Integrated Master in Bioengineering
Specialization in Biological Engineering

Optimization of a current driven system for Ammonia Recovery

Dissertation by Mariana Rodrigues

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WETSUS / Faculdade de Engenharia da Universidade do Porto

Supervisor WETSUS: **Dr. Philipp Kuntke**
Supervisor FEUP: **Professor Alexandra Pinto**

Department of Chemical Engineering

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Resumo

O rápido aumento da população mundial nas últimas décadas e consequentemente da demanda de nutrientes, causou um uso extremo de fertilizantes ricos em fósforo e amónia. O azoto extra, fixado pelo processo Haber-Bosch, requer uma quantidade significativa de energia durante a sua produção. Após o consumo de alimentos, este termina em cursos de água causando problemas como a eutrofização. Desta forma foram desenvolvidos processos para remover as formas reativas de azoto, mas até ao momento, as alternativas só o convertem para a sua forma gasosa, que é libertada para a atmosfera. Idealmente, para reduzir o custo e o consumo de energia associados à produção e remoção de amónia, é necessário um processo capaz de recuperar o mesmo. Assim, o objetivo deste trabalho foi dimensionar a maior escala e otimizar um sistema eletroquímico para remoção e recuperação de amónia a partir de urina sintética. Foram operados dois sistemas diferentes. Um *scale-up* de uma célula, com seis compartimentos, usando como elétrodos membranas bipolares e outro sistema para explorar o princípio da diálise de Donnan. Ambos os sistemas foram combinados com uma unidade TMCS (*transmembrane chemisorption - ammonia stripping*). Foi demonstrado que é possível melhorar a recuperação de amónia num sistema eletroquímico usando uma célula de diálise de Donnan. No entanto, nas condições de operação estudadas, a influência desta não foi significativa. O sistema obteve uma remoção máxima de 88% para uma entrada de energia de 14,2 kJ / gN. Também foi demonstrado que é possível usar membranas bipolares como elétrodos, para recuperar amónia. No entanto, para alcançar uma remoção de 80%, foi necessário melhorar o *design* da célula (espaçamento do campo de fluxo) e operar a célula com um maior Load Ratio (razão entre a corrente e concentração de amónia fornecida), o que se traduz num maior consumo de energia. O pH foi um fator determinante para a eficiência da recuperação de amónia em ambos os sistemas, pois apenas azoto gasoso (volátil) passa através da membrana permeável ao gás.

Abstract

The fast increase of the world population in the past decades and consequently of the nutrient demand, cause an extreme use of fertilizers rich in phosphorus and nitrogen. The extra nitrogen, fixed by the Haber-Bosch process, requires a significant amount of energy for its production. And after food consumption, it ends in water streams causing problems such as eutrophication. This way it was developed processes to remove the reactive nitrogen, but so far, the alternatives only convert it into nitrogen gas, that is released to the atmosphere. Ideally, to reduce the cost and energy consumption for nitrogen production and removal, it is necessary a process capable of not only remove but also recover. Thus, the aim of this work was to upscale and optimize an electrochemical system to remove and recover nitrogen from synthetic urine. It was operated two different systems. A stacked scale-up cell, with six compartments, using as electrodes bipolar membranes and other system to explore the Donnan dialysis principle. Both systems were combined with a TMCS unit, transmembrane chemisorption (transmembrane chemisorption - ammonia stripping). It was showed that is possible to enhance the recovery of ammonium in an electrochemical system using a Donnan dialysis cell. However, for these operation conditions the influence of the Donnan dialysis was not significant. The system obtained a maximum removal of 88% at an energy input of 14.2 kJ/g_N. It was also demonstrated that it is possible to use bipolar membranes as electrodes in a stacked system, to recover ammonium. However, to achieve a removal of 80% it was necessary to improve the design (spacing of the flowing field) and operate the cell at higher Load Ratio, which represents an increase of the energy input. The pH was a determinant factor for the efficiency of ammonia recovery in both systems, as only volatile ammonia passes through the gas permeable membrane.

Declaração

Declara, sob compromisso de honra, que este trabalho é original e que todas as contribuições não originais foram devidamente referenciadas com identificação da fonte.

I declare on my honour that this work is original and that all non-original contributions have been duly referenced with source identification.

Assinar e datar

Contents

Nomenclature

AEM – Anion exchange membrane

ANAMMOX– Anaerobic ammonium oxidation

BES – Bioelectrochemical system

BPM – Bipolar membrane

CANON – Completely autotrophic nitrogen removal over nitrite

CEM – Cation exchange membrane

ES – Electrochemical system

HRES – Hydrogen recycling system

LN – Load Ratio

MEA – Membrane electrode assembly

N_2 – Nitrogen gas

NH_3 – Ammonia

NH_4^+ – Ammonium

NO_2^- – Nitrite

NO_3^- – Nitrate

PP – Polypropylene

PMMA – Poly (methyl methacrylate)

PTFE – Polytetrafluoroethylene

SHARON – Single reactor system for high-rate ammonium removal over Nitrite

TAN – Total ammonia nitrogen

TMCS – Transmembrane chemisorption

WWTP – Wastewater treatment plant

j (A m^{-2}) – Current density

A (m^2) – Effective membrane area

$[NH_4^+]$ (g m^{-3}) – Concentration of ammonium

M (g mol^{-1}) – Molar mass

Q (m s^{-1}) – Feeding rate

F (C mol^{-1}) – Faraday constant

C_i (g L^{-1}) – Influent concentration

C_e (g L^{-1}) – Effluent concentration

E_{input} (kJ/ g_N) – Energy input

t_i (g m^{-2} day^{-1}) – TAN removal rate

V (V) – Voltage of the cell

t (s) – Time

t_{cation} (C day^{-1}) – Ion transport number

ΔC_{cation} (g L^{-1}) – Difference between the cation concentration of the influent and effluent

List of Figures

List of Tables

Background and Presentation of the Project

A recent report of the United Nations predicts an increase of the world population to more than 8 billion people by the year 2020, causing a subsequently growth of the nutrient and energy consumption. [1] For the same year, a Food and Agriculture Organization's report predicts a demand of about 120 million thousand tonnes of nitrogen to be use only as a fertilizer, representing approximately 75% of the consumption of this resource. [2,3]

Every day, more and more fertilizers are applied to ensure a higher crop production, compensating for the lack of nutrients in the soil due to agriculture intensification and climate changes. Nitrogen and phosphorus, being the main components of fertilizers, end up in the environment, by direct application on soil or after food consumption, causing the intensification of negative phenomena like eutrophication [4,5].

The abundance of nitrogen as an inert gas (N_2) in the atmosphere, unlike for example phosphorus, have postponed the development of energy efficient technologies capable of removing and simultaneously recovering ammonia. [6]

The N_2 gas conversion into a useful form of ammonia (NH_3), by the Haber-Bosch process, requires a considerable amount of energy. [5,7]. Moreover, it is estimated that the removal of the excess of nitrogen in water streams costs between 70 billion to 320 billion euros, just in Europe [8]. Therefore, it has become crucial to develop innovative technologies, more efficient and sustainable, capable of "reutilize" the reactive nitrogen present in the environment at a low energy consumption.

The nitrogen removal in wastewater treatment plants (WWTPs) is assured by the nitrification/denitrification process or ANAMMOX (anaerobic ammonium oxidation). [5,9] However, both share the disadvantage of converting into its inert gas form (N_2), releasing it to the atmosphere at the end of the process. These processes are also energy intensive and increase the emission of NO_2^- to the atmosphere. Therefore, different studies have explored electrochemical and bioelectrochemical systems as viable solutions to remove and recover nitrogen in wastewater treatment plants. [9,10]

Also, most of the conventional treatment plants are incapable of fulfil the new guidelines for total-nitrogen removal. [11,12] Therefore, upgrades of the conventional wastewater treatment plant become necessary, which include additional aeration tanks resulting in large investments. The installation of complementary techniques such as an electrochemical system might decrease the necessary capital investment and increase the removal capacity of the treatment plants.

Thus, the aim of this work is to develop and optimize an electrochemical system to remove and recover nitrogen from different wastewater streams.

Introduction

Nitrogen, as an inert gas (N_2), constitutes about 78% of Earth's atmosphere. It can be used by organisms in its reactive forms, nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and ammonia (NH_3). Nitrogen is a crucial element for the existence of life and diversity. [9,13]

The conversion between the multiple different chemical forms present in the ecosystems, is known as the nitrogen cycle. A biogeochemical cycle that includes nitrogen fixation, assimilation, ammonification, nitrification, and denitrification. [13,14]

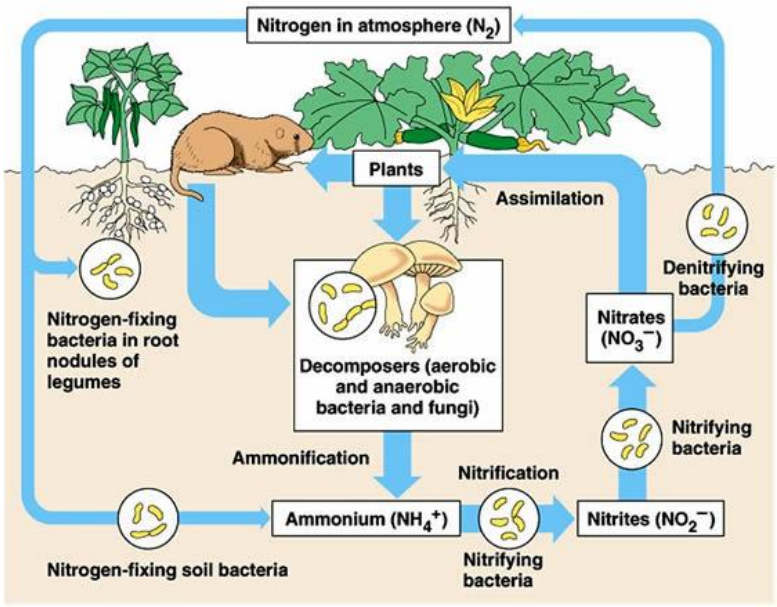


FIGURE 1. NITROGEN CYCLE [15]

Biologically, the fixation occurs due to nitrogen-fixing microorganisms, such as *Azotobacter* or *Clostridium*, from archaea and bacteria. [9,16] The enzyme nitrogenase present in these organisms, allows the conversion of atmospheric N_2 that can be later used by plants (symbiose) and consequently other levels of the food chain.

The inorganic forms of nitrate and ammonium (NH_4^+) are absorbed by plants, to be assimilated into amino acids, nucleic acids, etc. [14,17] The resulting organic nitrogen, present in remains or animal expelled waste, can be converted by bacteria or fungi, into inorganic ammonium. [16] In a primary stage of nitrification, *Nitrosomonas* species, oxidize ammonium to nitrites (NO_2^-) and consequently,

Nitrobacter oxidize nitrites into nitrates (NO_3^-). Denitrification completes the cycle. It is performed by anaerobic species such as *Pseudomonas*, that reduce nitrates back into N_2.

Industrially, nitrogen fixation is possible due to the Haber-Bosch process, where N_2 reacts with hydrogen gas, at elevated temperatures and pressure, resulting in ammonia. [17,18] This process consumes 37 kJ/g_N, representing about 2% of the worldwide energy consumption. [5,19]

Currently, just to satisfy the food production, humanity is using about 120 million tons of nitrogen in fertilizers, interfering severely with the nitrogen cycle. [2,9] The amount of NH_3 produced via the Haber–Bosch process, represents an excess of reactive nitrogen, considering the total amount fixed annually via natural processes. By direct application in agriculture or after food consumption (present in human urine or animal manure), this surplus ends up in waterways, soils and atmosphere. [9,20] The excess application of this compound contributes to the loss of nutrients such as calcium and potassium decreasing the soil fertility and can cause direct injury in plants, that require low concentrations for their normal metabolism. [7,13,20]

To avoid the waterbodies pollution and ensure the population safety, the European union has created directives to control the application of nitrogen and consequently the treatment of polluted streams. [12,21] The European legislation assures a 75% reduction of nitrogen, before releasing the streams into sensible water courses. [11]

The energy required to the elimination of this compound allied with the negative environmental consequences represent an economic extra on top of the production itself. To create a more sustainable use of nitrogen, it is necessary to develop a more efficient and environmentally friendly solution. Being capable of generate a product with low energy consumption, decreasing the need of the Haber-Bosh. Hence representing a decrease of energetic and economic costs, plus the decrease of its effects in the ecosystems. [8,13,22]

1.1. Wastewater treatment and ammonia removal

Nowadays, nitrification/denitrification and ANAMMOX process are well integrated in WWTPs. These systems convert the ammonium present in the domestic wastewater into nitrogen gas, as shown in Figure 2, mitigating its effect in the natural water courses. [9,22]

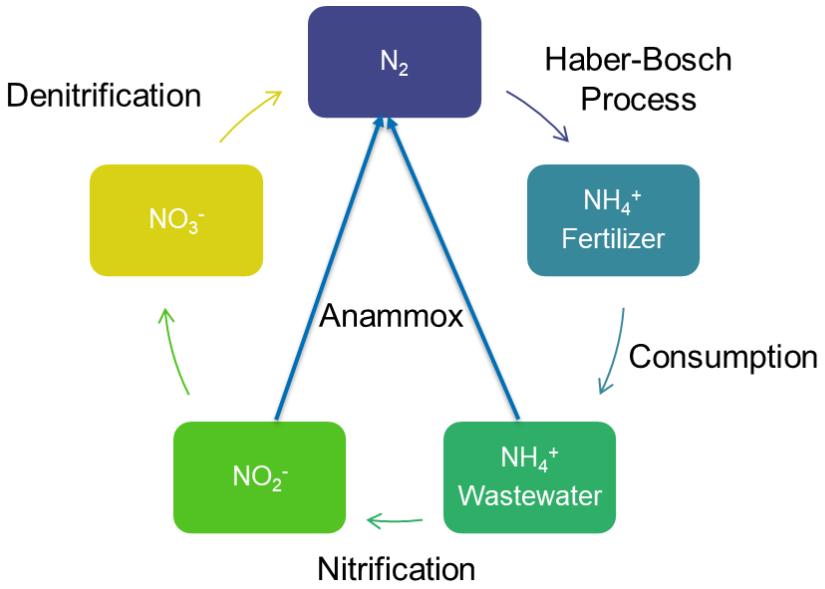


Figure 2. Anthropogenic Conversion of Nitrogen

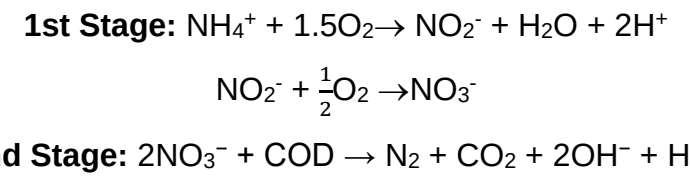
Besides the conventional processes, other alternatives have been studied for nitrogen recovery, including NH_3-stripping, struvite precipitation or use of zeolites. However, as independent processes they have not been tested beyond the lab/pilot scale and do not represent viable options due to the high energy consumption and/or high demand of chemicals during the treatment. [23]

To select the most suitable process, for nitrogen removal, it is necessary to consider different aspects including the concentration of nitrogen compounds in the influent, the required effluent quality, the possible combination with other treatment processes, the cost, reliability and flexibility.

Electrochemical systems and bioelectrochemical systems are being target of different researches due to their capacity to remove/recover compounds of different streams at a low energy input. But also, these systems can be combined with the existent processes.

1.1.2. Nitrification/Denitrification

The simultaneous process of nitrification/denitrification consists in the conversion of organic ammonium to nitrogen gas in a two steps process, according to the following equations. [24,25]



First, under aerobic conditions, autotrophic organisms such as *Nitrosomas* oxidized ammonium to NO_2^-. The *Nitrobacter* oxidize nitrite to NO_3^-. [9,19] Afterwards, in the denitrification step, with the help of an electric donor, the nitrate is reduced to inert gas, under anaerobic conditions. [26]

During this process, the ratio of nitrification time to denitrification can be adjusted according to the wastewater composition and volume. Therefore, it removes efficiently even for streams with low concentrations. [9,24]

However, the nitrification stage is highly affected by temperature, pH, the concentration of dissolved oxygen, chemical inhibitors, and slow growth of the nitrifiers species. [25] Plus, the need of aeration implies a high consume of energy in this phase. Consuming 45 MJ/kg_N for the all process. [25,27] Also, the requirement of an electric donor, in the second stage, adds other disadvantage for this process. [9]

1.1.3. ANAMMOX/SHARON

Anammox (anaerobic ammonium oxidation) may replace the conventional nitrification and denitrification process, due to the lower energy requirement compared with the conventional. During this process, half of the ammonium is oxidized to nitrite. Meanwhile, the other half of ammonium and the resulting nitrite, are directly converted to nitrogen, under anoxic conditions according to the next reactions. [9]

Aerobic stage: $NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+$

Anaerobic stage: $NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$

The first stage of this process can be operated in a SHARON (Single reactor system for High-rate Ammonium Removal Over Nitrite). The short residence time and elevated temperature in this reactor prevent the growth of NO_2^- oxidizing bacteria. [28]

Once this process does not require aeration, the energy input is only 16 MJ/kg_N. [9,27] Also, the biomass yield of anammox is very low, what means an inferior cost of the resulting sludge treatment. [28] Furthermore, the ANAMMOX reactions occur naturally in different ecosystems by autotrophic bacteria not requiring for any organic carbon sources. [9,28] This means a lower dosage of chemicals compared to the nitrification/denitrification process.

Nevertheless, this treatment requires a long start-up time of operation and it is limited to the high sensitivity of the bacteria to oxygen concentration and nitrite accumulation. [28] For high concentrations of nitrite the microorganisms are inhibited, but also for very low concentrations the growth does not occur. This way, ANAMMOX is strongly influenced by the concentrations of the influent stream. Hence, the main challenges consist in to overcome the defective growth of ANAMMOX bacteria, as well its competition with nitrite-oxidizing bacteria. [29,30]

1.1.4. CANON

To overcome the need of a ratio of 1:1 mixture of NH_4^+ and NO_2^-, for the ANAMMOX process, some studies presented the CANON reactor (Completely Autotrophic Nitrogen Removal Over Nitrite). [9,28]

The CANON can perform simultaneously aerobic ammonia oxidation and ANAMMOX, due to the operation at oxygen-limited conditions. The coexistence of aerobic and anaerobic conditions is guarantee by the formation of granular sludge. In the exterior grow the aerobic ammonium oxidizer, due to the interface in contact with oxygen. In the centre, there is the formation of an anaerobic

environment, suited for anammox bacteria activity. [28] Due to a low level of oxygen and at a high concentration of NH_4^+, the oxidation of NO_2^- to NO_3^- does not occurs. Compared with traditional nitrification/denitrification and SHARON/ANAMMOX process, CANON needs only one reactor, meaning less costs, and it is not dependent of the carbon source present in wastewater. However, this process is sensitive to the operation conditions such as oxygen concentrations and the distribution of the granular aggregates. [31] Additionally, it only converts the ammonium into volatile nitrogen like the previously techniques.

1.2. Ammonia recovery by stripping

The next two processes present less viable options when operated as single techniques to recover ammonia, due to chemical and energy requirements. However, they have been successful demonstrated at larger scale to remove and recover ammonia.

The solution pH is crucial parameter for ammonia recovery by stripping and TMCS (transmembrane chemisorption). The presence of unprotonated ammonia in the solution differs depending on the pH of the solution, as presented in Figure 3. [15]

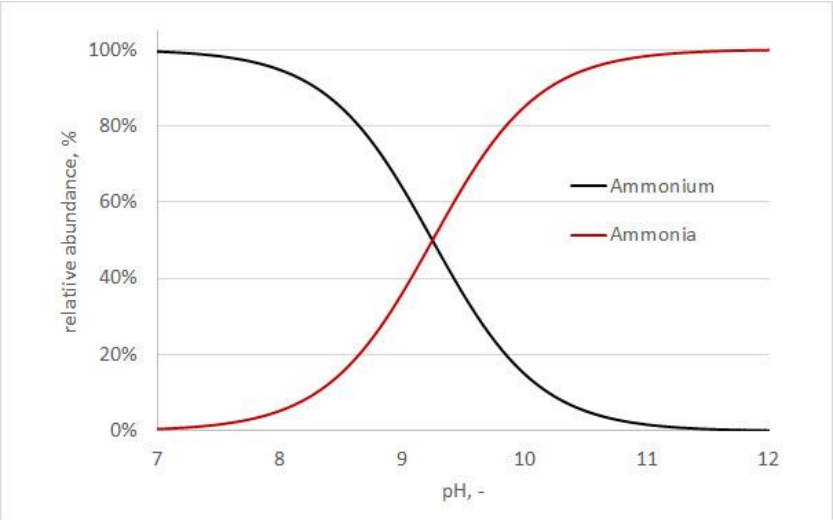


Figure 3. Ammonium concentration at different pH

As illustrated, at a pH 7 only ammonium ions are in the solution. At a pH 12, all ammonia is dissolved as a gas and it can be released from wastewater under proper conditions.

1.2.1. Conventional Stripping

Stripping consists in the dispersion of a gas through a highly concentrated solution to recover compounds, such as ammonia.

Ammonia can be found dissolved in water under a certain partial pressure. The reduction of the pressure decreases the solubility of ammonia in water, passing to the air phase. Ammonia can be removed from wastewater, by bubbling a large amount of air free of ammonia, called termed desorption. This process is also commonly known as ammonia stripping. The quantity removed is dependent of the concentration of unprotonated ammonia in the solution, gas-liquid surface area, mass transfer coefficient, and the partial pressure of the gas phase. For ideal ammonia stripping performance, it is necessary to increase the pH of the water to values in the range of 10.8-11.5, allowing the formation and reformation of water droplets in the stripping unit, and provide the circulation of large quantities of air to increase the air-water contact. Also the temperature is an important factor, a decrease of temperature decreases the volatility of ammonia. [32]

So, to achieve a high removal of ammonia, it is necessary to supply high gas flowrates and guarantee an elevated temperature and pH. This represents a high energy demand, 90 MJ/kgN, for the conventional stripping process. [19,27]

1.2.2. TMCS

Another studied method for ammonia stripping is transmembrane chemisorption (TMCS). The ammonia passing the gas permeable membrane can be absorb into an acid, such as phosphoric or sulfuric acid. [32]

Ammonia gas can be recovered from solution through microporous gas permeable hydrophobic membranes, like PTFE or PP based membranes. At a high pH, the concentration gradient between the concentrated solution formed at the ES and the acid, drives the passage of ammonia towards the acid. [33,34]

Bioelectrochemical and electrochemical systems can be used to concentrate ammonia, but to recover ammonia they need to be coupled to either TMCS or ammonia stripping units.

1.3. Bioelectrochemical systems for Ammonia Recovery

Other alternative that has been explored for ammonia recovery is Bioelectrochemical systems (BES). In a BES, either the oxidation or reduction it is carry out by microorganisms. The anode electrode is externally connected to the cathode where the reduction reaction occurs. [9,22] These compartments might be separated by an ion exchange membrane, which allow for anions and/or cations to be transported to maintain electron neutrality. The electron transport through the external circuit, forces the movement of ions across this membrane. BES can be distinguished into Microbial Fuel Cells or Microbial electrolysis cells, depending on the cathode reaction. [35] Microbial Fuel Cells reduce oxygen or other oxidant at the cathode, while electric current is harvested. [36] Microbial electrolysis cells produce hydrogen gas at the cathode, while this requires some energy input. [37,38]

These systems present some advantages compared to the previous techniques, due to their capacity of remove undesirable compounds from different streams, do not require chemical dosage and might produce energy. More specifically, BES allow for nitrogen recovery, creating a shortcut in the nitrogen cycle, as shown in Figure 4. The ammonium present in wastewater stream, can be directly recovered and concentrated to enable its re-use. [9]

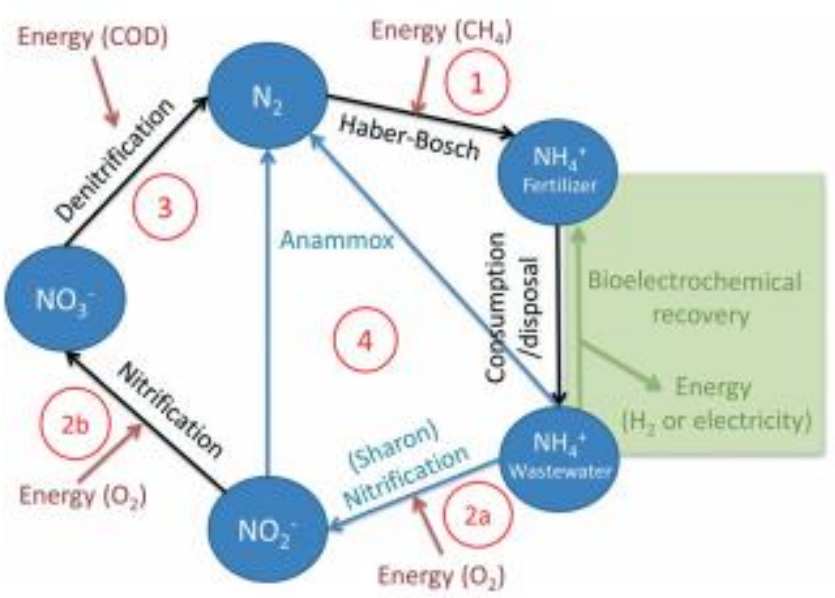


FIGURE 4.The nitrogen cycle in fertilizer production and wastewater treatment processes [39]

However, some issues remain open such as limited current generation, possible ammonia toxicity, substrate availability leading to limiting up scaling of the technology. [9,27,40] Likewise, the influence of other cations such as Na+ in the $NH4^+$ diffusion across the membrane might reduce the efficiency of these systems.

In order to ensure the proper functioning of a BES system, it is necessary to regulate the pH of both compartments. First, the conditions at the anode should allow the survival of the biomass (pH range from 6 - 8). Further, at the cathode, it is necessary to guarantee a basic environment (pH >9). This condition allows the conversion of NH_4^+ ions into gaseous NH_3, enabling its recovery.

Finally, the recovery of ammonia can be limited by the possibility of competition among different bacteria for the substrate, meaning less current available to ions transportation. [5,9]

1.4. Electrochemical systems

In the last years, Electrochemical Systems (ES) have been explored as an option to concentrate and/or dilute different solutions, utilizing ion exchange membranes to create physically separate compartments between the two electrodes. In an ES, all the reactions are uniquely electro-chemical. The formation of an electrical potential between the electrodes, due to the supply of current, causes the migration of cations towards the cathode. Depending on the presence of a cation-exchange (CEM) or anion-exchange (AEM) membrane, the cations pass through the membrane or are retained. In the same way, the anions migrate towards the anode, resulting in solutions depleted or concentrated in ionic species. [41] When comparing ES with BES, electrochemical systems present the advantage of not being influence by the presence of biomass, meaning an easily operation of the system. However, this also results in a higher energy input for ES than BES. Additionally, ESs can support higher current densities and work with streams at an extreme pH. [5,27]

The possibility of ion separation makes an ES a viable option for ammonia recovery. The supply of current to an ES drives ammonium and other positive ions through a cation exchange membrane towards the cathode, as presented in the Figure 5. The catholyte stream becomes concentrated in ammonium and other cations. At the same time, the pH of the catholyte increases due to the hydrogen evolution reaction ($2H_20 + 2e^- \rightarrow H_2 + 2OH^-$) and insufficient proton transport over the CEM. As a result, ammonium is deprotonated to ammonia ($NH_4^+ + OH^- \rightarrow NH_3$). The concentrated catholyte can be later pumped into a stripping unit, such as transmembrane chemisorption (TMCS) allowing the recovery of the ammonia. [27]

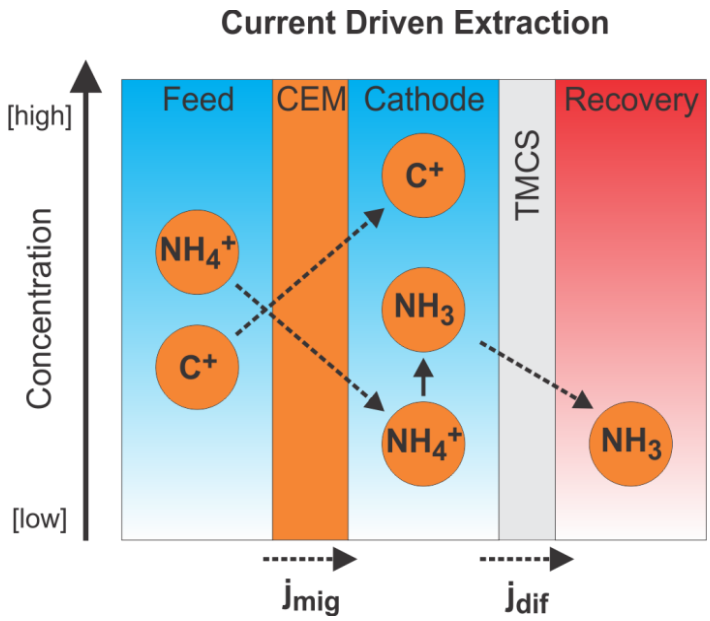


Figure 5. Current Driven Extraction of ammonia

1.5. Load Ratio

The concept of Load Ratio (L_N) was previously established as the ratio between the applied current density and the total ammonia nitrogen load (TAN, i.e., ammonium and ammonia). [27,39]

At a Load Ratio higher than one, more current is supplied than available TAN. Increasing the current considerably, only slightly increases the TAN removal after a certain Load Ratio. This occurs due to the presence of other cations (Na^+, K^+, etc.), in solution. With the increase of the supplied current these cations can be transported through the membrane, resulting in an increased energy demand for ammonia recovery. At a Load Ratio smaller than one, there is more TAN available than can be removed by the supplied current. In this case, the removal efficiency of the system is limited.

It was previously reported, experimentally and theoretically, that the Load Ratio should be approximately 1.3 for the system operate efficiently when it comes to removal and energy input, like present in Figure 6. [27,39]

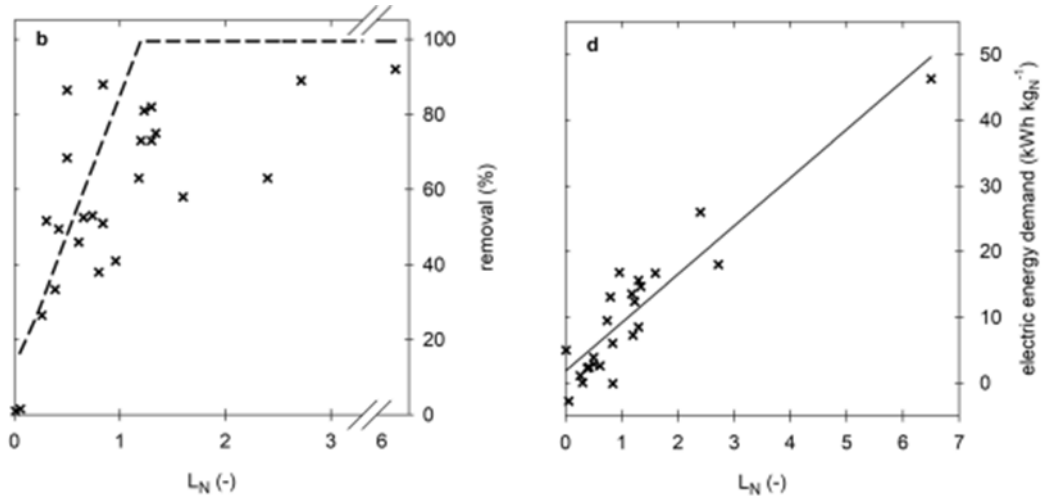


Figure 6. Relation between Load Ratio, TAN Removal and energy demand. Source: [27]

The performance of an HRES for TAN recovery can be define by different parameters including: removal efficiency, removal rate and necessary energy input. This way is possible to compare different systems, although it is necessary to take into consideration the final aim of the system. For example, if is required a high recovery, it is necessary a certain energy input. The combination of these factors allows to establish the necessary conditions for the system to perform at its best.

1.6. Hydrogen gas recycling electrochemical system

Kuntke and co-worker [5], developed an ESs including 3 compartments (anode, feed and concentrate) for ammonia recovery as shown in Figure 7. The hydrogen gas is oxidized at the anode. The electrons are moving from the anode through an external circuit towards the cathode, where the reduction of water occurs. The reduction reaction produces hydroxide ions and hydrogen. The hydroxide ions react with the ammonium ions, that migrate to the cathode resulting in water and NH_3. The formed NH_3 can be recovered using a gas permeable hydrophobic membrane.

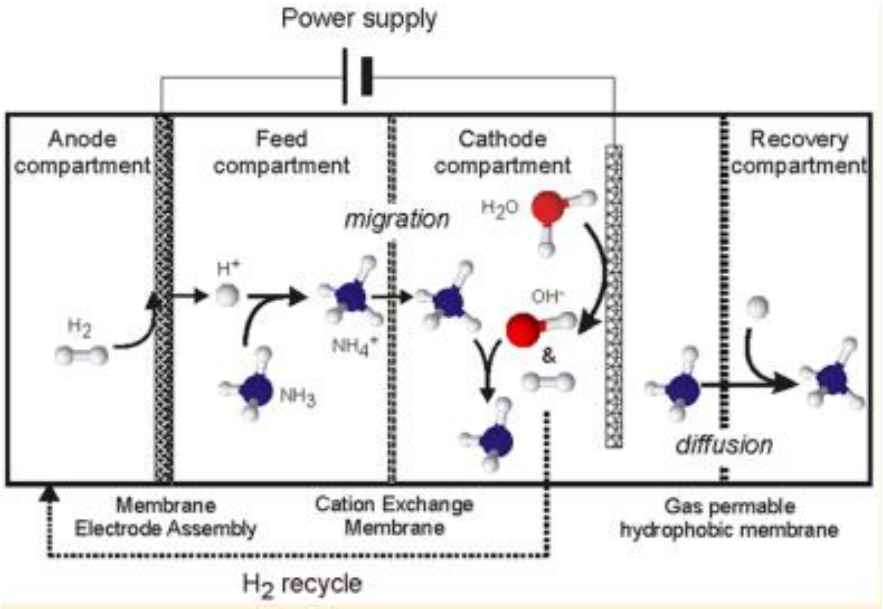


Figure 7. HRES for ammonia recovery [5]

This Hydrogen Recycling Electrochemical System (HRES) was suggested to overcome the formation of toxic products such as chlorine gas, chlorinated products and absorbable organic halides.

Also, with this new configuration, the hydrogen gas produced at the cathode, can be recycle back into the anode, decreasing the necessity of hydrogen gas supply. The direct supply of hydrogen to the anode, results in H_2 oxidation instead of water oxidation. The H_2 oxidation and water reduction occur at the same electrode potential, which lower the energy input of the ES compared with ES employing water splitting. [5]

ESs always require an energy input due to energy losses within the system. The necessary amount determines the success of the system and it is dependent on several factors, such as current density, ammonium loading rate (Load Ratio) and pH. [5,27].

In 2018, Kuntke and co-worker [42] presented a modified up-scaled system of the HRES shown in Figure 8.

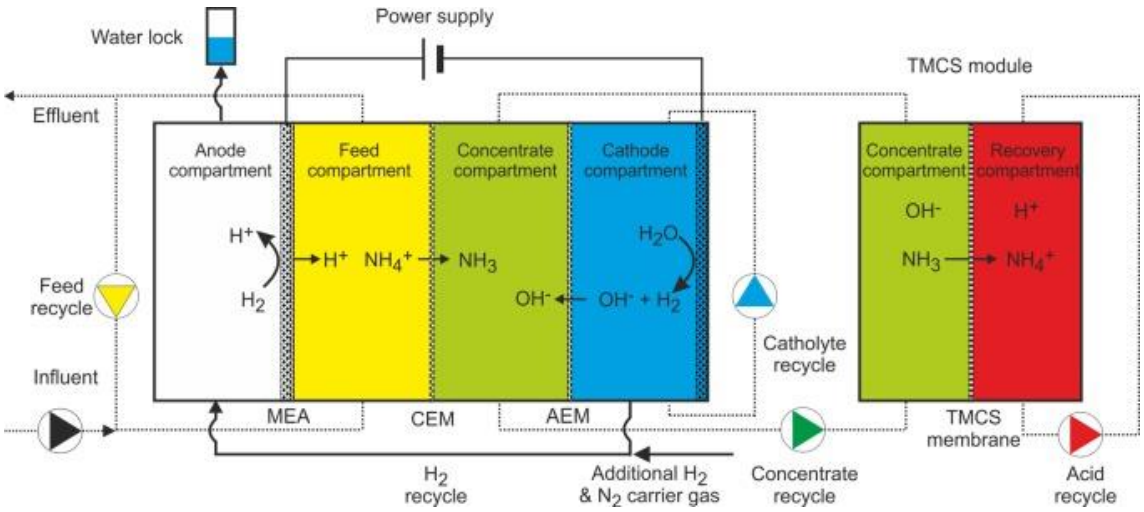


Figure 8. Modified HRES. [42]

The oxidation reaction occurring at the anode and the reduction at the cathode are the same as the previous system. However, this system includes one more compartment designated as the concentrate. This compartment is separated from the feed by a cation exchange membrane and from the cathode by an anion exchange membrane. The current supplied to the system drives the cations towards the cathode and the anionic species in the opposite direction. This way, the hydroxides formed at the cathode, cross the AEM to the concentrate. Likewise, the NH_4^+ oxidized at the feed, move through the CEM to the concentrate. The concentrate solution can then be pump into a TMCS unit similar to the previous system where the NH_3 is recovered.

With this extra compartment, it is possible to avoid the loss of the hydrogen gas through the TMCS unit. The hydrogen gas can be fed back to the anode, using N_2 as carrier gas, reducing the need of extra hydrogen and consequently decreasing the energy input.

1.6.1. Up-scaling by stacking

The treated volume capacity of an ES can be increase by using multiple cells or by stacking. This study evaluates the integration of a bipolar membrane into an HRES to allow stacking of multiple cell (membrane) pairs. Figure 9 presents the design of such a stacked system with 2 cell (membrane) pairs.

Bipolar membranes (BPM), have been developed in the last years among other ion exchange membranes to be integrated in different processes such as electrodialysis. A BPM integrates a cation exchange layer, an anion exchange layer and an interfacial layer. The interfacial layer is capable of generate protons and hydroxide ions from water molecules under direct current polarization. [43]

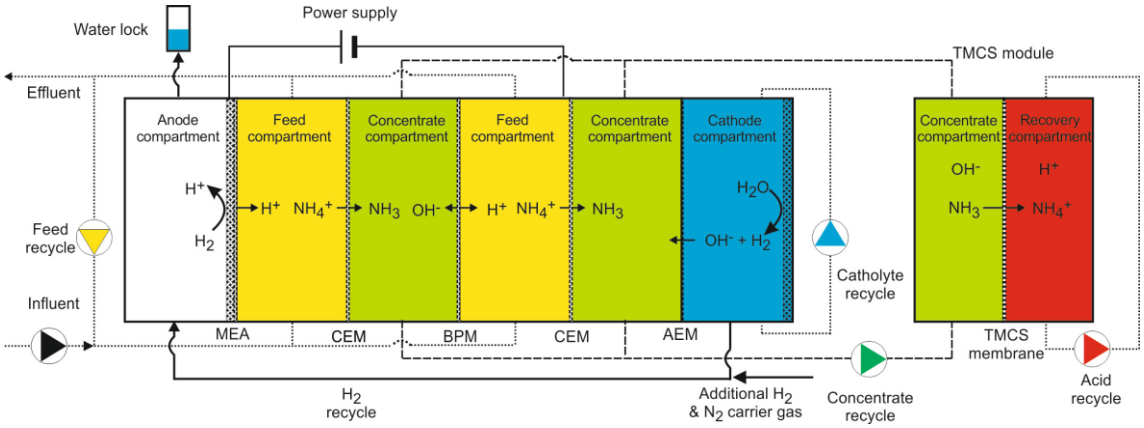


Figure 9. HRES with BPM

This configuration maintains the oxidation and reduction reactions happening at the electrodes. It also integrates the concentrate compartment for the possibility to reutilize the hydrogen gas at the anode. The cell includes two HRES units, divided by a BPM working as an electrode pair in between. On one hand, the anion side of the BPM allows the passage of the hydroxide formed in the middle layer to pass to the concentrate compartment. Here they react with the NH_4^+, like the previous system, forming NH_3. The NH_3 can be later recovered as previous explained. The cation side of the BPM supplies protons to the feed compartment. Like before, the protons result in the protonation of ammonia into ammonium, that can later cross over the CEM to the concentrate compartment.

The HRES with the BPM allows to treat a higher volume than the previous systems without increasing significantly the costs. Instead of multiple cells, it is possible to stack multiple units using BPM as electrodes.

1.7. Donnan Dialysis

The Donnan dialysis principle consists in the diffusion of ions through a membrane due to the formation of a concentration gradient. It can be used for ion separation, product recovery, synthesis of smart materials, and other innovative applications, being so far, the most popular application electrodialysis. [44,45]

The possibility of separate charged species (ions), makes the Donnan dialysis a potential technique to be combined with ES for ammonia recovery. In a current driven system for ammonia recovery, like previously showed, the supply of current forces the cations (Na^+, NH_4^+, K^+) to move from the feed into the cathode. Only ammonia is recovered from the catholyte. This way the cathode becomes concentrated in other co-ions (K^+ and Na^+). Due to the constant supply of current, the co-ions cannot return to the feed, building a concentration gradient between the two solutions.

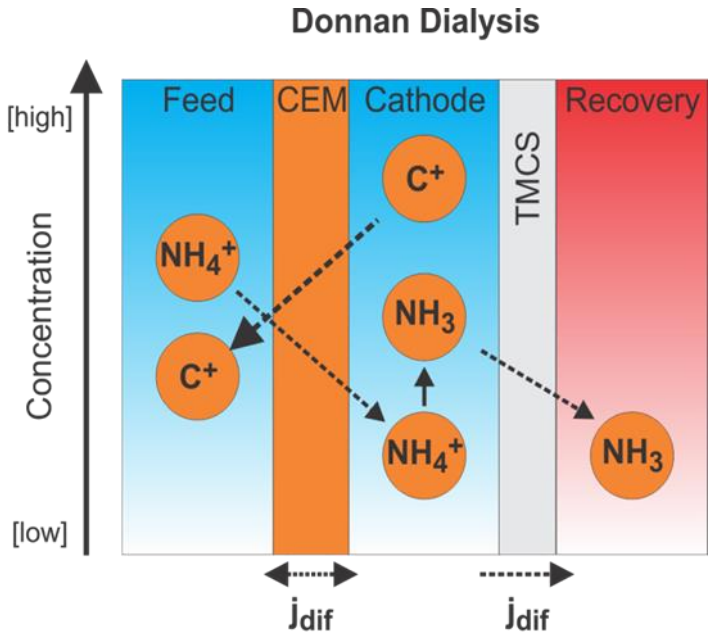


Figure 10. Donnan dialysis principle for ammonia recovery

During Donnan dialysis, no current is supplied to the cell. Due to the concentration gradient previously formed, the co-ions (Na^+ and K^+) move towards the less concentrated compartment, like illustrated in the Figure 10. The movement of the cations back to the feed must be compensated by similar charged species to maintain electroneutrality. Therefore, the ammonium ions

present in the feed will diffuse towards the cathode. This process can then be combined with an HRES to increase the recovery of ammonium from a feed stream, like in Figure 11.

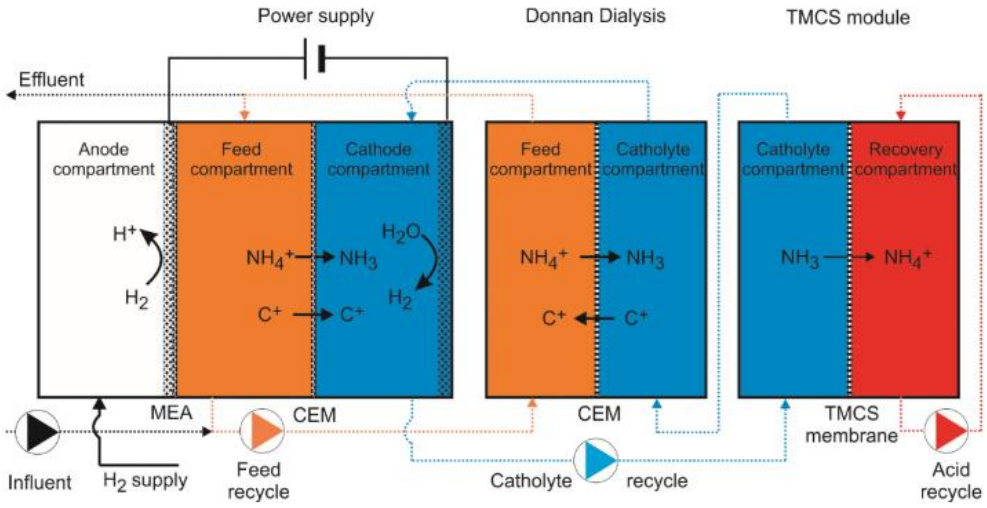


Figure 11. HRES with Donnan Dialysis

The first cell on the left, operates identically to the HRES system. The concentrated solution formed at the cathode is pumped into a TMCS unit where ammonia removal occurs. The ammonia depleted catholyte solution then passes through the Donnan dialysis cell. In the Donnan cell, co ions are transported towards the feed. This transport is compensated by the movement of the remaining ammonium from the feed towards the cathode.

1.8. Wastewater

In wastewater treatment plants, the nitrification/denitrification process receive as influent the stream from a primary settling, like presented in Figure 12. [46] However, the new alternatives for ammonia recovery have been exploring different streams such as urine, black water or rejected water.

A common central treatment plant receives a high volume of influent with low concentrations of nutrients, resulting in an increase of the cost of treatment. [47]

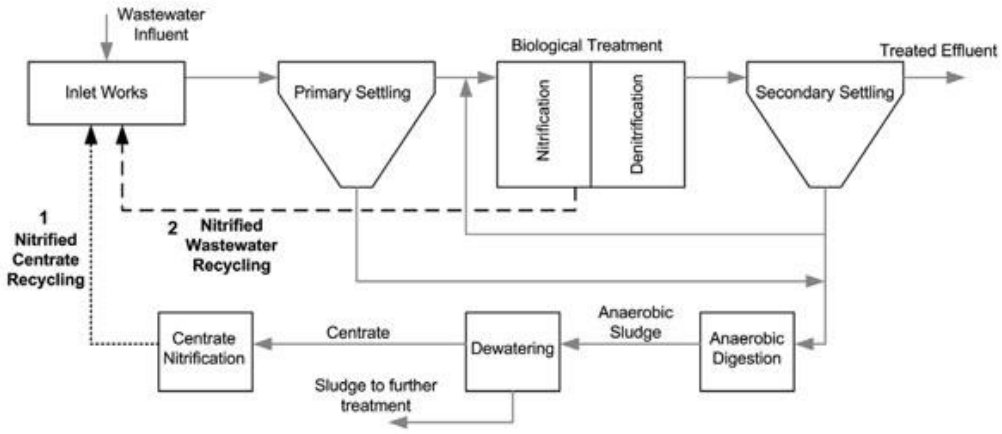


Figure 12. Nitrification/denitrification process in a WWTP [48]

The decentralized separated collection of nutrients from streams such as urine or blackwater may improve the energy efficiency of wastewater treatment system and allow a higher recovery. Also the collection at WWTP of rich streams such as rejected water, can result in a better final effluent at a lower cost. [42]

1.8.1. Urine

Urine is the main contributor of nutrients in domestic wastewater. It contains around 80% of the nitrogen, 50% of the phosphorus and 70% of the potassium, although it only represents 1% of the total volume. [19,47]

Urine is a balanced fertiliser with potential to be re-used in land fertilisation given its high content of nitrogen and phosphorus, the main components of fertilisers. [47] In the past it was used directly into the crop plantation. However, with the increase of urbanisation the main sources of urine are no longer near the agriculture areas. At the wastewater treatment plant, the nutrients from urine are already diluted around hundred times, representing a high effort to remove or recover them. Also, the separated transport of urine to a central treatment, has a high cost and increases the risk of spreading pathogens and micropollutants. So, to use this stream, there is the need to create a urine decentralised recovery.

The separation of urine reduces the nutrient load in wastewater treatment plants and allows an easier recovery and reuse of the nutrients. When treating urine with struvite precipitation to recover phosphorus, it is possible to obtain a product almost free of most micropollutants and with high marketable value for agricultural

use. Since the phosphorus nitrogen ratio in urine is not 1:1, 80 to 90% of the nitrogen in urine is not recovered. This way, the struvite crystallisation generates a highly rich stream in nitrogen, suitable to be fed to an HRES. [49]

Struvite crystallization has evolved in the past years as viable strategy to recover phosphorus, meaning the opening of an opportunity for electrochemical systems to recover the remain nitrogen. The combination of these treatments not only benefits both processes as increases the value of separated urine. [47]

1.8.2. Reject water

In a wastewater treatment plant, the produced sludge is dewatered to reduce its volume. From this process results a stream with a high concentration of ammonium known as rejected water. [22] The concentration can reach up to 1000 mg L^{-1}.

The reject water is normally recycled back to the nitrification reactor. This represents an increase of the load of nitrogen into the plant, that it must be removed again through the system. This, requires more reactors and chemical dosage, meaning an increase of the cost to achieve ammonium free effluents. [50]

Due to the high concentration of nutrients, more specifically ammonium, and a lower volume, reject water contains potential to be also treated by an HRES. The separated treatment of this stream would ensure a more efficient recovery of nitrogen, reducing the need of expansion of wastewater treatment plants and consequently reducing the economic investment. [51]

1.8.3. Blackwater after COD removal

Another source-separated stream with potential to recover ammonia, due to the high concentration of nutrients and lower volume, it is blackwater. [52] Black water results of the separation of the toilet stream from other wastewaters produced at home (laundry, showers, and kitchen). Blackwater contains around 70 % of the total domestic chemical oxygen demand (COD), 90% of the nitrogen and 80% of the phosphorus of domestic wastewater.

So far, anaerobic digestion has been explored as the preferential technique to remove the COD from black water. It allows energy and nutrient recovery, due to the conversion of organic matter into methane, which can be used to produce electricity and heat. After this process, the resultant effluent contains concentrations of ammonium exceeding sometimes 1000 mg L^{-1} and soluble COD/N ratios of around 1.0. [53]

After anaerobic digestion, around 90 % of the nitrogen is conserved in the liquid effluent, mainly as ammonium. Thus, it is possible to recover the nitrogen in the liquid phase with an HRES. [52]

Aim of the work

The aim of this research project is to optimization of a current driven system for ammonia recovery. Therefore, two concepts will be investigated; a) up-scaling of the technology via stacking of cell (membrane) pairs using bipolar membrane, and b) optimizing ammonia recovery by the concept of Donnan dialysis.

Materials and Methods

Two different systems were operated to test the Donnan dialysis principle and the up-scaling with bipolar membrane. The Materials and methods as well as the results will be presented separately.

2.1. Electrochemical systems design

i. Donnan Dialysis

The influence of the Donnan dialysis on ammonia recovery was studied with hydrogen gas recycling system as represented in the Figure 11. The system included two cells and one TMCS unit. The HRES cell was assembled according to the Figure 13.

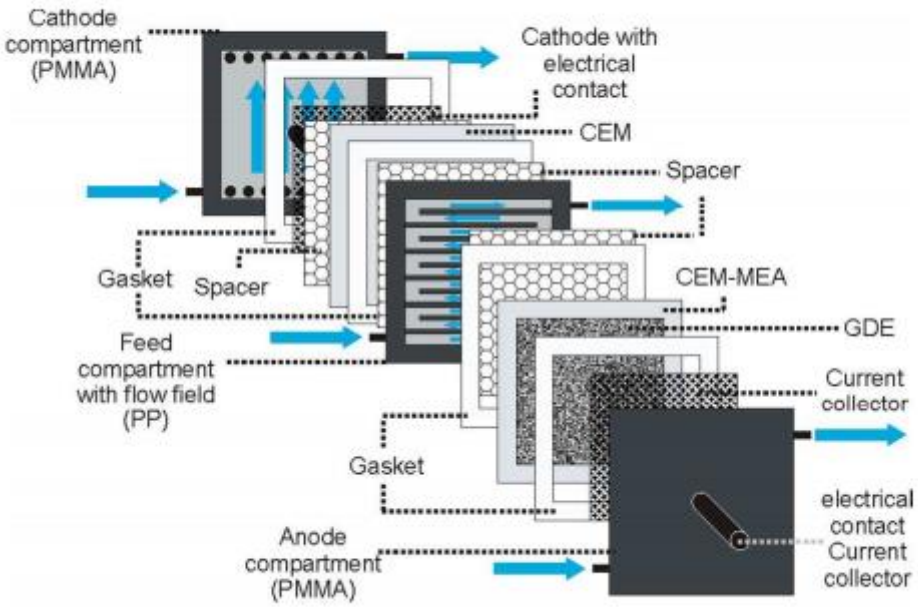


Figure 13. Schematic representation of the HRES cell design and its components

The HRES cell for ammonia recovery had three compartments, anode, feed and cathode. The cell frames were two PMMA (poly methyl methacrylate) panels (21 cm x 21 cm). The anode and cathode compartments had dimensions of 10 cm x 10 cm x 0.2 cm. The middle compartment (feed) was separated from the others

by two cation exchange membranes (CEM; 15 cm × 15 cm Nafion 117, Ion Power GmbH, Germany). The CEM between anode and feed was coated with a 10 cm × 10 cm of Platinum - Vulcan (carbon) catalyst (0.5 mg Pt cm^{-2}) and combined with a gas diffusion electrode (FuelCellsEtc Texas, USA), also known as a membrane electrode assembly (MEA). The catalyst side of the membrane was facing a current collector Pt coated titanium mesh electrode connected to an electrical circuit. The cathode compartment also included a Pt coated titanium mesh electrode with dimensions 9.8 cm × 9.8 cm, 5 mg Pt cm^{-2} (Magneto Special Anodes BV, The Netherlands) and nitril spacers (50% open). All ion exchange membranes and electrodes had a projected surface area of 100 cm^2. The feed compartment consisted of a custom-made polypropylene (PP) plate with dimensions 21 cm × 21 cm × 1.2 cm and including a serpentine shaped flow field (10 cm × 10 cm × 1.2 cm, 60% open). The feed was supplied at the bottom of the compartment and had the effluent channel at the top.

The supply of hydrogen gas to the anode was possible due to a support cell, not presented in the figure. This one was operated at constant current using as electrolyte a solution of 50 mM H_2SO_4. The hydrogen gas was supplied using as carrier gas N_2. A water lock was used to ensure oxygen free conditions the anode compartment.

The Donnan dialysis cell consisted in two compartments, feed and cathode. It included two PMMA (poly methyl methacrylate) panels (21 cm x 21 cm) separated by a cation exchange membrane (CEM; 15 cm × 15 cm MEGA a. s., Straž pod Ralskem, Czech Republic). The cell was supplied with the feed solution leaving the HRES cell and with the catholyte solution after the passage through the TMCS unit. Both compartments were fed at the bottom and had the effluent channel at the top.

The volatile ammonia was extracted from the catholyte by transmembrane chemisorption (TMCS) unit. The TMCS unit consisted in a custom-made polypropylene (PP) housing and a tubular gas permeable hydrophobic membrane (1.5 m, 0.2 µm pore size, V8/2 Type TP, MICRODYN-NADIR GmbH, Wiesbaden, Germany). Ammonia rich catholyte (lumen side) and 1 M sulphuric acid (shell side) solution were recirculated over the TMCS unit. The acid was replaced regularly before saturation occurred.

Ag/AgCl reference electrodes (+0.2 V vs NHE, QM711X, QiS-Prosence BV, Oosterhout, The Netherlands) were placed in the cathode and feed compartments to measure the membranes and electrode potentials. These were connected to a high impedance preamplifier (Ext-Ins Technologies, Leeuwarden, The Netherlands). The temperature and pH of the feed and catholyte solutions were measured using Orbisint CPS11D sensors connected to a Liquiline CM444 transmitter (Endress+Hauser BV, Naarden, The Netherlands). The conductivity of the feed and catholyte were measured using QC205X EC electrodes and P915-85 − Controller (QiS-Prosence BV, Oosterhout, The Netherlands). Constant current (CC) was supplied to the HRES cell by a Delta power supply (ES 030-5, Delta Elektronika BV, Zierikzee, The Netherlands). The pH, temperature, conductivity, current density, cell voltage, anode potential, and cathode potential were recorded by a Memograph M RSG40 datalogger (Endress+Hauser BV).

ii. Upscaled HRES with BPM

HRES up-scaling was studied by stacking of cell (membrane) pairs using a bipolar membrane, as presented in Figure 9.

The system integrated a double stack of two HRES separated by a bipolar membrane. It consisted in six compartments in the following order anode- feed – concentrate -feed -concentrate -cathode. Herein, the bipolar membrane acted as a pair of electrodes (anode and cathode). The anionic side acted as a cathode by supplying hydroxyl ions to the concentrate. The cationic side acted as an anode by supplying a proton to the feed.

The frame of the anode and cathode compartment were made of PMMA (poly methyl methacrylate) with a flow field of 20 cm × 20 cm × 0.2 cm and integrated influent and effluent channels for the four compartments. The anode compartment was separated from the feed by a MEA like previously describe for the HRES cell. For this system, the MEA was a 24 cm × 24 cm Nafion N117 CEM coated with a 20 cm × 20 cm platinum Vulcan (carbon) catalyst (0.5 mg Pt/ cm2). A Pt-coated titanium mesh in the anode compartment acted as current collector

was with dimensions 20 cm × 20 cm × 0.2 cm (5 mg Pt/cm2, Magneto Special Anodes BV).

The feed and concentrate compartments were separated by a CEM (CMH-PP Ralex, MEGA a. s., Straž pod Ralskem, Czech Republic). The two stacked pairs (anode/feed/concentrate from feed/concentrate/cathode) were separated by a bipolar membrane (Ralex, Membrane, Czech Republic) like presented in the figure 14. The feed and concentrate compartments had initially dimensions of 20 cm × 20 cm × 0.03 cm due to the custom-made rubber silica gaskets. Later, the feed and concentrate housing were replaced by silica gaskets plus PMMA plates resulting in compartments with dimensions 20 cm × 20 cm × 0.4 cm. A fixed structure of 4 spacers with 1.3mm thickness each was used to separate the membranes, in the feed and concentrate compartments.

The cathode compartment was separated by the concentrate by an anion exchange membrane (AEM) (AMH-PP Ralex, MEGA a. s.). The cathode compartment included a Pt-coated titanium mesh electrode (20 cm × 20 cm × 0.2 cm, 5 mg Pt/cm± Magneto Special Anodes BV). All ion exchange membranes and electrodes had a projected surface area of 400 cm^2.

As the previous systems, the ammonia was recovered using TMCS unit, including 4 gas-permeable hydrophobic membranes (1.5 m, 0.2 μm pore size, V8/2 Type TP, MICRODYN-NADIR GmbH, Wiesbaden, Germany) inside custom-made polypropylene (PP)modules assembled in parallel. The volatile ammonia was recovered from the concentrate stream.

The hydrogen gas produced at the cathode was carried by nitrogen gas at 15 mL/min to the anode, being injected near the MEA. This flow was enriched with approximately 10% of extra H2 from a custom-made electrolyser (operated at constant current and 50 mM H_2SO_4 as electrolyte).

Ag/AgCl reference electrodes were used in the cathode, feed and concentrate compartment (+0.2 V vs NHE, QM711X, QiS-Prosence BV, Oosterhout, The Netherlands) to measure the membranes and electrode potential. These were connected to a high impedance preamplifier (Ext-Ins Technologies, Leeuwarden, The Netherlands). The temperature and pH of the feed, concentrate and cathode solutions were measured using Orbisint CPS11D sensors connected to a Liquiline CM444 transmitter (Endress+Hauser BV, Naarden, The Netherlands). The conductivity of the same solutions was measured using QC205X EC

electrodes and P915-85 − Controller (QiS-Prosence BV, Oosterhout, The Netherlands). Constant current (CC) was supplied to the HRES cell by a Delta power supply (ES 030-10, Delta Elektronika BV, Zierikzee, The Netherlands). The pH, temperature, conductivity, current density, cell voltage, anode potential, and cathode potential were recorded by a Memograph M RSG40 datalogger (Endress+Hauser BV).

2.2. Basic operation consideration /Experimental Strategy

i. Donnan Dialysis

Two sets of experiments were performed in this system using always as influent synthetic urine. Synthetic urine was chosen as influent to be able to directly compare with previous work in HRES systems for ammonia recovery. The synthetic urine was prepared with the following concentrations: 13.7 g L^{-1} $(NH_4)_2CO_3$, 4.5 g L^{-1} NaCl, 1.9 g L^{-1} KCl and 1.04 g L^{-1} K_2SO4.

The system was operated with two configurations, using the HRES cell or both HRES and Donnan dialysis cell. Both configurations were operated at three different Load Ratio. For the Load Ratio 0.8, 1 and 1.3 the system was fed continuously at a rate of 0.39 mL min^{-1}, 0.51 mL min^{-1} and 0.63 mL min^{-1}, respectively. The system operated at a constant current density, 20 A m^{-2}. For each Load Ratio the system operated for a period of around 12 days, to guarantee that it was stable. The catholyte (synthetic urine) was replaced at the beginning of each experiment.

All liquids (feed, catholyte and acid) were recirculated using peristaltic pumps (Masterflex L/S, Metrohm Applikon BV, Schiedam, The Netherlands) at a rate of 80mL min^{-1}. The feed vessel had 1L. The catholyte consisted in a total recirculation volume of 0.5 L.

The 1M H_2SO_4 acid used in the TMCS unit was replaced once the concentration exceeded 20 g/L of ammonium-nitrogen. The system was operated at room temperature.

Table 1 summarizes all the experiments performed.

Table 1. Donnan Dialysis operation conditions

Experiment	Configuration	LN	Initial catholyte solution
1	HRES	0.8	Synthetic Urine
2	HRES	1	Synthetic Urine
3	HRES	1.3	Synthetic Urine
4	HRES+Donnan Cell	0.8	Synthetic Urine
5	HRES+Donnan Cell	1	Synthetic Urine
6	HRES+Donnan Cell	1.3	Synthetic Urine

ii. Upscaled HRES with BPM

The up-scaled system was operated using always as influent synthetic urine. The synthetic urine was prepared with the following concentrations: 13.7 g L^{-1} $(NH_4)2CO_3$, 4.5 g L^{-1} NaCl, 1.9 g L^{-1} KCl and 1.04 g L^{-1} K_2SO_4.

The system was operated at three different current densities, 10 A m^{-2}, 20 A m^{-2} and 50 A m^{-2}. The cell was fed continuously at a rate of 1.6 mL min^{-1}, 3 mL min^{-1} and 7.6 mL min^{-1}, respectively for each current density, to maintain a Load Ratio of 1.3.

Later, two more experiments at current density of 20 A m^{-2} and Load Ratio of 1.3 and 2, were performed using thicker feed and concentrate compartments. For each current density, the system was operated for a period of around 14 days, to guarantee that it was stable.

The concentrate and catholyte vessels were initially filled with synthetic urine. The catholyte and concentrate solutions were never replaced after. The composition of these solutions changed during the operation of the system, due to the ion accumulation in these compartments. The feed stream did not include a considerable recirculation volume. The cathode compartment had a total recirculation volume (vessel, cell and tubing) of 2.4 L. The concentrate

compartment had a total recirculation volume of 1.2 L. The cathode, feed and concentrate solution were recirculated by peristaltic pumps at a rate of 30 mL min^{-1} for the first experiments. Later, the recirculation was increased to 80 mL min^{-1}.

The 1M H_2SO_4 acid used in the TMCS unit was replaced once the concentration exceeded 20 g L^{-1} of ammonium-nitrogen. The acid was recirculated at 80 mL min^{-1}. The system was operated at room temperature.

Table 2 summarizes all the experiments performed.

Table 2. HRES with BPM operation conditions

Experiment	Configuration	LN	Current Density (A m-2)	Compartments thickness
1	HRES with BPM	1.3	10	0.03 cm
2	HRES with BPM	1.3	20	0.03 cm
3	HRES with BPM	1.3	50	0.03 cm
4	HRES with BPM	1.3	20	0.4 cm
5	HRES with BPM	2	20	0.4 cm

2.3. Analytical measurements

Daily samples from the influent, effluent, catholyte, concentrate (when applied) and acid were collected from both systems. All samples were diluted to satisfy the measurement IC limits. The samples were analysed in duplicate for cations (Na^+, K^+, NH_4^+) and anions (SO_4^{2-}, Cl^-), with a Metrohm Compact IC Flex 930 with a cation column (Metrosep C 4-150/4.0) and a Metrohm Compact IC 761 with an anion column (Metrosep A Supp 5- 150/4.0) each equipped with a conductivity detector (Metrohm Nederland BV, Schiedam, The Netherlands).

All samples, except the acid, were submitted to quantify organic carbon, inorganic carbon, and total carbon using a TOC analyser (TOC-L CPH, Shimadzu BENELUX, 's Hertogenbosch, The Netherlands).

The pH and conductivity were register daily for all samples collected.

2.4. Calculation

All calculations (Load Ratio, removal, energy input, TAN removal rate and ion transport number) showed in this section were adapted from [42].

The Load Ratio can be calculated using the following equation:

$$L_N = \frac{j}{\frac{[NH_4^+]}{M} \times Q \times \frac{F}{A}} \quad \textbf{(1)}$$

Where j is the current density (A m^{-2}), A is the effective membrane area (m^2), $[NH_4^+]$ is the concentration of ammonium (mol g^{-1}), M is the molar mass of NH_4^+ (g mol^{-1}), Q is the feeding rate (m^3 s^{-1}) and F is the Faraday constant of (96,485 C mol^{-1}).

The TAN removal was calculated as the difference between the NH_4^+ influent concentration ($C_{i[NH4+]}$; g L^{-1}) and the NH_4^+ effluent concentration ($C_{e[NH4+]}$; g L^{-1}) for every sample collected with 24h intervals.

$$Removal_{TAN} = \frac{C_i[NH_4^+] - C_e[NH_4^+]}{C_{i[NH_4^+]}} \quad \textbf{(2)}$$

The total energy input (E_{input}; kJ/g_N) for TAN recovery was described as the ratio between the supplied power and the TAN removal rate (t_i; g_N m^{-2} d^{-1})

$$\boldsymbol{E_{input} = \frac{j \times V \times 24}{t_i}} \quad \textbf{(3)}$$

where V is the voltage of the cell (V) and t_i is the TAN removal rate (g m^{-2} day^{-1}) and can be described as:

$$\boldsymbol{t_i = \frac{C_i\left[NH_4^+ - N\right] - C_e\left[NH_4^+ - N\right] \times Q \times t}{A}} \quad \textbf{(4)}$$

Where M_N is the molar mass of nitrogen and t is the time interval (86,400s).

The ion transport number (t_{cation}; C d^{-1}) was obtained using the following equation:

$$\boldsymbol{t_{cation} = \frac{\Delta C_{cation}}{M} \times Q \times F} \quad \textbf{(5)}$$

where ΔC_{cation} is the difference between the cation concentration of the influent and effluent (g L^{-1}) and M is the molar mass of the ion (g mol^{-1}).

Results and Discussion

i. Donnan dialysis

The performance of the HRES+Donnan cell was evaluated considering the removal, ion transport, TAN transported rate and energy input (total and loss over the membrane).

a) Removal

The removal of nitrogen was calculated considering the concentration of ammonium in the effluent and influent streams.

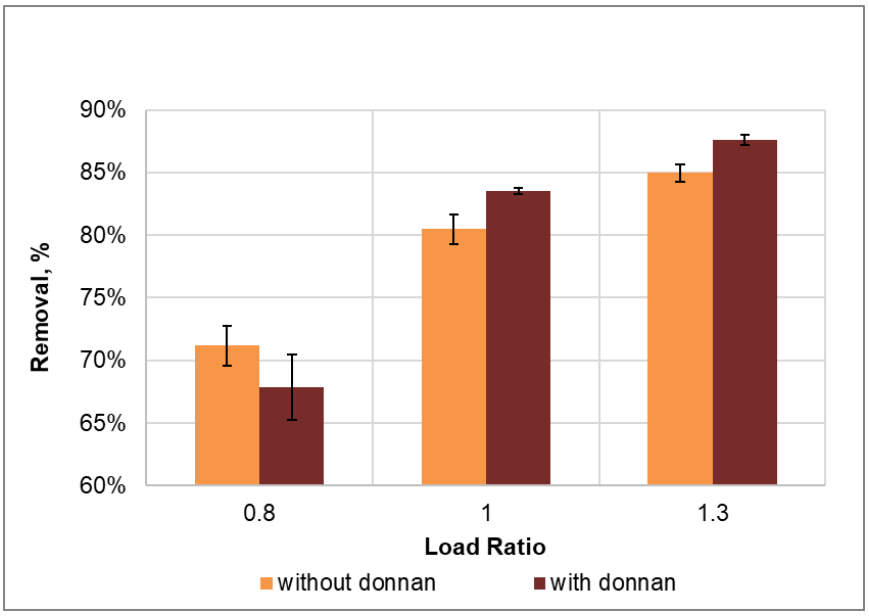


Figure 14.TAN Removal of the HRES and HRES+Donnan

As expected from the literature, the removal increases with the Load Ratio, Figure 14. [27]

Ammonia removal efficiency between 71% and 85% were obtained with the HRES without the Donnan cell. The ammonia removal efficiency between 68% to 88% were obtained with the HRES with the Donnan cell. In previous studies, ammonia removal efficiency was about 73 and 74% with a similar HRES and a modified HRES, respectively (see appendix, Section II). Those systems were also

operated at a LN=1.3 and current density of 20 A m^{-2}. The higher removal demonstrate an improvement of the system. [5,42]

The HRES + Donnan cell also showed a better performance compared to two electrochemical systems operating at 30 A m^{-2} and Load Ratio of 0.7 and 1, which obtained removal rate of 53% and 41%, respectively (see appendix, Section II). Although this comparison is not completely fair, due to the difference in operational condition of the systems. [54,55] Other aspects are the difference in influent compositions, which might affect ion transport over the membrane, and the method of extraction (stripping vs. TMCS).

Although it seems that the Donnan dialysis increases the removal, its influence was not found significant according to a student's t-test for LN 1 and 1.3 (see appendix, Section III).

At a Load Ratio 0.8, the Donnan cell decreases the removal. This can be explained by the lower pH of the cathode compared to the HRES without Donnan cell, which limits the extraction of ammonia.

b) Effect of pH on the Removal

As previous explained, the TMCS unit only removes gases. A solution with a pH 9.25 has 50% of ionic NH_4^+ and 50% of gaseous NH_3, which means that the amount of ammonium that can be recovered is limited. [15]

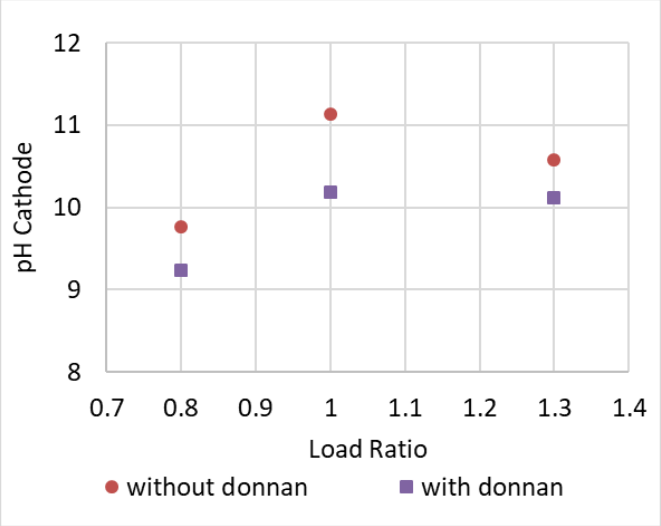


FIGURE 15.Cathode pH for the HRES and HRES+Donnan system

At a Load Ratio 0.8, the cathode pH was higher when operating only with the HRES compared to the combined HRES+Donnan cell, Figure 15. The removal efficiency with the HRES was higher, because at a higher pH more ammonia is present which can be extracted via the TMCS.

In general, the cathode pH was always lower for the combined HRES+Donnan cell. The Donnan dialysis prevents an increase of the pH. The exchange of Na+ and K+ with ammonium and protons lowers the cathode pH due to acid base reactions. Even though Donnan dialysis might increase the extraction of ammonium ions from the feed, the ammonia might not be recovered via the TMCS unit. The cathode pH is the crucial factor, a pH lower than 10 might limit the extraction**.**

c) Recovery

The TAN recovery was calculated considering the TAN supplied (influent), accumulated (cathode) and leaving (effluent) the system. Table 4 and Table 5 show the mass balances of the current driven ammonia recovery system without and with Donnan dialysis cell, respectively.

Considering the standard deviation of the removal is possible to conclude that there is no difference, between the removal and recovery.

Table 3. Mass balance for the HRES

LN	In (g)	Out (g)	Removed (g)	Cathode (g)	Removal (%)	Recovery (%)	Difference
0.8	**21.2**	6.1	15.1	0.4	71±2	69	2%
1	**16.9**	3.3	13.6	0.3	80±1	79	2%
1.3	**13.3**	2.0	11.3	0.2	85±1	83	2%

Table 4. Mass Balance for the HRES+Donnan cell

LN	In (g)	Out (g)	Removed (g)	Cathode (g)	Removal (%)	Recovery (%)	Difference
0.8	**20.6**	6.6	14.0	0.7	68±3	64	3%
1	**16.4**	2.7	13.7	0.3	84±0	82	2%
1.3	**12.9**	1.6	11.3	0.3	88±0	85	2%

d) Ti

The ionic transport numbers over the cation exchange membrane separating feed and cathode compartment were calculated for all the experiments.

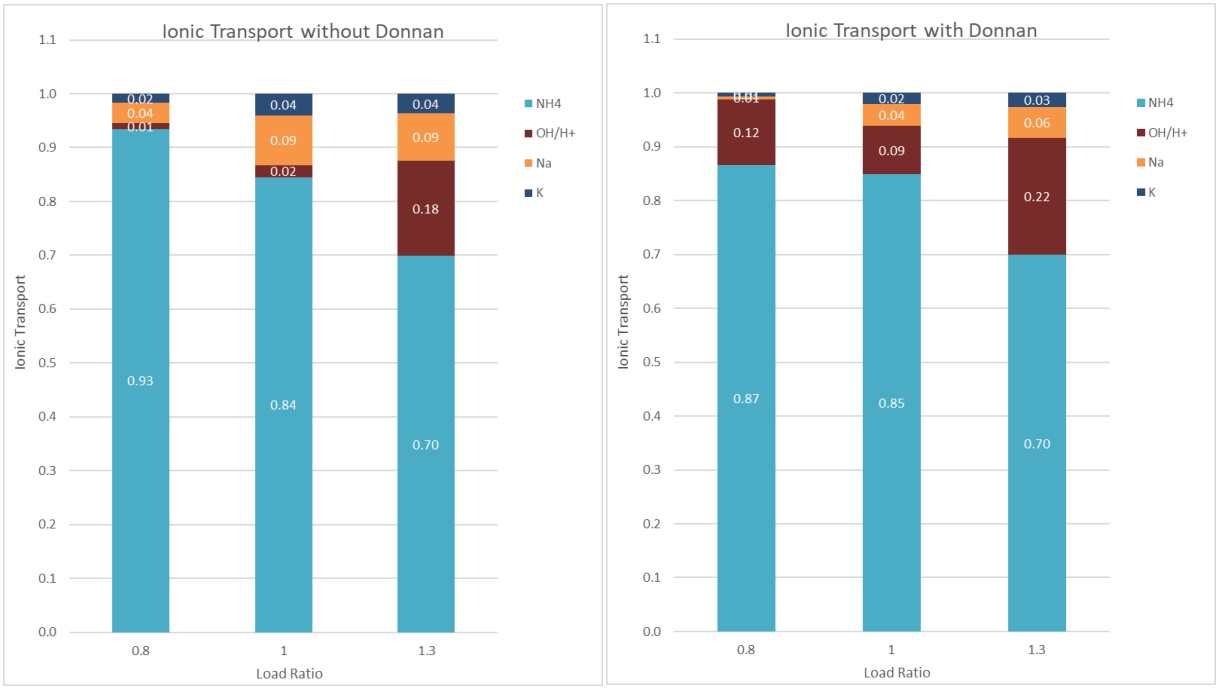


FIGURE 16. A) ionic transport over the CEM separating feed and cathode compartment in HRES B) ionic transport over the CEM separating feed and cathode compartment in HRES+Donnan.

For all the experiments, the main charged species transported over the membrane was ammonium, Figure 16. The ammonium transport decreases with the Load Ratio, as expected. [27] This happens due to the decrease in TAN loading with increasing Load Ratio, resulting in higher transport of other cations.

In general, K and Na transport was lower during experiment with Donnan dialysis than during experiment without Donnan dialysis at the repective Load Ratios. Unfortunately, this decrease is compensated by proton/hydroxyl ion transport instead of ammonium transport.

Similar to the observed removal efficiency, the difference for NH_4^+ transport with or without HRES+Donnan cell it was not significant for a Load Ratio 1 and 1.3. At a Load Ratio 0.8, the transport of NH_4^+ is lower when Donnan dialysis was used. This can be explained by the diffusion of ammonium ions to the feed in the Donnan cell, due to an insufficient extraction over the TMCS.

e) TAN Removal Rates

The TAN transported rates determined in experiments with the HRES (without Donnan dialysis) were 234.3±7.5 $g_N\ m^{-2}\ d^{-1}$, 211.8±6.4 $g_N\ m^{-2}\ d^{-1}$ and 175.2±3.9 $g_N\ m^{-2}\ d^{-1}$ for LN 0.8, 1 and 1.3 respectively.

The TAN transport rate determined in experiments with the HRES+Donnan cell were between 217.0±7.8 $g_N\ m^{-2}\ d^{-1}$, 213.0±2.7 $g_N\ m^{-2}\ d^{-1}$ and 175.3±2.7 $g_N\ m^{-2}\ d^{-1}$.

With the exception of Load Ratio 0.8, the TAN transported rates similar during operation with and without the Donnan dialysis cell. At a Load Ratio of 0,8, the pH of the catholyte influenced the ammonia recovery resulting in diffusion of ammonium back to the feed. This might explain the lower overall TAN transport. Nevertheless, the TAN transported rate was higher with this system than previously reported HRES hat obtained 151 $g_N\ m^{-2}\ d^{-1}$. [5] Overall, these values are also higher compared when with other studies (see appendix, Section II), representing a significant improvement in this system. Since it was possible to obtain a high TAN removal rate, it is possible to remove a given nitrogen load with a smaller and more compact system.

f) Energy

The energy input for TAN removal in an electrochemical system is determined by three main factors: cell voltage, applied current density, and the TAN transport rate. [5] The overall energy input was similar between configurations and

dependent on the Load Ratio. An energy input between 9.7 to 14.8 kJ/g_N. was determined for HRES and HRES+Donnan. In previous experiments, an energy demand of 26.1 kJ/g_N. was reported at a Load Ratio 1.3 and the same current density (20 A m^{-2}). [42] The lower energy input for a high TAN removal is an improvement for this new system. The comparison with other ES systems it is not entirely fair, due to the operation at a different current density. However, for Load Ratio 1, the HRES+Donnan required a much lower energy input (around 11.5 kJ/g_N) than an ES operated at the same Load Ratio (60.5 kJ/g_N) at a slightly higher current density. [54]

The total energy input was also lower than combination of the Haber−Bosch and the nitrification/denitrification processes, which uses 37 kJ/g_N (natural gas) and 45 MJ/kg_N (electricity), respectively. [19,42]

For further insides, the energy loss over for the TAN transport was quantified to assess the losses independently of the electrode reactions, Figure 17.

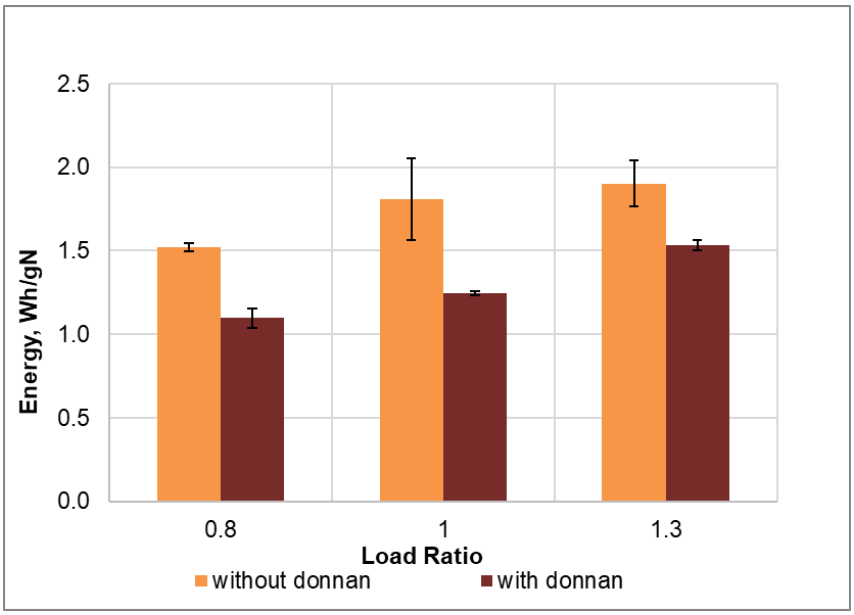


FIGURE 17. Energy Losses over the membrane

Therefore, the energy loss was composed of the ionic, the membrane and the equilibrium potential. The ionic losses originate from the electrolyte conductivity. The membrane transport originate from the transport of a positive ions (NH_4^+, Na^+ and K^+) over a negatively charged cation exchange membrane [56]. The equilibrium losses originate from the pH gradient between anode and cathode. Similar to the

overall energy input, the energy losses increased with the Load Ratio, as expected. [27]

During operation with the Donnan dialysis cell, the equilibrium losses were lower, due to the smaller difference between the feed and cathode pH. Furthermore, the decrease of the concentration gradient between feed and cathode, due to the diffusion of cations back to the feed, reduced the ionic loss and the membrane losses. Thus, there were less voltage losses during operating HRES+Donnan cell, meaning a lower overall energy loss during ammonia recovery.

A Load Ratio above 1, represents an insufficient TAN loading into the system, at a given current. [39]. This means, at higher Load Ratio, cations other than ammonium are transported, representing loss in current efficiency.

ii. Upscaling HRES with BPM

The up-scaled HRES using the bipolar membrane (HRES with BPM) was characterized by determining the TAN removal, ionic transport, TAN transported rate and total energy input.

a. Removal/recovery

The removal of nitrogen was calculated considering the concentration of ammonium in the effluent and influent streams of the system.

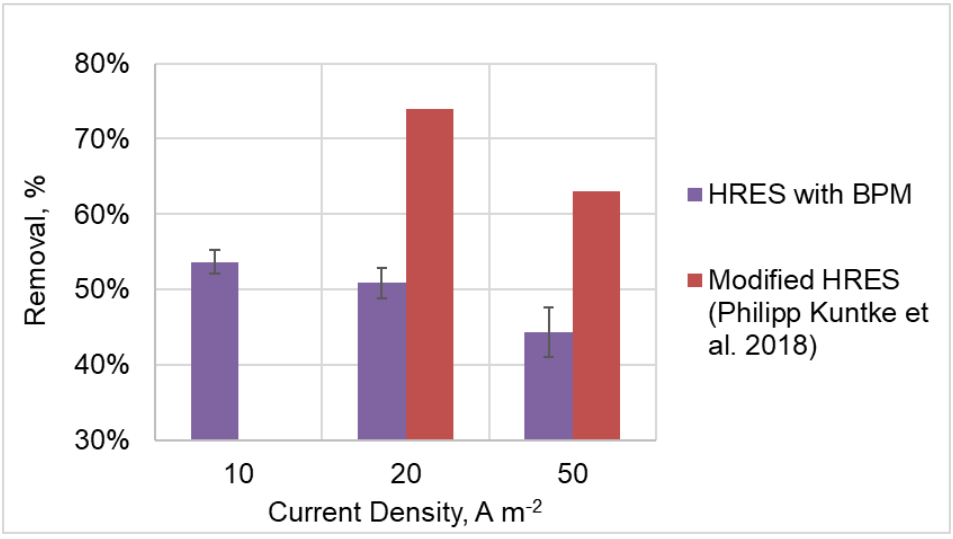


Figure 18. TAN removal of the up-scaled HRES modified and HRES with BPM

The removal decreases for higher current densities as previously observed, Figure 18. A similar decrease of removal with the increase of the current density was also observed for the modified HRES. [42] The decrease can be associated to the transport of other charged specie (Na^+ or K^+) over the membrane.
However, the HRES with BPM showed a significant lower removal, compared to the previous modified HRES that obtained a removal of 74% and 63% for 20 and 50 A m^{-2}, respectively. The inferior results can be result of several factors such as pH and recirculation.

The physical design (spacing of the flowing field) of the HRES with BPM did not allow feed flow rates higher than 30 mL min^{-1}. Accordingly, the HRES with BPM with thicker compartments was tested at a current density of 20 A m^{-2} at a Load Ratio 1.3 and 2.

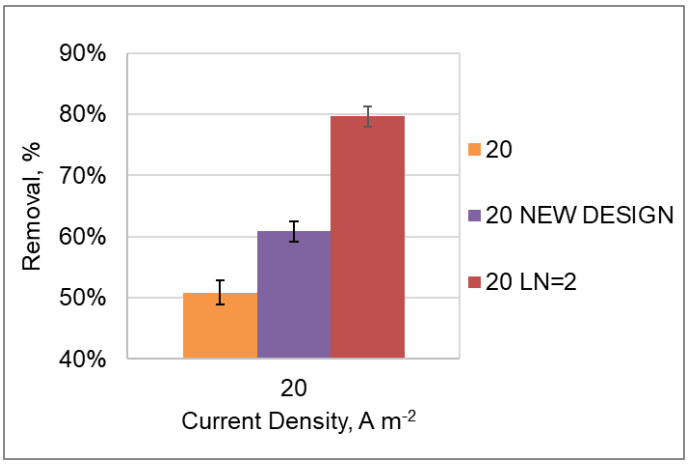


Figure 19. TAN Removal at 20 A m^{-2} for different design and LN

The increase of the dimensions of the feed and the concentrate compartment from 0.5 mm to 4 mm allowed to recirculate the liquid at 80 mL min^{-1}. The result presented in Figure 19, shows removal of 61%, 10% more than before. This shows that the performance of the cell is also affected by the fluid velocity inside the compartments.
Also, in Figure 19 is possible to see that the removal increased to 80% at a Load Ratio of 2. This means that a higher removal can be reached at higher Load Ratio, but it means an increases of the energy input and consequently a higher cost.[27]

b. Effect of pH on the Removal

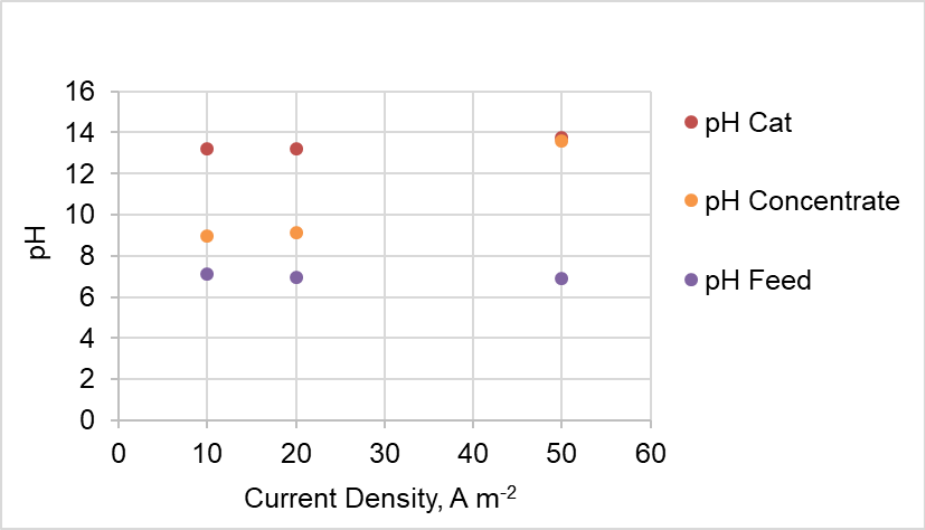


Figure 20. Cathode pH for the HRES with BPM

The pH of the concentrate was around 9 at a current density of 10 and 20 A m^{-2} (Figure 20). Similar to the previous experiments, this means the ammonia extraction via TMCS unit was limited. At a pH of 9 less than 50% of the nitrogen is in the gaseous form NH_3.

At a current density of 50 A m^{-2}, the concentrate pH was around 13 (Figure 20). Ideally, this would result in a high extraction considering that all TAN is in the form of volatile ammonia. However, the transport of ammonium to the concentrate was limited due to the reduced flow velocity (old spacer design). Based on these insights, operating at a higher current density and at higher flow velocities would lead to higher recoveries.

At a current density of 20 A m^{-2}, the cell with the larger spacing and higher recirculation rate had a concentrate pH of 13.3 leading to a higher removal.

c) Ti

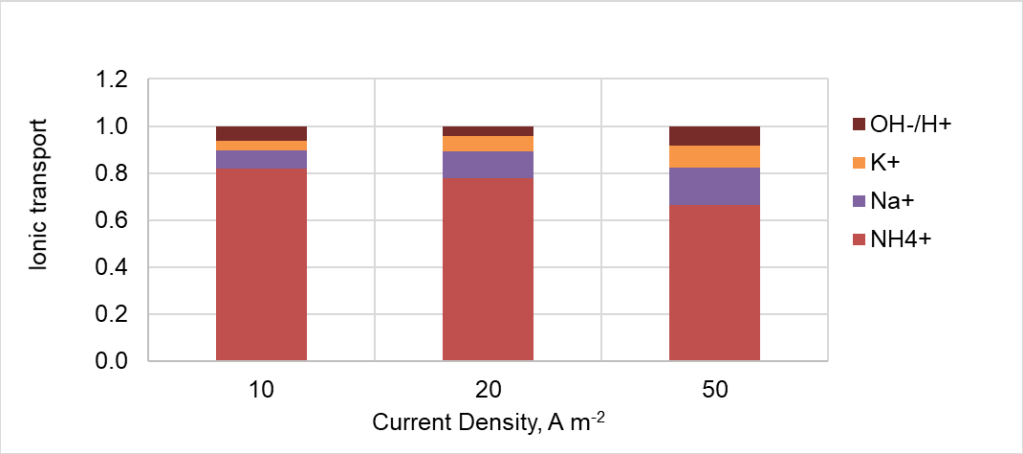


Figure 21. Ionic transport in the HRES with BPM

Ammonium ions accounted the majority of charge transported through the CEM separating feed and concentrate, as seen in Figure 21. When increasing the current supply to the system, the transport of other ionic species over the membrane increased. So, the transport of NH_4^+ decreases with the increase of the current density. Similar effects were observed in earlier work. [42]

The lower transport of NH4+ across the CEM at 50 A m^{-2} can also explain the lower removal obtained, considering that the pH conditions were ideally.

e) TAN Removal Rates

The TAN transported rates were 102.6±5.1 g_N m^{-2} d^{-1}, 195.8±13.5 g_N m^{-2} d^{-1} and 417±42.8 g_N m^{-2} d^{-1} for the current densities 10, 20 and 50 A m^{-2} respectively.

Considering that the system includes the equivalent of 2 HRES system, the TAN removal rates per CEM obtained was 51.3 g_N m^{-2} d^{-1}, 97.9 g_N m^{-2} d^{-1} and 208.8 g_N m^{-2} d^{-1} for the current densities 10, 20 and 50 A m^{-2}, respectively. At the current density of 20 A m^{-2}, this system shows a lower TAN transport rate than the HRES+Donnan cell and the HRES from previous work. At the same Load Ratio, TAN transport rates of 175.3 g_N m^{-2} d^{-1} and 151 g_N m^{-2} d^{-1} were obained, respectively. [5] This indicates that the operational conditions of this system are not optimized yet.

Also, the values obtained for at the current densities of 20 and 50 A m^{-2} were lower, compared to the HRES modified previously study. The HRES modified had obtained 141 g_N m^{-2} d^{-1} and 355 g_N m^{-2} d^{-1} (see appendix, Section II). [42]

Nevertheless, the TAN transport rate was higher than the previous systems when considering the full stacked system. This demonstrates that it is possible to remove nitrogen with this stacked system using bipolar membranes as electrodes.

f) Energy

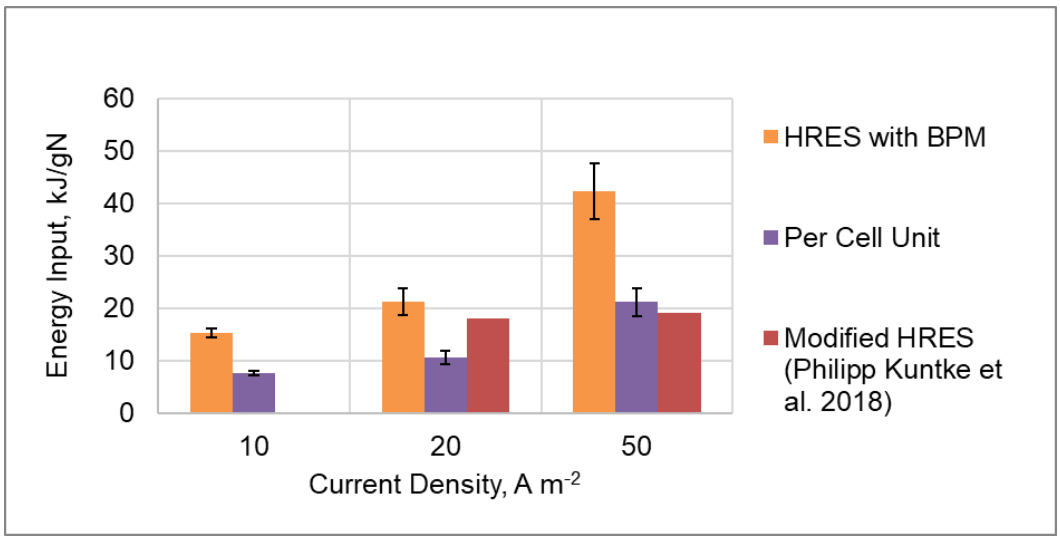


FIGURE 22. Energy input in the HRES with BPM

The energy input of the system was quantified per total energy of the cell (HRES with BPM) and per cell unit. Considering a cell pair, an anode separated from the cathode per an CEM and AEM, forming the feed and concentrate compartments. [41] The energy input was compared with a similar up-scaled system previously study (HRES modified). [42]

An increase of the current density means a higher energy input. At a current density of 20 A m^{-2}, the energy input per cell is lower than the modified HRES, Figure 22. At a current density of 50 A m^{-2}, the energy input is almost identical. Although the removal efficiency of this system was lower compared to previous studies, it requires a similar energy input per cell.

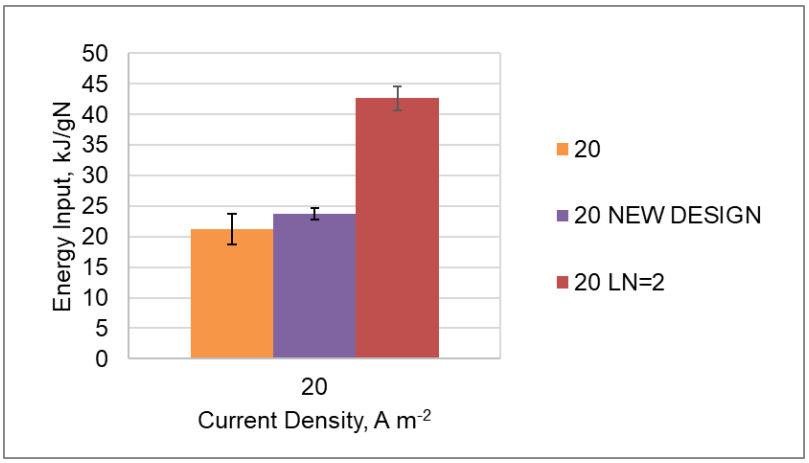


FIGURE 23.Energy Input at 20 A m^{-2} for different design and LN for HRES with BPM

As evident from Figure 23, increasing the spacing resulted in a higher removal (Figure 19) without a significant increase in energy input.

Furthermore, increasing the Load Ratio to 2, the energy input and removal increased.

Even though the energy input is higher for this LN (LN=2), the removal was significantly improved. This indicating a possible compromise of using more energy to achieve better removal when operating with these systems.

Conclusions

This study showed that it is possible to enhance the ammonium recovery in the electrochemical system using a Donnan dialysis cell. Nonetheless, for this specific system, the influence of the Donnan dialysis was not significant.

The system obtained a maximum removal of 88% at an energy input of 14.2 kJ/g_N, demonstrating an improvement against other systems previously studied.

It was also demonstrated that it is possible to use bipolar membranes as electrodes in a stacked system, to recover ammonium. However, to achieve a removal of 80%, it was necessary to improve the design (spacing of the flowing field) and operate the cell at a Load Ratio of 2. This represents an increase of the energy input to 42.6 kJ/g_N.

Nevertheless, the system can be optimized by increasing the re-circulation speeds, reducing the energy demand since more ammonium is recovered.

The 80% removal represents a positive result when comparing to other systems, considering that this *scale-up* treats a larger volume of influent and it is possible to maintain the removal. However, the increase of the Load Ratio for 2 means a higher energy input. It is necessary to reach a compromise to achieve the desired removal without increasing significantly the energy input.

The pH of the solution pumped into the TMCS unit was determinant for the ammonia recovery in both systems, as only volatile ammonia passes through the gas permeable membrane (TMCS unit).

Limitations and Future Work

Time was a limiting factor in this research. Suitable materials and designs had to be found to operate the systems. This led to limited time available for the actual experiments.

Future work is still needed to optimize both systems. For the HRES+Donnan, the addition of a second TMCS unit after the Donnan dialysis cell could potentially prevent the diffusion of ammonia back to the feed. The surface area of the Donnan dialysis cell could be further optimised. All the experiments should be performed in conditions where it is possible to achieve a cathode pH higher than 9, to guarantee an effective extraction.

For the HRES with the bipolar membrane, the main challenge should be a cell design that guarantees a better performance in terms of nitrogen removal and energy demand. Also, it would be interesting to test different Load Ratio values and higher current densities to study the system behaviour. Another important parameter to study is the recirculation of the liquids inside the electrochemical cell. The research indicates an increase of recovery when increasing the recirculation flow.

The finding that the bipolar membrane can be used as electrode in a stacked cell, opens a new possibility of stacking multiple cells capable of threating higher volumes of effluent without increasing significantly the energy demand and equipment cost.

Furthermore, as future work it would be important to combine both systems, bipolar membranes and the Donnan dialysis principle, to remove nitrogen from different effluents. Finally, research is needed with real wastewater streams to demonstrate the capabilities of this technology.

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Appendix

i. Influence of the pH on the recovery

The working principle of the Donnan dialysis was supported by measures feed pH. When increasing the Load Ratio, the feed pH generally decreases, which means more ions were extracted, and consequently a better removal. For a Load Ratio 1.3 the pH decreases severely, proving that almost all the ions were extracted.

When operating with the Donnan cell, the feed pH was higher than during operation without Donnan cell. This result was expected due to the return of co ions (Na+ and K+) that exchange with protons contribute to an increase of the pH..

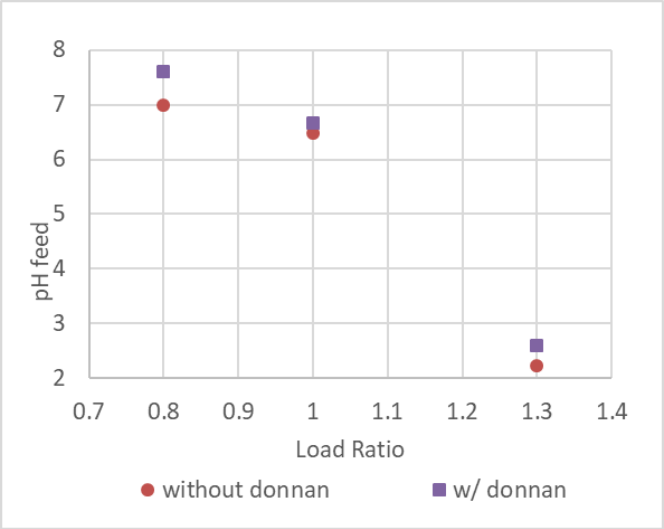

FIGURE A. FEED PH FOR THE HRES AND HRES+DONNAN CELL

ii. Summary of the literature and this study results

TABLE A. ENERGY INPUT, TAN RATE AND REMOVAL FROM DIFFERENT STUDIES

System	LN	j (A/m2)	E_{Input} (kJ/g_N)	Rate ($g_N m^{-2} d^{-1}$)	Removal (%)	Reference
HRES	1.3	20	26.1	151	73	[5]
HRES	0.8	20	9.7	234.3	71	(this study)
	1	20	11.5	211.8	80	
	1.3	20	13.4	175.2	85	
HRES Donnan	0.8	20	10.1	217.3	70	(this study)
	1	20	11.7	213.0	81	
	1.3	20	14.2	175.3	88	
HRES Modified	1.3	20	15.1	141	74	[42]
	1.3	50	19.8	355	63	
HRES BPM	1.3	10	15.2	102.6	54	(this study)
	1.3	20	21.2	195.8	51	
	1.3	50	42.3	417.5	44	
HRES BPM (0.4 cm plates)	1.3	20	23.7	218.7	61	(this study)
	2	20	42.6	246.9	80	
ES (synthetic wastewater)	1	30	60.5	95	41	[54]
ES (synthetic urine)	0.7	30	9.5		53	[55]

iii. Probabilistic test (t-test)

TABLE B. T-TEST TO THE HRES AND HRES+DONNAN RESULTS

Load Ratio	**A**		**std**	**B**		**std**	**dif(A-B)**	**dif(A-B)**	**p≤0.05**
0.8	4560	4590	21.2	1360	1390	21.2	3200	3200	5.13E-04
	4700	4660	28.3	1470	1460	7.1	3230	3200	
	4620	4660	28.3	1320	1330	7.1	3300	3330	
	4690	4680	7.1	1280	1300	14.1	3410	3380	
	4750	4750	0	1270	1270	0	3480	3480	
average		4666	62.6		1345	74.1			
	4630	4640	7.1	1670	1680	7.1	2960	2960	
	4650	4660	7.1	1460	1440	14.1	3190	3220	
	4370	4360	7.1	1420	1420	0	2950	2940	
	4600	4560	28.3	1380	1390	7.1	3220	3170	
	4470	4440	21.2	1360	1360	0	3110	3080	
average		4538	117.7		1458	118.9			
1			std			std	dif(A-B)	dif(A-B)	p≤0.05
	4540	4540	0	1000	999	0.7	3540	3541	0.444
	4570	4580	7.1	892	892	0	3678	3688	
	4550	4550	0	861	864	2.1	3689	3686	
	4590	4600	7.1	854	863	6.4	3736	3737	
	4780	4760	14.1	882	881	0.7	3898	3879	
average		4606	88.9		898.8	54.7			
	4420	4450	21.2	740	739	0.7	3680	3711	
	4470	4470	0	721	730	6.4	3749	3740	
	4460	4450	7.1	743	735	5.7	3717	3715	
	4400	4400	0	725	717	5.7	3675	3683	
	4560	4560	0	748	745	2.1	3812	3815	
average		4464	56.8		734	10.6			
1.3			Std			std	dif(A-B)	dif(A-B)	p≤0.05
	4630	4620	7.1	753	734	13.4	3877	3886	0.976
	4810	4800	7.1	749	721	19.8	4061	4079	
	4660	4690	21.2	709	718	6.4	3951	3972	
	4670	4670	0	658	670	8.5	4012	4000	
	4840	4830	7.1	694	698	2.8	4146	4132	
average		4722	87.3		710	31.3			
	4490	4490	0	588	585	2.1	3902	3905	
	4650	4660	7.1	588	585	2.1	4062	4075	
	4570	4620	35.4	564	560	2.8	4006	4060	
	4610	4640	21.2	560	561	0.7	4050	4079	
	4540	4530	7.1	548	537	7.8	3992	3993	
average		4580	64.9		568	18.0			