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MASTERS CHEMICAL ENGINEERING

STUDY OF NITROGEN RECOVERY FROM SLUDGE CENTRATE BY MEMBRANE CONTACTOR

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Executive Summary

This final masters' project was carried out at the Universitat Politècnica de València (UPV) under the Membrane Processes, Liquid Effluent Treatment and Optimization (PROMETEO) research group. The main objective of the project was to separate ammonium nitrogen (NH_4^+) from sludge centrate by a membrane contactor and establish the optimal operating conditions. The demand for NH_4^+ is always increasing due to its important applications within the fertiliser industry. With the current production method being very environmentally damaging, a sustainable alternative must be found. Currently, the sludge centrate is recirculated back to the head of the wastewater treatment plant (WWTP) but targeting this for NH_4^+ recovery provides a sustainable source and adds a profitable product rather than treatment.

Sludge undergoes treatment within the WWTP until the final by-product of sludge centrate is produced, which contains a high concentration of ammoniacal nitrogen (ammonia and ammonium). Therefore, by using a hollow fibre liquid-liquid membrane contactor (HF-LLMC), the NH_4^+ can be recovered from the sludge centrate. Sulphuric acid was used to strip the NH_4^+ from the sludge centrate, which resulted in the production of ammonium sulphate – a saleable product.

The experiments were set up using a commercial HF-LLMC (Liqui-Cel EXF – 2.5x8 Series (3M, USA)) in a closed-loop pilot plant. The parameters studied were feed solution temperature, stripping solution concentration and wastewater composition. Feed solutions were passed through the shell side of the HF-LLMC whereas the stripping solution was passed through the lumen side, both at a constant flow rate of 30 L/h. Samples were taken throughout and analysed to determine the concentration of NH_4^+ and other substances present in the feed solution at the end of the experiment. From this, the removal efficiencies were calculated to draw conclusions of the feasibility of the HF-LLMC.

The analysis of the results showed the HF-LLMC to be a suitable alternative for the recovery of NH_4^+. On average, 66.36% of NH_4^+ was removed from the sludge centrate with the highest removal being 71.52%. This occurred at a feed temperature of 35 ^oC, a stripping concentration of 0.1 M and a wastewater composition comprising of NH_4Cl, organic matter and ions. It was shown that the feed temperature and stripping concentration directly influenced the NH_4^+ removal efficiency, whereas the feed composition didn't. Recommendations for this study would be to collect further experimental data with different parameters to achieve a better overview of the optimal conditions for the NH_4^+ removal. The project overall showed promising results and great potential towards future research of the HF-LLMC and integrating this technology in a WWTP for nitrogen recovery from sludge centrate.

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Nomenclature

Abbreviation	Definition
PROMETEO	Membrane Processes, Liquid Effluent Treatment and Optimization
ISIRYM	Institute of Industrial, Radiophysical and Environmental Safety
TAN	Total Ammonium Nitrogen (ammonia and ammonium)
WWTP	Wastewater Treatment Plant
AD	Anaerobic Digestion
FO	Forward Osmosis
MC	Membrane Contactor
HF-LLMC	Hollow Fibre Liquid-Liquid Membrane Contactor
COD	Chemical Oxygen Demand
OM	Organic Matter

Symbol	Units	Description
P_{BT}	Pa	Breakthrough pressure
σ	N/m	Surface tension
θ	°	Contact angle
r	m	Pore radius
q	m/s	Permeate flux
k	m^2	Membrane permeability
ΔP	Pa	Transmembrane pressure
μ	Pa s	Viscosity of fluid
L	m	Membrane thickness
η	%	Performance efficiency
C_o	mg/L	Initial feed concentration at time 0
C_t	mg/L	Feed concentration at time, t
J_A	mol/m^2 s	Diffusion flux
D	m^2/s	Diffusion coefficient
$\frac{d\varphi}{dx}$	mol/m^3 m	Concentration gradient

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1 Introduction

1.1 Description of Organisation

This masters' project was carried out on behalf of the PROMETEO (Membrane Processes, Liquid Effluent Treatment and Optimization) research group, which specialises in the treatment of liquid effluents via membrane separation and purification. PROMETEO belongs to the University Institute of Industrial, Radiophysical and Environmental Safety (ISIRYM), which contains the largest number of academic personnel from the Department of Chemical and Nuclear Engineering. The institute is located within the Universitat Politècnica de València (UPV) which was established in 1971 and comprises of 10 schools across 5 campuses. The university primarily focuses on science and technology.

1.2 Motivation and Purpose of Project

Sustainable development and environmental contribution play a crucial role within many companies and industrial processes. The circular economy model has become a key feature of sustainability and focuses on three main goals: design out waste and pollution, keep products and materials in use and regenerate natural systems [1].

Ammonia (NH_3) is a key component within the fertiliser industry as it is the main source of nitrogen, the most important crop nutrient. Roughly 50% of the global food production requires fertilisation for growth, with approximately 80% of the NH_3 produced annually fuelling this [2]. A breakdown for the global applications of NH_3 is illustrated in *Figure 1.*

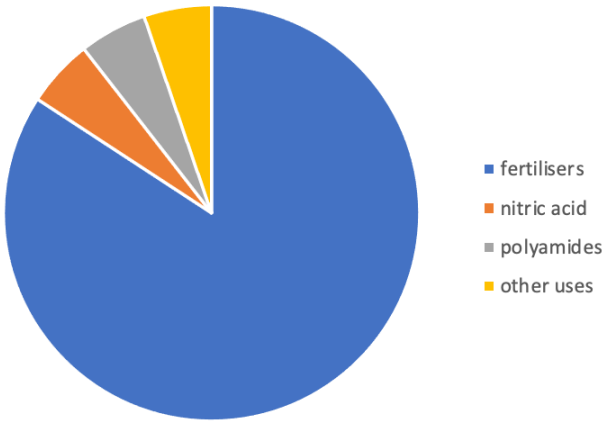

Figure 1: The Global Uses of Ammonia.

Currently, the majority of the world's NH_3 production is from the Haber-Bosch process, which occurs when nitrogen from the air is reacted with hydrogen produced from natural gas:

$$N_{2\,(g)} + 3H_{2\,(g)} \leftrightarrow 2NH_{3\,(g)} \qquad \text{(a)}$$

The Haber process requires very high and expensive operating conditions of pressures at 150 – 200 atm, temperatures of 400 ^{o}C and an iron catalyst to improve efficiency [3]. Annually, the reaction accounts for 1% of the total global energy production, as well as 1% of the global CO_2 emissions [4]. Although the Haber process is the largest producer of NH_3, it is one of the most in-efficient, expensive, and environmentally damaging industrial processes. As demand for food production increases, new challenges arise to find a more sustainable source of NH_3 to minimise harmful emissions and reduce raw material consumption.

As the need for wastewater treatment increases, the industry is always looking for ways to reduce their environmental impact and lower their waste. Specifically, the sludge centrate produced from anaerobic digestion is of key interest due to the high content of nutrients (nitrogen and phosphorus) present. Nitrogen is present within wastewater as ammoniacal nitrogen (total ammonium nitrogen (TAN) ammonia and ammonium). High concentrations can lead to issues with struvite blockage and nutrient accumulation which triggers eutrophication; a process which is toxic to aquatic life. Also, when emitted into the atmosphere, NH_3 can contribute to the formation of particulate matter and negatively impact climate change [5]. Although, the nutrients can be recovered and seen as an opportunity for sustainable fertiliser production and other industrial applications [6]. Therefore, the sludge centrate can be viewed as both a problem and an opportunity, depending on the option chosen for its management. The use of sludge centrate as a solution to the current NH_3 production method closely relates to the principles of a circular economy. It designs waste out from a wastewater treatment plant and keeps materials in use by finding an alternative application instead of disposal.

Traditional methods for the removal of TAN from wastewater include biological processes such as nitrification and denitrification. These methods alone account for between 50 – 70% of the total energy consumption of a wastewater treatment plant [7]. Such energy intensive methods can be costly and pose greater risk towards climate change and global warming.

In recent years, there has been a concentrated effort to find a new, cost-effective, and sustainable source of TAN to meet increasing population and industrial demands [8]. As well as being cost-effective, the energy consumption and environmental impact of the technology should be considered. The separation and recovery of TAN from the sludge centrate via membrane contactor has initially shown promising results and further investigation is required to determine the viability of this option. This project focuses on this further research and gathering of experimental data to determine the efficiency of such technology and if it is a suitable alternative for future implementation.

1.3 Objectives of Project

The main objective of this project was to research an environmentally safe and waste-free technology to treat the sludge centrate from wastewater treatment and recover nitrogen. In order to achieve this, the following aims were set:

1. Separate nitrogen from the synthetic sludge centrate via a membrane contactor.
2. Optimisation of the liquid-liquid extraction process by adjusting the following parameters: feed solution temperature and acid stripping solution concentration and study their influence.
3. Determine the influence of wastewater composition and contact time on the nitrogen removal.
4. Determine the feasibility of the membrane contactor technology for nitrogen recovery.

Alongside the technical objectives, personal learning objectives were also set:

1. Gain a comprehensive understanding of membrane contactors, wastewater treatment and the current challenges faced within the industry.
2. Improve practical analytical ability through gaining experience within a research team and the use of advanced laboratory equipment.
3. Improve report writing, time management and communication skills, especially when overcoming challenges such as language barriers.

The report will outline the theory behind wastewater treatment plants, with focus on the origin of sludge centrate and current separation techniques to deal with the nitrogen in it. It will also look in-depth at membrane separation technology, specifically membrane contactors and their benefits when compared to current available methods. Then, the materials, experimental and cleaning procedure used to achieve the project aims will be described. The results and discussion will focus on the analysis of the collected experimental data and detail any issues that occurred throughout the project. Finally, the report will draw conclusions from the set project objectives and provide recommendations for future studies to be carried out.

2 Background

The sludge centrate used in this study was synthetically made due to the complexity of obtaining it from an operating wastewater treatment plant (WWTP). The characteristics were simulated in a lab, using similar concentrations of substances (ammonium, organic matter, and ions) that are found in real sludge centrate, to achieve a suitable alternative for use in the experiments. Currently, wastewater contains a high concentration of nutrients, such as phosphorus and TAN, which are seen as an environmental hazard and require treatment or removal prior to disposal. It is suggested that, instead of disposal, nutrient waste can be recovered and utilised for use as a secondary source for fertilisers [6].

2.1 Wastewater Treatment Plants

2.1.1 Overview

WWTPs are designed to treat and remove pollutants from contaminated waters and ensure environmental standards are met before it is discharged. Urban wastewater is made up of wastewater generated by household, industrial and rainwater outflows [9]. The pollutants present in urban wastewater typically consist of organic matter, hydrocarbons, heavy metals, and nutrients [10]. TAN is present in high concentrations of 600 – 1500 mg/L, which is above most environmental disposal consent limits [11]. If left untreated, these pollutants can be toxic to aquatic ecosystems. Specifically, high concentrations of phosphorus and TAN can result in eutrophication, which occurs when a water source becomes enriched with nutrients and leads to an unwanted growth of algae and plants [12].

The wastewater treatment process can be broken down into four main stages: pre-treatment, primary treatment, secondary treatment, and tertiary treatment. *Figure 2* depicts a block flow diagram (BFD) showing the four main stages, alongside side processes and by-products. The treatment required varies depending on the characteristics of the wastewater and the desired product, therefore each WWTP is designed differently and may not contain all four stages.

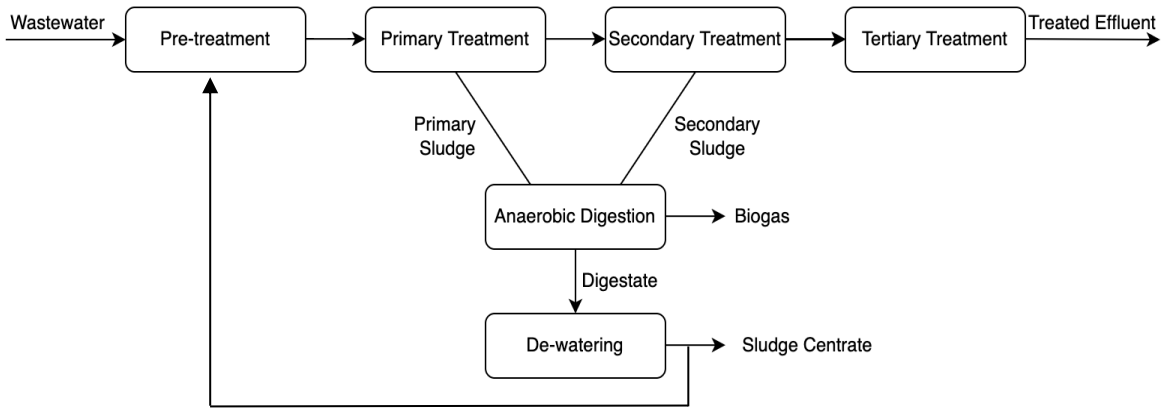

Figure 2: BFD of Wastewater Treatment Plant including Subsequent Steps and By-products.

2.1.2 Pre-treatment

The main objective of the pre-treatment stage is to remove large insoluble solids (metals), oils, and fats from the wastewater. This can be done through screening and grit removal, followed by grease removal [13]. Screening removes large non-biodegradable solids present in the wastewater; this prevents blockages from occurring further downstream. Next, the grit removal stage prevents sand and grit from causing erosion on equipment and pipes. This stage is monitored carefully to ensure the removed grit does not contain any biodegradable solids. The residence time is a key factor as it is important that it is long enough for the grit to settle and be removed, but short enough that the biodegradable solids don't. Pre-treatment may also include additional processes to stabilise the feed conditions such as flowrate, chemical oxygen demand (COD) load and pH [13].

2.1.3 Primary Treatment

Primary treatment consists mainly of sedimentation. Similar to the pre-treatment, the main objective is to remove and reduce the remainder of the suspended solids and organic matter present. As the wastewater passes through a sedimentation tank, the suspended solids settle at the bottom [14]. There are two output streams for the primary treatment process: primary effluent and primary sludge (the accumulation of solids at the bottom of the tank). Primary effluent is sent downstream and undergoes secondary and tertiary treatment prior to disposal. The primary sludge is removed from the sedimentation tank where it is combined with the secondary sludge [15].

2.1.4 Secondary Treatment

Secondary treatment focuses more on the removal of dissolved solids through the use of biological treatments. There are multiple processes included in secondary treatment: activated sludge, trickling filter, and oxidation ponds, although activated sludge is preferred. Approximately 85% of organic matter is removed during this stage [16]. Typically, if TAN concentrations are too high, an additional stage will be required [11], although current methods for this are very energy demanding. There are also two output streams for the secondary treatment process. The first, secondary effluent, is sent to a final tertiary treatment stage where it is disinfected before discharge. The remainder, secondary sludge, is nutrient-rich and is combined with the primary sludge.

2.2 Sludge Treatment

Sludge consists of the waste by-products from both the primary and secondary treatment stages, and is made up of organic and inorganic materials, primarily nutrients and organic chemicals. There are four main stages to sludge treatment: thickening, anaerobic digestion (AD), dewatering and disposal

[17]. As disposal is the final stage, the main objective of sludge treatment is to reduce its overall volume and stabilise the organic matter, preventing an environmental hazard from occurring [18].

Once the sludge has been combined it undergoes thickening, which allows for easier handling of the sludge. A tank, known as a gravity thickener, is used to increase the solids concentration whilst reducing the total volume of sludge, sometimes up to half its original value [18]. The sludge then undergoes AD where the organic matter is decomposed to increase its stability. Two tanks are used for AD, the first for degrading organic molecules into smaller, water-soluble molecules. The second tank then converts the sludge into biogas which can be harnessed and used as an additional energy source for the first tank [17]. Finally, the sludge passes through a dewatering stage, most commonly a centrifuge due to its shorter residence time and lower running costs compared to other technologies. The solid fraction (biosolids) is then removed and can be disposed of, whereas the liquid fraction (sludge centrate) is either recycled back to the head of the plant for further treatment or extracted for nitrogen recovery.

2.3 Nitrogen Recovery in Sludge Centrate

The sludge centrate contains approximately 10 - 30% of the nitrogen load of a WWTP [19]. This occurs from the AD stage, where the nitrogen present in the organic materials is released as TAN. Typically, it is removed from the system using the method of biological nitrification-denitrification. Nitrification can be broken down into two steps; the first where NH_4^+ is oxidised into nitrite (NO_2^-), *reaction b*, and the second where the NO_2^- is oxidised into nitrate (NO_3^-), *reaction c* [11].

$$NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \quad \text{(b)}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad \text{(c)}$$

Denitrification consists of a multi-stage process where NO_3^- is reduced to NO_2^-. The NO_2^- is then further reduced until gaseous N_2 is produced, which can be safely released into the atmosphere. The four half reactions are shown below [20]:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \quad \text{(d)}$$

$$NO_2^- + 2H^+ + 2e^- \rightarrow NO + H_2O \quad \text{(e)}$$

$$2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O \quad \text{(f)}$$

$$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O \quad \text{(g)}$$

In addition to nitrification-denitrification, there are other techniques which have been deeply studied for NH_4^+ removal from sludge centrate such as: air stripping, ion exchange, struvite precipitation, zeolite adsorption and electrochemical treatment [21][22][23]. Air stripping involves wastewater

being brought into contact with air, in which NH_3 gas is stripped from the wastewater [24]. The ion exchange method focuses on the dissociation of NH_4^+ from wastewater, where it is collected on an insoluble resin bed [22]. These methods are all capable of removing nitrogen, but at higher operating costs and larger energy usage.

However, the option of nitrogen recovery rather than elimination is preferred from an economical and environmental point of view. The recovery of nitrogen can provide a profitable alternative, whilst preventing its disposal into the environment. From this, membrane processes provide an important advantage due to their applicability and effectiveness. A combination of forward osmosis (FO) and nanofiltration [25], vacuum membrane distillation [26] and membrane contactors are novel, relevant membrane-based techniques currently being studied for the separation of TAN from sludge centrate. FO and nanofiltration have shown potential in the separation and recovery of TAN from landfill leachate [27]. Although, throughout studies conducted, issues arose surrounding the efficiency of the processes and permeability of the water [28][29].

3 Membrane Contactors

Membrane contactors (MC) have been researched for a variety of applications across many industries, for both product recovery and waste management solutions [30]. They have been investigated for their performance in processes such as the degasification of water [31], and the extraction and removal of CO_2 and TAN from waste gas and water effluent [32]. This technology has gained interest in recent years due to its ability to combine separation with other chemical processes such as extraction or absorption. The advantages of both processes being fully integrated into one piece of equipment allows for high selectivity and driving force, irrespective of concentration difference [33]. Other advantages over traditional separation technologies include higher efficiency, lower energy consumption and more economical operating conditions.

3.1 Membrane Theory

Membranes act as a semipermeable barrier to prevent the dispersion of one phase into another (gas-liquid or liquid-liquid), whilst mass transfer occurs. The barrier allows separation of molecules and particles, such as ions, based on the size of the membrane pores. An aqueous feed solution travels through the membrane with the retentate stream consisting of particles unable to pass through the membrane pores. The permeate stream contains the filtered solution as seen in *Figure 3* [34].

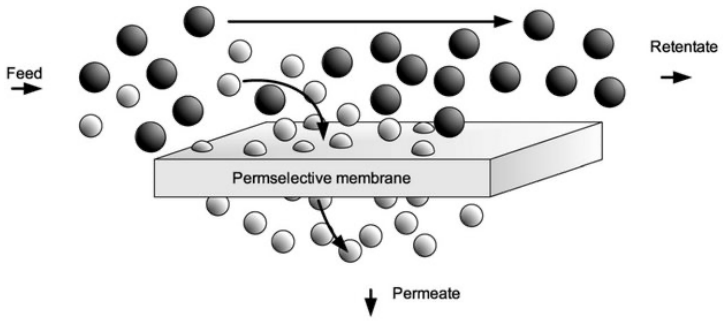

Figure 3: Schematic of Membrane Process.

The liquid phase can be organic or aqueous and the membrane is typically hydrophobic [35]. Hydrophobic materials prevent the aqueous solution from penetrating the pores, providing the pressure of the feed is lower than the breakthrough pressure (P_{BT}) (*Equation 1)*. This is the pressure required to force the aqueous solution through the pores of the membrane and into contact with the other phase.

$$P_{BT} = \frac{(2\sigma cos\theta)}{r} \tag{1}$$

The diffusion of the phases through a membrane occurs due to a driving force, usually a difference in concentration, temperature or pressure [6] [36]. However, in a single phase system, the mass diffusion

is caused by a concentration difference [37]. The rate at which an aqueous solution travels through a porous membrane is known as the permeate flux (q) and is represented by Darcy's Law (*Equation 2).*

$$q = \frac{k\Delta P}{\mu L} \tag{2}$$

The performance efficiency *(Equation 3)* of a membrane can be determined using the initial and final concentration of the substance being removed:

$$\eta = \frac{C_o - C_t}{C_o} \times 100 \tag{3}$$

3.2 Hollow Fibre Liquid-Liquid Membrane Contactors

Hollow fibre liquid-liquid membrane contactors (HF-LLMC) have a similar geometric structure to a shell and tube heat exchanger. They are divided into two sides: the lumen and shell, where the feed and stripping solution flow. *Figure 4* [38] shows the typical configuration of a HF-LLMC, where fluid 1 represents the lumen (hollow fibres) and fluid 2, the shell.

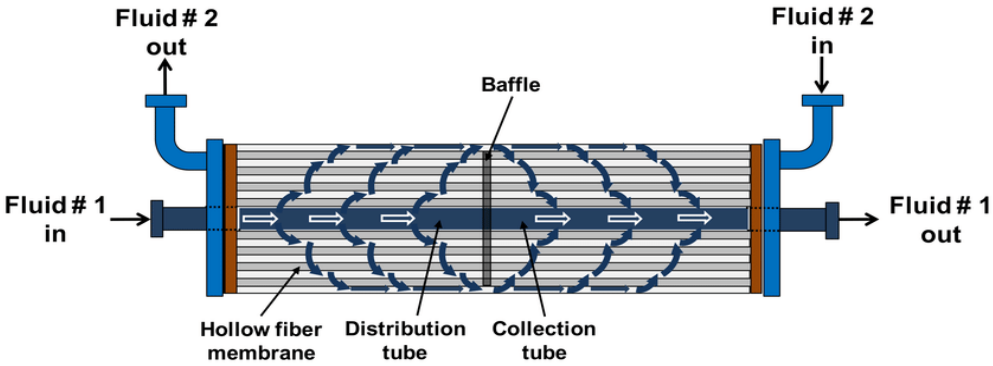

Figure 4: Cross-Sectional of Hollow Fibre Membrane Contactor.

Shell and tube configurations are typically used as this protects the hollow fibre membrane and requires limited space for operation [39]. The only disadvantage is that irreversible fouling damage may occur, but this can be prevented to some degree depending on the flow configuration chosen. The two flow options within the HF-LLMC are: (1) feed solution in the shell side and stripping solution in the lumen and (2) feed solution in the lumen side and stripping solution in the shell. Configuration (1) of feed in the shell side is preferable as it can prevent fouling from occurring on the hollow fibres [39]. Alongside flow configuration, the two solutions can interact co-current, counter-current or cross-flow to each other. The hollow fibres are usually constructed from highly porous, hydrophobic polymers such as polyethylene (PE), polypropylene (PP) and polytetrafluoroethylene (PTFE) [32][40].

3.3 Types of Hollow Fibre Membranes Modules

3.3.1 Longitudinal Flow Modules

Longitudinal flow is the most common type of module used within research. The two phases flow parallel to each other on opposite sides of the MC as shown in *Figure 5* [41]. The phases can flow in both co-current and counter current arrangement. As the structure is similar to that of a shell and tube heat exchanger; the module can be easily manufactured, and the fluid dynamics are well documented [42]. Although, the mass transfer efficiency is low when compared to cross-flow modules. A study conducted by *Yang and Cussler* [43] investigated the construction of longitudinal modules, which aided future design of MC modules in studies where the two phases are the same.

Figure 5: Schematic of Longitudinal Flow Module.

3.3.2 Cross-flow Modules

Cross-flow modules allow the solution to flow across the membrane surface tangentially. The feed passes through the MC and the desired product for removal accumulates at the other end of the MC. There are two configurations for cross-flow modules, seen in *Figure 6* [44]. Hollow fibre, cross-flow modules are favoured due to their many advantages compared to other module types. Some of these advantages include higher mass transfer coefficients, low pressure drop and prevention of irreversible fouling which can improve the membrane lifespan [42], [44].

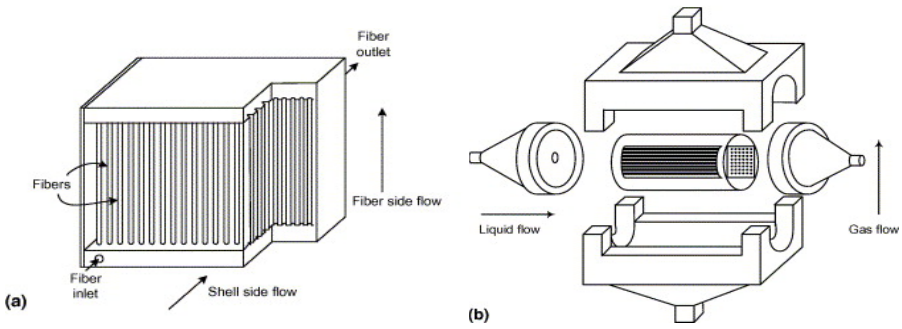

Figure 6: Schematic of Cross-flow Modules.
(a) Module 1 from TNO, The Netherlands and (b) Module 2 from study by Dindore and Versteeg.

3.3.3 Coiled Modules

Coiled modules have been the focus in studies involving nanofiltration and ultrafiltration. As the module has a curved surface, this creates a secondary flow known as Dean Vortices which intensifies the overall process. As a result of these vortices, the mass transfer across both the shell and lumen side of the MC improves drastically [42]. In a study conducted by *Liu et al.* the mass transfer for coiled modules was found to be double that of longitudinal modules [45]. Although this module provides improved mass transfer rates compared to other modules, its presence is uncommon in recent research.

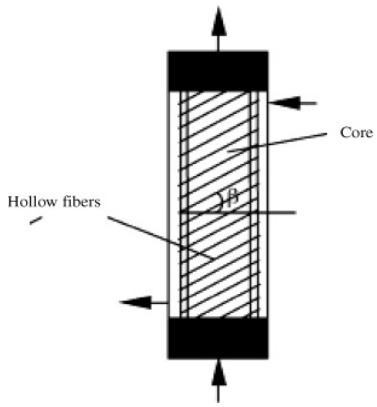

Figure 7: Schematic of Coiled Membrane Module.

3.4 Other Configurations of Membrane Contactors

3.4.1 Flat-Sheet Membranes

Typically, flat-sheet membranes have been used in studies focusing on the capture and removal of CO_2 from various industrial processes [46]. The flat-sheet membrane is constructed of parallel modules placed on top of each other, separated by a spacer, and held together by an external frame as seen in *Figure 8* [47]. They have the advantage of being able to handle high solid concentrations and can be easily cleaned or replaced as required [48]. As well, they are thought to have a simple scale up due to ease of manufacture. On the other hand, when compared with hollow fibre membranes, the flat-sheet has a lower packing density and efficiency making it less favourable overall [49].

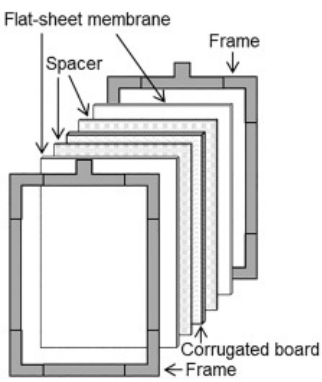

Figure 8: Schematic of Flat-Sheet Membrane.

3.4.2 Tubular Membranes

Tubular membranes are constructed of two tubes: inner (membrane tube) and outer (shell). They work by allowing the feed solution to flow tangentially across the membrane tube and filter into the outer tube, illustrated in *Figure 9* [50]. The concentrate is then collected at the opposite end of the membrane tube [51]. This configuration has applications within the wastewater industry, where high concentrations of dissolved and suspended solids, and oils are present. Compared to other membranes, the tubular configuration provides the lowest pressure drop across it [52]. They are also less susceptible to fouling and can handle more robust cleaning procedures, including harsh chemicals and mechanical cleaning techniques [51]. Tubular membranes typically have larger inner diameters, which leads to larger flowrates and the use of a pump to provide such flowrates. The additional requirement of a pump results in higher capital and operating costs compared to other configurations.

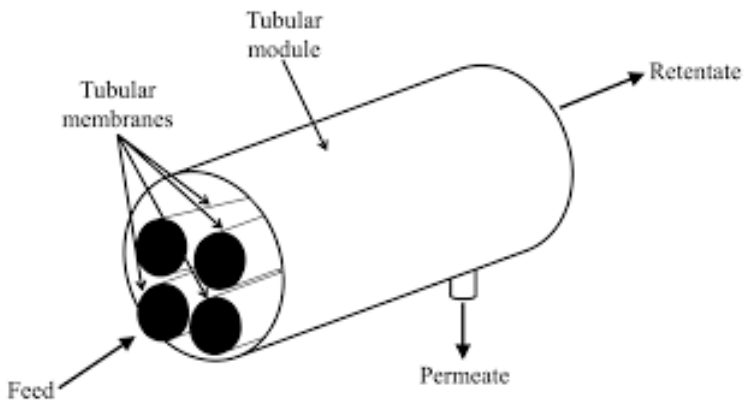

Figure 9: Schematic of Tubular Membrane.

3.5 Membrane Contactor for Nitrogen Recovery

Due to their ability to efficiently remove and recover nitrogen from the sludge centrate, as show in pilot plant studies, HF-LLMCs are becoming an increasingly popular choice for future implementation into WWTPs. As the HF-LLMC works with the aid of an acid stripping solution, the selection of acid can provide a valuable product at the end of the process. Typically, the stripping acid is phosphoric, nitric, or sulphuric acid. These can react with the TAN from the wastewater to form a saleable product which is normally a fertiliser.

The pH of a solution greatly influences the proportion of NH_4^+ to NH_3 present within. Increasing the pH leads to an increase in OH^- ions which converts NH_4^+ into NH_3. The chemical equation showing this relationship is shown below *(reaction h).* A pH of 9 or above favours the conversion to NH_3 gas [53].

$$NH_{4\,(g)}^{+} + OH^{-} \rightarrow NH_{3\,(g)} + H_2O \qquad \text{(h)}$$

The NH_3 gas diffuses from the sludge centrate solution into the pores of the HF-LLMC. As the hollow fibres are hydrophobic, only the NH_3 can enter the pores, the water remains in the feed solution. Once present in the pores, the NH_3 is absorbed by the stripping solution where it can be recovered. This is shown in *Figure 10.*

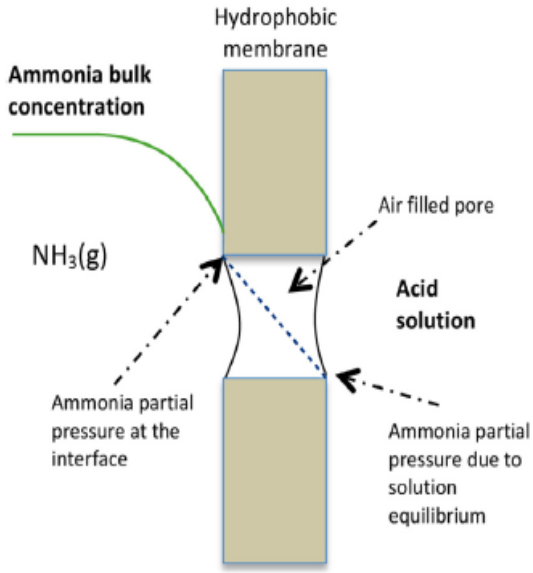

Figure 10: Diagram for the Removal of NH_3 in HF-LLMC.

In this project, the stripping solution used was sulphuric acid. The NH_3 gas is absorbed by the sulphuric acid, where it reacts to produce ammonium sulphate:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \quad \text{(i)}$$

The formation of ammonium sulphate provides a profitable product that can be sold on for use in multiple industries. It is mostly used within the fertiliser industry, when both nitrogen and sulphur based fertilisers are required [54]. It is also a key component within the bread-making process where it activates yeast, allowing bread to rise, and can also increase the shelf-life of such products [55].

4 Materials, Methodology and Analysis

4.1 Materials

4.1.1 Membrane Contactor

The MC used in this study is a commercial HF-LLMC, manufactured by Liqui-Cel, 3M (USA), specifically EXF – 2.5 x 8 Series. Membrane specifications can be found in *Table 1 [32].*

Table 1: Specification of the Hollow Fibre Membrane Contactor.

Hollow-fibre membrane module	2.5 x 8 Liqui-Cel Membrane
Membrane fibre / potting material	Polypropylene / Polyethylene
Fibre outer diameter / inner diameter	300 / 220 µm
Membrane porosity	40%
Membrane area	1.4 m^2
Liquid flow limits	
Shell side	0.16 – 1.8 m^3/h
Lumen side	0.1 – 0.7 m^3/h
Priming volume	
Shell side	0.4 L
Lumen side	0.15 L
Maximum shell side allowable working temperature / pressure	40 °C / 7.2 bar
Maximum lumen side allowable working temperature / pressure	70 °C / 4.8 bar
Pore diameter	0.03 µm

4.1.2 Feed Solutions

Three wastewater compositions were used as the feed solution in this study:

1. ammonium chloride (NH_4Cl)
2. ammonium chloride and organic matter (OM)
3. ammonium chloride, organic matter, and ions

OM consisted of peptone, meat extract, glucose, and K_2HPO_4. Calcium chloride and magnesium chloride were chosen to represent the ions. The feed solutions were prepared by dissolving NH_4Cl, along with OM and ions, where applicable, in 2 L and 2.5 L of distilled H_2O for 20 °C and 35 °C respectively. Prior to the experiment, the pH was altered using 1 M NaOH until pH 10 was reached. All calculations to determine masses required for the feed solutions can be found in *Appendix A-2.*

4.1.3 Stripping Solution

The stripping solution was prepared using sulphuric acid (H_2SO_4, 96%) dissolved in 2.5 L of distilled H_2O. Two concentrations were required: 0.05 and 0.1 M. The respective volumes required to achieve each concentration were 6.941 and 13.881 mL. Calculations to determine these volumes can be found in *Appendix A-2.*

4.1.4 Cleaning Solutions

The MC cleaning procedure required both an alkaline and acidic solution to be circulated through the shell-side system. The alkaline solution was 1 M sodium hydroxide (NaOH), pH 12, prepared in 1.4 L of distilled H_2O. The acidic solution was 1 M citric acid ($C_6H_8O_7$), pH 1, prepared in 1.4 L of distilled H_2O. To prevent waste of chemicals, both solutions were reused 3 times before being discarded. Storage at room temperature was sufficient.

4.2 Methodology

The experiments conducted as part of this study had the following varying parameters: wastewater composition, acid stripping concentration and feed solution temperature. The flowrate of feed and stripping solutions was kept constant at 30 L/h. A summary of the conditions can be seen in *Table 2.* Room temperature was assumed to be 20 °C.

Table 2: Summary of Experimental Conditions for this Study.

Experiment no.	Feed composition	Acid concentration (M)	Feed temperature (°C)
1	NH_4Cl only	0.05	20
2	NH_4Cl & OM	0.05	20
3	NH_4Cl, OM & ions	0.05	20
4	NH_4Cl only	0.05	35
5	NH_4Cl & OM	0.05	35
6	NH_4Cl, OM & ions	0.05	35
7	NH_4Cl only	0.1	20
8	NH_4Cl & OM	0.1	20
9	NH_4Cl , OM & ions	0.1	20
10	NH_4Cl only	0.1	35
11	NH_4Cl & OM	0.1	35
12	NH_4Cl, OM & ions	0.1	35

4.2.1 Experimental Procedure

All experiments were conducted in a closed-loop, counter-current configuration. Pressure was monitored at multiple locations to ensure no pressure increase occurred throughout the system. Flow indicators were also used to monitor a constant flow throughout. *Figure 11* illustrates the experimental set up. The synthetic sludge centrate feed solution was passed through the shell of the HF-LLMC, whereas the stripping solution was passed through the lumen side. Additionally, photos of all equipment and analytical kits used are located in *Appendix A-3.*

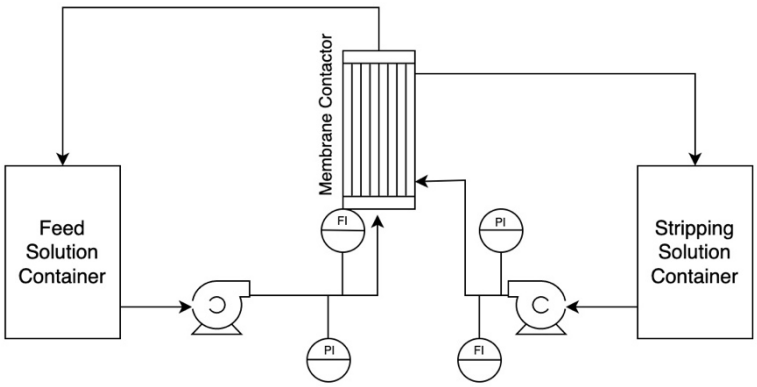

Figure 11: Schematic Diagram of Experimental Set Up.

4.2.1.1 Initial Tests

At the pre-experiment stage, initial tests were carried out on the pilot plant using distilled H_2O in both the shell and lumen side. The shell container was filled with 2 L of distilled H_2O and the pump was turned on and adjusted until a flowrate of 30 L/h was reached at which a timer was started. At time intervals of 0, 5 and 10 minutes, the time taken to obtain a 250 mL sample was recorded to calculate the flowrate. After 10 minutes, the pump was switched off and the same method was followed to obtain the results for the lumen side. Once both sides were completed individually, the flowrates were then measured running simultaneously. Similar to before, the flowrate for both was set at 30 L/h, although the time taken to obtain a 250 mL sample was recorded only at 0 minutes.

4.2.1.2 Experimental Tests

The feed solution was prepared following the method discussed in *4.1.2 Feed Solutions.* Two samples were taken prior to the beginning of the experiment: one before the pH was altered and one after pH 10 was achieved. The feed solution was then decanted into the feed container on the pilot plant. Similar, the acid solution was prepared following *4.1.3 Stripping Solution.* The acid solution was decanted into the lumen container on the pilot plant. No samples of the acid solution were required.

Depending on the experiment carried out, adjustments had to be made to achieve the desired feed solution temperature. For experiments at 20 °C, no further adjustments were required. Conditions for 35 °C feed temperature required a digital thermometer and thermistor to monitor and control the temperature. Both were fully submerged within the feed container and the thermistor turned on. Once a temperature of 35 °C was recorded, the experiment could proceed. As the temperature was controlled manually, a range of $\pm$ 2 °C was allowed. Throughout the experiment, the thermometer was monitored closely, and the thermistor turned off / on as required to maintain the operating temperature.

Both the shell and lumen pump were switched on and adjusted until a flowrate of 30 L/h was read on the flow meter. Once this was achieved, the timer was started, and the time taken to obtain a 250 mL sample was recorded on both sides. At time interval 15 minutes, the time taken to obtain a 250 mL sample was recorded again on both sides, with an approx 25 mL sample from the feed solution being taken for further analysis. This method was repeated at time intervals of 30, 60, 90 and 120 minutes. For the experiments carried out at 35 °C, the temperature of both the shell and lumen side were recorded at each time interval to monitor the heat transfer between the two.

4.2.2 Cleaning Procedures

The HF-LLMC was cleaned in-between each experiment. A recommended cleaning procedure document was provided by the manufacturing company and the appropriate procedure was chosen: *'Recommended Cleaning Procedure for Routine/Maintenance for Fouling'* [45]. This was selected as the best option due to the nature of the experiment; the contactor was not exposed to harsh water conditions. Adjustments were made to the recommended duration of each step to best suit the contactor. All H_2O flushes were carried out in an open-loop configuration whereas the alkaline and acidic flush were closed-loop.

Once the experiment was finished, the shell and lumen containers were emptied, with their contents discarded. Both containers were rinsed 2 times with tap H_2O, then filled with distilled H_2O. The pumps were turned on and set to 30 L/h. Distilled H_2O was left to flush through the plant, with the containers refilled as needed. This was carried out until a conductivity of approx 36 µS was noted in both discharge streams. The next step was an alkaline (NaOH) flush which was circulated only in the shell side, for 30 minutes. An alkaline flush helps to remove any biofouling which may have occurred in the MC. The feed side was then flushed again with distilled H_2O until a conductivity of 50 – 100 µS was recorded in discharge. After, an acidic flush ($C_6H_8O_7$) was circulated through the shell side for 30 minutes. An acid solution helps removal mineral scaling and neutralize the previous alkaline flush.

Finally, both the shell and lumen side were flushed with distilled H2O until a conductivity of 50 – 100 µS was recorded in discharge.

4.3 Analysis

Samples taken throughout were analysed for: pH, conductivity, NH_4^+ concentration, chemical oxygen demand (COD) concentration, calcium (Ca^{2+}) concentration and magnesium (Mg^{2+}) concentration. COD concentration was only measured experiments using feed solution compositions 2 and 3, whereas the Ca^{2+} and Mg^{2+} concentrations were only measured when feed solution composition 3 was used. The samples were stored in a fridge when not in use (to avoid degradation) and were allowed to acclimatise to room temperature prior to carrying out analytical tests.

4.3.1 Conductivity and pH

The conductivity was measured using a *Conductimeter GLP31+* (Crison, Spain). Conductivity was only measured in the initial feed solution sample and the initial feed solution after pH 10 adjustment. The probe was placed in the sample and the reading was left to stabilise. Once stabilised, the conductivity reading was recorded in µS/cm.

The pH of the samples were measured using a *pH-Meter GLP21* (Crison, Spain). pH was only measured in the initial feed solution sample. The probe was placed in the sample and the pH meter was set to stability mode. The reading was left to stabilise before recording the final value.

4.3.2 NH_4^+ Concentration

NH_4^+ concentration was measured using a cell test kit from Merck (ref. 1.14559.0001), with a range of 4.0 – 80.0 mg/L NH_3-N. The samples had to be diluted prior to testing due to the range of the test kit. The dilution rates were: 1:10 for initial feed sample and initial feed sample after pH10, 1:5 for feed solution at t15 and t30, 1:4 for feed solution at t60 and t90 and then 1:3 for feed solution at t120. After the reagent had been added to the cell, the concentrations were measured using a Merck *NOVA 30 Spectrophotometer.* The spectrophotometer results were then multiplied by the corresponding dilution rate to achieve the final NH_4^+ concentration of each sample.

4.3.3 OM Concentration

The OM concentration was calculated in respect to COD. It was also measured using a cell test kit from Merck (ref. 1.14541.0001) for a COD range of 25 – 1000 mg/L. Only the initial feed solution after pH adjustment and feed solution at t120 were measured for their COD concentration, both at a dilution rate of 1:3. The COD cell had to be heated to 148 °C for two hours using a Merck *TR 300 Thermoreactor.*

After two hours, the cells were left to cool down for thirty minutes before the COD value could be determined using the spectrophotometer. The values were multiplied by three for the final COD concentrations.

4.3.4 Ca^{2+} and Mg^{2+} Concentration

Both the Ca^{2+} and Mg^{2+} concentration were measured using cell test kits from Merck (ref. 1.00858.0001 and ref. 1.00815.0001 respectively). Similar to the COD cell test kit, only the initial feed solution after pH adjustment and the feed solution at t120 were measured, both at a dilution rate of 1:3. The calcium test kit had a range of 10 – 250 mg/L Ca and magnesium a range of 5 – 75 mg/L Mg. The reagents were added to their respective cell kits and left to stand for 3 minutes. Once done, both concentrations were determined using the spectrophotometer and multiplied by three for the final Ca^{2+} and Mg^{2+} concentrations.

5 Results and Discussion

5.1 Overview

Table 3: Summary of Experimental Conditions and their respective NH_4^+ Removal Efficiencies.

Exp No.	Feed Comp	Acid Conc (M)	Feed Temp (°C)	NH_4^+ Removal (%)
1	NH_4Cl only	0.05	20	63.55
2	NH_4Cl & OM	0.05	20	60.92
3	NH_4Cl, OM & ions	0.05	20	65.98
4	NH_4Cl only	0.05	35	64.42
5	NH_4Cl & OM	0.05	35	66.86
6	NH_4Cl, OM & ions	0.05	35	69.77
7	NH_4Cl only	0.1	20	64.56
8	NH_4Cl & OM	0.1	20	63.40
9	NH_4Cl, OM & ions	0.1	20	64.34
10	NH_4Cl only	0.1	35	69.82
11	NH_4Cl & OM	0.1	35	66.33
12	NH_4Cl, OM & ions	0.1	35	71.52

From the experiments conducted, it was found that the HF-LLMC was able to effectively separate NH_4^+ from synthetic sludge centrate. The NH_4^+ removal efficiency from the feed solution was calculated using *Equation 3*, with the results displayed in *Table 3*. An average removal efficiency was then calculated by taking an average of that achieved across the twelve experiments, with a value of 66.36% being achieved. A study conducted by *Tan et al.* using the same HF-LLMC, but different operating parameters also achieved efficiencies in the range of 60% [56]. Other studies obtained higher average efficiencies of 70 – 99%, although these operated with longer contact time between the two phases and different stripping solutions, therefore they were not a fair comparison with the results from this study [6][32]. From *Table 3*, experiment 12 (highlighted yellow) provided the highest NH_4^+ removal efficiency of 71.52% with optimal conditions being a feed temperature of 35 °C and an acid concentration of 0.1 M. The wastewater composition for these conditions consisted of NH_4Cl, organic matter, and ions.

Repeating each of the experiments and analytical tests would have allowed for a comparison in the data recorded and an average could have been taken. It also minimises the margin of error on the current data obtained from this study. The additional data would have given more precise and reliable results for a conclusion to be drawn. Other improvements to the experiment itself include more

frequent samples taken at smaller time intervals. This would have improved the graphical relationship of the experimental variables against time and any inconsistencies may have been observed earlier.

5.2 Influence of Feed Temperature

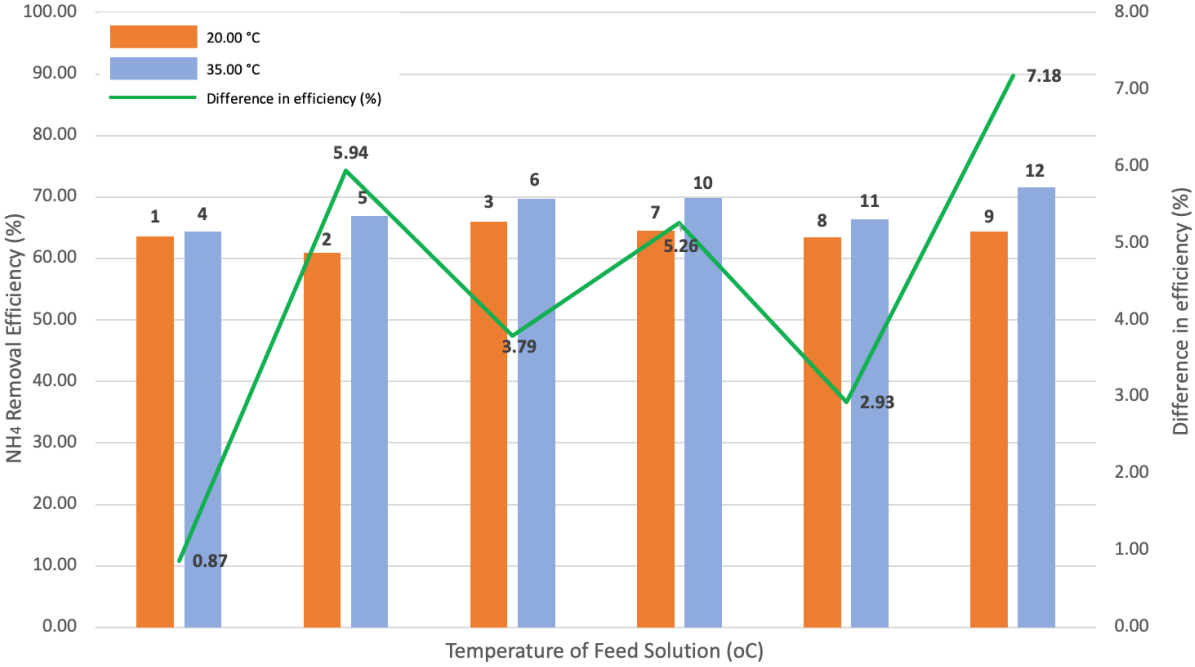

Figure 12: Comparison of NH_4^+ Removal Efficiency at Feed Temperatures of 20 °C and 35 °C

Figure 12 shows that the removal efficiency increases as the temperature increases. When the temperature increased from 20 °C (orange) to 35 °C (blue), the average efficiency increased from 63.79% to 68.12%. The green line shows the difference in efficiency between each of the compared experimental data, which gives the average increase of 4.3% between the feed temperatures. When comparing the difference in efficiency achieved, it can be seen that experiments 1 and 4 had the lowest difference, whereas 9 and 12 had the greatest difference. This could be down to additional influence from the acid concentration as experiments 1 and 4 were conducted with 0.05 M concentration, with 9 and 12 conducted at 0.1 M concentration. A study conducted by *Noriega-Hevia et* al. compared similar temperatures, 25 °C and 35 °C, and also observed a trend of the temperature increase resulting in a higher removal efficiency [57].

The increase is attributed to an increase in mass diffusion rate at higher temperatures as the molecules gain more kinetic energy and travel faster through the membrane [58][59]. As the pilot plant is set up in a closed-loop configuration, an increase in mass diffusion rate will result in the feed solution passing more frequently through the HF-LLMC and an increase in contact time between the two solutions. This will allow more NH_4^+ to be stripped from the feed solution and absorbed into the acid solution, thus increasing the removal efficiency. The optimal operating temperature for the

removal of NH_4^+ in the MC is 35 °C. Although this may require more energy, the higher removal efficiency achieved outweighs a slightly larger energy consumption.

When carrying out the experiments at 35 °C, the temperature was manually controlled by monitoring a digital thermometer submerged in the feed solution and switching a thermistor on/off. This resulted in the temperature fluctuating and falling below or exceeding the operating condition. An allowance of $\pm$ 2 °C was set. Although the temperature was not maintained throughout, this was thought to cause minimal impact to the data obtained and overall results of the study as they still aligned with the expected (and documented) trend. Recommendations for improving this could include the use of an automatic temperature control, to reduce the chance of human error. Introducing a temperature bath for the feed solution container would provide a constant temperature throughout the experiment.

5.3 Influence of Acid Stripping Concentration

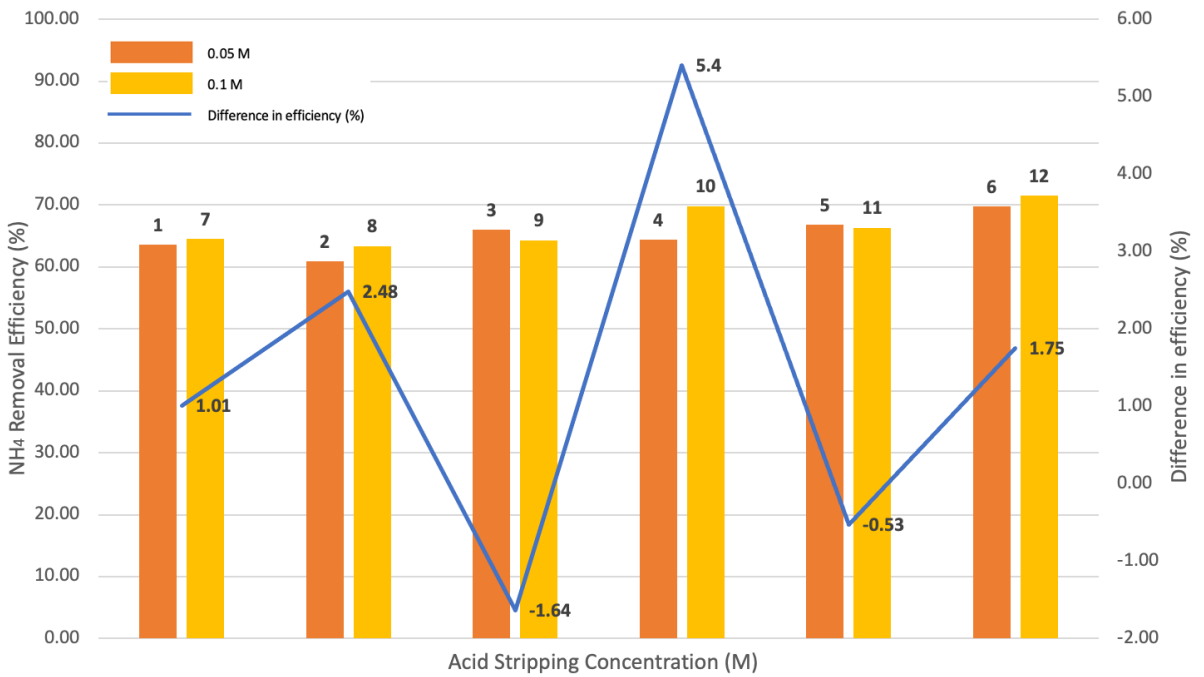

Figure 13: Comparison of NH_4^+ Removal Efficiency at Stripping Concentrations of 0.05 M and 0.1 M.

Figure 13 shows the relationship between the NH_4^+ removal efficiency and the concentration of the acid stripping solution. From 0.05 M (orange) to 0.1 M (yellow), the average removal efficiency increased from 65.25% to 66.66%. Other studies observed the same trend, albeit one used a different type of MC and the other a different acid stripping solution, they both exhibited an increase in removal efficiency as the acid concentration increased [60][61]. This increase is thought to occur due to Fick's

law of diffusion *(Equation 4)* which states that the rate of diffusion is proportional to the difference in concentration [62]. Fick's law assumes there is a uniform pressure throughout the system.

$$J_A = -D\frac{d\varphi}{dx} \tag{4}$$

Similar to that mentioned previously in *5.2 Effect of Temperature,* an increase in the diffusion rate through a closed-loop configuration will increase the contact time between the two solutions in the MC and result in more NH_4^+ being stripped and reabsorbed by the acid solution.

On *Figure 13*, the blue line indicates the difference in efficiency between each of the compared experimental data, which gave an average increase of 1.41% between the stripping concentrations. The negative values represent where the efficiency from the 0.05 M experiment was higher than that of the 0.1 M. This could have been down to human error due to a such a small average increase.

Although the comparison between experiment 4 and 10 showed a definitive increase in removal efficiency, increasing the concentration from 0.05 M to 0.1 M did not provide a significant increase. It is important to view this from an economical point to determine if higher concentration costs would benefit the overall removal of NH_4^+. This assumption was based on the results achieved from this study and may vary depending on the volume of sludge centrate being treated and the scale of the WWTP.

5.4 Influence of Wastewater Composition

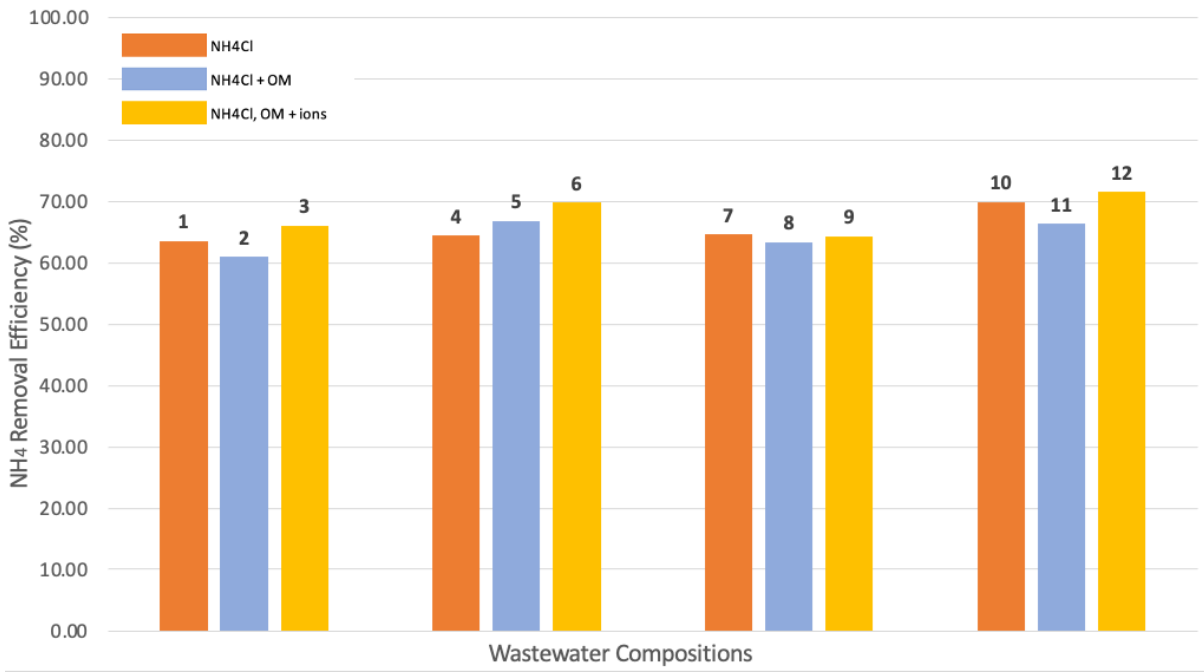

Figure 14: Comparison of NH_4^+ Removal Efficiency at Varying Wastewater Compositions.

Figure 14 illustrates that the highest removal efficiencies occurred when the synthetic wastewater comprised of NH_4Cl, OM, and ions (yellow). NH_4Cl alone (orange) provided an average efficiency of 65.59%, the addition of OM (blue) gave 64.38% and with ions added gave 67.90%. Although there were slight variations in the removal efficiency, a direct relationship or trend could not be identified. It was assumed that the wastewater composition had no influence on the NH_4^+ removal from the sludge centrate. This result was to be expected as sludge centrate obtained from a real WWTP will always have other substances such as OM and ions present. It is important to highlight that as these results show the addition of other substances does not affect the removal efficiency, the membrane contactor is ideal for the NH_4^+ removal from sludge centrate.

To justify the assumption of a lack of trend within the wastewater composition influence, an additional experiment using a synthetic wastewater of NH_4Cl and ions would be recommended. The results from this experiment would allow for discussion into whether the presence of ions could enhance the removal efficiency or whether the previous assumption of no trend is correct. Further experiments using real sludge centrate would provide a comparison between that and the synthetic sludge centrate to verify whether the results achieved in this study mimic that of a real WWTP.

One study, by *Ashrafizadeh et al.,* researched the effect of excess ions present within the feed solution [32]. They observed that the additional ions did not influence the removal of TAN and therefore their results agree with that of this study. Other than this study, it was challenging to find additional research that agreed or was comparable with the experimental data achieved in this one. This was due to the majority of studies conducting their experiments on sludge centrate obtained from a commissioned wastewater plant, rather than creating a synthetic version in the lab. These feed solutions would have already contained the substances rather than observing their influence.

5.5 Influence of Contact Time

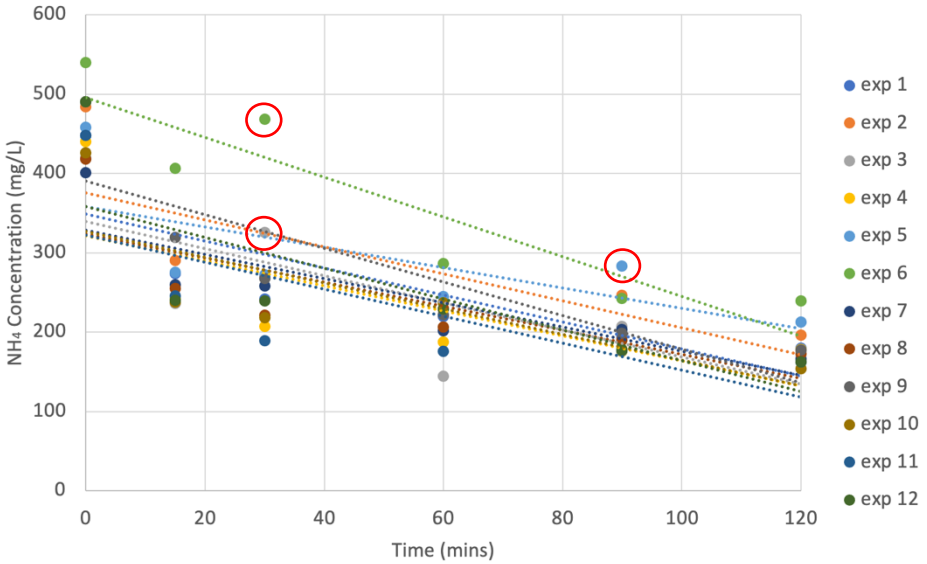

Figure 15: NH_4^+ Concentration vs Time.

The contact time between the two solutions directly influenced the removal efficiency of NH_4^+. *Figure 15* illustrates how the NH_4^+ concentration decreased with time. After two hours, it can be seen that the majority of the NH_4^+ is removed from the sludge centrate in each of the twelve experiments although there were some noticeable outlier points (red circles). These discrepancies could have occurred from either difficulty controlling the 35 ^oC feed temperature or an error in measurements, rather than the contact time itself. Although some of the points at x = 0 may appear as outliers in regard to their line of best fit, they were ruled out as the experiment had not begun when these initial concentrations were calculated. Another graph, located in *Appendix A-4.1,* was plotted to show an additional version of the relationship between the removal efficiency and contact time.

The relationship between the contact time and the NH_4^+ concentration can be explained following a similar theory of that mentioned within the influence of feed temperature and acid stripping concentration. This relationship is in agreement with that observed in a study conducted by *Ashrafizadeh et al.* which used the same type of MC and stripping solution [32]. Further experiments for studying the influence of this parameter would be to increase the total duration of the experimental procedure and compare the results obtained from that and two hours.

5.7 Future Research Opportunities

From the experimental data collected in this study and the analysis of the results, it is clear there is an opportunity for future research to be conducted surrounding the HF-LLMCs use for nitrogen recovery. Although the study was based on a synthetic sludge centrate, it shows promising results that can hopefully be recreated using sludge centrate from a commissioned WWTP. Had more time been available for this study, the next step in the continuation of it would be to repeat these experiments, under the same operating conditions, using real sludge centrate. Achieving similar results between the synthetic and real sludge centrate would confirm the beneficial aspect of carrying out this project and show its contribution towards the more economical route for the removal and recovery of nitrogen. Comparable results could also aid the process of introducing HF-LLMCs into WWTPs in the future.

With the same pilot plant set-up, further experiments could be carried out by adjusting the operating parameters already selected. This includes increasing the feed temperature higher than 35 ^oC, an acid stripping concentration greater than 0.1 M and allowing the experiment to run for longer than 2 hours. Increasing the operating range of these conditions would provide further clarification on their influence on the removal efficiency. It could also identify more optimal operating conditions than that found in this study.

Additional experiments with different operating parameters could also be used in order to study their influence and gain a more comprehensive understanding into the overall optimal conditions for the removal of nitrogen from sludge centrate. Some of these parameters include:

1. Using different acid compositions, including phosphoric and nitric acid. It may also be interesting to identify if a mix of two acids can provide a greater benefit to the removal efficiency.
2. Vary the flowrate of both the feed and stripping solutions. Whilst this project didn't focus on this parameter, a similar theory of increasing the contact time between the solutions within the HF-LLMC was discussed. Using different flowrates would provide a direct comparison between the contact time and removal efficiency.
3. Adjust the pH of the feed solution. The conversion of NH_4^+ to NH_3 gas is directly affected by the pH therefore this would also relate to studying the influence of the initial NH_4^+ concentration in the feed solution. Recommended pH's would be 9 and 11.
4. Using different configurations of membrane contactors. Although HF-LLMC are the preferred within wastewater treatment, conducting experiments with flat-sheet and tubular modules will give an overview into any potential applications they have within the industry and confirm if HF-LLMC is the most suitable choice.

6 Economics

6.1 Feed, Stripping and Cleaning Chemicals Used

An estimate of prices of chemicals consumed throughout the experiments was calculated. Additionally, the potential selling price of ammonium sulphate was calculated based on total volume produced across the 12 experiments and the current buying price. All prices were obtained from Merck [63], with the closest specification to that used in the project chosen. A full summary of the costs can be found in *Table 4.*

Table 4: Cost Breakdown of Chemicals Used and Produced.

Chemical	Price per mass / volume	Total mass / volume required for experiments	Total Price
CHEMICALS CONSUMED			
Ammonium Chloride	62.24 € / 500 g	42.67 g	5.31 €
Peptone	309.4 € / 500 g	1.43 g	0.89 €
Meat Extract	303.45 € / 500 g	1.43 g	0.87 €
Glucose	178.50 € / 500 g	3.18 g	1.13 €
K_2HPO_4	76.52 € / 500 g	0.35 g	0.05 €
Calcium Chloride	298.69 € / 500 g	2.66 g	1.59 €
Magnesium Chloride	90.20 € / 500 g	2.44 g	0.44 €
Sulphuric Acid (0.05 M)	148.75 € / 250 mL	41.65 mL	24.78 €
Sulphuric Acid (0.1 M)	148.75 € / 250 mL	83.29 mL	49.56 €
CHEMICALS PRODUCED			
Ammonium Sulphate	19.03 € / 1000 g	53100 g	1010.39 €

As mentioned previously in *Section 4.1.4*, both the alkaline and cleaning solutions were used three times before being discarded. Due to the high volume of distilled H_2O consumed throughout the experiments, it was unfeasible to predict a total consumption value. The price per 1 L of distilled H_2O is provided for future calculations when a reasonable value can be determined [64]. *Table 5* shows a breakdown of costs for the chemicals required in the cleaning procedure.

Table 5: Cost Breakdown for Cleaning Procedure Chemicals.

Chemical	Price per mass / volume	Total mass / volume required for experiments	Total Price
Citric Acid	71.28 € / 500 g	804 g	114.62 €
Sodium Hydroxide	28.08 € / 500 g	168 g	9.44 €
Distilled Water	1.25 € / L	-	-

6.2 Equipment

All cell test kits used were from manufacturer, Merck. Four different kits were used, as mentioned in *Section 4.3*, for measuring the concentration of substances within the samples. All kit prices were obtained from Merck [63].

Table 6: Cost Breakdown of Cell Test Kits.

Cell Test Kit	Price (€)
NH_4^+	135
COD	97.50
Ca^{2+}	175
Mg^{2+}	155
TOTAL	562.50

The membrane contactor used was a commercial HF-LLMC, constructed by company 3M. The specific model was: Liqui-Cel EXF – 2.5 x 8 Series. Due to a lack of available information for the cost of the HF-LLMC and time constraints for obtaining quotes from the manufacturer, an accurate price could not be determined. Although, based on similar membrane contactors available, an estimate cost of 1500 € was taken.

6.3 Personnel Cost

Additional costs were considered for personnel such as technicians and engineers. *Table 7* shows a summary breakdown for hourly costs of both personnel.

Table 7: Cost Breakdown for Personnel.

Item	Hourly Cost (€/h)	Hours	Total Cost (€)
Technician	60	100	6000
Engineer	80	10	800
		TOTAL	6800

6.4 Total Budget

It is necessary to add an additional 10% of the total budget costs to account for electrical and other potential direct costs (DC). Additionally, 25% must be added for value added tax (VAT). This is shown in *Table 8*.

Table 8: Overall Cost Breakdown Including DC and VAT.

Item	Cost (€)
Lab Materials	208.67

Equipment	2062.50
Personnel	6800
TOTAL COST	9071.17
10% DC	907.12
25% VAT	2267.79
TOTAL BUDGET	12,246.08

Therefore, the final budget of this project was TWELVE THOUSAND, TWO HUNDRED AND FORTY SIX EUROS AND EIGHT CENTS (12,246.08 €), VAT included.

7 Conclusion

Twelve experiments were conducted on a hollow fibre liquid-liquid membrane contactor (HF-LLMC) to separate ammonium nitrogen (NH_4^+) from a synthetically made sludge centrate. The experiments had varying operating conditions in order to study their influence on the removal efficiency of nitrogen and identify the optimal operating conditions. The highest nitrogen removal efficiency was 71.52%, recorded in experiment 12. The conditions were: a feed temperature of 35 ^oC, a sulphuric acid stripping concentration of 0.1 M, feed and stripping flowrates of 30 L/h, and a wastewater composition of ammonium chloride (NH_4Cl), organic matter (OM) and ions.

The study concluded that the key operating parameters that directly influenced the removal of nitrogen were the feed solution temperature and acid stripping concentration. As both of these variables increased, this led to an increase in the removal efficiency. These relationships were driven by an increase in mass transfer rate which allowed more NH_4^+ to be stripped from the feed solution and reabsorbed by the sulphuric acid. It was also shown that an increase in contact time of the two solutions within the HF-LLMC led to more NH_4^+ being removed from the sludge centrate. Contrastingly, the experimental data showed the wastewater composition had no influence on the removal efficiency.

Recommendations towards this study include introducing the use of an automatic temperature control system, such as a temperature bath. This would provide a constant feed solution temperature throughout the experiment. Additionally, it was suggested to carry out a further experiment with a wastewater composition of NH_4Cl and ions. The data obtained from this would allow for confirmation that the wastewater composition does not influence the removal efficiency.

The overall average efficiency across the twelve experiments was calculated to be 66.36%, with a minimum and maximum efficiency of 60.92% and 71.52%. As the majority of the ammonium nitrogen was removed, it can be assumed that the HF-LLMC is a feasible technology for the recovery of nitrogen from the sludge centrate.

8 Personal Reflection and Review

At the beginning of the project, I set myself personal objectives to work towards throughout and overall, I feel all objectives were met. Working within the PROMETEO research team at UPV provided an in-depth insight into WWTPs and membrane technologies. By having access to the others masters' students and their project work, I was able to gain a thorough understanding of the work being conducted by this research group contributing to resolving issues within the wastewater industry and providing sustainable alternatives.

Prior to this project, my experience within a lab setting was limited and at the beginning I required supervision to carry out experimental and analytical tests. I became familiar with the practical tests very quickly to the extent that no supervision was required, my advisors were confident in my abilities, and I was confident sharing the results of my experiments and explaining how my pilot plant operated to academic staff within the UPV team.

Prior to this project, my knowledge of the current challenges of a wastewater treatment plant and membrane technology was very limited. Modules completed at Strathclyde for example: Environmental Technology, Advanced Separations and Mass Transfer & Separations, provided a basic understanding of the topics, which still proved helpful. Had I not had this knowledge beforehand, I believe I would have experienced difficulty grasping the basic concepts, and with moving on to the more in-depth and complex research. Carrying out this study allowed me to apply the theoretical information learned in lectures and put it into practise in a practical situation. Furthermore, completing modules such as Chemical Engineering Design (completed in both Year 3 & 4) provided me with some experience of writing and structure of a research report. Completing this solo project, compiling the report, and delivering the presentation has given me valuable project and life experience, which I am sure will be really valuable skills to apply and develop in my future career.

Initially, there was a slight delay to the start date of my research work, due to the allocation of research projects identified by UPV. In considering deadlines set by both UPV and Strathclyde, I was keen not to fall behind at an early stage and therefore before beginning any experiments, I decided to start the initial theory research of my report. I began researching the background of wastewater treatment plants and trying to familiarise myself with the membrane contactor technology prior to experiments. Starting the theory portion of the project early ensured I was engaged in the work and, on reflection, showed me that I was confident to use my initiative and not wait for instructions to start. It also made me focus on my time-management skills ensuring a balanced workload once my experiments

commenced, whilst at the same time settling into living in a new country and sharing accommodation with fellow students.

The biggest challenge I faced working in a foreign country I faced was the ability to communicate effectively with colleagues given the language barrier with some. This was especially evident in a technical environmental where it was not just conversational Spanish being used by UPV staff and other masters' students. I found myself having to be more considerate of the pace at which I spoke and how I described things. One of my advisors took the time to teach me the basics of Spanish for lab equipment so I was able to communicate better with the other students in the lab and this was extremely helpful and boosted my confidence. In return, I was able to help her improve her spoken English slightly and through this exchange we were able to build a really good working and productive relationship. The opportunity to improve my communication skills and build good working relationships with the research team has, to me, been an important part of my overall project and I have gained valuable experience which will be also beneficial in my future professional career. I also enjoyed learning the basics of a new language and am considering continuing with this after the exchange.

In summary, undertaking this project in Valencia has provided me with invaluable life experience and I am grateful to have had this opportunity. Moving to a foreign country pushed me outside of my comfort zone and showed me I am capable of adapting to a new culture and lifestyle. I have become more confident asking for support and guidance, and living and working in a new, and unfamiliar, environment. The personal goals I set myself have definitely been met and the new skills I have learned will benefit me greatly when I move into a graduate role to begin my professional career.

9 References

[1] Ellen MacArthur Foundation, 'Circular economy introduction: What is a circular economy?', 2022. https://ellenmacarthurfoundation.org/topics/circular-economy-introduction/overview (accessed Feb. 16, 2022).

[2] thyssenkrupp, 'Ammonia in agriculture: The engine of plant growth', 2022. https://www.thyssenkrupp.com/en/stories/sustainability-and-climate-protection/ammonia-in-agriculture:-the-engine-of-plant-growth (accessed Mar. 09, 2022).

[3] BYJUS, 'Haber's Process for the Manufacture of Ammonia & Its Uses', 2022. https://byjus.com/chemistry/haber-process/ (accessed Mar. 09, 2022).

[4] L. K. Boerner, 'Industrial ammonia production emits more CO2 than any other chemical-making reaction. Chemists want to change that', *Chem. Eng. News*, vol. 97, no. 24, Jun. 2019, [Online]. Available: https://cen.acs.org/environment/green-chemistry/Industrial-ammonia-production-emits-CO2/97/i24

[5] S. N. Behera, M. Sharma, V. P. Aneja, and R. Balasubramanian, 'Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies', *Environ. Sci. Pollut. Res.*, vol. 20, Aug. 2013.

[6] X. Vecino, M. Reig, B. Bhushan, O. Gibert, C. Valderrama, and J. L. Cortina, 'Liquid fertilizer production by ammonia recovery from treated ammonia-rich regenerated streams using liquid-liquid membrane contactors', *Chem. Eng. J.*, vol. 360, pp. 890–899, Mar. 2019, doi: 10.1016/j.cej.2018.12.004.

[7] Z. Guo, Y. Sun, S.-Y. Pan, and P.-C. Chiang, 'Integration of Green Energy and Advanced Energy-Efficient Technologies for Municipal Wastewater Treatment Plants', *Int. J. Environ. Res. Public. Health*, vol. 16, no. 7, p. 1282, Apr. 2019, doi: 10.3390/ijerph16071282.

[8] Persistence Market Research, 'Ammonia Market', May 2021. https://www.persistencemarketresearch.com/market-research/ammonia-market.asp (accessed Apr. 02, 2022).

[9] eurostat: Statistics Explained, 'Glossary:Urban wastewater', Feb. 26, 2019. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Glossary:Urban_wastewater (accessed Jan. 25, 2022).

[10] A. Oghenerobor, D. A. Otohinoyi, T. D. Olaolu, and J. B. I. Aderiye, 'Pollutants in Wastewater Effluents: Impacts and Remediation Processes', *Int. J. Environ. Res. Earth Sci.*, vol. 3, no. 3, pp. 50–59, Mar. 2014.

[11] V. Magueijo, 'Lecture 6: Wastewater Treatment: Principles of biological treatment II', University of Strathclyde, 2020.

[12] N. O. and A. A. US Department of Commerce, 'What is eutrophication?', May 10, 2017. https://oceanservice.noaa.gov/facts/eutrophication.html (accessed Jan. 26, 2022).

[13] V. Magueijo, 'Lecture 4: Wastewater treatment: General overview + Preliminary and Primary Treatment', University of Strathclyde, 2020.

[14] A. Ambulkar and J. A. Nathanson, 'Wastewater Treatment', Feb. 02, 2021. https://www.britannica.com/technology/wastewater-treatment (accessed Jan. 27, 2022).

[15] S. Oakley, 'Preliminary Treatment and Primary Sedimentation', *Water Sanit. 21st Century Health Microbiol. Asp. Excreta Wastewater Manag.*, Jul. 2018, [Online]. Available: https://www.waterpathogens.org/book/preliminary-treatment

[16] United States Environmental Protection Agency, 'How Wastewater Treatment Works.. The Basics'. May 1998. [Online]. Available: https://www3.epa.gov/npdes/pubs/bastre.pdf

[17] J. Patel, '4-Step Wastewater Sludge Treatment Process', Apr. 03, 2018. https://www.wateronline.com/doc/step-wastewater-sludge-treatment-process-0001 (accessed Jan. 28, 2022).

[18] A. Holst, 'Clean Water Act | United States [1972] | Britannica', in *Encyclopaedia Britannica*, 2015. [Online]. Available: https://www.britannica.com/topic/Clean-Water-Act

[19] M. C. M. van Loosdrecht and S. Salem, 'Biological treatment of sludge digester liquids', *Water Sci. Technol.*, vol. 53, no. 12, pp. 11–20, Jun. 2006, doi: 10.2166/wst.2006.401.
[20] A. Sapkota, 'Nitrification vs Denitrification- Definition, 15 Differences, Examples', *Microbe Notes*, Jan. 02, 2022. https://microbenotes.com/nitrification-vs-denitrification/ (accessed Apr. 11, 2022).
[21] United States Environmental Protection Agency, 'Wastewater Technology Fact Sheet: Ammonia Stripping'. Sep. 2000.
[22] T. C. Jorgensen and L. R. Weatherley, 'Ammonia removal from wastewater by ion exchange in the presence of organic contaminants', *Water Res.*, vol. 37, no. 8, pp. 1723–1728, Apr. 2003, doi: 10.1016/S0043-1354(02)00571-7.
[23] X. Wu and O. Modin, 'Ammonium recovery from reject water combined with hydrogen production in a bioelectrochemical reactor', *Bioresour. Technol.*, vol. 146, pp. 530–536, Oct. 2013, doi: 10.1016/j.biortech.2013.07.130.
[24] L. Kinidi, I. A. W. Tan, N. B. Abdul Wahab, K. F. B. Tamrin, C. N. Hipolito, and S. F. Salleh, 'Recent Development in Ammonia Stripping Process for Industrial Wastewater Treatment', *Int. J. Chem. Eng.*, vol. 2018, p. e3181087, Jul. 2018, doi: 10.1155/2018/3181087.
[25] S. Jafarinejad, H. Park, H. Mayton, S. L. Walker, and S. C. Jiang, 'Concentrating ammonium in wastewater by forward osmosis using a surface modified nanofiltration membrane', *Environ. Sci. Water Res. Technol.*, vol. 5, no. 2, pp. 246–255, 2019, doi: 10.1039/C8EW00690C.
[26] M. S. EL-Bourawi, M. Khayet, R. Ma, Z. Ding, Z. Li, and X. Zhang, 'Application of vacuum membrane distillation for ammonia removal', *J. Membr. Sci.*, vol. 301, no. 1, pp. 200–209, Sep. 2007, doi: 10.1016/j.memsci.2007.06.021.
[27] M. Qin, H. Molitor, B. Brazil, J. T. Novak, and Z. He, 'Recovery of nitrogen and water from landfill leachate by a microbial electrolysis cell–forward osmosis system', *Bioresour. Technol.*, vol. 200, pp. 485–492, Jan. 2016, doi: 10.1016/j.biortech.2015.10.066.
[28] I. A. Talalaj, 'Removal of nitrogen compounds from landfill leachate using reverse osmosis with leachate stabilization in a buffer tank', *Environ. Technol.*, vol. 36, no. 9, pp. 1091–1097, May 2015, doi: 10.1080/09593330.2014.982207.
[29] M. Xie, H. K. Shon, S. R. Gray, and M. Elimelech, 'Membrane-based processes for wastewater nutrient recovery: Technology, challenges, and future direction', *Water Res.*, vol. 89, pp. 210–221, Feb. 2016, doi: 10.1016/j.watres.2015.11.045.
[30] R. Klaassen, P. Feron, and A. Jansen, 'Membrane contactor applications', *Desalination*, vol. 224, no. 1, pp. 81–87, Apr. 2008, doi: 10.1016/j.desal.2007.02.083.
[31] A. Mandowara and P. K. Bhattacharya, 'Membrane contactor as degasser operated under vacuum for ammonia removal from water: A numerical simulation of mass transfer under laminar flow conditions', *Comput. Chem. Eng.*, vol. 33, no. 6, pp. 1123–1131, Jun. 2009, doi: 10.1016/j.compchemeng.2008.12.005.
[32] S. N. Ashrafizadeh and Z. Khorasani, 'Ammonia removal from aqueous solutions using hollow-fiber membrane contactors', *Chem. Eng. J.*, vol. 162, no. 1, pp. 242–249, Aug. 2010, doi: 10.1016/j.cej.2010.05.036.
[33] R. Klaassen, P. H. M. Feron, and A. E. Jansen, 'Membrane Contactors in Industrial Applications', *Chem. Eng. Res. Des.*, vol. 83, no. 3, pp. 234–246, Mar. 2005, doi: 10.1205/cherd.04196.
[34] D. De Meis, *Overview on porous inorganic membranes for gas separation*. 2017. doi: 10.13140/RG.2.2.35571.53287.
[35] P. B. Kosaraju and K. K. Sirkar, 'Novel solvent-resistant hydrophilic hollow fiber membranes for efficient membrane solvent back extraction', *J. Membr. Sci.*, vol. 288, no. 1, pp. 41–50, Feb. 2007, doi: 10.1016/j.memsci.2006.10.050.
[36] M. Stanojevic, B. Lazarevic, and D. Radic, 'Review of membrane contactors designs and applications of different modules in industry', *FME Trans.*, vol. 31, no. 2, 2003, [Online]. Available: https://www.mas.bg.ac.rs/_media/istrazivanje/fme/vol31/2/stanojevic_mirko.pdf

[37] P. Grassia and I. Burns, 'CP302: Mass Transfer and Separation Processes, Part 1 - Introduction to Mass Transfer', University of Strathclyde, 2020.
[38] H. Estay, E. Troncoso, R. Ruby-Figueroa, and J. Romero, 'Assessment of Industrial Modules to Design a GFMA Process for Cyanide Recovery Based on a Phenomenological Model', *Processes*, vol. 6, no. 4, p. 34, Apr. 2018, doi: 10.3390/pr6040034.
[39] M. Darestani, V. Haigh, S. J. Couperthwaite, G. J. Millar, and L. D. Nghiem, 'Hollow fibre membrane contactors for ammonia recovery: Current status and future developments', *J. Environ. Chem. Eng.*, vol. 5, no. 2, pp. 1349–1359, Apr. 2017, doi: 10.1016/j.jece.2017.02.016.
[40] A. Hasanoğlu, J. Romero, B. Pérez, and A. Plaza, 'Ammonia removal from wastewater streams through membrane contactors: Experimental and theoretical analysis of operation parameters and configuration', *Chem. Eng. J.*, vol. 160, no. 2, pp. 530–537, Jun. 2010, doi: 10.1016/j.cej.2010.03.064.
[41] Aurora Alcaraz Segura, 'Ammonium removal from wastewater by liquid-liquid contactors', Universidad Politécnica de Catalunya, Barcelona, 2012. [Online]. Available: https://upcommons.upc.edu/bitstream/handle/2099.1/18480/TFM%20Diciembre%2012.pdf
[42] A. Mansourizadeh and A. F. Ismail, 'Hollow fiber gas–liquid membrane contactors for acid gas capture: A review', *J. Hazard. Mater.*, vol. 171, no. 1, pp. 38–53, Nov. 2009, doi: 10.1016/j.jhazmat.2009.06.026.
[43] M.-C. Yang and E. L. Cussler, 'Designing hollow-fiber contactors', *AIChE J.*, vol. 32, no. 11, pp. 1910–1916, Nov. 1986, doi: 10.1002/aic.690321117.
[44] V. Y. Dindore and G. F. Versteeg, 'Gas–liquid mass transfer in a cross-flow hollow fiber module: Analytical model and experimental validation', *Int. J. Heat Mass Transf.*, vol. 48, no. 16, pp. 3352–3362, Jul. 2005, doi: 10.1016/j.ijheatmasstransfer.2005.03.002.
[45] L. Liu, L. Li, Z. Ding, R. Ma, and Z. Yang, 'Mass transfer enhancement in coiled hollow fiber membrane modules', *J. Membr. Sci.*, vol. 264, no. 1, pp. 113–121, Nov. 2005, doi: 10.1016/j.memsci.2005.04.035.
[46] N. Ghasem and M. Al-Marzouqi, 'Modeling and experimental study of carbon dioxide absorption in flat sheet membrane contactor', *J. Membr. Sci. Res.*, vol. 3, no. 2, pp. 57–63, Jun. 2017, doi: 10.22079/jmsr.2016.20226.
[47] T. Sano, Y. Koga, H. Ito, L. V. Duc, T. Hama, and Y. Kawagoshi, 'Effects of structural vulnerability of flat-sheet membranes on fouling development in continuous submerged membrane bioreactors', *Bioresour. Technol.*, vol. 304, May 2020, doi: 10.1016/j.biortech.2020.123015.
[48] K. Scott, 'Introduction to Membrane Separators', *Handb. Ind. Membr.*, pp. 3–185, 1995, doi: https://doi.org/10.1016/B978-185617233-2/50004-0.
[49] Synder Filtration, 'Plate and Frame Membranes', Jul. 22, 2014. https://synderfiltration.com/learning-center/articles/module-configurations-process/plate-and-frame-membranes/
[50] R. Sarbatly, 'Membrane Fabrications', in *Membrane Technology for Water and Wastewater Treatment in Rural Regions*, 2020, p. 21.
[51] Synder Filtration, 'Tubular membranes', Jul. 22, 2014. https://synderfiltration.com/learning-center/articles/module-configurations-process/tubular-membranes/ (accessed Apr. 13, 2022).
[52] I. G. Wenten, *Recent Development in Membrane and Its Industrial Applications. Membrane Technology in Oil and Gas Industry*. 2005.
[53] 'The Role of pH In The Aquarium Nitrogen Cycle', *BeChewy*, Dec. 11, 2014. https://be.chewy.com/the-role-of-ph-in-the-aquarium-nitrogen-cycle/ (accessed Apr. 14, 2022).
[54] Mosaic, 'Ammonium Sulfate', *Mosaic Crop Nutrition*, 2022. https://www.cropnutrition.com/resource-library/ammonium-sulfate (accessed Feb. 14, 2022).
[55] 'Ammonium Sulfate | Aluminum Sulfate | Aluminum Manufacturers'. https://www.aluminummanufacturers.org/aluminum-sulfate/ammonium-sulfate/ (accessed Apr. 13, 2022).

[56] X. Tan, S. P. Tan, W. K. Teo, and K. Li, 'Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water', *J. Membr. Sci.*, vol. 271, no. 1, pp. 59–68, Mar. 2006, doi: 10.1016/j.memsci.2005.06.057.

[57] G. Noriega-Hevia, J. Serralta, L. Borrás, A. Seco, and J. Ferrer, 'Nitrogen recovery using a membrane contactor: Modelling nitrogen and pH evolution', *J. Environ. Chem. Eng.*, vol. 8, no. 4, p. 103880, Aug. 2020, doi: 10.1016/j.jece.2020.103880.

[58] W. Riedl, 'Membrane-Supported Liquid-Liquid Extraction – Where Do We Stand Today?', *ChemBioEng Rev.*, vol. 8, no. 1, pp. 6–14, 2021, doi: 10.1002/cben.202000032.

[59] Sciencing, 'What Effect Does Temperature Have on the Process of Diffusion?' https://sciencing.com/effect-temperature-process-diffusion-10046049.html

[60] F. Rivera, R. Muñoz, P. Prádanos, A. Hernández, and L. Palacio, 'A Systematic Study of Ammonia Recovery from Anaerobic Digestate Using Membrane-Based Separation', *Membranes*, vol. 12, no. 1, Art. no. 1, Jan. 2022, doi: 10.3390/membranes12010019.

[61] C.-L. Lai, S.-H. Chen, and R.-M. Liou, 'Removing aqueous ammonia by membrane contactor process', *Desalination Water Treat.*, vol. 51, pp. 5307–5310, Jul. 2013, doi: 10.1080/19443994.2013.768788.

[62] 'Fick's Laws of Diffusion: Formulas, Equations, & Examples', *Science Facts*, Jul. 10, 2020. https://www.sciencefacts.net/ficks-laws.html (accessed Mar. 31, 2022).

[63] 'Merck | United Kingdom'. https://www.sigmaaldrich.com/GB/en (accessed May 04, 2022).

[64] 'Distilled Water - Buy 25 Litre Distilled Water Online with Fast Delivery', *Distilled Water Supplies*. https://www.buydistilledwater.co.uk/distilled-water/4-25-litre-distilled-water.html (accessed May 04, 2022).

[65] 'What is Total Suspended Solids (TSS)?', *Water & Wastes Digest*, Apr. 16, 2021. https://www.wwdmag.com/suspended-solids-monitors/what-total-suspended-solids-tss (accessed Apr. 14, 2022).

[66] 'What is Total Dissolved Solids (TDS)?', *Water & Wastes Digest*, Jul. 12, 2021. https://www.wwdmag.com/what-articles/what-total-dissolved-solids-tds (accessed Apr. 14, 2022).

[67] O. US EPA, 'How Does Anaerobic Digestion Work?', Mar. 18, 2019. https://www.epa.gov/agstar/how-does-anaerobic-digestion-work (accessed Apr. 14, 2022).

[68] 'SEMIPERMEABLE Definición y significado en inglés', *Lexico Dictionaries | English*. https://www.lexico.com/en/definition/semipermeable (accessed Apr. 11, 2022).

Appendices

A-1 Glossary

Table 9: Glossary.

Term	Definition
Ammoniacal Nitrogen	General term used to describe both free ammonia and ammonium within a sample.
Sludge Centrate	The liquid fraction produced from anaerobic digestion stage within wastewater treatment plant.
Struvite	A phosphate mineral crystal formed in water, composing of magnesium, ammonia, and phosphate.
Eutrophication	Excessive richness of nutrients in a lake or other body of water which causes dense growth of plant life and algae [12].
Organic Matter	Carbon-based compounds found in natural and aquatic environments. In this study it composes of peptone, meat extract, glucose, and K_2HPO_4.
Suspended Solids	Amount of tiny solid particles that remain suspended in wastewater, that exceed 2 µm in size [65].
Dissolved Solids	Dissolved organic matter and inorganic salts present in wastewater [66].
Anaerobic Digestion	A process which uses bacteria to break down organic matter, in the absence of oxygen [67].
Semipermeable	A material or membrane allowing certain substances to pass through (allow passage of solvent but not certain solutes) [68].
Lumen	The inside (hollow fibres) of the membrane contactor.
Hydrophobic	A property or substance which repels water.
Thermistor	Temperature-dependent resistor used for measurement and control.

A-2 Feed and Stripping Calculations

A-2.1 Feed Solution Calculations

Concentrations of TAN present within urban wastewater vary from 600 – 1500 mg/L, with a value of 600 mg/L chosen for the experiments. Based on this concentration, the mass required was calculated using the data from *Table 10* and *Equation 5.*

Table 10: Data Required to Calculate NH_4 Mass Required.

Component	Symbol	Value	Unit
Molecular Weight NH_4Cl	MW_{NH4Cl}	53.49	g/mol
Molecular Weight NH_4	MW_{NH4}	18	g/mol
Desired Concentration	$c_{desired}$	600	mg/L
Volume of Solution	V_{sol}	2 / 2.5	L

$$m_{NH4Cl} = \frac{c_{desired} MW_{NH4Cl} V_{sol}}{MW_{NH4}} \tag{5}$$

Organic matter in urban wastewater ranges from 600 – 900 mg/L. As this study investigated the sludge centrate, a concentration of 400 mg/L was chosen to allow for partial removal in prior stages. The initial 'recipe' for organic matter was based on 500 mg/L, therefore needed to be scaled down. Data from *Table 11* was used in *Equation 6* to calculate the mass. C_{500} defines the concentration at 500 mg/L.

Table 11: Data Required to Calculate OM Mass Required.

Component	Concentration at 500 mg/L
Peptone	0.113
Meat extract	0.113
Glucose	0.25
K_2HPO_4	0.028

$$m_{400} = \left(\frac{400}{500}\right) c_{500} V_{sol} \tag{6}$$

Calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) represented the ions present within wastewater. The data in *Table 12 and 10* were used with *Equation 7 and 8* to calculate the ions mass.

Table 12: Data Required to Calculate $CaCl_2$ Mass Required.

Component	Symbol	Value	Unit
Molecular Weight $CaCl_2$	MW_{CaCl2}	110.99	g/mol
Molecular Weight Ca	MW_{Ca}	40.078	g/mol

Desired Concentration	$c_{desired}$	120	mg/L
Volume of Solution	V_{sol}	2 / 2.5	L

$$m_{CaCl2} = \frac{c_{desired} MW_{CaCl2} V_{sol}}{MW_{Ca}} \quad (7)$$

Table 13: Data Required to Calculate $MgCl_2$ Mass Required.

Component	Symbol	Value	Unit
Molecular Weight $MgCl_2$	MW_{MgCl2}	203.30	g/mol
Molecular Weight Mg	MW_{Mg}	24.305	g/mol
Desired Concentration	$c_{desired}$	60	mg/L
Volume of Solution	V_{sol}	2 / 2.5	L

$$m_{MgCl2} = \frac{c_{desired} MW_{MgCl2} V_{sol}}{MW_{Mg}} \quad (8)$$

A full summary of the final masses required for each component at both 2 L and 2.5 L can be found below.

Table 14: Summary of Wastewater Components Masses for Feed Solution Volume of 2 L and 2.5 L.

Component	Mass Required for 2 L (g)	Mass Required for 2.5 L (g)
Ammonium chloride	3.556	4.458
Peptone	0.179	0.224
Meat Extract	0.179	0.224
Glucose	0.397	0.496
K_2HPO_4	0.044	0.056
Calcium Chloride	0.665	0.831
Magnesium Chloride	0.609	0.761

A-2.2 Stripping Solution Calculations

The volume required for both an acid concentration of 0.05 M and 0.1 M was calculated using the data in *Table 15* and *Equation 9.*

Table 15: Data Required to Calculate Volume of H_2SO_4 for both 0.05 M and 0.1 M Concentration.

Component	Symbol	Value	Unit
Density	ρ_{H2SO4}	1840	kg/m^3
Molecular Weight	MW_{H2SO4}	98.08	g/mol
Purity	R_{H2SO4}	0.96	-

Desired Concentration	$c_{desired}$	0.05 / 0.1	mol/L
Volume of Solution	V_{sol}	2.5	L

$$V_{H2SO4} = \frac{c_{desired} V_{sol} MW_{H2SO4}}{\rho_{H2SO4} R_{H2SO4}} \quad (9)$$

A-3 Apparatus

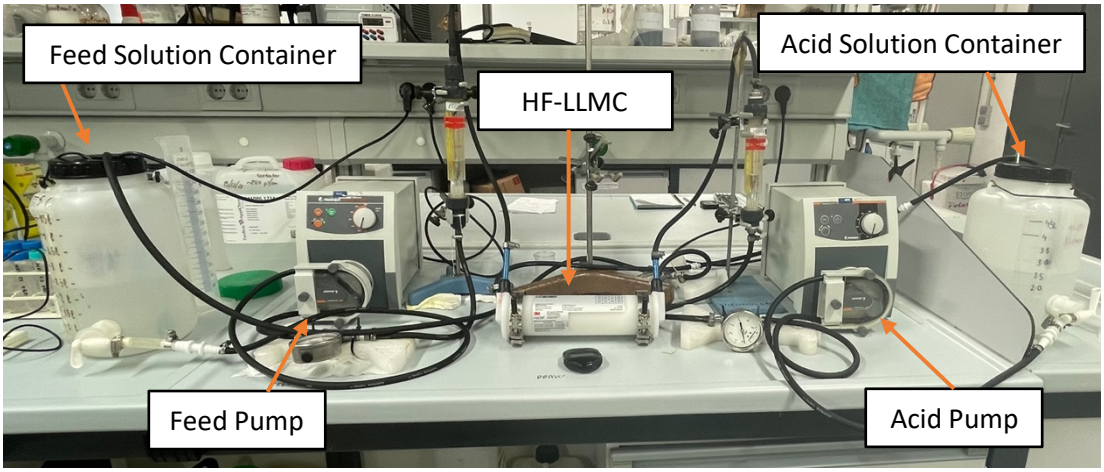

Figure 16: Labelled Diagram of Pilot Plant Set-up.

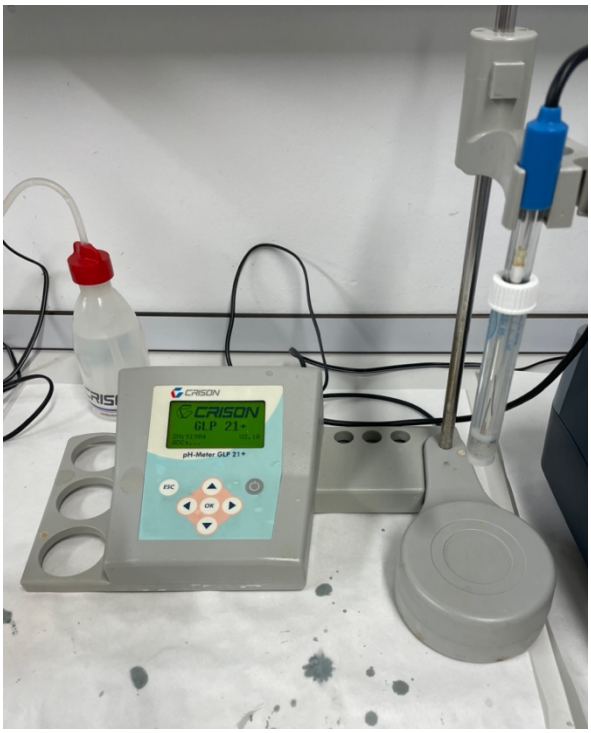

Figure 17: pH-Meter GLP21.

Figure 18: Conductimeter GLP31.

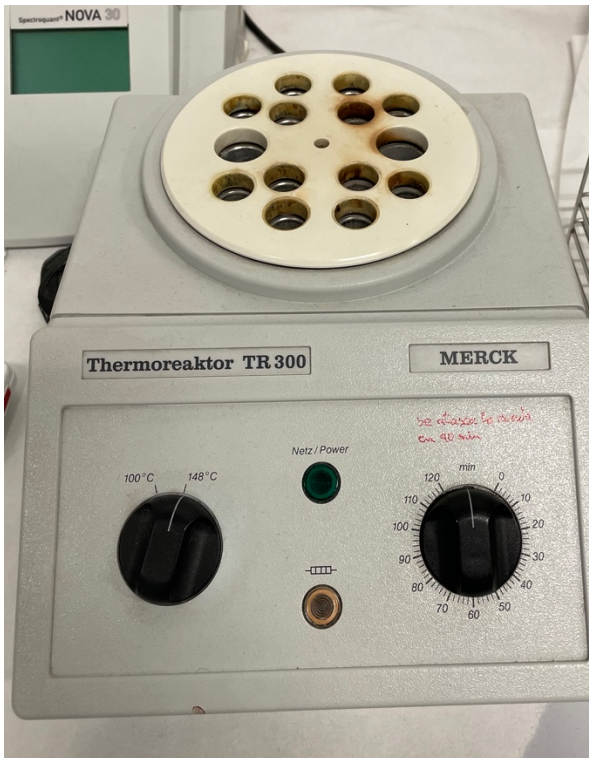

Figure 19: Merck Thermoreactor TR300.

Figure 20: Merck NOVA 30 Spectrophotometer.

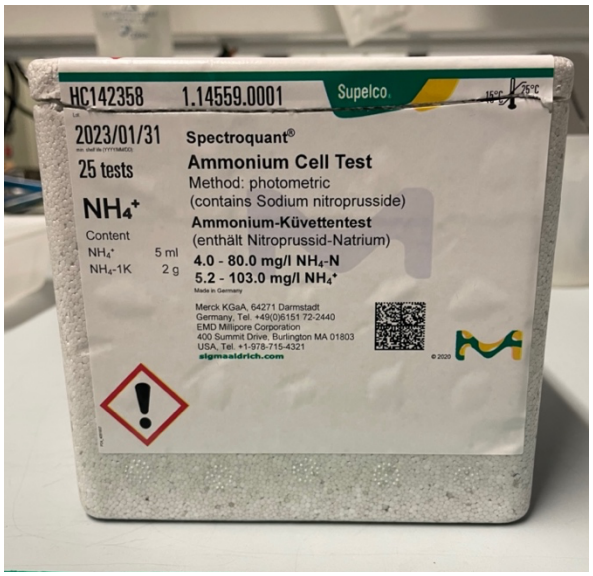

Figure 21: Ammonium Cell Test Kit.

Figure 22: COD Cell Test Kit.

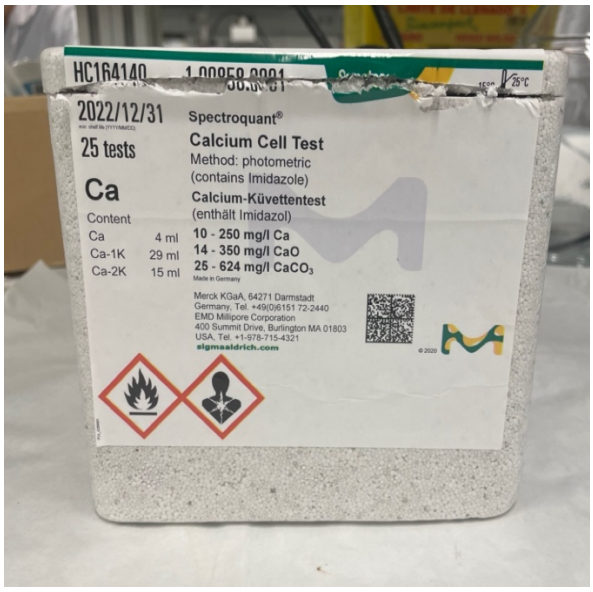

Figure 23: Calcium Cell Test Kit.

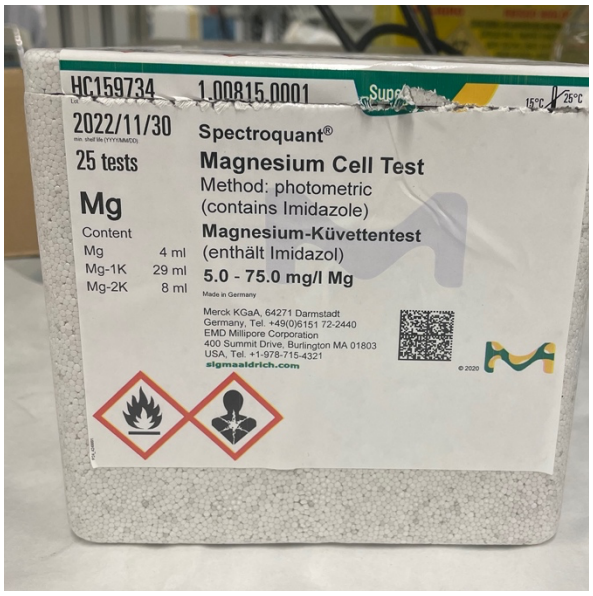

Figure 24: Magnesium Cell Test Kit.

A-4 Results and Discussion

A-4.1 Influence of Contact Time

The efficiency seen at t0 (orange circle) was calculated using the initial concentration of the feed solution after preparation and the concentration of the feed solution after the pH had been adjusted to a value of 10. Although this is an insignificant efficiency when compared to others throughout the experiment, it shows the ability to remove (convert) NH_4^+ by simply increasing the pH of the solution and provides evidence to further investigate the influence of pH as an additional optimal parameter.

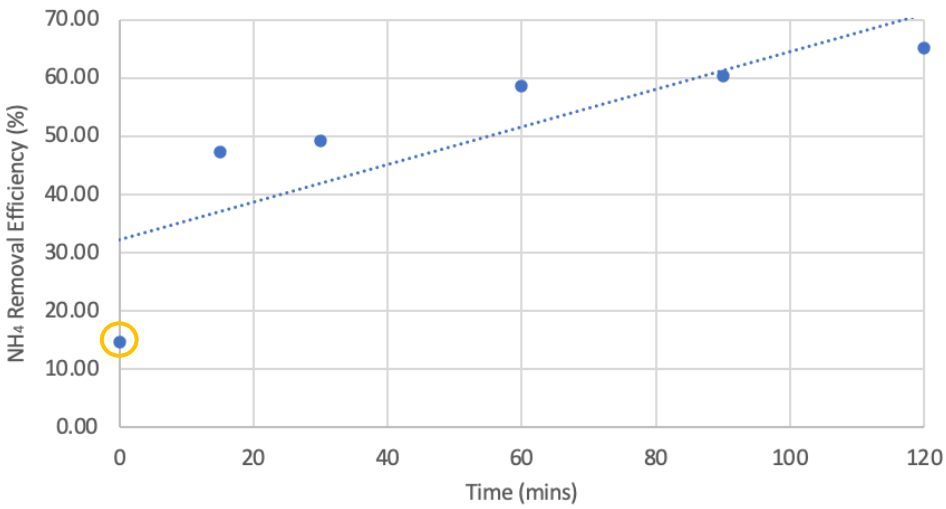

Figure 25: Average NH_4^+ Removal Efficiency at Sample Time Intervals.