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Nitrogen harvesting from liquid waste streams using hydrophobic gas permeable membranes

Master's thesis under examination for a degree of Master of Science

In Espoo 13.4.2018
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Tiivistelmä

Jäteveden käsittely pyrkii typen poistoon talteenoton sijasta. Sekä typen poisto että sen sitominen ilmakehästä reaktiiviseen muotoon ovat energiaintensiivisiä prosesseja (Liu, 2014). Merkittävä osuus käsittelyprosessiin tulevasta kuormasta on peräisin laitoksen omien mädättämöiden rejektivesistä. Typen talteenotto rejektivedestä vähentäisi käsittelyprosessin kustannuksia ja tarvetta sitoa typpeä ilmakehästä. Osoitamme tässä tutkimuksessa, että typpeä voidaan ottaa talteen käyttäen hydrofobista, kaasuselektiivistä kalvoa. Kahdeksan tunnin viipymäajalla saavutettiin 60 % talteenottotehokkuus ja menetelmän arvioitiin olevan taloudellisesti kannattava, kun talteenottotehokkuus on 55 ja 85 % välillä. Lisäksi totesimme, että kalkkipohjaiset tuotteet ovat tehokkaita esikäsittelyssä sekä pH:n säädössä. Tulokset vahvistavat, että typen talteenottomenetelmät ovat mahdollinen keino saavuttaa korkeampi ravinteiden kiertotehokkuus ja vähentää energian kulutusta. Ennustamme, että typen talteenottomenetelmien tutkimuksen suosio kasvaa, koska typpirikkaat nestevirrat ovat ominaisuuksiltaan hyvin erilaisia ja lisätutkimus on tarpeellista, jotta teknologian potentiaali saadaan hyödynnettyä.

!Avainsanat Typpi, talteenotto, kalvo, pilotti

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Abstract

The focus for nitrogen treatment in a wastewater treatment plant (WWTP) is removal instead of recovery. Both nitrogen treatment and creation of reactive nitrogen are energy intensive processes (Liu, 2014). A major fraction of nitrogen load on the treatment process originates from reject water from WWTP’s own digesters. Nitrogen recovery from reject water would decrease treatment process costs and the need to bind nitrogen from atmosphere. Here, we show that nitrogen can be recovered from liquid waste using gas-permeable hydrophobic membranes. Recovery efficiency of 60 % was reached with 8-hour retention time. The method was estimated to be economically feasible for a specific WWTP when the recovery efficiency is between 55 % and 85 %. Furthermore, we also concluded that lime products are suitable option for pre-treatment and pH control. Our results demonstrate that nitrogen recovery methods are a viable pathway to reach higher nutrient recycling rate and lower energy consumption. We anticipate that research for nitrogen recovery methods will gain momentum: nitrogen-rich liquid streams have very diverse properties and further research is necessary to utilize the maximum potential of the technology.

Keywords Nitrogen, recovery, membrane, pilot

Foreword

This thesis is a part of Aalto University's project called NPHarvest, which is aiming at researching and developing technology to recover nutrients from liquid waste streams. In order to keep the workload appropriate for a master's thesis, the topic is limited to investigating nitrogen cycle and harvesting with different technologies, one of which is used to run the experiment. This means that other aspects of the process, such as phosphorous removal and pre-treatment with lime products are not discussed. The contents of this thesis were included in an article which was presented in NRR-LWWTP2017 conference and is currently under revision. The work is based on tests and ideas of D. Sc. Surendra Pradhan and D. Sc. (Tech) Anna Mikola, who both are also the instructors for this thesis. During the work, they also proved to be invaluable support for guiding this work. Lab personnel, led by Aino Peltola, and intern Pierre Bernard also helped with running the pilot and analysing the results. Sara Saukkonen provided invaluable aid with finishing touches for the thesis. Supervisor for this thesis is professor Riku Vahala. The thesis has been funded by European Regional Development Fund with kind support from Helsinki-Uusimaa Regional Council and Häme Regional Council. In addition, the Ministry of Environment has funded the entire project with 457 499.7 euro from the program "Enhancing nutrient recycling and the condition of Saaristomeri." In addition, Nordkalk Oy and Gasum Oy financially supported the project. The project is a part of the larger project called "A breakthrough in the circular economy and clean solutions" project by the Finnish government. During this work Surendra Pradhan was partly supported by Nessling Foundation grant decision 2015.

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Juho Kaljunen

Contents

Markings

$Ca(OH)_2$	Calcium hydroxide
H_2SO_4	Sulphuric acid
H_3PO_4	Phosphoric acid
$MgNH_4PO_4 \cdot 6H_2O$	Magnesium ammonium phosphate hexahydrate
$NaOH$	Sodium hydroxide
N_2	Nitrogen gas
NH_3	Ammonia
NH_4	Ammonium
$(NH_4)_2SO_4$	Ammonium sulphate
Nr	Reactive nitrogen
NH_x	General term for ammonia or ammonium
NO_x	General term for nitrogen oxides
N_2O	Nitrous oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
K^+	Kalium ion

Abbreviations

BES	Bioelectrochemical systems
C-BNF	Cultivation induced nitrogen fixation
CEM	Cation ion exchange membrane
COD	Chemical oxygen demand
HRT	Hydraulic retention time
MAP	Magnesium ammonium phosphate hexahydrate
N-BNF	Natural biological nitrogen fixation
Nr	Reactive nitrogen
pH	Measurement scale for acidity or basicity
RW	Reject water
SS	Suspended solids
TSS	Total suspended solids
WWTP	Wastewater treatment plant

1 Introduction

Nitrogen is one of the most common elements found on Earth and its cycle covers the Earth's grand schemes. Nitrogen is present in atmosphere as inert gas as well as oxidized products. Additionally, soil and aquatic environments have plenty of nitrogen compounds, such as ammonia, nitrate and nitrite and nitrous oxides. A large amount of nitrogen is bound in life forms as building blocks for proteins. For the past 150 years, the importance and use of nitrogen has increased due to the need to enhance yields to provide food for the growing human population. This has led to several changes in the nitrogen cycle. The focus of this thesis originates from these changes and their mitigation.

Nitrogen is fixed naturally from the inert atmospheric form N_2 to its reactive forms by organisms and lightning. The species capable of breaking the triple covalent bond of N_2 are few and the natural rate of conversion to reactive forms is limited. In most types of environment, nitrogen has been the limiting factor for growth. However, this natural nitrogen cycle has been interfered by the anthropogenic nitrogen cycle: in order to feed the growing population, nitrogen has been taken from the atmosphere by Haber-Bosh process for the past 100 years. The anthropogenic cycle consists of fertilizers, plants, feedstock, the human population and, finally, the wastewater treatment where nitrogen is returned to the atmosphere. This, however, is not a closed loop due to nitrogen "leaking" to the environment in every step.

While use of fertilizers, especially nitrogen fertilizers, has increased the food production, it has interfered the nitrogen balance and created changes in the environment at the same time. Currently, reactive nitrogen is more abundant than ever before in the cycle, leading to eutrophication and hypoxia in aquatic environments, in addition to ozone layer depletion in the stratosphere and ocean acidification. Steffen et al. (2015) defined the planetary boundary for biochemical nitrogen flows and listed it as being "beyond the zone of uncertainty (high risk)". This means that there is a high risk of changing the environment permanently.

Another point of view to the situation is the energy balance of the anthropogenic cycle: nitrogen is first bound to reactive form from atmosphere, it then cycles through natural environment and, finally, is released back to the atmosphere. This is not energy efficient: to turn the current climatological development, it is vital to decrease energy consumption on a global scale. The purpose of this thesis is to research technology that enables energy savings by promoting nutrient recovery and circulation, thus short-cutting the anthropogenic nitrogen cycle.

Circular economy and closed loops within the society's material flows are trending in today's world, compared to the old "cradle to grave" type of thinking. In nitrogen's case, the circular economy would mean that new nitrogen based products would not be produced from atmospheric N_2 but instead from by-products and waste flows containing nitrogen. This sort of system thinking offers many advantages over production from virgin materials. For the feasibility of any modern technology, and to decrease the impact on the environment, it is important to increase or create value for processes and by-products that would otherwise be considered as waste and processed as such. One of the objectives, in addition to researching the technology itself, is to estimate its economic impact at a specific wastewater treatment plant.

This thesis was conducted as part of Aalto University NPHarvest-project. The goals for this project are to research new energy efficient methods or technology to recover nutrients from waste streams and to estimate the economic opportunities related to them. It is a 3-year project with this thesis being the first part. The objectives for this phase were to build a continuously working reactor and test it to prove that the process could work in larger scale. The technology utilized for this experiment is a combination of already existing ideas implemented in a new way and is based purely on physical phenomena without biological processes. The purpose of the tests was to find the optimal running conditions for the reactor and to obtain enough information to scale the process from laboratory scale to an actual pilot scale, including size and preliminary design choice for the next phase's reactor. Furthermore, the economic feasibility was assessed based on the results of the tests. The thesis is focused only on nitrogen recovery, while phosphorous and calcium are discussed in another thesis (Pihl, 2017).

2 Literary review

This chapter of the thesis presents the motivation for the global development of nitrogen recovery processes and explore (1) where nitrogen is available, (2) how its chemistry works through the natural systems, (3) nitrogen production, usage, its treatment and harvesting methods.

2.1 Global nitrogen cycle: nitrogen availability

The high occurrence of nitrogen makes it a vital element globally. It is present everywhere on Earth: atmosphere, soil, marine environments, fresh water, biosphere and Earth's crust. However, it is not always in the same form. The simplest way to categorize these compounds is to divide them into reactive and non-reactive nitrogen: atmospheric nitrogen gas, N_2, is not reactive and the rest are classified as reactive (Nr). The most relevant and common reactive forms related to wastewater treatment are NH_x, NO_x and N_2O. To fully grasp the impact of nitrogen, it is important to understand the so-called nitrogen cascade: the nitrogen cycle is not an actual cycle but a network where nitrogen flows from one form to another. Cascade means that a single nitrogen atom bound from the atmosphere to ammonia fertilizer could be involved in several different phenomena. For instance, the same nitrogen atom could contribute to the eutrophication of a water body, affect climate change as nitrous oxide for decades or be the building block for the proteins before returning to the atmosphere as inert nitrogen gas. This is the reason why the anthropogenic impact of increased availability of nitrogen is difficult to predict. (Galloway et al., 2003)

Before looking at nitrogen cycle in detail, it is a good idea to take a look at Earth's nitrogen budget as estimated by Johnson and Goldblatt (2015) in the article "The nitrogen budget on Earth." If nothing is excluded, most of the nitrogen is in Earth's crust. This is called bulk silicate earth. However, this is not relevant because the nitrogen is not exploitable when bound in the crust. The 2nd largest nitrogen storage is the atmosphere, followed by oceans and biomass. Figure 1 illustrates the distribution of nitrogen storages.

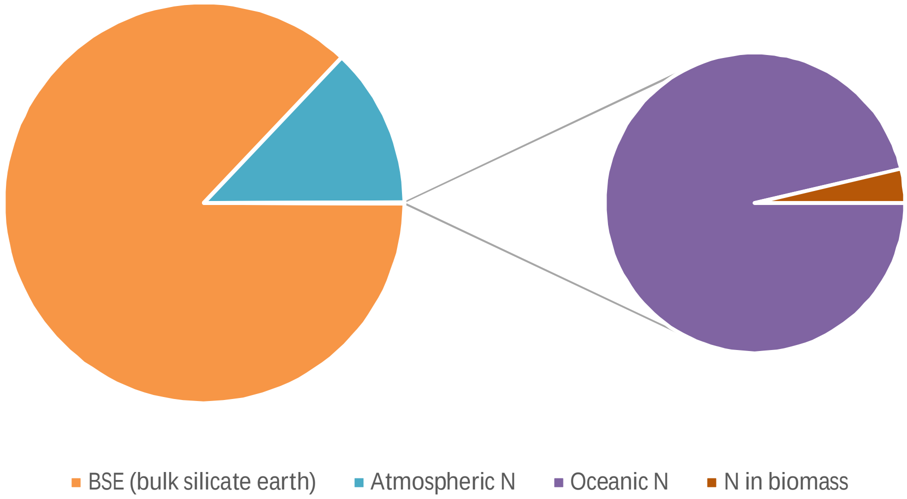

Figure 1. Nitrogen budget on Earth (modified from Johnson and Goldblatt, 2015).

As seen in Figure 1, the amount of reactive nitrogen compared to the amount of atmospheric nitrogen is insignificant. This is why atmospheric nitrogen can be treated as an infinite nitrogen source. Moreover, it also explains why one of the objectives of this thesis focuses on the reduction of energy consumption rather than nitrogen consumption.

Most of the nitrogen in the atmosphere is N_2 but there are still airbound NH_x, NO_x and N_2O compounds. Same holds true for the oceans, shown in Figure 2. Figure 3 also shows the distribution of nitrogen in the biomass. Most of the nitrogen in the biomass is still in the oceans.

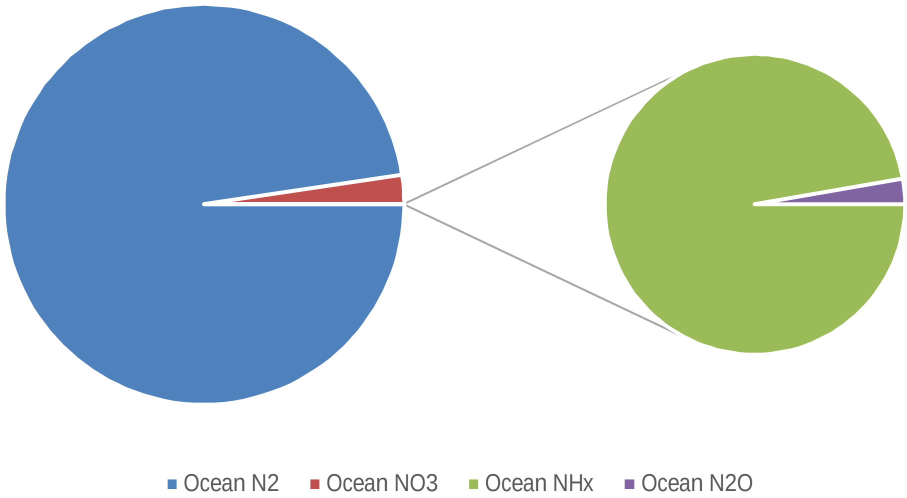

Figure 2. Oceanic nitrogen budget (modified from Johnson and Goldblatt, 2015).

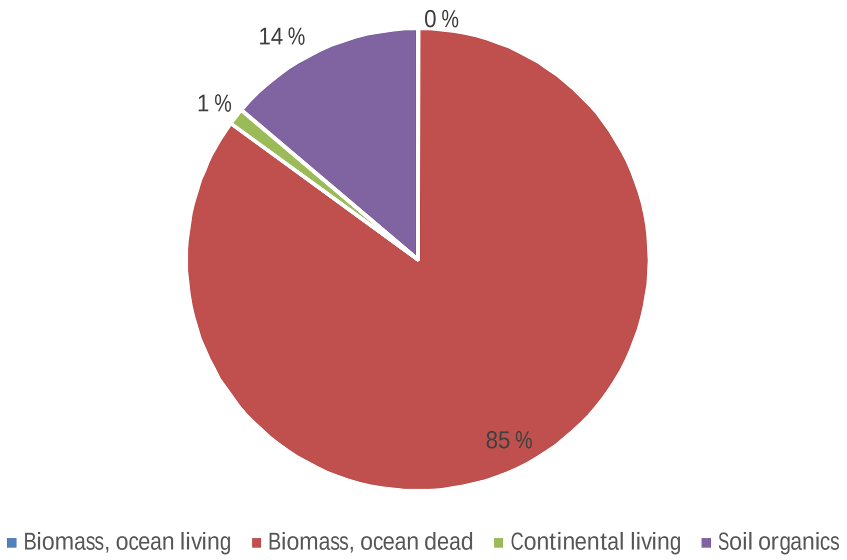

Figure 3. Distribution of nitrogen in biomass. The blue sector is not visible in the chart due to its relatively low portion (modified from Johnson and Goldblatt, 2015).

Based on these charts, it seems that the amount of nitrogen available for our terrestrial activities is rather insignificant. However, now that the distribution of nitrogen in different environments is better understood, let us take a look at the cycles in detail.

2.2 Global nitrogen cycle: flows

It is important to understand the cycle from the chemical point of view before looking at the full cycles. Figure 4 below describes the main interactions: from atmospheric nitrogen N_2 the nitrogen is transformed to ammonia (NH_3) for living organisms to use. After going through that phase, ammonia goes through mineralization to ammonium (NH_4^+). A type of bacteria utilizes ammonium to transform the compound further into nitrogen oxides. Finally, another type of bacteria transforms the nitrogen back to its inert gaseous form in a process called denitrification. Nitrous oxide (N_2O) is produced as a side product. (Galloway et al., 2004) This process is explained in more detail later in the section 2.8.

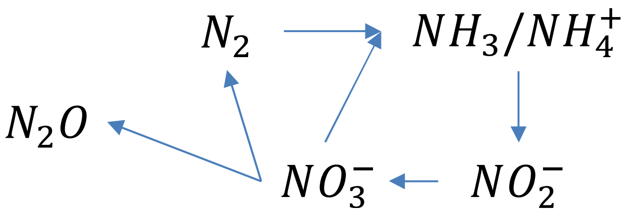

Figure 4. Simplified nitrogen cycle.

The global cycle is described in Figures 5 and 6. The volume of nitrogen flows in pre-industrial era (1860), current situation (late 1990s) and future prediction (2050) is shown in tons per year. Data originates from the article “Nitrogen cycles: past, present, and future” by Galloway et al. (2004). Even though the figures describe a cycle, they do not look like one because the atmosphere has been split into two boxes for the sake of clarity. The N_2 in Atmosphere-boxes can be thought as being connected. The thicknesses of the flows reflect the flow quantities. This means that flows can be compared with each other at a glance. However, the sizes of the boxes have no significance.

Nitrogen flows from atmosphere by both natural pathways and artificial pathways: natural pathways include lightning fixation and natural bacterial nitrogen fixation (N-BNF). Artificial pathways include the Haber-Bosch process, cultivation induced nitrogen fixation (C-BNF) and burning of the fossil fuels. These artificial pathways are not present or are insignificant in the pre-industrial time as presented in Figure 4. The pathways lead to Continents, NOx in Atmosphere and Oceans. Continents include terrestrial and freshwater environments. From these points onwards, the cycle acts like a net between Continents, reactive nitrogen compounds in atmosphere and the Oceans. The effect of nitrogen cascade is present. It is noteworthy that Oceans represents the open ocean and there are no interactions with Continents: the nitrogen flow from terrestrial environments to marine environments is represented in Estuary and shelf-box to represent. This also explains why nitrogen fixation to oceans and marine denitrification stays the same for all three timeframes (Gruber and Galloway, 2008).

After the network-like section in the chart, nitrogen is returned to the atmosphere by denitrification. Estuary and Marine denitrification represent the nitrogen flows from coastal and open ocean waters; regarding the topic of this thesis they are not relevant. This is a blessing because estimating the amount of denitrification on a global scale is difficult and the values could be inaccurate. Instead, the most important aspect of these three figures is the balance of the Continents-box and the flow quantities between the reactive forms.

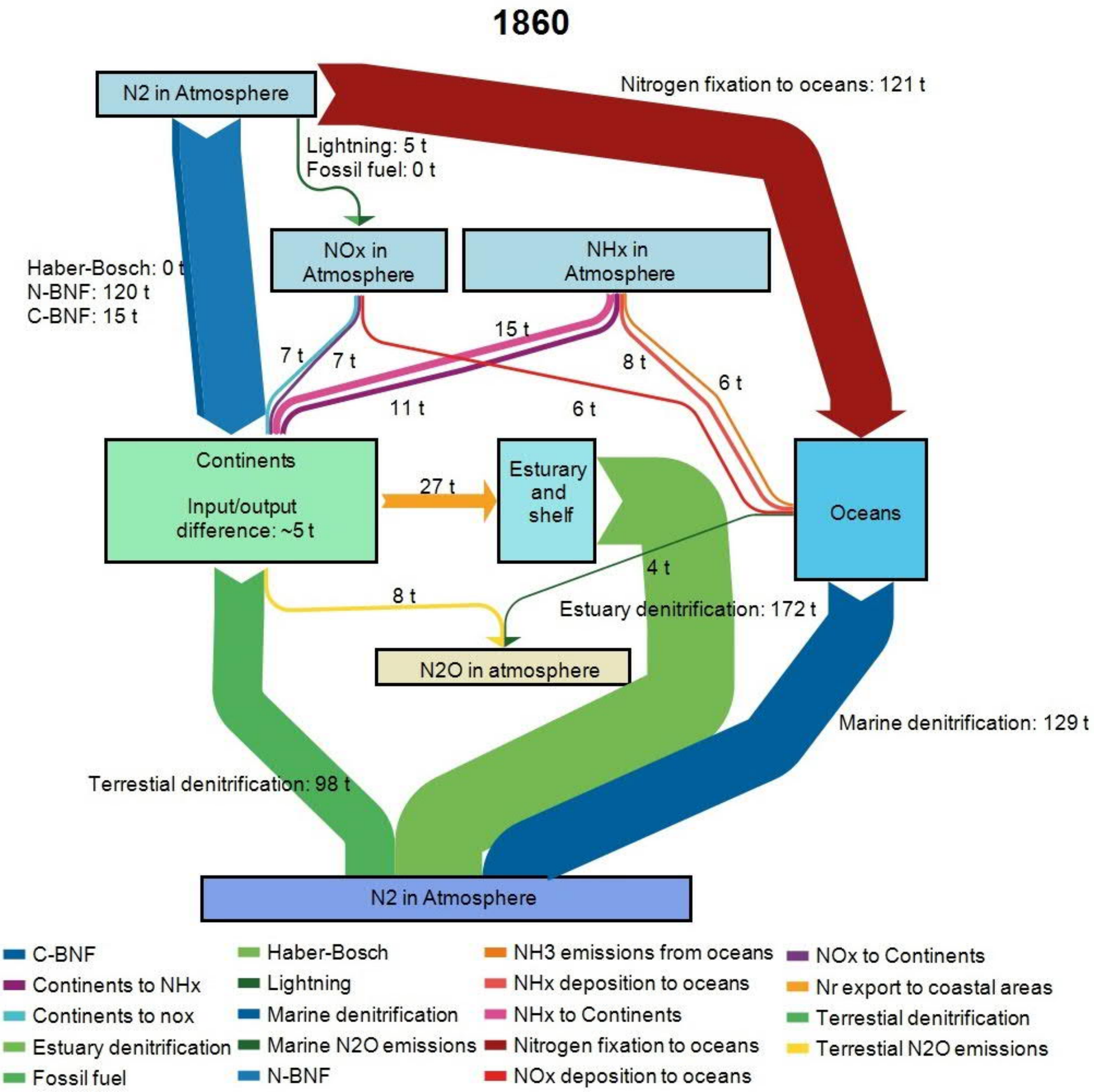

Figure 5. Nitrogen flows in 1860 (modified from Galloway et al., 2004).

For the pre-industrial era the nitrogen flows for the Continents-box are in neutral balance and the flows between the reactive forms of nitrogen are almost non-existent compared to the late 1990s or the future prediction: for 1990, the balance of Continents-box is 80 tons more inflow than outflow and for 2050, the net gain is 127 tons. This indicates that nitrogen is accumulating in the terrestrial environments. The origin of this change is easy to find: the nitrogen flow for the Haber-Bosch process is zero in pre-industrial time but increases significantly for the later timeframes. The same effect can be seen for nitrogen flow caused by the burning of fossil fuels. An increasing effect can be observed

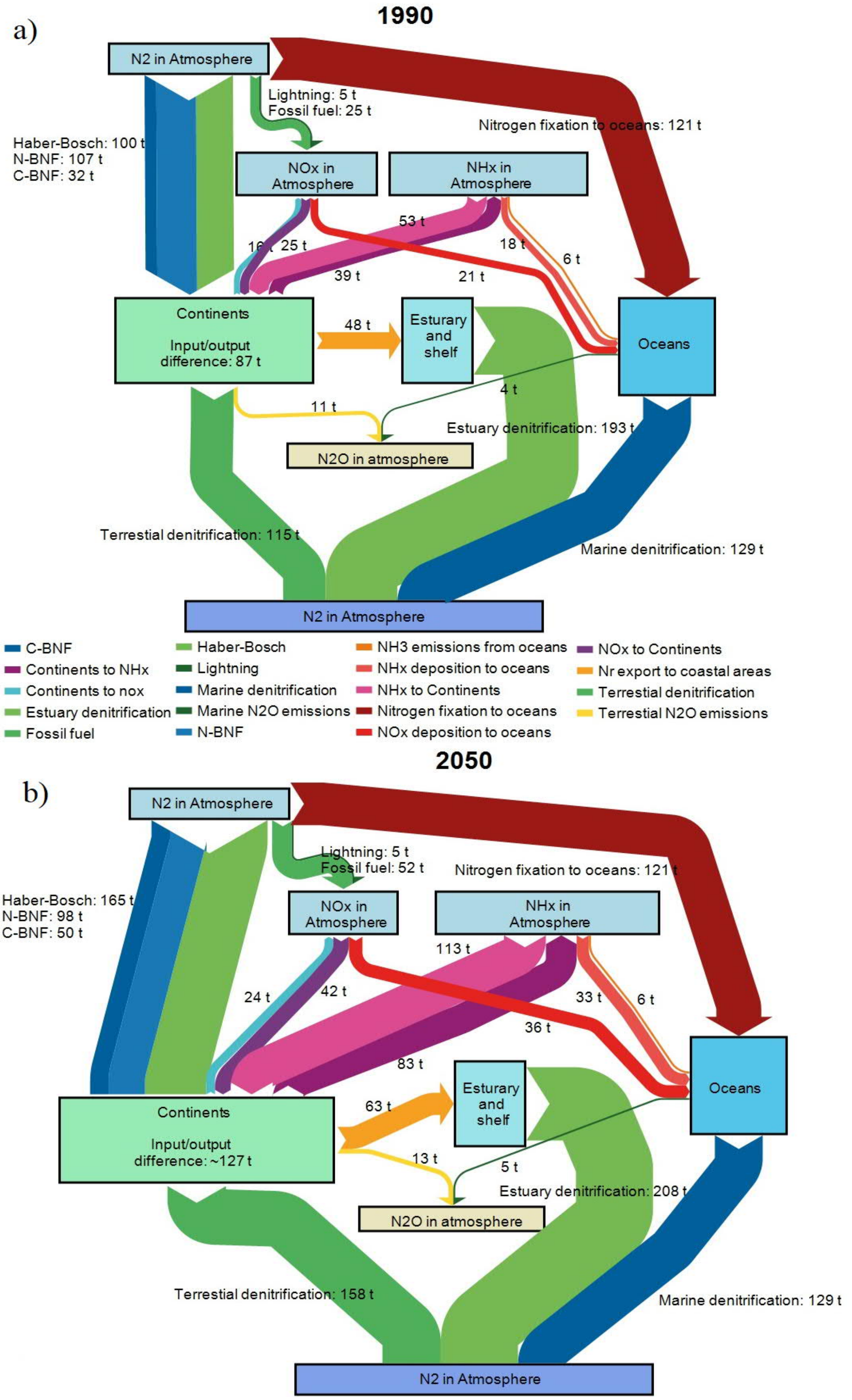

Figure 6a and b. Nitrogen flows in 1990 and an estimation for 2050 (modified from Galloway et al., 2004).

also when examining the flows between the reactive forms in the atmosphere and the ocean: the flow quantities increase significantly over time. Nitrous oxide flows to the atmosphere increase considerably as well. Nitrous oxide is very stable substance in the atmosphere, and thus, its deposition is not considered for these timeframes.

Based on Figures 5 and 6, it can be concluded that the reactive nitrogen is accumulating in the terrestrial and atmospheric environment and that the trend will continue in the future with increasing population and the need for fertilizers. This a significant environmental change: nitrogen is the limiting factor for the growth in many environments and having an abundance of it changes these ecosystems. A good example is the Baltic Sea and its eutrophicated state. However, the impacts of increased nitrogen availability are not limited to eutrophication: nitrous oxide is a greenhouse gas and promotes climate change and nitrogen has a role in ocean acidification, to name a few changes. (Follet and Hatfield, 2001)

2.3 Planetary boundaries

Environmental changes are typically labelled as problems. However, there are different degrees of significance associated with problems in general, and the changes caused by nitrogen are not an exception. Before labelling abundance of nitrogen as a problem on a global scale, it would make sense to understand how much of a change is a problem: after all, change is a never-ending factor in the nature. Thus, there is need for better definition for a problem.

Steffen et al. (2015) have developed a useful term to describe this situation: planetary boundary. Their idea is that there is a “safe operating space:” a range where changes can occur but are not irreversible. The systems on Earth have been divided into categories as shown in Figure 7. Our interest lies mainly in biochemical flows and especially in nitrogen. However, the categories interact with each other, and thus, it is important to look the system as a whole.

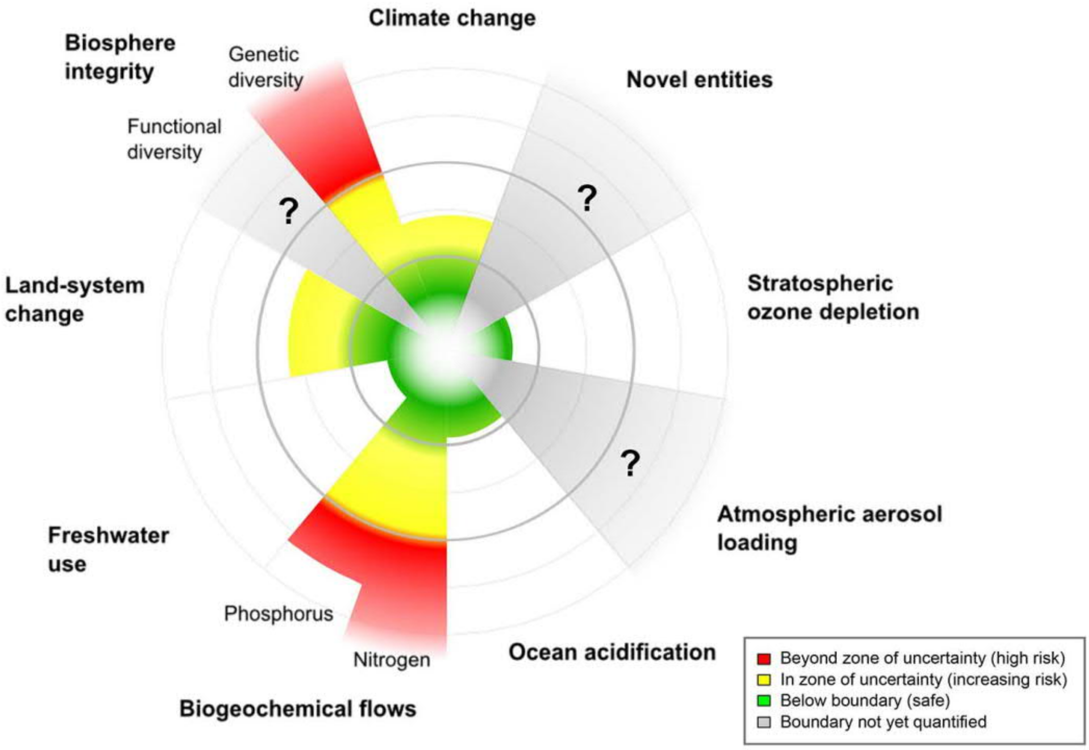

Figure 7. Statuses of planetary boundaries (Steffen et al., 2015).

The boundary is divided into three zones: safe zone (green), uncertain zone (yellow) and high-risk zone (red). Nitrogen flows are clearly in the high-risk zone, which means that the change is irreversible i.e. there is a permanent change in the environment. The evidence suggests that this change is mainly caused by human actions (Galloway et al., 2004) and could have unpredictable consequences in the future due to nitrogen flows being linked to at least climate change, stratospheric ozone depletion and ocean acidification (Steffen et al., 2015). Furthermore, environmental changes can affect the biosphere integrity and biodiversity. Unfortunately, decreasing nitrogen usage is out of the question while human population is growing.

2.4 The Haber-Bosch process

As explained before, the industrial fixation of nitrogen gas (N_2) to ammonia (NH_3) is called the Haber-Bosch process. It was invented in the beginning of the 20th century and has been developed and used for 100 years. The simple reaction formula is

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

The process is most likely one of the most important chemical reactions in the world; without it the growth of human population from around 2 billion to over 7 billion would not have been possible. (Glibert et al., 2014) The process is, however, energy intensive: a single set of process equipment requires reaction pressure of 10-15 MPa and energy consumption of 27.2 GJ. Total energy consumption for this process is 2 % of the world's energy consumption and it releases carbon dioxide worth of 1.6 % of world's CO_2 emissions. (Liu, 2014)

2.5 Nitrogen fertilizer use

Reactive nitrogen produced with the Haber-Bosch process is used as raw material to create multiple products such as plastics, resins, feed supplements and explosives (Galloway et al., 2008). However, the largest portion of nitrogen is still bound in fertilizers, and fertilizer consumption and production have been growing steadily over time (Heffer and Prud'homme, 2008). Steffen et al. (2015) also estimated the high-risk areas when assessing the planetary boundaries, as shown in Figure 8. Clearly, the most highly populated areas are also most high-risk areas: mid-USA, central Europe, northern India and eastern China.

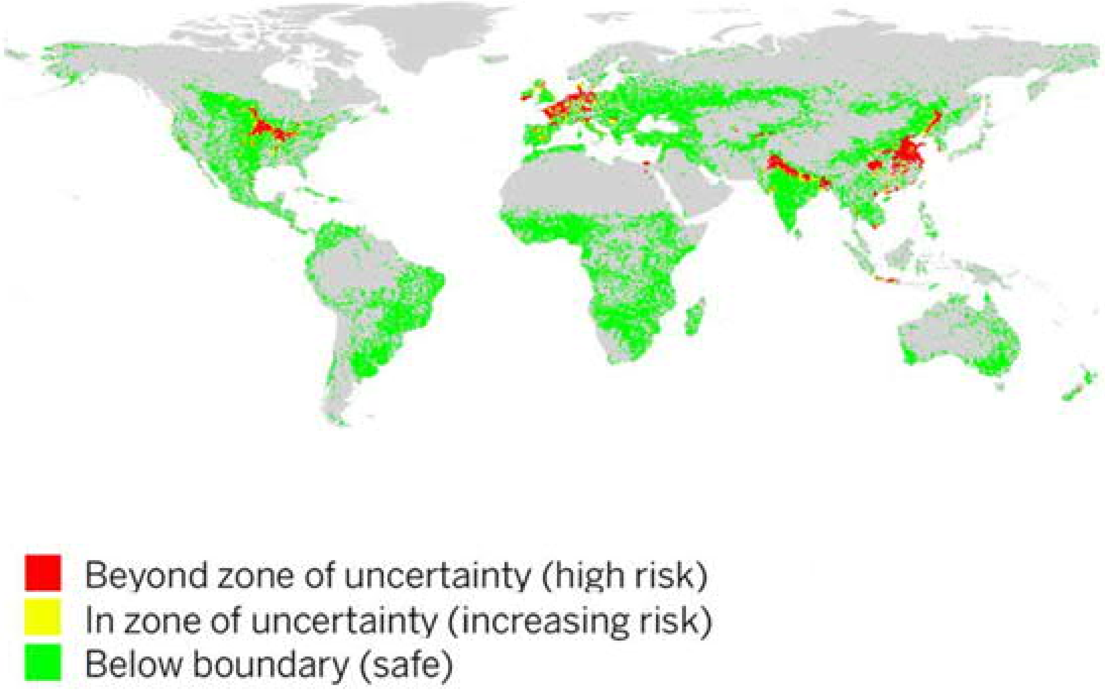

Figure 8. The global distribution of risk for biochemical flow of nitrogen (Steffen et al., 2015).

Figure 9 shows the distribution of the traded quantity of nitrogen contained in fertilizers (Galloway et al., 2008). The total traded amount was 31 million tons of nitrogen. As expected, the locations of the thickest arrows coincide with the high-risk areas, which were presented in Figure 8. Overall total nitrogen demand in 2013 was 141.5 million tons while nitrogen supply was 150.4 million tons with an annual increase of 2-3 %. (Heffer and Prud'homme, 2013)

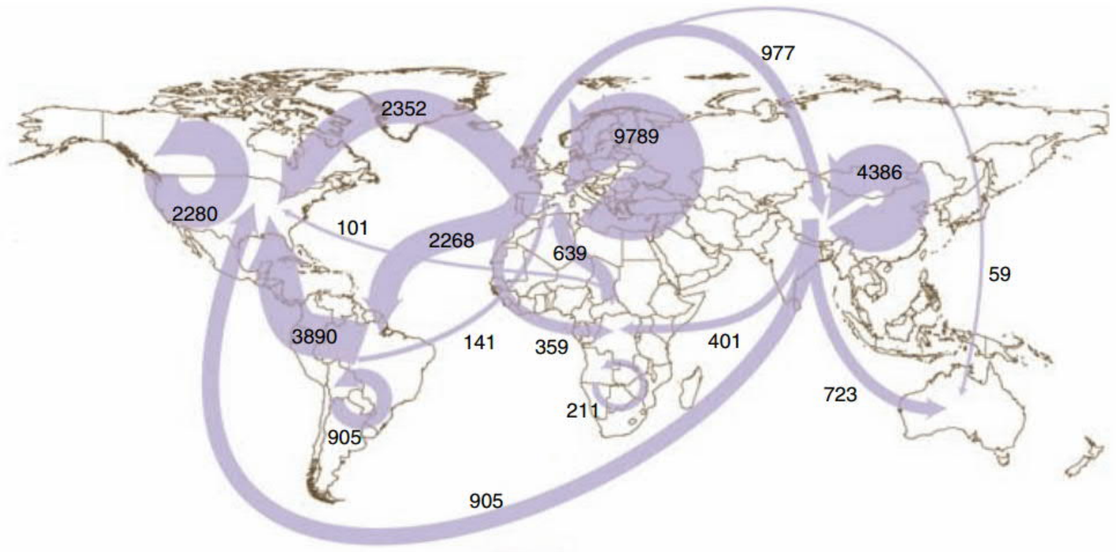

Figure 9. Nitrogen in internationally traded fertilizer as flows. Units are thousands of tons and data is from 2004 (Galloway et al., 2008).

2.6 Reduction of reactive nitrogen

There is not a single strategy that could solve the problems caused by abundant nitrogen while sustaining the food producing capacity for the growing population. Galloway et al. (2008) propose few strategies: controlling NOx emissions, increasing nitrogen uptake efficiency of crops, improving animal management strategies and aiming to have sewage water treatment to convert Nr to N_2 gas. These all reduce the amount of new Nr created annually.

However, this thesis explores another approach to the problem: closing the loop of the nutrient cycle by harvesting nitrogen from waste streams. This would decrease the amount of nitrogen bound by the Haber-Bosch process and, thus, decrease the energy consumption. Decreasing energy consumption would help combat climate change in global scale because most of the world’s energy is still produced with fossil fuels

(Yearbook.enerdata.net, 2016). Figure 10 illustrates a simplified description of our approach.

While the possibilities of harvesting nitrogen seem plenty in theory, as nitrogen exists almost everywhere, locating a suitable testing environment and acquiring nitrogen-rich source material is not a simple task. For this purpose, nitrogen flows and storages in Finland were investigated. Antikainen et al. (2005) have conducted a thorough analysis of nitrogen in Finnish food production and consumption system as well as for the forest industry. However, the amount of nitrogen in forest industry is insignificant compared to food production system (Antikainen, Haapanen and Rekolainen, 2004) and is excluded from this thesis.

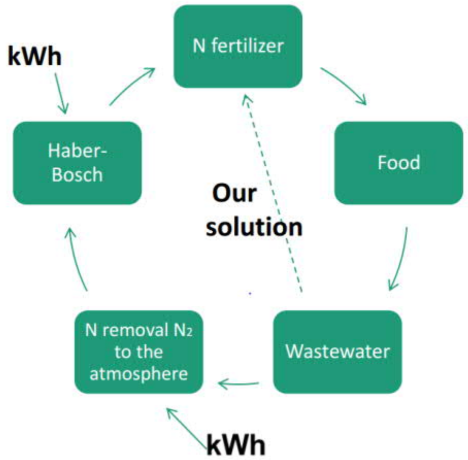

Figure 10. The approach of this thesis on improving nitrogen cycle.

2.7 *Nitrogen flows in Finland*

Figure 11 shows the nitrogen flows in the Finnish food production system. Similarly, to the previous sankey-flowchart, the thicknesses of the flows reflect the amount of nitrogen in the flow but the sizes of the boxes are not related to the actual storage values. The data is from late 1990s and, thus, fairly old. However, even if the values have most likely increased in these 20 years, the proportions are still accurate. Unlike the global nitrogen cycle, this figure does not attempt to describe a full cycle but a network of pathways that has subcycles inside, namely with the flows that return to the atmosphere. The point where nitrogen disappears from this chart is the water systems; after entering rivers and lakes the return nitrogen flow is insignificant and can be considered to exit the Finnish system. This network is entirely inside the Continents-box and the atmospheric Nr-boxes in Figures 5 and 6.

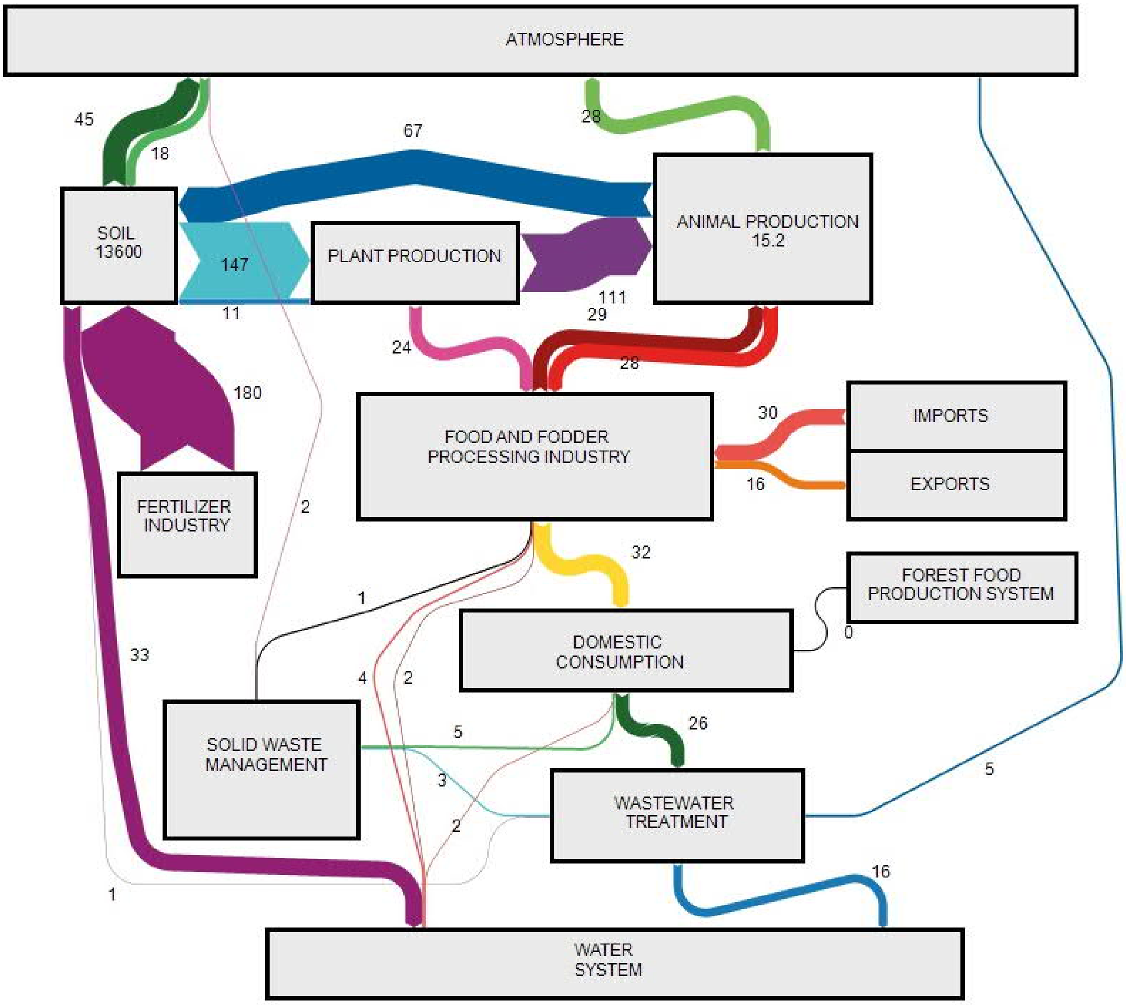

Figure 11. Nitrogen stocks and flows in the Finnish food production system. Values are 1000 t and 1000 t per year, respectively. Data was collected throughout years 1995-1999 (modified from Antikainen et al., 2005).

Clearly, the top part of the chart has more nitrogen flowing than the lower part. However, the flows already have a function as a fertilizer or raw material and, thus, it would be meaningless to harvest nitrogen from them except to decrease possible transportation costs from a location to another. The flow from Soil to Water system would be ideal. However, this is in the form of runoff from fields and harvesting it is difficult in practice. Another significant flow is the flow from Domestic consumption to Wastewater treatment and further on from Wastewater treatment to the Water system. Wastewater treatment is an industrial-size process and, in this sense, more natural place to test new technology. Therefore, the tests conducted for this thesis utilized the nitrogen flow related to wastewater treatment.

2.8 Finnish wastewaters and existing treatment methods

Figure 11 has some nationwide values for nitrogen flows but they are rather out-dated. More recent numbers are provided by SYKE (2013): in 2013, the total wastewater discharge that was processed was 497 million m^3 and included 29 500 t nitrogen. The average nitrogen concentration was 52.1 mg/l. After treatment, the average nitrogen concentration was 21.9 mg/l and the total load to the environment was 10 900 t. Comparing to the values in Figure 10, the nitrogen load to wastewater treatment has increased but the load on the water systems has decreased. Yet, the nitrogen removal efficiency was only 57.9 %. This is partially because only the coastal areas in Finland have a 70 to 80 % total nitrogen removal requirement while in inland often only nitrification is required. This is because most of the primary production in lakes is limited by phosphorous. Additionally, the cold climate in Finland complicates denitrification process for some of the smaller treatment plants.

Wastewater has one problem for our harvesting technology of choice: the nitrogen concentration is rather low. However, inside wastewater treatment plant there are nitrogen-rich flows. Figure 11 illustrates the conventional treatment process: first, large solid particles are removed by screening and grit removal. Ferrous sulphate is added for chemical phosphorous removal and lime for pH control. The biological treatment, also called as active sludge process, handles nitrogen removal: both nitrification and denitrification. This process also degrades and removes organic material from the waste flow as microbes consume the carbon and nutrients in the waste. The bacteria transform ammonia or ammonium to nitrogen gas with several steps in the process. Excess sludge has to be removed from the process. This sludge together with the raw sludge removed in the primary clarifiers is used for biogas production in the digesters. After digestion, the digestate is dewatered using polymers to enhance the dewatering. Water coming from the dewatering is called reject water and is rich in nitrogen content. It is recycled back to the treatment process. This reject water is the source material chosen for the experiment run for this thesis.

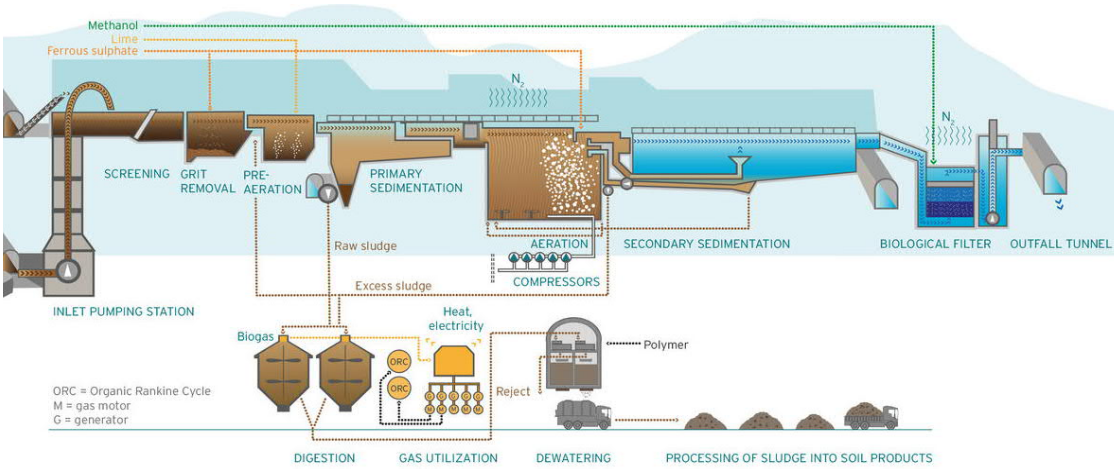

Figure 12. Wastewater treatment process in Viikinmäki WWTP. Source: www.hsy.fi [18.12.2017]

2.9 Nitrogen harvesting methods

Harvesting nitrogen is not a new idea and there are several different methods for recovering it. This section presents few of these methods. They can be divided into two categories: biological recovery methods and physiochemical methods. Table 1 summarises the harvesting methods. The process costs were estimated by the author of this thesis, with the idea of implementing the solution to Finnish environment.

Table 1. Different harvesting methods and their aspects. The process is more expensive if it has higher amount of + signs.

Method	Research stage	Process costs	End product	Other benefits	Source
Microalgae	Lab, bench, few full-scale plants	++	Biofuel	Economical in areas with lots of sunlight?	[1], [2]
Bioelectro-chemical systems (BES)	Lab scale	+	Ammonium sulphate, electricity		[3]
Zeolite	Lab scale	+	Supplementary fertilizer		[4]
Struvite	Full	+	Fertilizer	Well researched, useful in controlling precipitate problem of bioP sludge digesters	[5], [6]
Stripping+ scrubbing	Industrial scale	++	Ammonium sulphate	Works	[7], [8]
Membrane contactors	Lab scale	+	Ammonium sulphate	Reduction in existing treatment costs	[8], [9]

[1] Cai, Park and Li, 2013 [2] Christenson and Sims, 2011 [3] Rodríguez Arredondo et al., 2015 [4] Taddeo, Prajapati and Lepistö, 2017 [5] Darwish et al., 2015 [6] El Diwani et al., 2007 [7] Jiang et al., 2014 [8] Boehler et al., 2014 [9] Amaral et al., 2016

2.9.1 Biological methods

The first biological method is recovery by microalgae. The idea is straightforward: microalgae grow in the liquid stream with high nutrient content. Nutrients, such as nitrogen and phosphorous, as well as toxic compounds are removed from the liquid to feed the microalgae. The algae are selected so that they produce lipids, which can be used for biofuel production. After lipid extraction the by-product, algae biomass residue, can be used as a nitrogen source for animal feed or fertilizer for crops. There are many advantages for this system: microalgae grow rapidly and they fix carbon dioxide from the atmosphere, reducing the greenhouse effect and improving air quality. However, the research is still in lab scale. The contents of wastewater are more complex than simply nutrients and microalgae require careful growth conditions and bioengineering to succeed. (Cai, Park and Li, 2013)

Bioelectrochemical systems (BES) are another interesting approach. BESs are combinations of electrodes and microorganisms in an electrochemical cell. Organisms catalyse the chemical reactions taking place at anode where organic matter is degraded. Ammonia in wastewater is transported over a cation ion exchange membrane (CEM) to the cathode chamber where high catholyte pH allows ammonia recovery. Ammonia is stripped by the produced hydrogen and subsequently absorbed to sulphuric acid. Main advantage is that it produces electricity during the purification/recovery process instead of consuming it. However, currently the removal/recovery efficiencies are around 30 %. (Rodríguez Arredondo et al., 2015)

2.9.2 Physiochemical methods

The most conventional method for ammonia recovery is stripping with a gas feed and then absorbing it with an acid with sulphuric acid being the most common solution. This method produces good results with 90 % ammonia recovery. However, it is rather energy intensive due to aeration flows for stripping. It consumed 9.7 kWh/kg-$N_{harvested}$ after using CO_2 stripping to decrease NaOH-consumption. (Jiang et al., 2014, Boehler et al., 2014).

Instead of stripping ammonia, it is possible to precipitate nitrogen with struvite, also known as magnesium ammonium phosphate hexahydrate (MAP) ($MgNH_4PO_4 \cdot 6H_2O$). Struvite precipitation has been researched intensively for wastewater treatment during the last decade and the results look promising: it is possible to significantly reduce the chemical costs in wastewater treatment while recovering over 90 % of ammonia nitrogen (Darwish et al., 2015). The core idea is that by adding a magnesium source to the water and controlling the conditions, it is possible to precipitate ammonia and phosphorus and use the precipitate as a fertilizer. The most important process condition is the correct balance of nitrogen, phosphorus and magnesium. Thus, it is more suitable for wastewaters with higher dissolved phosphorous concentration, such as the reject water of a bioP sludge digestate. If chemical precipitation is used for phosphorus removal, this method is not applicable. Furthermore, the presence of calcium-ions supresses the MAP formation process. (El Diwani et al., 2007)

Ammonia in wastewater is usually in its ammonium form ($NH_4^{+)}$. A new approach is to use ion exchange as a basis for adsorbing the ammonia to a mineral, for instance to zeolite. Zeolites are hydrated aluminium-silicate minerals with an overall negative charge. Negative charge enables adsorbance of positive cations, such as NH_4^+ or K^+. However, industrial scale applications are few and the development for wastewaters with high concentration of NH_4^+ is still in early phase. (Taddeo, Prajapati and Lepistö, 2017)

Other research teams are experimenting stripping by membrane contactors (Amaral et al., 2016, Boehler et al., 2014). This method is presented in section 3.3. While the basic technology is based on membranes, many options for pre-treatment affect the system efficiency. Most common factors differing from project to another are the chemical used to control pH, pH itself, the method for handling solids in the process, pressure applied to the membrane system and the properties of the membrane. Boehler et al. (2014) used a reactor described in Figure 13. They had three reactor units in series and reject water was heated up to 54 °C with flow rate varying between 600 and 1200 l/h. The ammonium nitrogen concentrations tested were from 700 to 3400 mg/l.

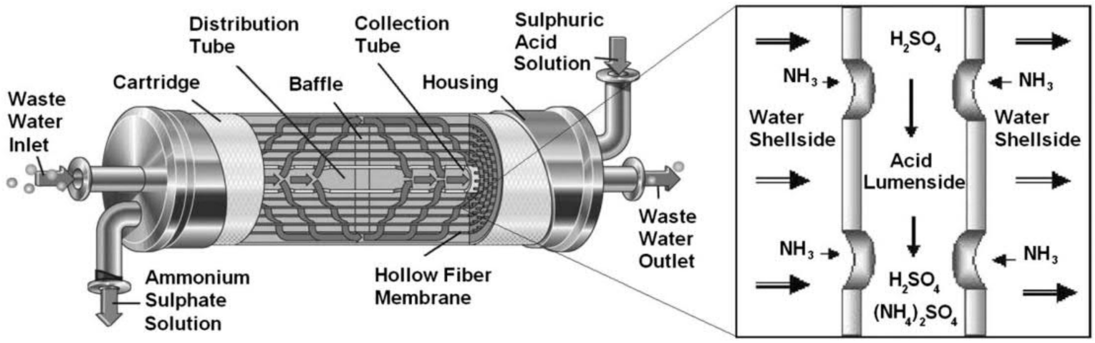

Figure 13. A membrane contactor module used by Boehler et al. (2014).

Amaral et al. (2016) used more humble setting, shown in figure 14. They processed landfill leachate with ammonium nitrogen concentration of 881 ± 61 mg/l and microfiltered the source water. The leachate tank and extraction solution tank (sulphuric acid) were 3 litres and 2 litres in volume, respectively. The leachate and extraction solution come into contact in a membrane contactor outside the tanks which is a suitable instrument setup for a lab scale pilot. Both liquid flows, leachate and acid, were recycled and transferred back to their respective reservoirs. Temperature was kept at 25 °C. Both teams used NaOH to adjust pH before the process.

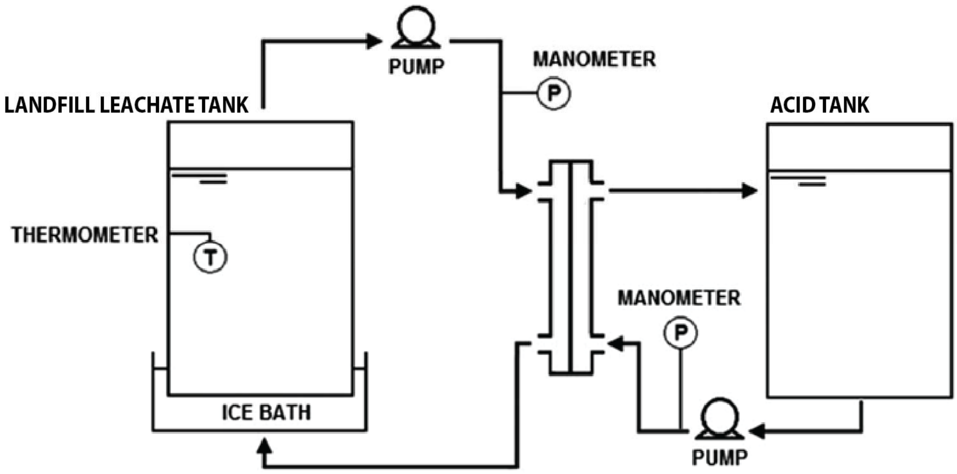

Figure 14. Process schematic used by Amaral et al. (2016).

3 Material and methods

The tests conducted for this experiment involved optimizing a lab scale continuous reactor using reject water from a wastewater treatment plant. The utilized technology for nitrogen recovery is a stripping process using a membrane, combining already existing ideas and implementing them in a new manner. The process is based on physical phenomena without any biological factors involved.

3.1 The reactor

A continuous-flow reactor with a volume of 2 litres was built for this experiment. The design process to implement the membrane technology in the reactor started from hydraulic retention times (HRT). The purpose was not to maximize the recovery efficiency alone but instead to develop a process with a reasonably short HRT. Suitable retention times were below 20 hours. The length of the reactor was decided to be 45 cm, resulting in a cylinder shape reactor with a volume of 1.9 litres. With this volume, the discharges were suitable for the lab pumps to create retention times from 2 hours to 16 hours.

The reactor had two membrane tubes with a diameter of 10.008 mm, wall thickness of 0.495 mm and absolute membrane surface area of 0.28 m^2. The membrane surface area to volume ratio was 14.6 m^2/m^3. Based on literature, sulphuric acid was selected as the extraction liquid. The acid circulation direction in the reactor was set against the reject water flow. The acid container was placed approximately 20 cm above the reactor to keep a mildly higher pressure inside the membrane but not too high to cause a rupture. A constant amount of 120 ml acid was used throughout the experiment. The reject water container was air tightly sealed apart from replacement air tube which offset the pressure drop caused by reject water leaving the container. Figure 15 shows the process schematic and the instrument setup in the lab. Reject water flows from the container in the right, through the heated water bath, through the reactor and ultimately to the sink behind the water bath. Reject water container also functions as a settler for solids in the pre-treated reject water. The acid circulates from the acid container, upwards through the reactor and back to the acid container. Finally, the mixing was implemented with magnets rotating along its inner wall and slowly rotate the fluid inside the reactor. Table 2 summarises the pilot system parameters.

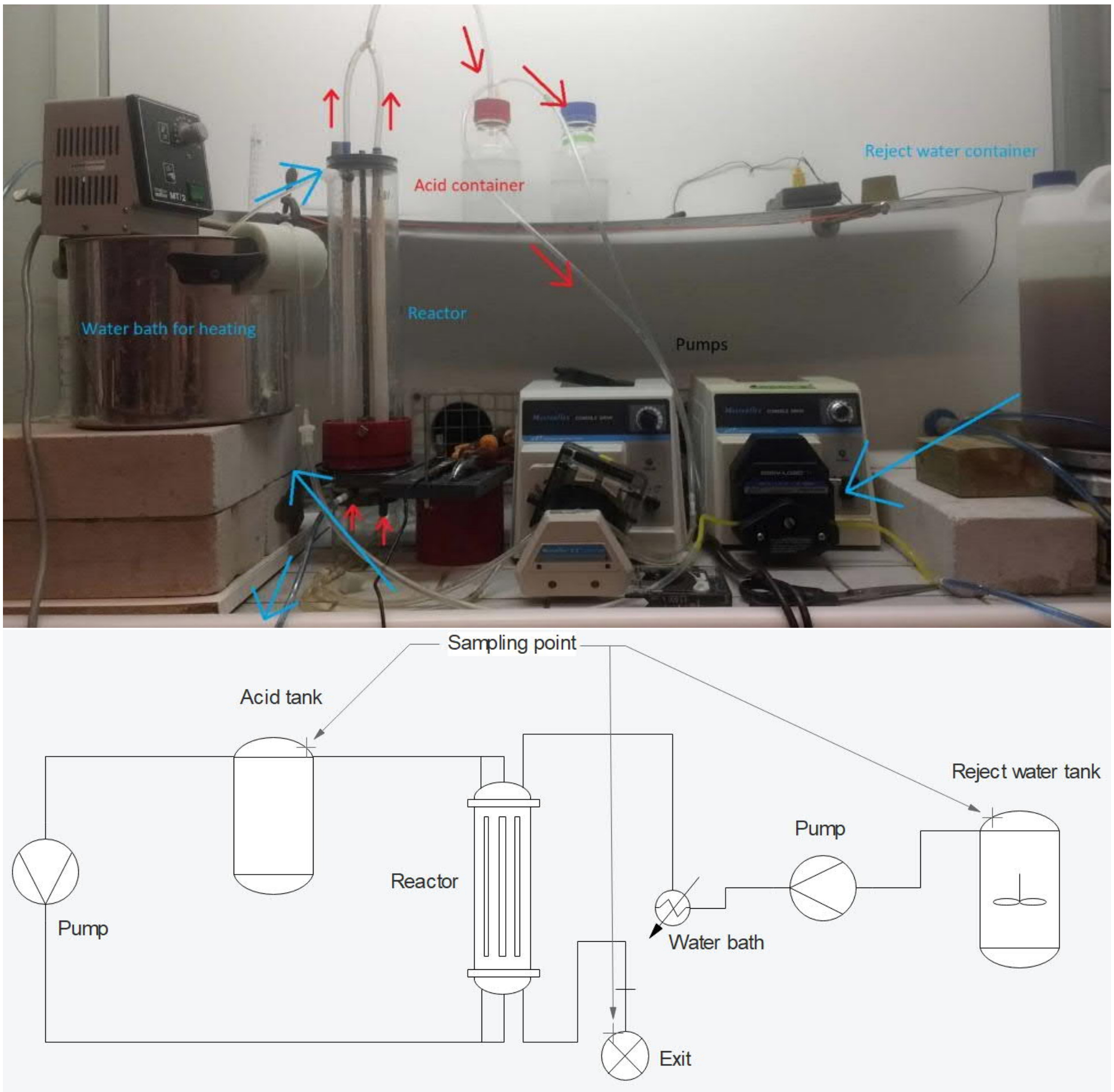

Figure 15. Lab pilot setup and process schematic. Reject water flows linearly while acid circulates back to the container. Blue arrows and texts describe reject water flow and red arrows and texts the acid flow.

Table 2. Pilot design parameters.

System parameter	Value
Volume (l)	1.9
Membrane surface area (m^2)	0.028
Membrane surface area per volume (m^2/l)	14.6
Reactor Length (m)	0.45
Reactor Diameter (m)	0.074
Membrane tube diameter (m)	0.01
Membrane wall thickness (mm)	0.495
Mixing	Poor
Temperature (°C)	35-45

3.2 Properties of reject water

The liquid waste stream used in this study was reject water from Viikinmäki wastewater treatment plant's digesters after the dewatering of the sludge. The reject water used in the experiments was taken after gravity settling at the plant. Properties of the reject water are presented in Table 3.

Table 3. Properties of the reject water. Values were calculated over the year 2016 from 52 samples.

Property	Average	Min	Max
BOD_7ATU (mg/l)	530	320	1140
SS (mg/l)	980	560	4200
Total-P (mg/l)	13	10	47
PO_4-P (mg/l)	1.4	0.5	2.7
Total-N (mg/l)	980	820	1250
NH_4-N (mg/l)	790	680	900
pH	8	7.5	8.1
Alkalinity (mmol/l)	67	57	77
COD_{Cr} sol (mg/l)	1380	860	2100

3.3 Experiment details

The core idea of the recovery process is based on the hydrophobic gas permeable membrane. As seen in Table 3, most of the nitrogen in reject water is in the ammonium form. When pH is increased, ammonium-ammonia balance shifts towards ammonia which is a soluble gaseous compound. Ammonia can and will pass through the membrane because there is always an ammonia concentration gradient over the membrane, shown in Figure 16. The gradient remains constant because the ammonia inside the membrane reacts with sulphuric acid (H_2SO_4) to form ammonium sulphate ($(NH_4)_2SO4$), rendering ammonia concentration inside the membrane to zero.

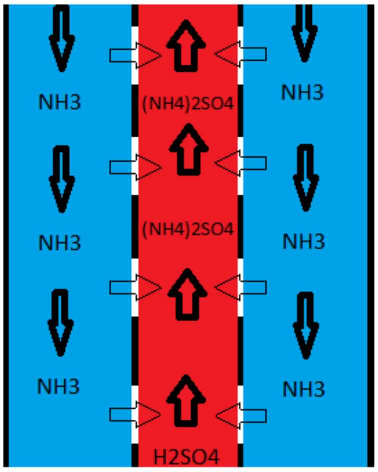

Figure 16. GPHM function principle. [1]

As seen in Table 3, the suspended solids content in the reject water is high which is a problem in the reactor with the high pH environment because solids floc and precipitate naturally when pH is increased. To avoid clogging of the membranes or any other parts of the system, a simple 30+ minutes settling pre-treatment phase was used after increasing pH up to 12+ with calcium hydroxide ($Ca(OH)_2$) powder. This process decreased SS concentration from 1300 mg/l to approximately 600 to 800 mg/l. Influent to the reactor was also heated up to 35-40 °C to simulate actual digester environment.

Once the system was running, the following parameters were tested and optimized regarding ammonia transfer over the membrane: hydraulic retention time, acid flow rate, membrane thickness with thinner membrane, acid type with 1 mol/l phosphoric and sulphuric acid and reject water pH with pH 10, 11 and 12. Table 4 lists all the conducted tests.

Table 4. Tests conducted during the research.

Dates	Number of runs	HRT (h)	Acid flow (l/m^2/h)	Acid type	Notes
8.5.-17.5.17	4	8	30-320	H_2SO_4	Acid flow rate optimization
19.5.-31.5.17	6	2-12	320	H_2SO_4	HRT optimization
5.6.-9.6.17	5	2-12	320	H_2SO_4	Repeat experiment for HRT optimization

[1] Modified from Hansruedi Siegrist and Marc Boehler, *Eawag, 8600 Duebendorf, Switzerland*, 6th and 7th of July 2017, POWERSTEP Summer School, Vienna (slides)

20.6.-23.6.17	2	8	320	H_2SO_4	Reject water pH optimization with pH 10, 11 and 12
27.6.17	1	8	320	H_3PO_4	Different acid type
3.7.17	2	8	320	H_2SO_4	Membrane thickness
28.9.17	1	8	320	H_2SO_4	Membrane surface area

The effectiveness of a run was determined based on the ammonia content in the acid container. Detailed explanation is in section 3.4. Otherwise, suspended solids (SS), NH_4, chemical oxygen demand (COD), total phosphorous, total nitrogen and total suspended solids (TSS) were measured and analysed from three points in the process: reject water container (influent), effluent and acid container. Standards used in sample analysis are listed in Table 5.

Table 5. List of standard analysing methods.

Property	Standard
NH_4	ISO 11732, dated 2005, by flow analysis (FIA) and spectrometric detection; Tecator 5012 Analyzer, 5042 Detector
SS	SFS-EN 872, v.2005; Filter: Whatman GF/A glass fiber filter
PO_4	SFS-EN ISO 15681-1, dated 2005 by flow analysis (FIA) and spectrometric detection using tin chloride method; FOSS Tecator, FIAstar 5000 Analyzer + Sampler 5027
COD	SFS 5594, dated 1988 (in Finnish); Hach DRB 200 reactor; Metrohm Dosimat 775
Total Nitrogen	SFS-EN-ISO 11905-1 v.1998, Standard Methods for the examination of water & wastewater (v. 2005, 21. edition, pages 4-120), Standard Methods (v.2005) 4500 B. Ultraviolet Spectrophotometric Screening Method, Ganimede N equipment manual; Ganimede N
Total Phosphorus	SFS-EN ISO 6878 v. 2004, SFS-EN-ISO 15681-1, flow analysis (FIA) v. 2005; Foss: FIAstar 5000 Analyzer
TSS	SFS 3008

3.4 Economic feasibility analysis

An economic estimation was also conducted for WWTP which produces 2500 m^3 reject water a day, corresponding to a plant which receives wastewater from approximately one million inhabitants. Currently, reject water is often recycled back to the normal treatment process, contributing approximately 20 % of its nitrogen load. If the reject water was treated with NPHarvest technology, the ammonia load to primary treatment process would decrease and it would be more cost-effective to run. The assumptions behind the estimation are that the current nitrogen removal process of the wastewater treatment plant costs 8 €/kg-N and that the conventional costs increase linearly with removal efficiency.

This cost was estimated based on discussion regarding the treatment costs from several WWTPs and biogas plants and selected to represent the average end of the price range.

Costs for NPHarvest are estimated with yearly equipment costs using 15-year lifetime and an interest rate of 5% as well as operational costs including chemical costs. Calcium hydroxide ($Ca(OH_2)$) was estimated to cost 93 €/t and sulphuric acid (H_2SO_4, 98 % w/v) cost 290 €/t (Rothrock, Szögi and Vanotti, 2013) The final product contained around 6 g/l ammonia sulphate. However, due to large volume of acid used, this translates to 0.6 mass-% solution. No value was calculated for the final product. Energy costs were estimated to be insignificant.

3.5 Process mass balance

To measure the effectiveness of the process, it is critical to understand and measure the mass balances of the process. A methodology to evaluate the pace of the ammonia transfer was developed for this process.

As the process is continuous, it is more meaningful to work with loads instead of absolute concentrations of nutrients. In this pilot experiment, the liquid flows are:

$Reject\ water\ flow, Q$ [l/s]
$Acid\ flow, F$ [l/s]

However, we are mostly interested in ammonia loads:

$Influent\ ammonia\ load, I$ [g/s]
$Effluent\ ammonia\ load, E$ [g/s]
$Ammonia\ flux\ through\ the\ membrane, A$ [g/s]

Influent and effluent ammonia loads are the product of reject water flow Q and their respective ammonia concentrations:

$$I = Q * [I] \tag{1}$$

$$E = Q * [E], \qquad [2]$$

where [I] and [E] are the ammonia concentrations in influent and effluent, respectively, after the reactor has reached a relatively stable state or equilibrium. In this situation, the mass balance equation is:

$$I = E + A \qquad [3]$$

However, since the acid is circulating, the ammonia flux through the membranes, A, cannot be measured as simply as other flows. Figure 17 illustrates the ammonia concentrations in effluent and acid, over the length of a single run.

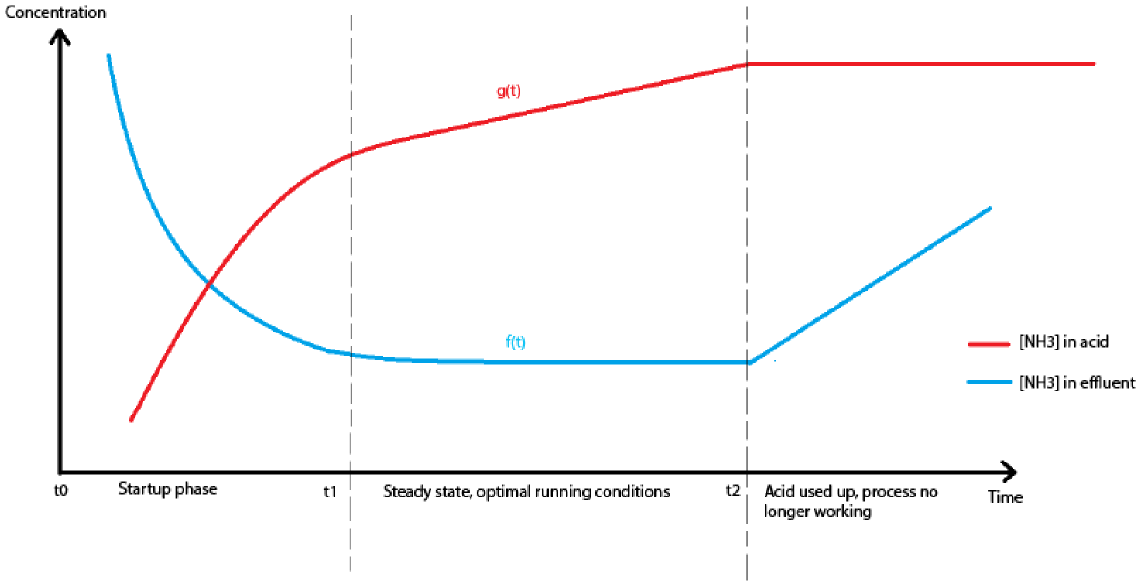

Figure 17. Visualization of a conceptual run.

In start-up phase, the ammonia concentration in the reactor (used here interchangeably with ammonia concentration in the effluent) decreases aggressively while ammonia concentration increases in the acid is in a logarithmic manner. After reaching steady state at t1, the ammonia concentration in the reactor is constant until t2. It should be noted that influent is assumed to be constant due to mixed source material container.

The ammonia transfer over the membrane during the steady state (between t1 and t2) is the first differential coefficient for g(t) while t1<t<t2, g’(t). The value for this differential coefficient is constant. Thus, mass balance equation can be formed as follows:

$$I = E + g'(t), \qquad while\ t1 < t < t2 \tag{4}$$

In practical sense, this means that the effectiveness of the process is evaluated by measuring ammonia content in the acid container and calculating their differential coefficients as ammonia transfer rates.

3.6 A test run in practice

Based on section 3.5, it is important to reach steady state for each test. Therefore, every run that began with an empty reactor, the process was driven for four hours before the actual test started. To accurately measure the process effectiveness, the acid was replaced for each run i.e. the ammonia concentration in acid was zero at the start of each run. Every run was as long as its HRT, meaning 2-hour run had 2 h HRT and 10-hour run had 10 h HRT. The reason for this was to keep the test times as short as possible while observing the process over the time period of at least one complete turnover of the reactor content.

Samples were collected at the start of the run and four times during a run at times equally apart from each other (n * HRT/4, where n is the sample number). Samples were collected from the source liquid container (influent) by extracting the sample through the replacement air tube, reactor exit tube (effluent) and acid exit tube by removing acid tube from the acid container and pumping the sample into the sampling vial. Influent and effluent samples were approximately 11 ml in volume because a 10-ml sample was needed for ammonia concentration analysis. Acid sample was less than 2 ml due to the sample being diluted to 10 ml during the analysis. Furthermore, the acid volume could not drop below 100 ml without risking instrumental failure so the acid samples had to be small in volume. A few composite samples were also collected during the experiment.

4 Results

The results are divided into ammonium nitrogen results and secondary findings. Ammonium nitrogen results are related to process parameters that are subject to optimization, such as acid flow rate or reject water HRT, and have an effect on process efficiency, while secondary effects, including but not limited to SS and COD, are measured to understand what happens during the process in detail. It is important to keep in mind that controlling pH with calcium hydroxide affects some of the other parameters, most significantly SS. The economic feasibility estimation is also presented and discussed.

4.1 Ammonium nitrogen results

Ammonium nitrogen results are all based on NH_4 measurements. As explained in section 3.5, process efficiency is estimated by monitoring ammonia balance. It is important to keep in mind that ammonia transfer is based only on NH_4 measurements from the acid flow, while harvesting efficiency is calculated through ammonia nitrogen concentration difference in influent and effluent.

4.1.1 Acid flow rate

The hypothesis for the relationship between flow rate and transfer rate was that the faster the flow rate, the better ammonia transfer through the membrane, up to a point. This assumption was based on the idea that ammonia transfer rate is the most efficient when ammonia molecules do not linger on the surface of either side the membrane. On the acid side of the membrane, this means that faster acid flow removes ammonia molecules faster from the surface of the membrane and opens spaces for the adjacent ammonia molecules to diffuse through the membrane. Meaning that faster acid flow is better for maintaining the maximum ammonia concentration difference over the membrane. To test this, a series of runs were conducted with acid flow rate varying from 30 to 320 $l/m^2/h$ while keeping other parameters constant. Results are presented in Figure 18.

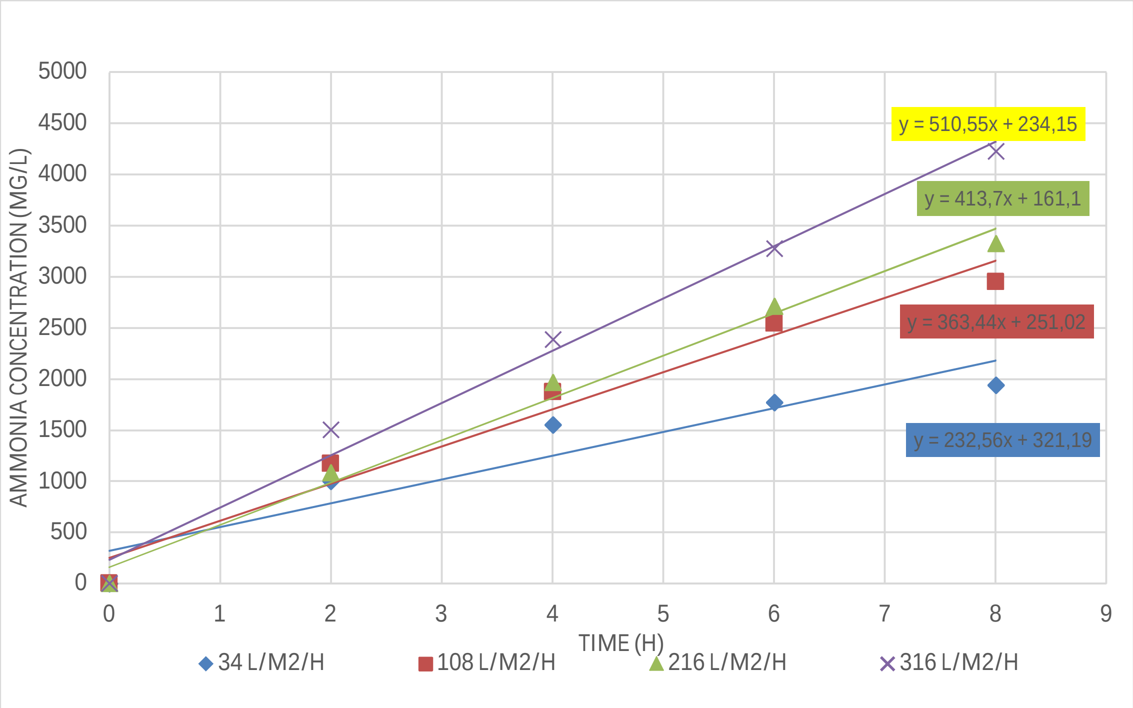

Figure 18. Ammonia concentration in acid with different acid flow rates. Flow rates are in litres per membrane area in square metres per hour.

Data sets have a linear trendline to accurately describe the slope of the curve, which is the ammonia transfer rate. As seen in the figure, the original assumption was correct: with faster flow rate, a better transfer rate is achieved. To estimate the most optimal flow rate in regard of ammonia transfer, the differential coefficients of the equations in Figure 18 were analysed in an acid flow, transfer rate-chart, shown in Figure 19. A linear trendline could also represent the four data points in the chart, however, the process ceases to function when flow rate is zero i.e. the transfer rate is also zero. Thus, the trendline is logarithmic and not linear.

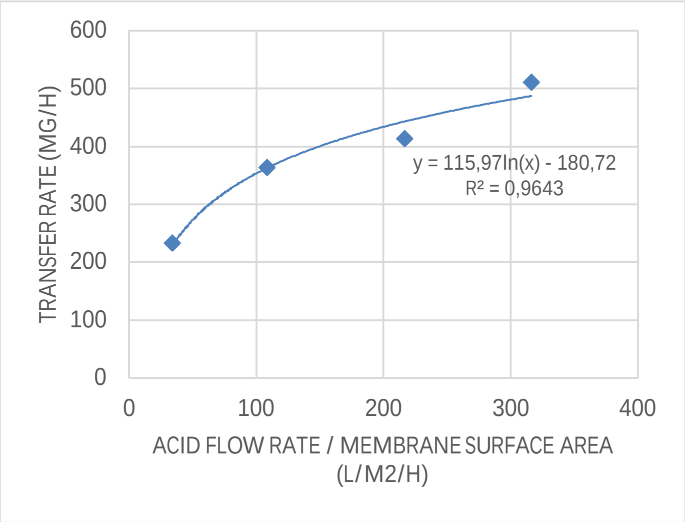

Figure 19. Ammonia transfer rate as a function of acid flow rate.

Based on this logarithmic trendline, there are diminishing returns with the acid flow rate. Further calculating the actual benefit of increasing acid flow rate, the data was extrapolated in Table 6. The first differential coefficient reflects the benefit achieved when increasing acid flow rate. The benefit of increasing flow rate above 320 l/m^2/h was insignificant and the rest of the experiment was conducted using this acid flow rate.

Table 6. Differential coefficients for the equation presented in Figure 19.

Acid flow rate per surface area (l/m2/h)	dy/dx
34	7.25
108	2.27
216	1.14
316	0.77
424	0.58
531	0.46
637	0.39

4.1.2 Hydraulic retention time

Similar to acid flow rate, there was a hypothesis with the HRT. Batch tests conducted before the continuous reactor had proved that with a long enough experiment, 99 % of nitrogen can be harvested with this technology. However, the objective was to optimize the process to a short HRT. The shorter the HRT is, the better is the economic feasibility of the process. In this section, the effects of HRT are presented from two points of view: ammonia transfer rate and harvesting efficiency.

4.1.2.1 Ammonia transfer

Acid ammonia concentrations for different HRTs are presented in Figure 20.

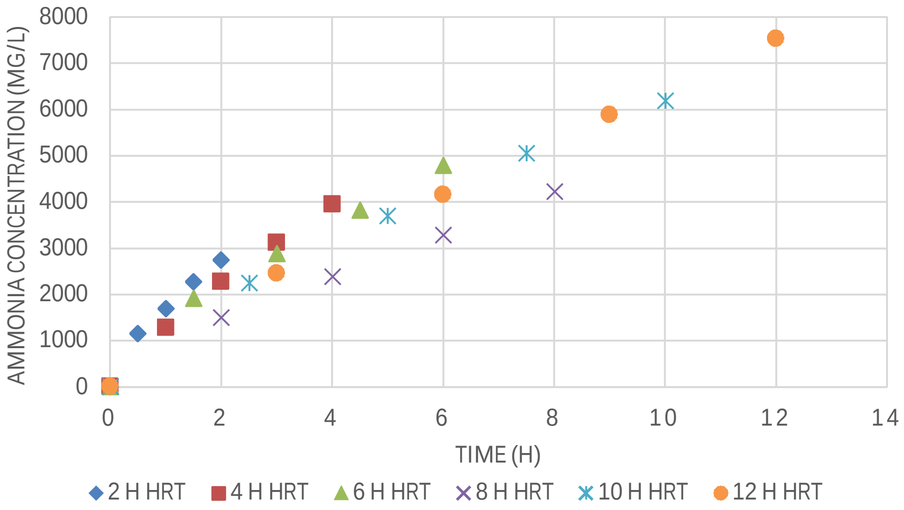

Figure 20. Ammonia transfer with varying HRTs.

As seen in Figure 18, ammonia concentration increases over the duration of tests in linear fashion while the HRT was between 2 and 12 hours. This is natural but it is noteworthy that the ammonia transfer rates are very close to each other. Meaning that the ammonia flux over the membrane is not affected by the HRT. This is understandable: the key parameters affecting the transfer rate are membrane surface area, concentration gradient over the membrane and the rate of mixing. These three were constant throughout the experiment.

4.1.2.2 Harvesting efficiency

The effect of the HRT was tested with a second set of tests to confirm the result. The data sets had similar results as can be seen in Figure 20. All figures except for Figure 21 show only one data set to maintain clarity. Figure 21 compares the harvesting efficiencies of the runs with different HRTs. It is important to keep in mind that harvesting efficiency is calculated by comparing ammonia concentration in effluent and influent streams.

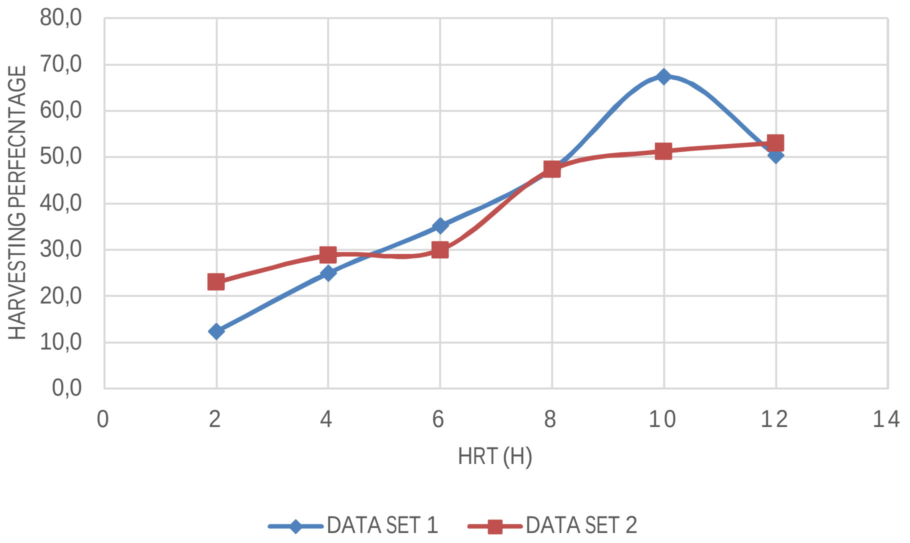

Figure 21. Harvesting efficiency for each HRT for the original test run and the repeatability test.

While there are clear differences in the harvesting efficiencies for specific HRTs, the trend is clear: the longer the retention time is, the higher the harvesting efficiency. This is natural since the contact time for reject water and ammonia is longer when HRT is longer, meaning that a larger portion of ammonia passes through the membrane.

4.1.2.3 Reject water pH

Reject water pH is relevant because it affects the ammonia-ammonium balance. With higher pH the balance shifts towards ammonia. Figure 20 shows a simple linear representation on the effect of pH and harvesting efficiency. The test conditions were not yet fully optimized, and thus, the efficiency is lower. However, it is relevant to compare these three runs with each other. It is clear that pH 12+ is the best in terms of harvesting efficiency.

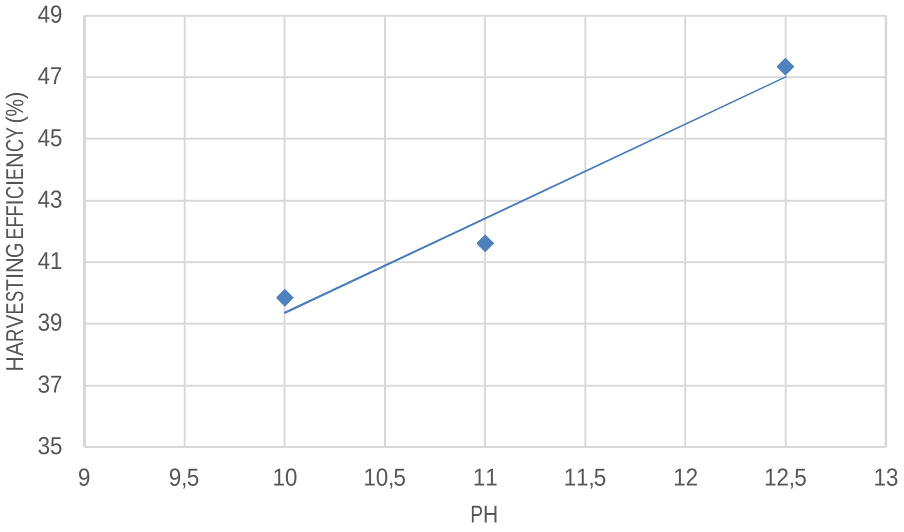

Figure 22. Effect of reject water pH to harvesting efficiency.

4.1.2.4 Membrane surface area

One test was conducted by shutting down one of the two membranes inside the reactor in order to study the influence of the membrane area. Results are illustrated in Figure 23. Ammonia concentration is lower with only half the membrane, supporting the assumption that larger membrane surface area increases the harvesting efficiency.

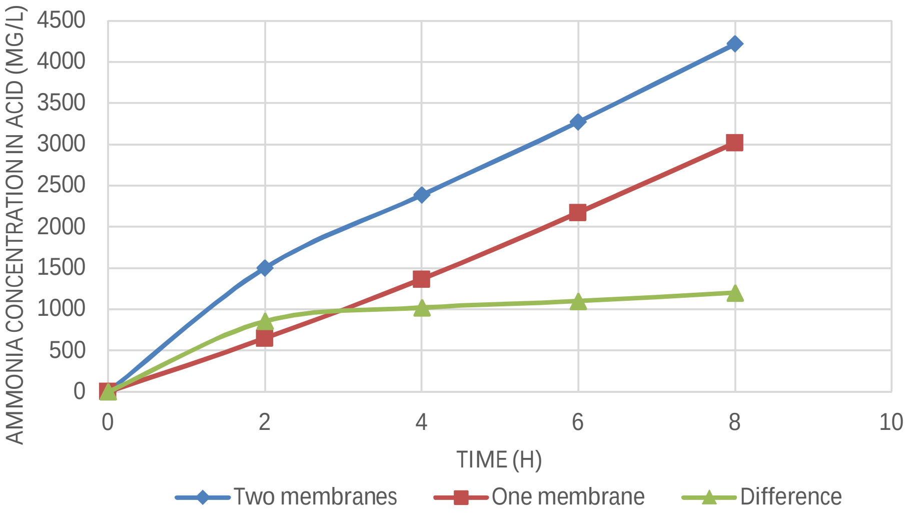

Figure 23. Ammonia concentration in acid with full membrane surface area and only half of it.

4.1.2.5 Different acid and membrane thickness

The tests were also conducted with 1 mol/l phosphoric acid and using another reactor configuration. The different reactor configuration had close to the same membrane surface area, however, it had four membranes with thinner membrane walls (0.229 mm) and smaller diameters (5.2 mm inside diameter). The results for different reactor configuration were inconclusive but it seems there is not much difference with membrane thickness. Phosphate acid performed equally well compared to sulphuric acid. The graphs for these parameters are presented in Appendix 1.

4.2 Secondary findings

One of the most significant problems in the process is the suspended solids concentration which causes fouling of the membranes and clogging of the reactor and tubes. Our system solution uses low pressure to mitigate this problem and decrease the need to pre-treat the reject water. However, it was clear that monitoring SS is important. As seen in Table 3, the variance for SS in the raw reject water is quite large, from 500 to over 4000 mg/l. Table 7 summarises a single run’s measurements.

Table 7. Comparison with settled reject water, the influent and the effluent values. The data is from a single 12-hour run. Five measurements were conducted for each parameter. The values are in mg/l.

mg/l	Settled reject water			Influent			Effluent		
	Average	Min	Max	Average	Min	Max	Average	Min	Max
NH4	840	840	850	550	420	730	310	230	430
SS	1290	1240	1340	1090	830	1630	890	630	1150
Pt	13.1	12.8	13.4	7.6	7.2	8.5	7.3	7.0	7.9
Nt	1050	1050	1050	800	770	810	480	430	600
COD	8980	8760	9200	7180	6680	8010	6390	4460	7090
TSS	2.5	2.4	2.5	2.7	2.5	3.2	2.5	2.5	3.2

On average, our raw reject water batches contained 1000-1300 mg/l SS before settling. The influent to the reactor typically had 600-700 mg/l SS and the effluent 500-600 mg/l SS. This indicates that solids are accumulating in the reject water container and the reactor. Most of the accumulated SS settled to the bottom of the reactor instead of fouling the membranes. The reactor had to be flushed occasionally to remove the accumulated solids from the bottom of the reactor. Overall, the SS concentrations are rather high because the pre-treatment is not aimed to remove it particularly efficiently. Still despite this, the process performs well despite this.

COD was also measured throughout a test run. Our measurements consistently show a value between 6000 and 9000 mg/l. However, the data from the wastewater treatment plant's measurements range reject water COD between 800 and 2100 mg/l. Regardless of absolute value for COD, there is a slight drop when reject water is settled but no significant difference during the treatment process. This is true also for TSS: the concentration values are consistently between 2 and 3 mg/l from pre-settling to reactor effluent.

Total phosphorous and total nitrogen were measured. They behave similarly: during settling the total phosphorous concentration drops from 12-13 mg/l to 6-7 mg/l and total nitrogen from 1000-1100 to 700-800 mg/l. Total phosphorous does not change significantly during the treatment process. In contrast, total nitrogen drops further during the membrane reactor phase, especially during the longer runs corresponding to the higher recovery efficiency of nitrogen. The lowest measured value for total nitrogen was approximately 400 mg/l. The values measured at the treatment plant and in the university laboratory reflect each other.

Phosphate phosphorous is precipitated during the settling but its fraction of the total phosphorus was insignificant: the flocs that are settling adsorb solid particles with phosphorous bonded with them. This explains the drop of phosphorous concentration during settling. The remaining phosphorus flows through the process. Some nitrogen is lost during the settling to the atmosphere before the supernatant is sealed in an airtight container. The further drop in total nitrogen concentration shows that the process works as intended.

4.3 Economic estimation for the technology

A rough estimate of the economic viability was prepared. Assuming that the final product (6 g/l; 0.6 mass-% liquid ammonium sulphate for our experiments) would have any market value is too optimistic. However, the ammonium sulphate created with the process can be given away for free. Figure 24 shows the result of the estimate. The figure compares conventional process costs and NPHarvest process costs. The grey line represents the costs of conventional treatment described in section 2.8. The curve starts at 30 % because 30 % removal was estimated to be the extent of nitrogen removal in the process that could be achieved without any increased cost related specifically to nitrogen removal. The dashed lines are sub costs for NPHarvest: investment, calcium hydroxide cost and sulphuric acid cost. Investment costs include all the equipment and infrastructure costs and increases in exponential manner because several reactors in series would be required to reach higher harvesting efficiency. Chemical costs increase linearly. The green line is the sum of the three dashed lines.

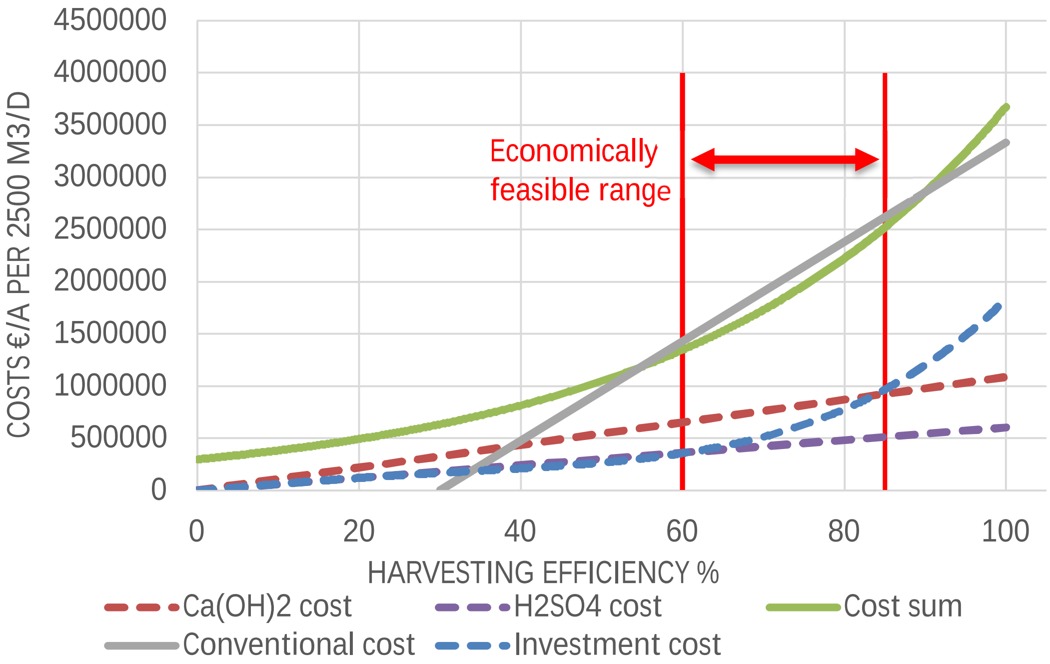

Figure 24. Economic estimation of NPHarvest viability.

Based on this estimation, a wastewater treatment plant that produces around 2500 m^3 reject water a day would be more cost-effective to run if the harvesting efficiency is between 60 and 85 %.

5 Discussion

Results were positive and encouraging: the process works in a continuous manner. However, the results are not entirely without problems. This section discusses and analyses the sources of uncertainty and the results. Furthermore, the reactor design for the next phase is presented and different nitrogen recovery methods are compared.

5.1 Sources of uncertainty

One of the most significant sources of uncertainty lies with the ambitious objective to reach steady state for the test runs. In an ideal situation, the effluent ammonia concentration is constant throughout the test run; in practice, most of the runs the effluent ammonia concentration decreased, particularly when the HRT was longer than six hours. Figure 23 shows the effluent ammonia concentrations for different HRTs. The reason for this was limited operational time during the day: typically, after a run, the reactor was left full of reject water but acid was removed from the membranes for the night. The following day operation started from this situation but the vertical ammonia gradient through the reactor had evened out during the night.

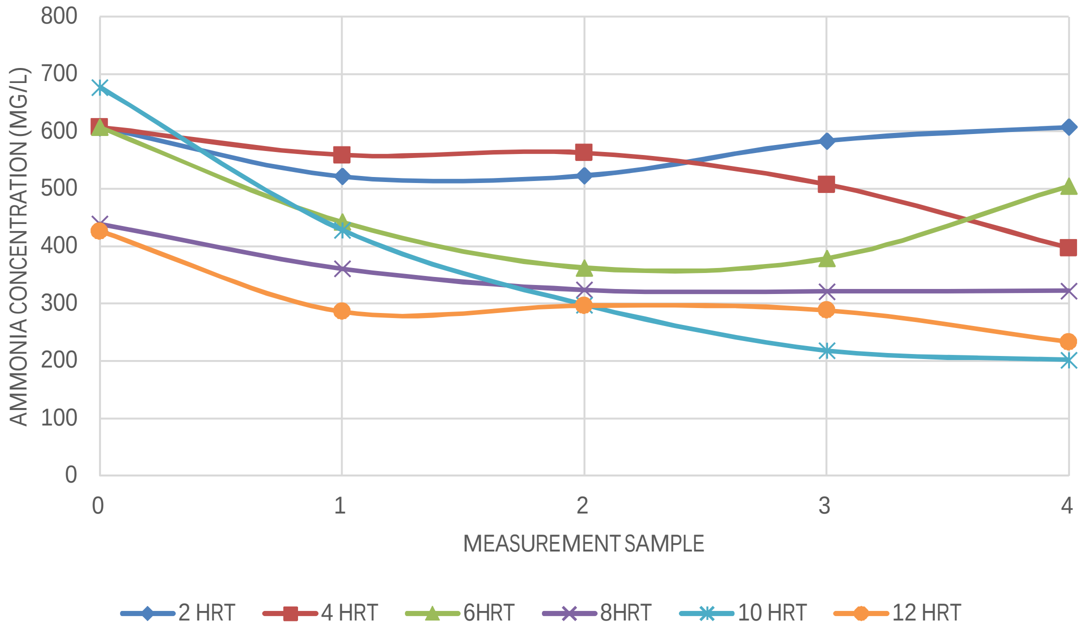

Figure 25. Effluent ammonia concentration for a set of test runs.

While calculating harvesting efficiencies the average of last three samples of each run was taken into account to negate the higher ammonia concentration at the beginning of the run. However, the calculations for acid transfer rate over the membrane are based on the assumption that the reactor conditions are constant. Strictly speaking, this was not true for the runs. Thus, a linear trendline for ammonia concentration in acid container for a run as a representation for the ammonia transfer rate over the membrane is not accurate. The error caused by this is, however, not significant in the grand scheme.

Another unfortunate uncertainty was the mixing. As mentioned earlier, it was applied after the reactor was built and its efficiency reflects this. The mixer, along general dispersion forces, mixed the content of the water in horizontal circles around the reactor. Ideal mixing instruments would mix the content from edges of the reactor towards the centre along the radius in order to keep ammonia rich water in touch with the membranes. As a consequence, the overall efficiency of the reactor was lower compared to the possibilities of an efficient mixing. The scaled-up reactor for next phase has a better design in this regard.

Another factor for running the pilot was the variety of reject water batches. This affected mostly the $Ca(OH)_2$ consumption but also comparing results between runs that use reject water from different batches was more unreliable.

5.2 Analysing the results

The process works well in a continuous manner and is relatively efficient when taking into account the scale of the pilot and the running conditions. Optimal operational conditions could be defined for parameters affecting ammonia transfer over the membrane: acid flow rate and reject water pH. The optimal hydraulic retention time depends on the desired application, but based on the results in this experiment, it is possible to keep HRT short by optimizing other parameters of the process, including mixing efficiency and suitable pre-treatment.

The design choice of non-pressurized system seems to have been the correct one: the membranes gained some colour but did not foul up to the point of restricting the ammonia transfer. This also decreases the need to have a highly efficient pre-treatment: the solids in the process act as an inert material that flows through the system rather than being an obstacle for the ammonia recovery. Not using high pressure is also an advantage in energy consumption. However, the tests conducted were relatively short and for the next phase it is important to assume that pre-treatment is still required and that the membranes need occasional washing.

According to our results, the most effective pH is above 12. Research conducted by Amaral et al. support this result: the optimal pH for their experiments was set at 11.5 (Amaral et al., 2016). The experiments in this thesis tested pH only on intervals of one, thus if the most effective pH is indeed between 11 and 12 and the effectiveness is assumed to stay the same after the breaking point, it would not show in our results. However, in theory, pH 10 should be sufficient as the ammonium/ammonia balance shifts towards ammonia when pH increases (Siegrist, Laureni and Udert, 2013). Figure 26 illustrates the ammonia fraction in regard to pH. According to this figure, the transfer efficiency for pH of 11 and 12 should be the same because the ammonia concentration should be almost the same, but in our experiments the efficiency increased linearly. It is not clear why this phenomenon happens. It may be related to some colloidal matter reacting in higher pH, and thus, favoring the access of ammonia to the membrane but more research would be needed to fully understand the detailed diffusion mechanic.

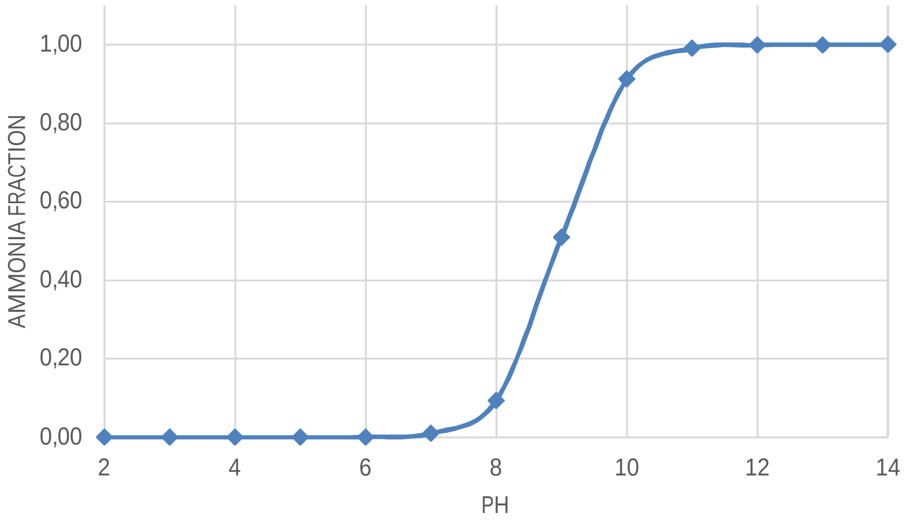

Figure 26. Estimation of ammonia fraction from Total Ammonia Nitrogen (TAN) in regard to pH.

Earlier it was stated that more membrane surface area in the same reactor volume increases the ammonia transfer rate, and thus, the recovery efficiency. The test results from the run with half the membrane surface area support this, at least when comparing the final ammonia concentration in acid. However, more than one test would be needed to confirm this: if the surface area to volume ratio would have the effect we expected, also the transfer rate, the angle of the curve, would be steeper for full membrane test compared to half membrane run. However, as Figure 23 shows, besides the beginning of the run, the curves have almost the same slope. This would indicate that the ammonia transfer rate in the middle of the run was the same. This conclusion cannot be fully trusted due to the length of time between the runs, different reject water batch and problems with mixing. Furthermore, even if we assume that larger membrane surface area improves ammonia transfer, there will be a point where mixing is hindered if there is too much membrane inside the reactor.

Secondary findings behave throughout the run as expected. The increase of pH with calcium hydroxide in the pre-treatment phase creates flocs which settle efficiently, removing suspended solids and some phosphorus and COD from the reject water. Some nitrogen is also lost during the settling phase; however, it does not precipitate easily so losing it to the atmosphere is a probable explanation. Only nitrogen is removed from the reject water flow during the membrane reactor. Phosphoric acid did not prove to be better than sulphuric acid and using it as the acid would increase the process costs.

Economic estimation is rough but it provides a guideline on how the process would be implemented as a system to reduce existing treatment costs, rather than for producing ammonium sulphate with an economic value. The cost estimate is based on the direct operating costs of a wastewater treatment plant which may vary depending on the location and industry. For some biogas plants, the treatment cost for their wastewater is 10-20 €/kg-$N_{treated}$, thus, increasing the economic feasibility of the process significantly. Furthermore, economic efficiency of the process can be increased by using lime and acid by-products from other processes.

5.3 Reactor design for the next phase

Based on the acquired data, preliminary design draft was drawn for up scaled phase for the research, as it is one of the objectives of the study. The reactor for the next phase was designed with a 200-litre reactor volume. It is only a preliminary design and will most likely change with the requirements from the membrane provider. The reactor would be 1.25 m high with a square bottom with a side length of 0.4 m. The membranes inside would be in plates instead of tubes. The aimed membrane surface area to volume ratio would be 40 or 60, depending on the price and practicalities with membrane plate dimensions. The number of plates needed would be between 15 and 23. While sparing 5 cm spare space between the walls of the reactor and the membrane plates, the dimensions of a single sheet would be 0.9 m x 0.3 m. The mixing system would be a hyperbolic mixer at the bottom of the reactor. Figure 25 illustrates the design concept of the reactor.

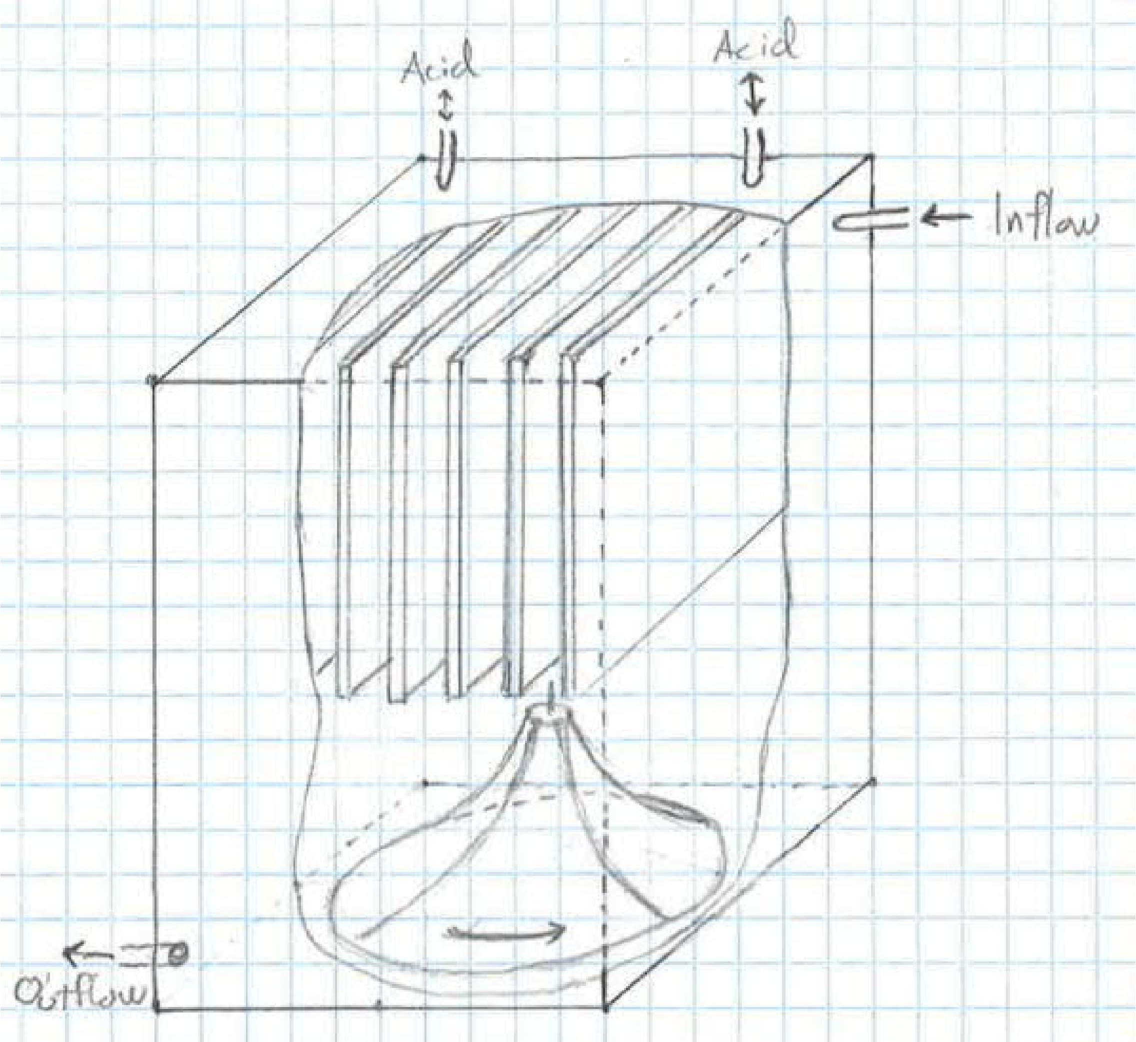

Figure 27. Conceptual design of the next phase's reactor.

5.4 Comparison with other recovery methods

Comparing biological methods with NPHarvest technology is unfair due to the early stages of research for algae and bioelectrochemical systems. Therefore, comparing the potential of the technologies is more appropriate approach. While some algae species are able to reach 70 % and above total nitrogen harvesting efficiencies, the removal time used in the tests has been several days or up to weeks (Cai, Park and Li, 2013). This would not be suitable for the applications NPHarvest is intended for as the shorter the removal time or hydraulic retention time is, the more economically viable the process is. Furthermore, in the Nordic environment, the use of biological methods provides an additional challenge: light is a limited resource during the winter time. Therefore, the process would require artificial lighting and the fluctuation of outside temperature could hinder the process or at least increase the heating costs. The long retention time would also mean that the process would have to be heated to maintain the optimal 35 °C temperature. Thus, a biological process would most likely not be suitable for Nordic environment. Although, microalgae technology has an advantage to offset this: the production of materials for biofuel industry. However, due to the research being in so early stage, it is difficult to assess and compare the economic potential for it. Furthermore, there are still challenges in extracting the biofuel and drying the biomass. Bioelectrochemical systems have the similar problems: although, the process produces electricity, the current ammonia harvesting efficiency from urine is around only 30 % (Rodríguez Arredondo et al., 2015). This could prove useful as a method for producing energy in some applications while having an extra harvesting system alongside it, but as a pure harvesting method the efficiency is too low. In addition, the electrodes are subject to biofouling which is a problem. If the efficiency improves in the future, the process becomes more viable for reject water because there is no light requirement and the retention times are short. For wastewaters, in general, the Nordic environment could prove to be too challenging due to temperature variation.

Another method still in its early phase research is the use of zeolite and ion exchange for ammonia recovery. The idea is interesting and seems promising: ammonium removal of approximately 70 % was reached within 2 hours in batch tests conducted with zeolite. However, removal efficiency was subjective to concentration of total solids in the wastewater. Noticeable decrease in removal efficiency in the tests of Taddeo et al. (2017) seemed to happen when TSS concentration was above approximately 5 g/l. For the reject water, this would not be a problem because the TSS concentration is usually below 3 g/l. Zeolite would also work as a supplementary material to common fertilizers, so it would have the same functionality as the ammonium sulphate NPHarvest process produces. (Taddeo, Prajapati and Lepistö, 2017) The challenges of this technology are related to the possible regeneration of the zeolite: it is difficult to know what is the nitrogen concentration from the regeneration process or if it is possible to utilize it. In case the zeolite would be used as fertilizer as such, the sheer amount of it would be great.

Assuming 2500 m^3/d reject water flow, 1000 mg/l NH_4^+ concentration and 70 % recovery efficiency, the daily need for zeolite would be over 200 tons (estimation based on the results of Taddeo, Prajapati and Lepistö (2017)). Further research will show if this technology can be applied on a continuous flow and its potential efficiency.

Other recovery methods are at more advanced stage. The conventional method for recovering ammonia is stripping with air and then scrubbing with an acid. This method has been implemented for a longer time and is an efficient way to recover ammonia: recovery efficiency can be as high as 85 to 90 % (Jiang et al., 2014, Boehler et al., 2014). However, it is more complex and energy consuming process than NPHarvest, hence the reason for developing membrane technology. Boehler et al. (2014) estimated that their system of CO_2-stripping + NH_3-stripping + NH_3-scrubbing consumes 9.7 kWh/kg-$N_{harvested}$ for plant operation and chemicals. Assuming electricity cost of 0.11 €/kWh, the cost for their stripping process is 1.1 €/kg-$N_{harvested}$. Compared to the costs for NPHarvest, except energy consumption costs, this is on the same level as the acid cost used in the economic analysis: the acid would cost 0.94 €/kg-$N_{harvested}$ (Rothrock, 2013) in an optimal situation. The NPHarvest technology would be less energy intensive because the effective stripping method is passive transportation over the membrane and it does not require energy input, unlike stripping by aerated air. They also tested membrane technology but did not compare the energy consumption. However, the recovery efficiency was approximately as high as with conventional scrubbing. Energy consumption was not measured for the tests concluded for this thesis, and thus comparing accurate energy consumption values is not possible.

Struvite is possibly the most significant competitor for membrane technology as a new and energy efficient method for nitrogen recovery. The recovery efficiency is high if the process conditions are optimized: removal efficiency of approximately 90 % can be reached within 15 minutes to an hour (Darwish et al., 2015). While this is on the same levels as membrane contactors are able to achieve, the time required to reach these removal/harvesting efficiencies is much shorter in comparison. However, the struvite precipitation process is not cheaper by default: the most important process parameter is Mg:N:P ratio and this has to be maintained by adding chemicals. It is a pre-requisite that the phosphorus is in soluble form. Furthermore, NPHarvest process utilizes lime as pH control chemical and Ca^{2+}-ions supress MAP formation. Current research is focused on finding cheaper chemicals (Darwish et al., 2015). The technology is in use for many full-scale plants which use biological phosphorus removal with waste streams rich with both nitrogen and phosphorous. As such, it is not be suitable for the WWTP where the source material used in this experiment originates. However, if the process can become economically more viable, struvite is suitable for agriculture as a slow releasing fertilizer as such (Darwish et al., 2015, Di Iaconi et al., 2010, El Diwani et al., 2007).

There are few other research teams conducting tests with membrane contactors. Both Boehler et al. (2014) and Amaral et al. (2016) reached approximately 90 % removal efficiency within five hours. This is much higher efficiency compared to tests conducted for this thesis. However, both used extensive pre-treatment to remove solids from the influent to prevent fouling of the membranes. With Boehler et al. (2014) process, the pressure was much higher than NPHarvest and this increases the risk of fouling. They also used three contactor units in series, totalling membrane surface area to 120 m^2. According to the product catalogue of the reactor manufacturer (Liqui-Cel) the volume for a membrane unit is 75 litres at its maximum. Thus, the surface area to volume ration is approximately over 500 m^2/m^3. This is much higher than the pilot used in this experiment (14.6 m^2/m^3). Thus, it is questionable if the process is economically viable: it is strongly dependent on the market value of ammonium sulphate. Approach of NPHarvest is different, aiming for reduction of treatment costs for current treatment processes while recovering nitrogen to be used as a raw material, for instance, for fertilizers. Yet, the results of other teams prove that by optimizing our process further, it is possible to increase the effectiveness. However, the objective for the next phase is to do so without using extensive pre-treatments or increase in pressure. Table 8 summarises the comparison for recovery methods.

Table 8. Comparative summary for the recovery methods.

Method	Pros	Cons
Algae	• Useful by-product: biofuel	• Long retention time • Not suitable for Nordic
BES	• Electricity production • Short HRT	• Low harvesting efficiency
Zeolite	• Short HRT	• Requires a great volume of material • Unknown quality of nitrogen from regeneration
Conventional stripping	• Known and functions well	• Energy intensive
Struvite	• Short HRT	• Difficult and/or expensive process to maintain • Requires high concentration of both N and P
Membrane contactors	• In theory an energy efficient solution	• Requires pre-treatment • Easy to implement on existing technology for benefit

6 Conclusions

The aim of the experiment was to design, build and optimize a continuously functioning lab scale reactor which separates nitrogen as ammonia from liquid waste flow using hydrophobic gas permeable membrane. After being separated by the membrane, ammonia was captured by an acid. The system was designed to withstand relatively high concentration of suspended solids to avoid excessive pre-treatment to reduce the process cost, chemical consumption and energy usage.

The reactor was optimized for ammonia transfer efficiency by controlling hydraulic retention time, acid flow rate and pH. Also, acid type, membrane thickness and membrane surface area were tested. Furthermore, an economic estimation was calculated based on the results. The experiment shows that harvesting nitrogen works with this kind of reactor setup and it is easy to reach harvesting efficiency of 60 % with 8-hour hydraulic retention time with pH over 12. Increasing HRT increases the yield but it does not affect the ammonia transfer rate over the membrane. It is affected by the acid flow rate and mixing efficiency. Increasing membrane surface area in a fixed volume increases the yield. However, membrane thickness or acid type did not affect the harvesting efficiency or the ammonia transfer rate.

The reactor affects only the nitrogen in the reject water flow but the pre-treatment affects other parameters of the reject water. Increasing pH with calcium hydroxide flocs solids and subjects them to precipitation. During this process, some of the phosphorous is removed from the water. COD also decreases while ammonia escapes to the atmosphere. The economic estimation showed that in comparison with an average conventional nitrogen removal cost, the process would be economically viable when the harvesting efficiency is between 60 and 80 % for a treatment plant that produces around 2500 m^3/d reject water.

Thus, it may be concluded that this experiment achieved its purpose and proved that this technology works and is economically viable at least in certain cases. Further research is needed to show if it is viable to scale up the process and how modifiable it is for different liquid waste streams.

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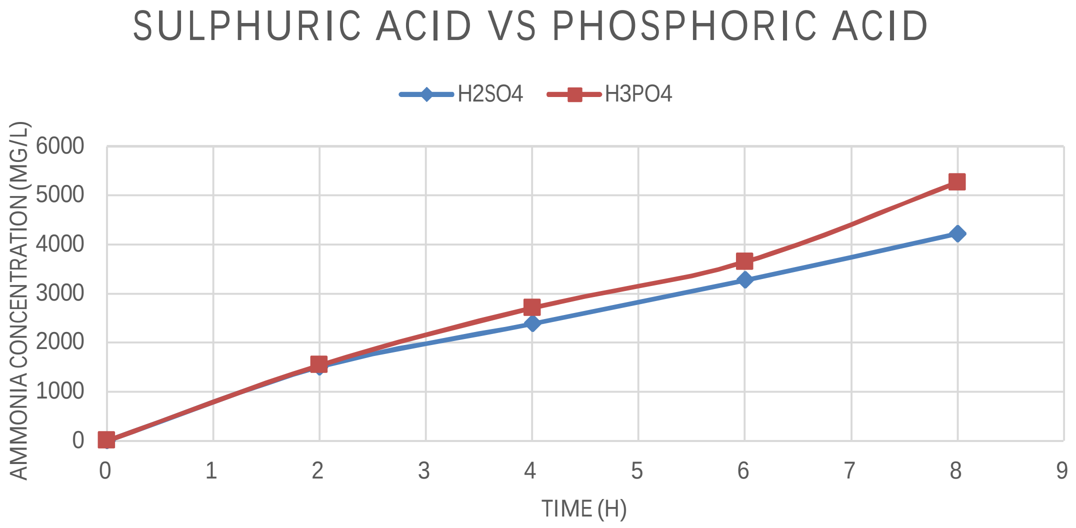
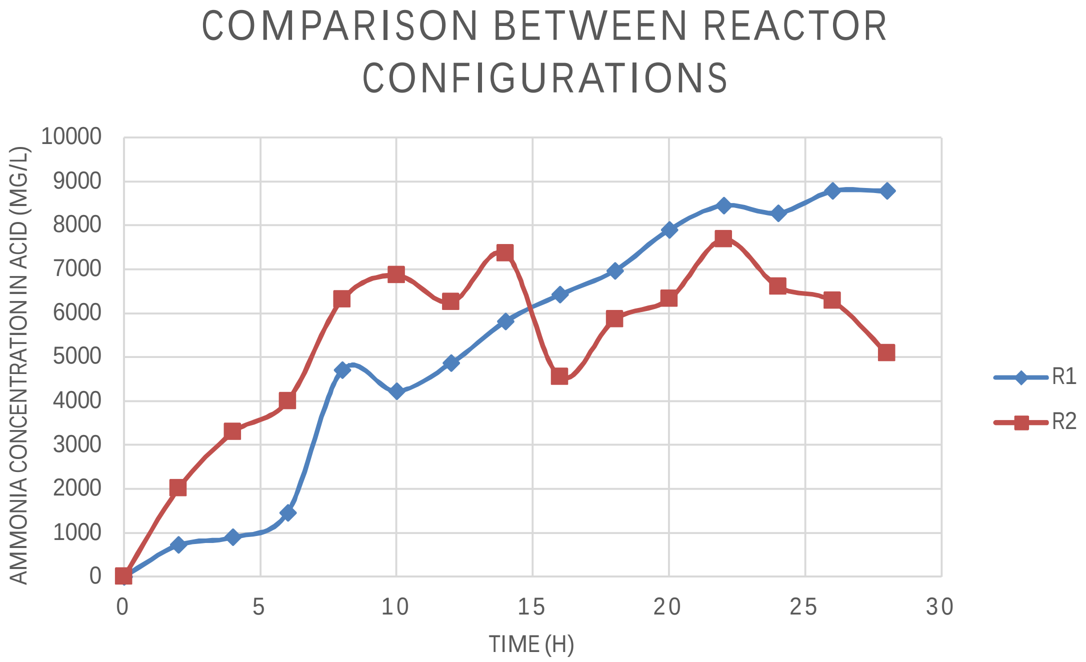
Appendix

Appendix 1. Figures for different acid and membrane thickness tests.



Comparison between different acids.



Comparison between two different membrane thicknesses. R1 is the thicker membrane and R2 is a thinner membrane.