} \right) \left[\frac{m}{s \cdot bar} \right] \quad (5)$$

$$L_A = \left(\frac{N_A}{C_{A1} \cdot f - C_{A2}} \right) \left[\frac{m}{s} \right] \quad (6)$$

Where:

N_B is the water flux density through the membrane [m/s]

K_L is a polarization parameter [m/s]

N_A is the ammonia flux density through the membrane [mol/m²·s]

C is a parameter obtained from reducing permeability's difference between experiments

m meters

n is a parameter obtained from reducing permeability's difference between experiments

s seconds

R is the rejected feed

f is the polarization, which relates the solution's concentration with the concentration touching the membrane

L_B is the water permeability through the membrane [m/s·bar]

L_A is the ammonia permeability through the membrane [m/s]

$pK_A := 9,25$ $M_{NH_3} := 17 \frac{g}{mol} = 0,017 \frac{kg}{mol}$ $S := 35,3 m^2$
 $NDP := 13,57 \text{ bar}$ $pH_1 := 8,97$ $pH_2 := 7,55$ $\Pi := 2,60 \text{ bar}$
 $C_{AT1} := \frac{1535,5 \frac{mg}{L}}{M_{NH_3}} = 90,3235 \frac{mol}{m^3}$ $C_{AT2} := \frac{376,6 \frac{mg}{L}}{M_{NH_3}} = 22,1529 \frac{mol}{m^3}$ $P := 0,53 \frac{m^3}{hr}$ $R := 3,02 \frac{m^3}{hr}$
 $N_B := \frac{P}{S} = 4,1706 \cdot 10^{-6} \frac{m^3}{m^2 \cdot s}$ $N_A := \frac{C_{AT2} \cdot P}{S} = 9,2391 \cdot 10^{-5} \frac{mol}{m^2 \cdot s}$
 $C_{A1} := \text{solve } pK_A = pH_1 + \log_{10} \left(\frac{C_{AT1} - x \frac{mol}{m^3}}{x \frac{mol}{m^3}} \right); x; 0; C_{AT1} \quad \frac{mol}{m^3} = 31,0875 \frac{mol}{m^3}$
 Hi ha molt poc amoniac perquè es transforma ràpidament en amoni
 $C_{A2} := \text{solve } pK_A = pH_2 + \log_{10} \left(\frac{C_{AT2} - x \frac{mol}{m^3}}{x \frac{mol}{m^3}} \right); x; 0; C_{AT2} \quad \frac{mol}{m^3} = 0,4334 \frac{mol}{m^3}$
 $C := 0,005$ $n := 0,33$
 $f := \exp \left(\frac{N_B}{C \frac{m}{s} \frac{1-3 \cdot n}{1-n} \cdot R^n} \right) = 1,0087$ $k_L := C \frac{m}{s} \frac{1-3 \cdot n}{1-n} \cdot R^n = 0,0005 \frac{m}{s}$
 $L_{B1} := \frac{N_B}{NDP - \Pi \cdot (1-f)} = 3,08 \cdot 10^{-7} \frac{m^3}{m^2 \cdot s \cdot bar}$ $L_{A1} := \frac{N_A}{(C_{A1} \cdot f - C_{A2})} = 3 \cdot 10^{-6} \frac{m}{s}$

Figure 7 SMATH Studio mathematical mode for a Reverse Osmosis process, example for pH=9 and 15% of ammonia recovery

Figure 7 shows how is implemented the model in SMATH Studio for a particular case. Then changing the concentrations and pH, the software recalculates automatically the results which are tabulated in Appendix 1.

For obtaining the C and n parameters which are necessary to calculate the polarization, they were iterated until the permeabilities for the same recovery value were as much constant as possible.

4.1.2.3. Results obtained from the simulation

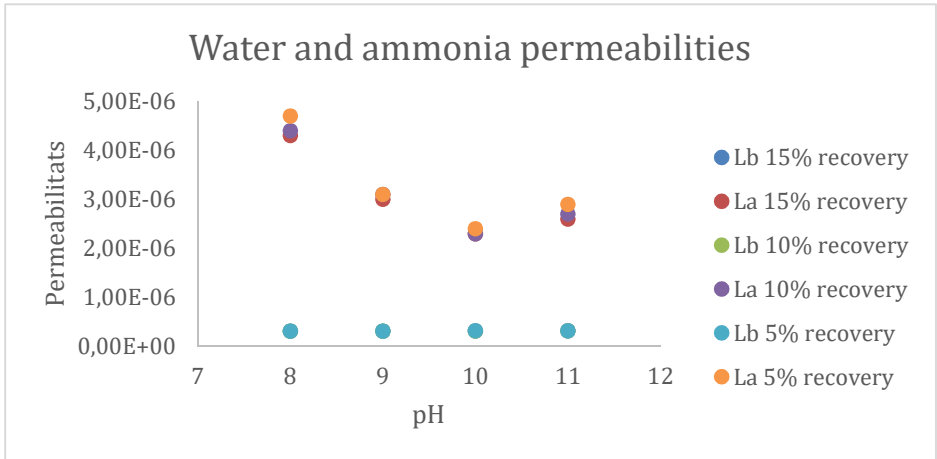


Figure 8 Water and ammonia permeabilities in function of pH and % of ammonia recovery

As results reflect, the water permeability (L_B) is more constant than ammonia permeability (L_A) with pH variation. Besides, both permeabilities are practically constant with different % of ammonia recovery. Although theoretically both permeabilities should be independent of pH, ammonia's concentration is very dependent of pH, and as the concentration calculation is based on an approximated pH, it would be really difficult to get constant ammonia permeability values. On the other hand, water concentration is not affected by pH, so its permeability remains constant.

Nevertheless, the values for both permeabilities can be considered constant and their average value will be used for the computational simulation of FO processes.

The average values obtained from Reverse Osmosis processes are:

- L_A : $3 \cdot 10^{-6}$ m/s
- L_B : $3,15 \cdot 10^{-7}$ m/s·bar

All the results from ROSA's simulated experiments are on Appendix 1.

4.2. FORWARD OSMOSIS COMPUTATIONAL SIMULATION

Using the parameters data obtained on the previous chapter, an alternative process was studied.

The FO processes were simulated by an own created mathematical model using Smath Studio, and VM was used to obtain the speciation of both vessels along the evolution of the experiments.

The different experiments at different pH conditions were carried out with several constant parameters, as:

1. Same initial volume for both vessels: 1L
2. Total ammonium/ammonia initial concentration on the feed solution: 1000 ppm
3. Total ammonium/ammonia initial concentration on the permeate solution: 5000 ppm.
4. Temperature: 25°C
5. Two different values for the initial pH of the feed solution: 9-10
6. Three different values for the initial pH of the permeate solution: 6-7-8

Figures 9 and 10 show the VM interface, which was used to calculate the pH and Osmotic pressure for each vessel.



Figure 10 VM main menu

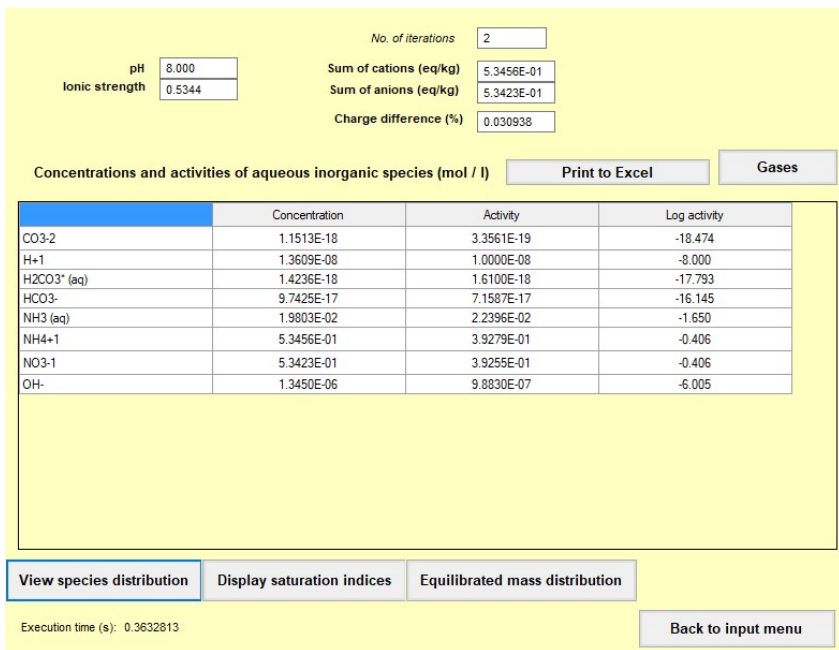


Figure 9 VM Output interface

4.2.1. Mathematical model's inputs

The following parameters were introduced as inputs for the calculation of the FO simulated experiments:

1. pK_a : Acid dissociation constant of ammonia/ammonium equilibrium
2. M_{NH_4} : Molecular mass of ammonium [kg/mol]
3. $M_{NH_4NO_3}$: Molecular mass of ammonium nitrate [kg/mol]
4. $M_{NH_4CO_3}$: Molecular mass of ammonium carbonate [kg/mol]
5. M_{CO_3} : Molecular mass of carbonate [kg/mol]
6. M_{NO_3} : Molecular mass of nitrate [kg/mol]
7. S : Surface of membrane in contact with both solutions [m^2]
8. R : Gas constant [J/mol·K]
9. V_F : Feed solution's vessel
10. V_D : Draw solution's vessel
11. T : Temperature [K]
12. L_B : water permeability through the membrane [m/s·bar]
13. L_A : ammonia permeability through the membrane [m/s]
14. pH_1 : Feed solution's pH
15. pH_2 : Draw solution's pH
16. f : polarization, obtained from the RO simulation
17. Δt : amount of time between each calculation cycle [s]
18. t_{emps} : initial time [s]
19. s : membrane parameter [μm]
20. D_S : ammonium nitrate's water diffusion [m^2/s]
21. k_D : membrane parameter calculated with the s and the D_S
22. k_L :
23. C_{FCO_3} : carbonate's concentration in the feed solution [mg/L]
24. C_{DNO_3} : nitrate's concentration in the draw solution [mg/L]

25. C_{FNH} : ammonium-ammonia total concentration in the feed solution [mol/m³]
26. C_{DNH} : ammonium-ammonia total concentration in the draw solution [mol/m³]
27. C_{FNH3} : Free ammonia concentration in the feed solution, calculated from the total ammonium-ammonia concentration and pH [mol/m³]
28. C_{DNH3} : Free ammonia concentration in the draw solution, calculated from the total ammonium-ammonia concentration and pH [mol/m³]

4.2.2. Mathematical model's equations

The first step after introducing all the inputs to the Smath Studio created program, was the osmotic pressure's calculation with VM. Once the Osmotic pressures were calculated, the first calculation cycle started.

In every calculation cycle, both solution's osmotic pressure touching the membrane and the water flux were calculated by iteration. First, with the osmotic pressures calculated with VM and an estimated water flux density, both osmotic pressure's touching the membrane were calculated. With these two parameters, water flux density was calculated and the cycle was repeated until the three parameters remained constant. Also, the ammonia flux density was calculated with the free ammonia concentrations and the ammonia permeability:

$$\pi_{Dw} = \pi_D \cdot e^{-\frac{J_w}{k_D}} \text{ [atm]} \quad (7)$$

$$\pi_{Fw} = \pi_F \cdot e^{\frac{J_w}{k_L}} \text{ [atm]} \quad (8)$$

$$J_w = L_B \cdot (\pi_{Dw} - \pi_{Fw}) \left[\frac{m}{s} \right] \quad (9)$$

$$J_s = L_A \cdot (C_{FNH3} - C_{DNH3}) \left[\frac{mol}{m^2 \cdot s} \right] \quad (10)$$

Where:

π_D is the draw solution's Osmotic pressure [atm]

π_{Dw} is the draw solution's Osmotic pressure touching the membrane [atm]

π_F is the feed solution's Osmotic pressure [atm]

π_{Fw} is the feed solution's Osmotic pressure touching the membrane [atm]

J_w is the water flux density through the membrane [m/s]

J_s is the ammonia flux density through the membrane [mol/m²·s]

After calculating the ammonia and water flux densities, the second calculation cycle started and the new ammonia-ammonium and water quantity in every vessel were calculated:

$$N_{FNH} = C_{FNH} \cdot V_F - (J_s \cdot S \cdot \Delta t) \text{ [mol]} \quad (11)$$

$$N_{DNH} = C_{DNH} \cdot V_D + (J_s \cdot S \cdot \Delta t) \text{ [mol]} \quad (12)$$

$$V_F = V_F - (J_w \cdot S \cdot \Delta t) \text{ [m}^3\text{]} \quad (13)$$

$$V_D = V_D + (J_w \cdot S \cdot \Delta t) \text{ [m}^3\text{]} \quad (14)$$

Where:

N_{FNH} is the total quantity of ammonia-ammonium in the feed solution [mol]

N_{DNH} is the total quantity of ammonia-ammonium in the draw solution [mol]

V_F is the feed solution's volume [m³]

V_D is the draw solution's volume [m³]

In this second calculation cycle, VM was used again to calculate the new osmotic pressure and pH for each vessel, getting the inputs for the following cycle of calculation. The next calculation cycles were identical to the second one, and they were executed until the target time was achieved.

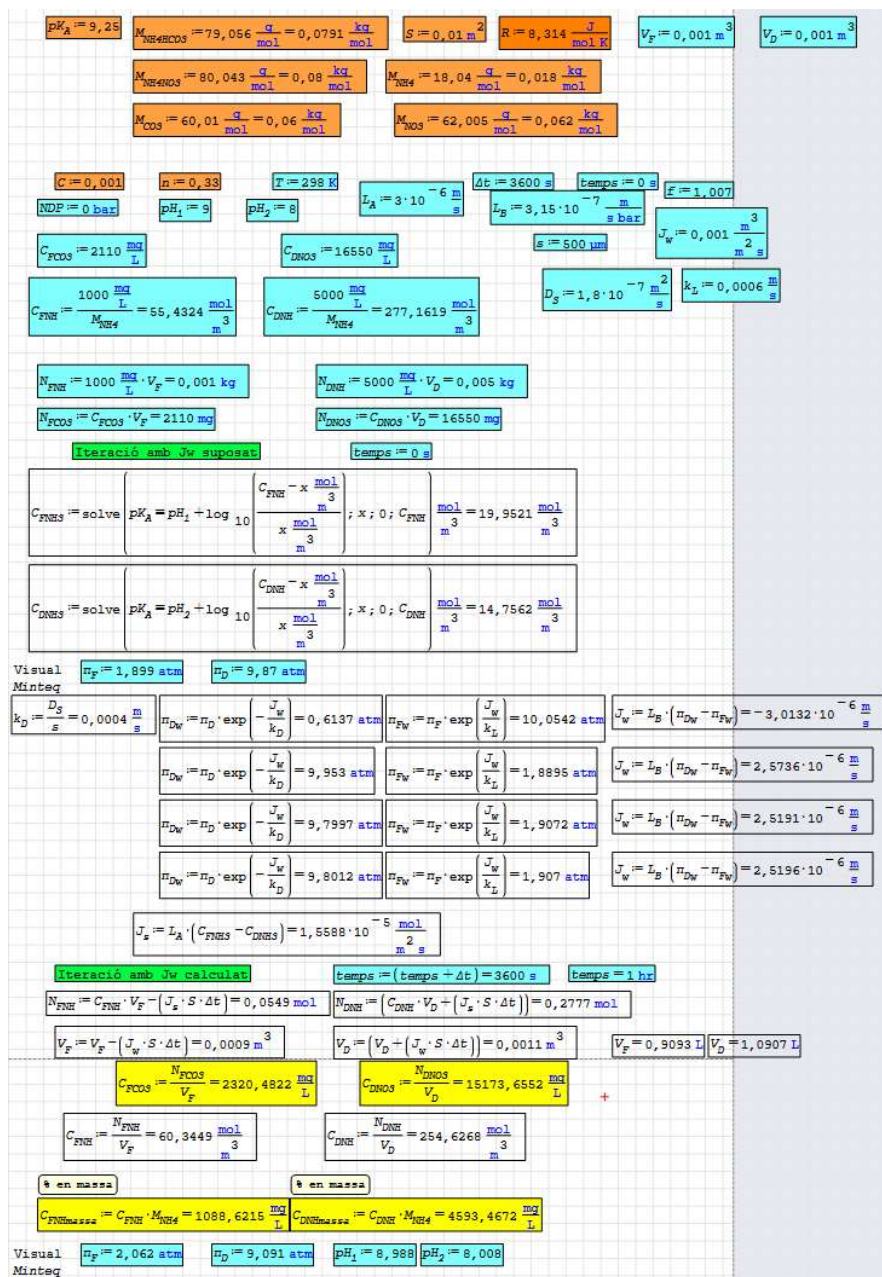


Figure 11 Smath Studio mathematical mode for a FO process, example for Feed's pH=9 and Draw's pH=8

Figure 11 shows how the model is implemented in SMATH Studio for a particular case. The picture shows the first and second cycle of calculation. Because of the slow speed of the process, the amount of time between each calculation cycle was relatively long, 1 hour, as pH and water and ammonia flux densities changed very slowly.

4.2.3. Results obtained from the simulation

Figure 12 shows the results that were obtained from the simulated experiments. As can be seen, ammonia recovery increases as the pH in the feed solution increases as well, and as the pH difference between both vessels gets greater. From the data obtained it can also be concluded, and in perspective to a possible operation, that the feed's solution pH has got a more important impact on ammonia recovery than the draw solution's pH.

Furthermore, the difference of ammonia recovery between pH=6 and pH=7 (difference between the green and the red, and between light blue and orange) in the draw solution is significantly less important than between pH=7 and pH=8 (difference between dark blue and red, and between purple and light blue). In perspective to a possible operation, spending resources on decreasing draw's solution pH below 7 could be a waste.

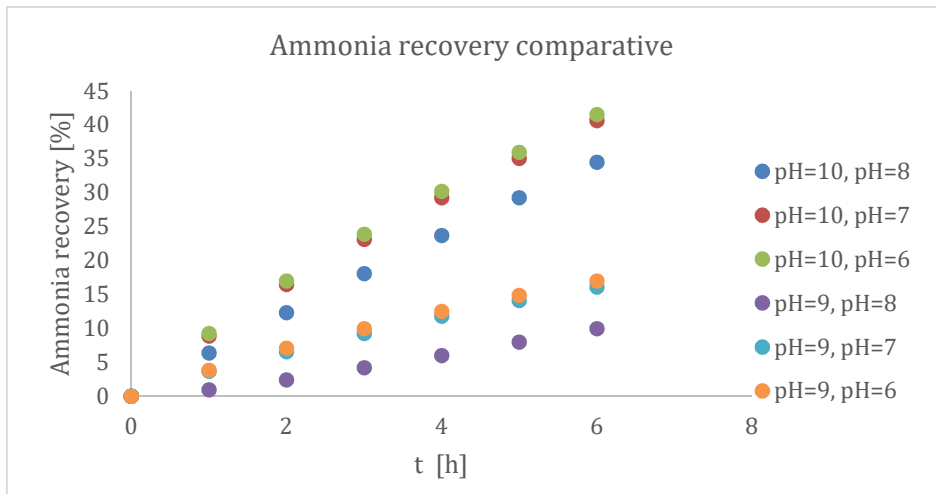


Figure 12 Ammonia recovery results for Forward Osmosis, first pH refers to feed solution, and the second one to draw solution

The maximum ammonia recovery obtained was above 40%. Despite the limited velocity of the simulated experiments, the results show that the system hasn't approached the equilibrium at the end of the simulation. Although the process speed was slow (6 hours to get 40% recovery), its limited velocity was probably caused by the limited membrane area (100 cm²) that was used for 1 L vessels.

These parameters were used for approaching as much as possible to the university's laboratory units, in case that empirical experiments were carried out in the future. If the area/volume ratio from the commercial membranes like the one studied in the RO process (SW30HR-380) were used, the kinetics of the processes would have been quicker, and the ammonia recovery could have been significantly higher.

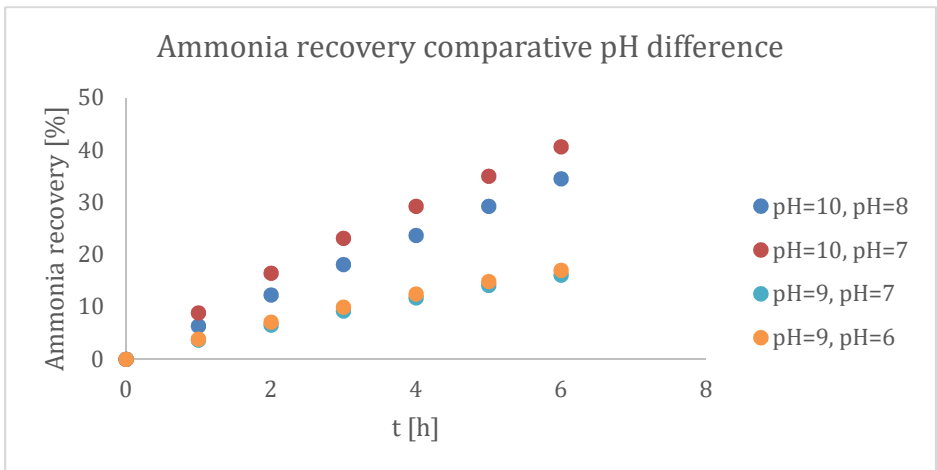


Figure 13 Ammonia recovery comparative for the same pH difference, first pH refers to feed solution, and the second one to draw solution

As Figure 13 shows, with the same difference of pH between both vessels, high pHs are more likely to recover ammonia, since the pH on the feed solution, and therefore, its NH₃ concentration are the parameters with the most impact. According to the results obtained, and in perspective to a possible operation, it will be advisable to spend more resources on increasing feed solution's pH than decreasing draw solution's pH.

The possibility of increasing the feed solution's above 10 was not studied in this project as the N added to the swine manure would be much bigger than the initial concentration of the WW, interfering in the purpose of reducing the total N concentration of the solution.

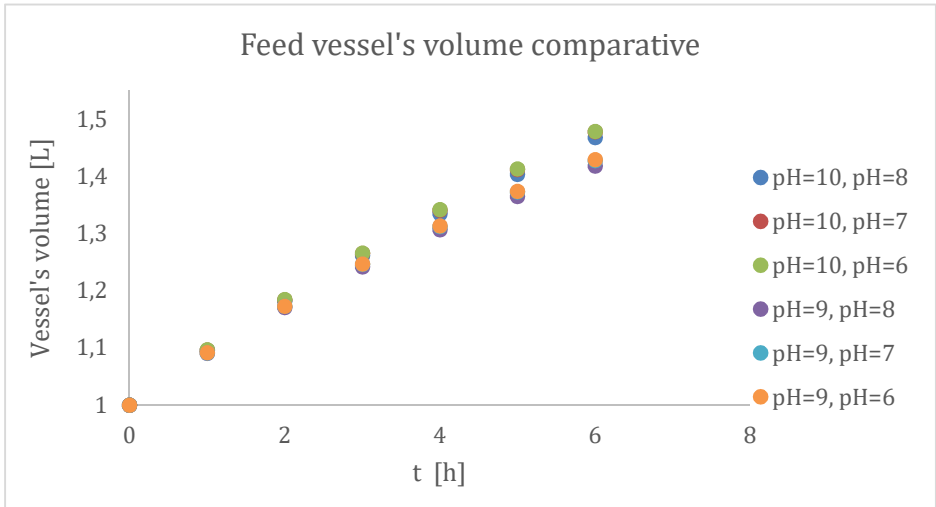


Figure 15 Feed vessel's volume comparative, first pH refers to feed solution, and the second one to draw solution

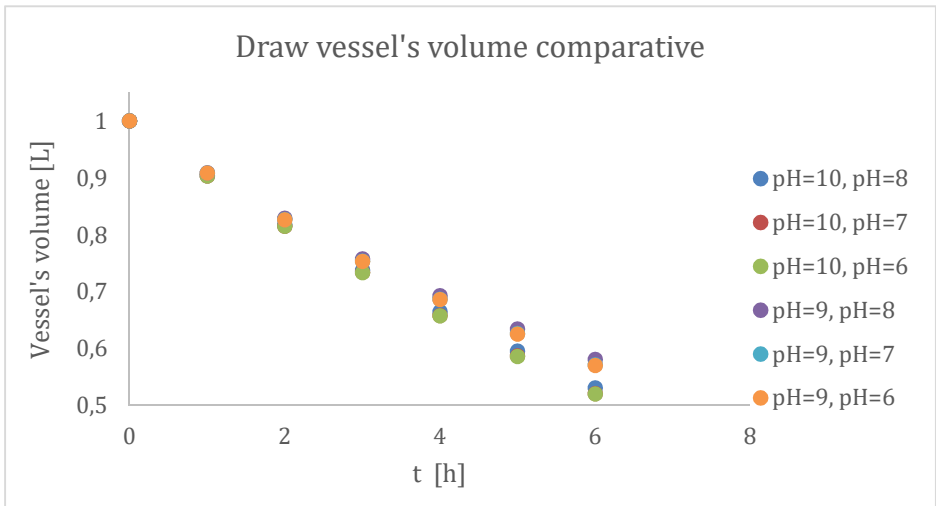


Figure 14 Draw vessel's volume comparative, first pH refers to feed solution, and the second one to draw solution

Figures 14 and 15 show the vessels volume along the time for each pH condition. As can be seen in those figures, when the feed solution's pH is higher, the water flow is significantly greater as well. Water flow depends on the Osmotic pressure difference between both vessels, and as the different simulated experiments were carried out with the same total N concentration, the

bicarbonate concentration had to be lower for pH=10 than for pH=9, and therefore the solution's Osmotic pressure.

Also, in both figures can be seen a little variation of the volumes for different draw solution's pH. As explained in the case of the feed solution, the experiments were carried out with the same total ammonium-ammonia concentration, and the nitric acid concentration had to increase to decrease pH. Because of this increment of the nitric concentration, the osmotic pressure on the draw solution increased as well, and therefore the water flux from the feed solution to the second one.

All the results from FO simulated experiments are on Appendix 2.

5. CONCLUSIONS

During the project, the problems caused by the presence of N in WW, the current state of the ammonia recovery technologies and the Forward Osmosis gas membrane processes were studied.

Then, a research for an alternative process using not hydrophobic membranes was performed, using computational simulations.

The conclusions achieved are following:

- The elimination of N from WW is necessary due to it is one of the causes of eutrophication problems.
- The majority of the practices for NH₃ production are energy intensive and contribute to global warming, therefore, developing new methods for removal and recovery of NH₃ it's an interesting line of research.
- The most common membrane for FO is ePTFE, as well as other hydrophobic membranes.
- Sea water desalination membranes have a high permeability for gases like ammonia.
- Water permeability is more constant with pH variation than ammonia permeability, although both can be considered constant in approximate simulations.
- In FO ammonia recovery, feed solution's pH is a very influent parameter.
- Both ammonia and WW have good recovery rates with not hydrophobic membranes.
- FO ammonia recovery with not hydrophobic membranes seems a viable alternative capable of reducing both ammonia and WW emissions from an anaerobic digester.
- It would be advisable to perform empirical experiments to support the viability of this alternative process.
- More research should be performed in order to optimize the process conditions to maximize both ammonia and water recovery rates.

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ACRONYMS

(WW) Waste Water

(N) Nitrogen

(RO) Reverse Osmosis

(FO) Forward Osmosis

(VM) Visual Minteq ver. 3.1

(WWTP) Waste Water Treatment Plant

APPENDICES

APPENDIX 1: REVERSE OSMOSIS SIMULATED EXPERIMENTS

Table 3 ROSA's simulated experiments reports

Test	S [m ²]	Feed pH	Recovery [%]	LMH	F [m ³ /h]	R [m ³ /h]	NH ₄ +NH ₃ [ppm]	π [bar]	P [m ³ /h]	NH ₄ +NH ₃ [ppm]	NDP [bar]	Rejection
1	35,3	8	15	15	3,53	3	1227,45	2,79	0,53	68,59	13,53	0,944
2	35,3	8	10	15	5,30	4,77	1163,16	2,71	0,53	67,76	13,42	0,942
3	35,3	8	5	15	10,59	10,06	1105,56	2,63	0,53	66,88	13,31	0,940
4	35,3	9	15	15	3,55	3,02	1535,54	2,60	0,53	376,61	13,57	0,755
5	36,3	9	10	15	5,30	4,77	1471,24	2,52	0,53	375,84	13,40	0,745
6	35,3	9	5	15	10,60	10,07	1413,64	2,46	0,53	374,96	13,29	0,735
7	35,3	10	15	15	3,53	3	2023,82	2,12	0,53	865,01	13,36	0,573
8	35,3	10	10	15	5,30	4,77	1959,54	2,06	0,53	864,17	13,29	0,559
9	35,3	10	5	15	10,59	10,06	1901,94	2,00	0,53	863,28	13,20	0,546
10	35,3	11	15	15	3,53	3	2156,48	1,94	0,53	997,67	13,32	0,537
11	35,3	11	10	15	5,30	4,77	2092,19	1,89	0,53	996,83	13,25	0,524
12	35,3	11	5	15	10,59	10,06	2034,59	1,84	0,53	995,93	13,18	0,511
13	35,3	12	15	15	3,53	3	2173,14	1,92	0,53	1007,13	13,32	0,537
14	35,3	12	10	15	5,30	4,77	2108,41	1,87	0,53	1006,70	13,25	0,523
15	35,3	12	5	15	10,59	10,06	2050,45	1,82	0,53	1006,24	13,18	0,509

Table 4 Smath Studio's calculated membrane parameters

pH	Recovery [%]	$L_A \cdot 10^6$ [m/s]	$L_B \cdot 10^7$ [m ³ /m ² ·s·bar]
8	15	4,3	3,09
8	10	4,4	3,11
8	5	4,7	3,14
9	15	3	3,08
9	10	3,1	3,12
9	5	3,1	3,14
10	15	2,3	3,13
10	10	2,3	3,14
10	5	2,4	3,16
11	15	2,6	3,14
11	10	2,7	3,15
11	5	2,9	3,17

APPENDIX 2: FORWARD OSMOSIS SIMULATED EXPERIMENTS

Table 5 FO simulation results, pH=10, pH= 8

pH=10, pH=8					
Temps [h]	N _{FNH} [mol]	N _{DNH} [mol]	V _F [L]	V _D [L]	Ammonia recovery [%]
0	0,055	0,277	1,000	1,000	0,0
1	0,052	0,281	0,904	1,096	6,4
2	0,049	0,284	0,818	1,182	12,3
3	0,045	0,287	0,738	1,262	18,1
4	0,042	0,290	0,665	1,335	23,7
5	0,039	0,293	0,596	1,404	29,3
6	0,036	0,296	0,531	1,469	34,5

Table 6 FO simulation results, pH=10, pH= 7

pH=10, pH=7					
Temps [h]	N _{FNH} [mol]	N _{DNH} [mol]	V _F [L]	V _D [L]	Ammonia recovery [%]
0	0,055	0,277	1,000	1,000	0,0
1	0,051	0,282	0,904	1,097	8,9
2	0,046	0,286	0,815	1,185	16,5
3	0,043	0,290	0,734	1,266	23,1
4	0,039	0,293	0,659	1,342	29,3
5	0,036	0,297	0,588	1,412	35,1
6	0,033	0,300	0,521	1,479	40,6

Table 7 FO simulation results, pH=10, pH= 6

pH=10, pH=6					
Temps [h]	N _{FNH} [mol]	N _{DNH} [mol]	V _F [L]	V _D [L]	Ammonia recovery [%]
0	0,055	0,277	1,000	1,000	0,0
1	0,050	0,282	0,903	1,097	9,3
2	0,046	0,287	0,815	1,185	17,0
3	0,042	0,290	0,734	1,267	23,9
4	0,039	0,294	0,658	1,342	30,2
5	0,036	0,297	0,587	1,414	36,0
6	0,032	0,300	0,521	1,480	41,6

Table 8 FO simulation results, pH=9, pH= 8

pH=9, pH=8					
Temps [h]	N _{FNH} [mol]	N _{DNH} [mol]	V _F [L]	V _D [L]	Ammonia recovery [%]
0	0,055	0,277	1,000	1,000	0,0
1	0,055	0,278	0,909	1,091	1,0
2	0,054	0,279	0,829	1,171	2,4
3	0,053	0,280	0,758	1,242	4,2
4	0,052	0,281	0,693	1,307	6,0
5	0,051	0,282	0,635	1,366	8,0
6	0,050	0,283	0,581	1,419	10,0

Table 9 FO simulation results, pH=9, pH= 7

pH=9, pH=7					
Temps [h]	N _{FNH} [mol]	N _{DNH} [mol]	V _F [L]	V _D [L]	Ammonia recovery [%]
0	0,055	0,277	1,000	1,000	0,0
1	0,053	0,279	0,909	1,092	3,7
2	0,052	0,281	0,827	1,173	6,6
3	0,050	0,282	0,754	1,246	9,3
4	0,049	0,284	0,687	1,313	11,8
5	0,048	0,285	0,627	1,373	14,1
6	0,047	0,286	0,572	1,428	16,1

Table 10 FO simulation results, pH=9, pH= 6

pH=9, pH=6					
Temps [h]	N _{FNH} [mol]	N _{DNH} [mol]	V _F [L]	V _D [L]	Ammonia recovery [%]
0	0,055	0,277	1,000	1,000	0,0
1	0,053	0,279	0,908	1,092	3,8
2	0,052	0,281	0,827	1,173	7,1
3	0,050	0,283	0,753	1,247	10,0
4	0,049	0,284	0,686	1,314	12,5
5	0,047	0,285	0,626	1,375	14,9
6	0,046	0,287	0,570	1,430	17,0

