

# WALNUT

## D2.7 - Report on Ion exchange and membrane contactors processes and Smart BBF formulation

WP2, T2.6 Ion exchange and membrane contactor process

[Version 1.0 - 07/03/2023]

**Authors:** Guillermo Noriega-Hevia, Alicia González-Míguez and Álvaro Mayor (CETAQUA)

**Website:** [walnutproject.eu](http://walnutproject.eu)

**Twitter:** [@walnut\\_project](https://twitter.com/walnut_project)



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement 101000752.

## Disclaimer

The content of this deliverable reflects only the author's view. Neither the Research Executive Agency (REA) nor the European Commission is responsible for any use that may be made of the information it contains.

## Copyright notice

©2021 WalNUT Consortium Partners. All rights reserved. WalNUT is a HORIZON2020 Project supported by the European Commission under contract No. 101000752. For more information on the project, its partners and contributors, please see the WalNUT website ([www.walnutproject.eu](http://www.walnutproject.eu)). You are permitted to copy and distribute verbatim copies of this document, containing this copyright notice, but modifying this document is not allowed. All contents are reserved by default and may not be disclosed to third parties without the written consent of the WalNUT partners, except as mandated by the REA contract, for reviewing and dissemination purposes. All trademarks and other rights on third party products mentioned in this document are acknowledged and owned by the respective holders. The information contained in this document represents the views of WalNUT members as of the date they are published. The WalNUT consortium does not guarantee that any information contained herein is e-free, or up-to-date, nor makes warranties, express, implied, or statutory, by publishing this document.



## Technical references

Grant Agreement n°	101000752
Project Acronym	WalNUT
Project Title	Closing waste water cycles for nutrient recovery
Project Coordinator	Francisco Corona, PhD FUNDACIÓN CARTIF fraenc@cartif.es
Project Duration	Sep 2021 – Feb 2026

Deliverable No.	D2.7
Dissemination level*	Public
Work Package	WP2 – Technologies for nutrient recovery from waste water streams
Task	T2.6 – Ion exchange and membrane contactors processes
Lead beneficiary	CETAQUA
Contributing beneficiary/ies	Guillermo Noriega-Hevia, Alicia González-Míguez & Álvaro Mayor
Due date of deliverable	28/02/2023
Actual submission date	15/03/2023

v	Date	Author(s)	Reviewers	Comments
0.1	15/02/2023	Guillermo Noriega, Alicia González, Álvaro Mayor	-	
0.2	20/02/2023	Guillermo Noriega, Alicia González, Álvaro Mayor	Edward Someus	Minor changes Relation with other activities
0.3	02/03/2023	Guillermo Noriega, Alicia González, Álvaro Mayor	Miriam Bayers Sander Bruun	Minor changes Typos
0.4	07/03/2023	Guillermo Noriega, Alicia González, Álvaro Mayor		
1.0	08/03/2023	Guillermo Noriega, Alicia González, Álvaro Mayor	Francisco Corona, Sergio Sanz Bedate	Minor changes



## Table of Contents

<b>EXECUTIVE SUMMARY .....</b>	<b>6</b>
<b>1. INTRODUCTION .....</b>	<b>7</b>
1.1. PURPOSE, SCOPE AND TARGET GROUP .....	7
1.2. CONTRIBUTION PARTNERS .....	7
1.3. RELATION TO OTHER ACTIVITIES IN THE PROJECT .....	7
<b>2. STATE OF ART .....</b>	<b>8</b>
<b>3. MATERIAL AND METHODS .....</b>	<b>11</b>
3.1 SETUP .....	11
3.2 FEEDSTOCK CHARACTERISATION.....	12
3.3 ANALYTICAL PROCEDURE.....	12
3.3.1 Pre-treatment selection.....	12
3.3.2 Adsorption/Desorption of N with zeolite.....	12
3.3.3 Lifespan determination .....	13
3.3.4 HFMC recovery system for NH <sub>4</sub> <sup>+</sup> salts production .....	13
3.3.5 PGPB selection and evaluation .....	14
<b>4. RESULTS AND DISCUSSION.....</b>	<b>15</b>
4.1 FEEDSTOCK CHARACTERISATION.....	15
4.2 PRE-TREATMENT SELECTION.....	15
4.3 FLOW-RATE SCREENING TRIALS .....	16
4.4 REGENERANT SELECTION .....	17
4.5 REGENERANT CONCENTRATION .....	18
4.6 LIFESPAN ASSAY .....	18
4.6.1 Cation exchange capacity evolution .....	18
4.6.2 Kinetics evolution.....	19
4.6.3 Cation affinity in zeolite structure.....	20
4.6.4 Pilot plant operation conclusions .....	20
4.6.5 Chemical balance .....	22
4.7 HFMC RECOVERY SYSTEM FOR NH <sub>4</sub> <sup>+</sup> SALTS PRODUCTION .....	22
4.7.1 Feed flow rate effect .....	22
4.7.2 Acid flow rate effect .....	23
4.7.3 Final product concentration .....	24
4.8 PGPB SELECTION AND EVALUATION.....	25
4.8.1 Objective 1: Selection of microorganisms. ....	25
4.8.2 Objective 2: Testing the growth of the selected bacteria in a culture medium based on ammonium salts and struvite to be used as a biofertiliser.....	25
<b>5. NEXT STEPS .....</b>	<b>30</b>
<b>6. CONCLUSIONS .....</b>	<b>31</b>
<b>7. REFERENCES .....</b>	<b>32</b>

## List of Tables

Table 3-1: HFMC assays .....	14
Table 3-2: Fertilisers obtained in the recovery process .....	14
Table 4-1: Feedstock characterisation .....	15
Table 4-2: TSS content depending on the pre-treatment applied .....	15
Table 4-3: Fertiliser final concentrations in each assay.....	24



Table 4-4: PGPB selected.....	25
Table 4-5: Experiment 1 results.....	26
Table 4-6: Results of experiment 2.....	27
Table 4-7: Results of experiment 3 (in bold the best condition for each fertiliser).....	27

## List of Figures

Figure 2-1: Ion exchange scheme .....	9
Figure 2-2: Hollow-fibre membrane contactor scheme.....	10
Figure 3-1: Treatment train setup scheme .....	11
Figure 3-2: Treatment train setup image .....	11
Figure 4-1: V30 tests carried out .....	16
Figure 4-2: Flow rate effect over saturation step.....	16
Figure 4-3: Regenerant effect over the regeneration .....	17
Figure 4-4: NaOH concentration effect .....	18
Figure 4-5: Cation Exchange Capacity (CEC) evolution during the time operation in terms of BV .....	18
Figure 4-6: Ammonium absorbed in the column evolution showing saturation (S) and regeneration (R) steps .....	19
Figure 4-7: Ammonia adsorbed .....	20
Figure 4-8: Percentage of ammonium desorbed.....	20
Figure 4-9: Ammonium adsorbed during each saturation .....	21
Figure 4-10: Ammonium desorbed.....	22
Figure 4-11: Flow rate effect over the membrane performance .....	23
Figure 4-12: Acid flow rate effect on membrane performance .....	24
Figure 5-1: Pilot plant layout.....	30



## Executive Summary

The aim of this task was to study and optimise the operational conditions of the technology proposed in WalLAB for nitrogen recovery, in order to scale-up this technology in further WalNUT activities.

In this regard, several tests were performed concerning ion exchange and membrane contactor technologies.

For the optimisation of the ion exchange technology, optimal location of the pilot plant, pre-treatment of the waste water used (WW), flow rate and regenerant type and concentration were determined. The lifespan of the adsorbent used was also calculated. The pilot plant was decided to be settle in Ourense and operated as follows: 5 µm filtration as pretreatment, 70 mL/min flow rate for adsorption process, which will be stopped once 20 Bed Volume (BV) of WW had been treated, and NaOH 0.35 as regenerant at 100 mL/min for the regeneration process, which will also be stopped after 10 BV of regenerant flow through the column.

For membrane contactor technology optimisation, different types of acid at variable concentrations were tested. Flow rate was optimised maximising the ammonia transfer rate at a flow rate higher than 400 mL/min. The maximum nitrogen content in the product was 29 g N/l which is similar to industrial production.

Finally, different Plant Growth Promoting Bacteria (PGPBs) were tested to produce a SMART fertiliser by blending the recovered ammonium salt, recovered struvite with the following bacteria species: *Pseudomonas putida*, *Bacillus megaterium*, *Azospirillum brasilense* and *Pseudomonas aeruginosa*.

**Keywords:** Smart BBF, nitrogen recovery, ion exchange, hollow-fiber membrane contactor, biobased fertiliser.



# 1. Introduction

## 1.1. Purpose, scope and target group

The aim of this task is to develop a system for ammonium salt recovery from urban WW and sewage sludge, and to transform recovered nutrients into Smart biobased fertilisers (BBFs) by incorporating Plant Growth Promoting Bacteria (PGPB).

The system for N recovery will consist of an ion exchange process with zeolites coupled to membrane contactors. The ion exchange process will be tested at laboratory scale with different urban WW and sewage sludge provided by VIAQUA from the WWTP operated by them.

## 1.2. Contribution partners

CETAQUA is the lead and the only partner involved in this task.

Table 1: Contribution of partners

Partner	Contribution
CETAQUA	Design and operation the pilot and analysis of the results

## 1.3. Relation to other activities in the project

This deliverable is aligned with task 3.6 which created the foundation which is useful for to the scale up of the technology. However, both tasks have relations to tasks from WP4 due to the analysis of the fertilizer in soil as well as to WP5 in terms of the data production to evaluate the impact and footprint of the technology and the fertiliser obtained in that WP.

Table 2: Relation to other activities in the project

Task	Description
3.6	Design, construction, and installation of Pilot plant 5 are going to be based on these results.
4.3	This work shows the first step to produce the biofertilisers which application are going to be demonstrate.
5.1	Development and implementation of data compilation strategy, literature review, shortlisting of technologies for further analysis, alignment of scope
5.2	Provide technical data for the inventory analysis, modelling environmental emissions and soil fertility improvements and upscaling of technology performances
6.2	Policy recommendations for the BBF regulatory, market and user acceptance
7.1	Identification of BBF business opportunity
7.2	Develop WWT business model



## 2. State of art

Population growth and the uncontrolled use of resources in the last decades force us to develop new sustainable alternatives to face the increase of this consume. For that reason, new alternative sources of resources were analysed, identifying water and waste water as one of the most important. Both act as a sink in nature and in human agglomeration for lots of nutrients and compounds. One of the compounds that appears in waste water in remarkable concentrations is nitrogen, mainly as urea in urban agglomerations and as other nitrogen forms due to its use in agriculture as fertilisers, because it is an essential chemical element for the growth and development of plants.

This nitrogen fertiliser production is commonly carried out by the Haber-Bosch process which uses atmospheric nitrogen and the hydrogen of natural gas as main sources. It is an electricity-intensive and natural gas dependent process. It is estimated that this process has an energy consumption of  $6.4 \cdot 10^{12}$  MJ/year, which is equivalent to the energy consumed of 80,000,000 people in terms of global warming (Razon, 2014). Because of that, it is needed to develop new, more sustainable ways of nitrogen fertilisers production.

In this framework the use of waste water as a source of nitrogen appears as a very promising alternative which increases the nutrient circularity and reduces the impact of Haber-Bosch nitrogen fertiliser production. For that purpose, different technologies have been developed in the last decades: ion exchange, stripping, bioelectrochemical systems, struvite crystallisation or membrane technologies.

In this work, the treatment train proposed included two main steps: an ion exchange unit, to concentrate the ammonium with zeolites and a membrane contactor unit for nitrogen recovery as a marketable product.

Ion exchange is a physico-chemical process which consists of the exchange of ions between an adsorbent and the treated stream. This adsorbent can be a natural zeolite, mainly clinoptilolite, or a synthetic resin. This adsorbent has a microporous structure which offers a high exchange capacity in a reduced space (Lubensky et al., 2019). This technology can be applied as a technology for nitrogen recovery or as to concentrate the ammonia, as in this case. Zeolites are a natural aluminosilicate microporous adsorbent able to capture the ammonium of the feed solution by ion exchange. After that, a regenerant solution, mainly NaOH or NaCl, is put in contact with the zeolite to revert the initial condition favouring the release of ammonium. However, due to the high pH of this solution, ammonium is present as free ammonia. Figure 2-1 shows a scheme of the process. This technology presents high efficiency, operation simplicity and low costs. However, its costs depend on the reagent used in the regeneration process (Vaneekhaute et al., 2017).





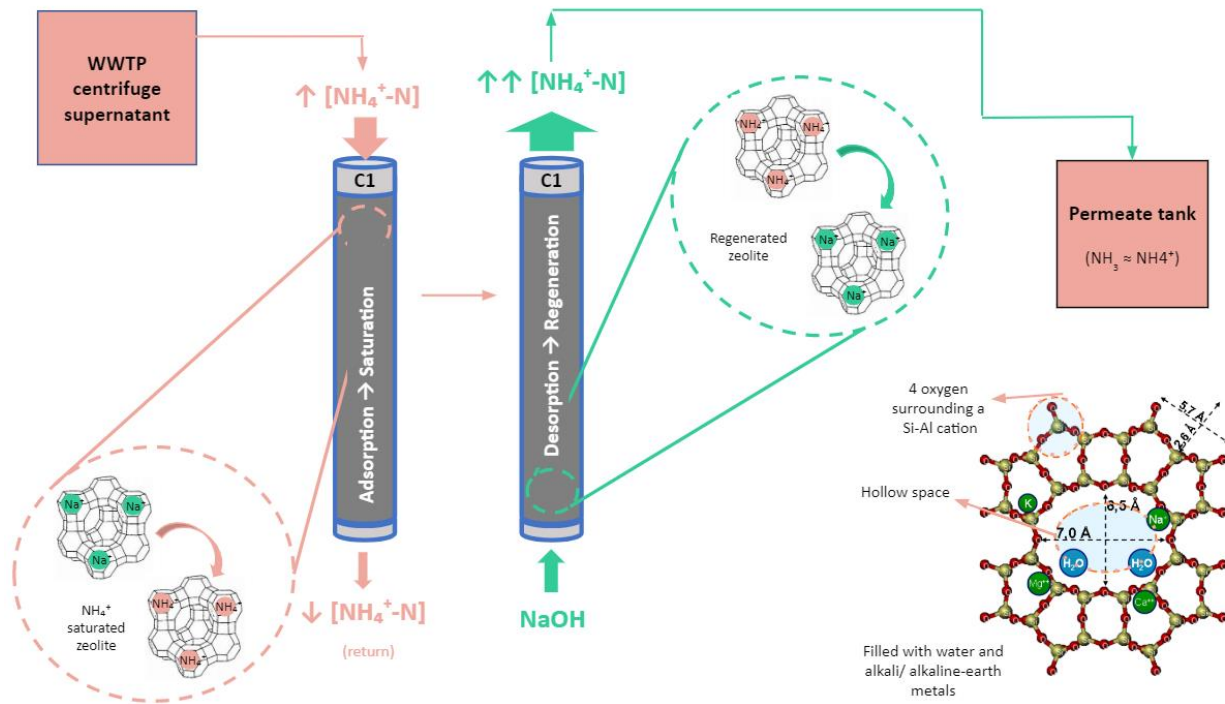


Figure 2-1: Ion exchange scheme

Regarding membrane technologies, hollow-fibre membrane contactor (HFMC) is one of the most promising technologies for nitrogen recovery. It is a gas-permeable membrane, normally made of polypropylene, which offers a high contact surface between two streams. Due to its hydrophobicity only, gaseous substances are able to cross the membrane, so, in case of ammonia, the ammonia rich solution should have a high pH to transform ammonium to free ammonia gas by chemical equilibrium.

Once free ammonia crosses the membrane by diffusion, it is captured by an acid solution, usually sulphuric, phosphoric or nitric acid, which will determine the marketable salt obtained: ammonia sulphate, ammonia phosphate or ammonia nitrate, respectively. Due to the passing of free ammonia through the acid solution, the proton concentration is decreasing, obtaining at the end of the process a salt dilution at neutral pH. When the pH is near neutral, ammonia transfer decreases dramatically because the driving force is minimal at that pH.

At the same time, the pH in the nitrogen rich solution also varied. Once the free ammonia gas crosses the membrane, the ammonia-ammonium equilibrium is modified: the ammonium is transformed into ammonia, releasing protons and decreasing the pH. This fact provokes a reduction in the free ammonia concentration which can stop the process. Because of that, a pH higher than 8.6 is needed to maintain the driving force (Noriega-Hevia et al., 2020). Figure 2-2 shows a scheme of the technology.

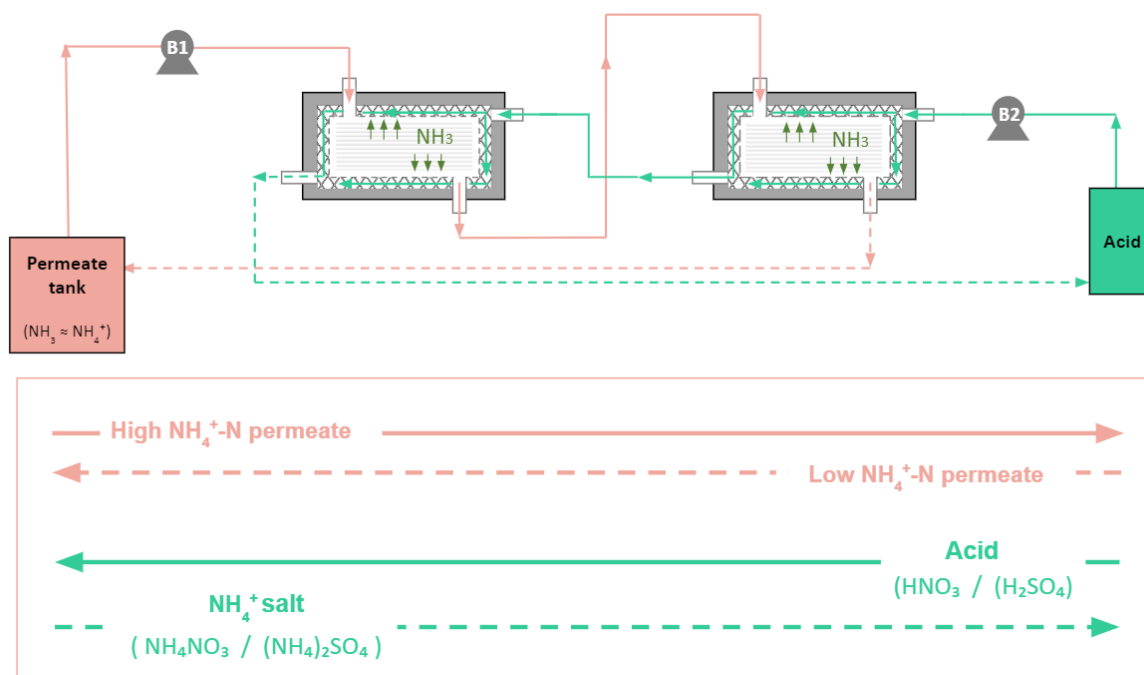


Figure 2-2: Hollow-fibre membrane contactor scheme.

The main advantages of this technology are:

- Low energy consumption given that the driving force is the ammonia concentration gradient between both sides of the membranes
- Low space requirements
- Modularity
- High ammonia selectivity because its hydrophobicity only permits the passage of gas substances.
- High quality products because the hydrophobic character of the membrane prevents the passage of heavy metals or PTFEs or OMPs to the final product.
- High range of ammonia concentration in the feedstock.

Although the ammonia content of the feed solution has no influence on the recovery efficiency of the membrane, it has important economic implications: The lower the ammonia concentration in the feed, the higher the reagents costs to increase the pH per gram of ammonia recovered. Because of that, it is necessary to select the most concentrated ammonia stream of the WWTP, which is the anaerobic supernatant. The ammonia concentration of this stream normally varies from 600 to 800 ppm of  $\text{NH}_4^+\text{-N}$ . However, a previous step of ion exchange with natural zeolites is included in the treatment train to reduce costs and optimised the recovery process.

Although, the ammonium rich solution is a marketable product, **the aim of this task is not only to optimise the treatment train for nitrogen recovery applying zeolites and hollow-fibre membrane contactors, but also to create an added-value fertiliser.** For that reason, in this task the first test to design a Smart Bio-Based Fertiliser (Smart BBF), is also included.

A Smart BBF is a fertiliser that allows to control the rate, timing and duration of nutrient release. In our case we are going to blender the ammonium salt recovered with recovered struvite and a selection of Plant Growth Promoting Bacteria (PGPB) to modify the nutrient release



## 3. Material and methods

### 3.1 Setup

In order to test the technologies proposed for N recovery a two-units set up was built in Cetaqua's facilities. The nitrogen recovery took place in two different steps, which corresponded with two different units in our pilot setup (shown in Figure 3-1):

- Unit 1: Adsorption/desorption of  $\text{N-NH}_4^+$  with zeolites.
- Unit 2: Membrane recovery system as  $\text{NH}_4^+$  salts.

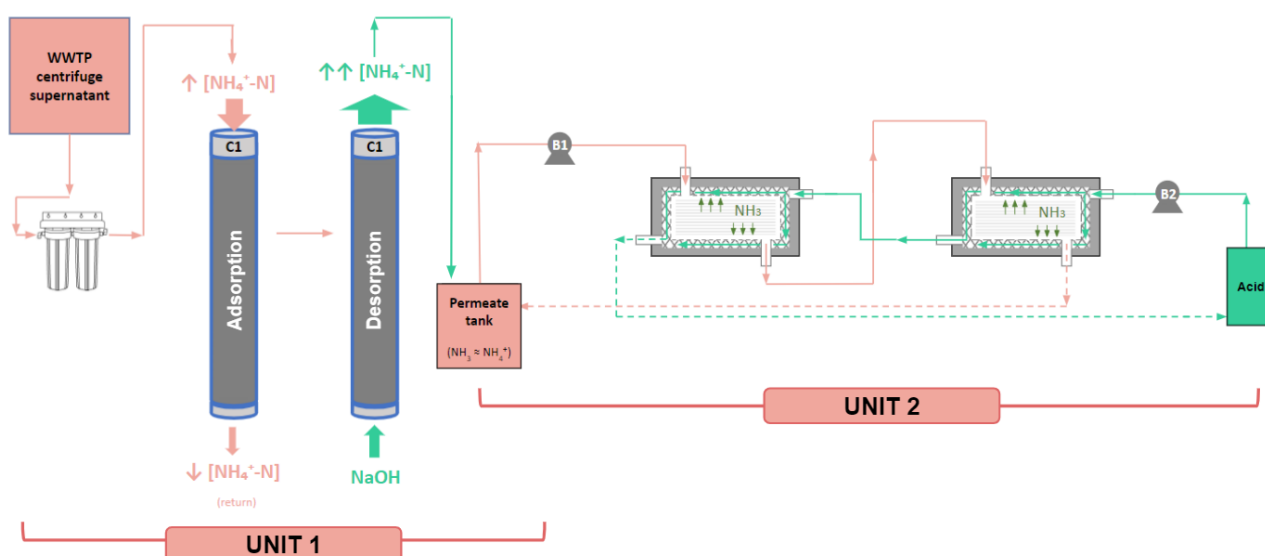


Figure 3-1: Treatment train setup scheme

Real setup layout, the one built in Cetaqua's laboratory, is shown in Figure 3-2.

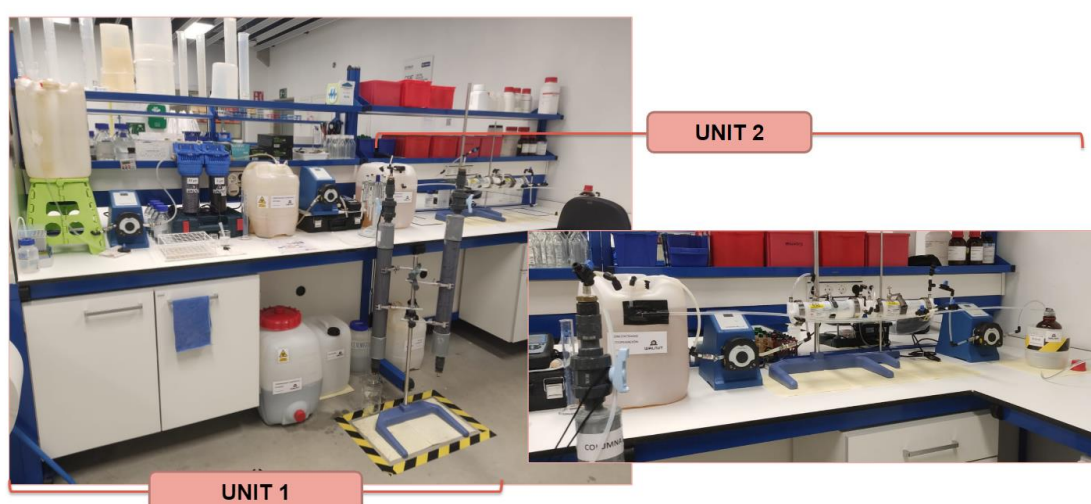


Figure 3-2: Treatment train setup image

### 3.2 Feedstock characterisation

Two different anaerobic digestion supernatants from two different Waste Water Treatment Plants (WWTP) were characterised in order to select the best location for subsequent pilot assays

The feedstock used in adsorption/desorption assays was characterised before each assay in terms of: pH, conductivity, alkalinity, COD, P,  $\text{PO}_4^{3-}\text{-P}$ , N,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{SO}_4^{2-}\text{-S}$  and total suspended solids (TSS). Occasionally, total solid (TS) were also analysed.

For pH and conductivity measurements PHC101 and CDC401 Hach™ sounds were used respectively. For analyte measurements Hach™ kits LCK014, LCK350, LCK338, LCK340, LCK302, LCK303 and LCK153 were used.

The decantability of the feedstock was also evaluated by the V30 test, it represents the volume of sludge settled in 30 minutes

### 3.3 Analytical procedure

#### 3.3.1 Pre-treatment selection

In order to determine the need of waste water (WW) pre-treatment, decantation tests were conducted. 1L Imhoff sedimentation cones were used for this purpose. Waste water used in adsorption trials was sedimented for 30 minutes, samples were taken from the upper part of the cone, and then total suspended solids (TSS) were determined using 0.45 mm pore size filters. Microfiltration was also tested as a pre-treatment by using a set of two consecutive filters (20  $\mu\text{m}$  and 5  $\mu\text{m}$ ).

TSS values were compared between not-treated WW, supernatant of the decanted WW and filtered WW.

#### 3.3.2 Adsorption/Desorption of N with zeolite

Adsorption and desorption of N were performed in two 69x6.6 cm polyvinyl chloride columns filled with zeolite 2- ZEOCAT 0-1 mm. Total volume of this column was 2360  $\text{cm}^3$ .

After the columns were built and filled with zeolite, activation of those zeolites was performed. The activation process consisted in soaking the zeolites in 0.4M NaOH solution for 24h. Then, zeolites were washed with water and adsorption/desorption trials could be started.

Columns were filled with 1970.2 g for these trials and the calculated BV was 1.06L.

Samples of water that flowed out of the column, both in adsorption and desorption assays, were taken each 5-15 minutes, respectively, and  $\text{N-NH}_4^+$  was analysed.  $\text{NH}_4^+\text{-N}$  measurements were done using Hach LCK302 and LCK303 kits.

##### 3.3.2.1 Adsorption flow rate screening trials

Firstly, flow rate screening tests were performed in order to determine flow rate effects on adsorption capacity. Several flow rates were tested: 135, 75, 60 and 30 mL/min. All of them were performed in duplicate. Water flow took place from top to bottom through the column.

The used pumps were calibrated for flow rate adjustment. Nevertheless, the flow rate was manually adjusted to ensure the highest possible accuracy.



### 3.3.2.2 Desorption of N: regenerant selection

Two different types of regenerants were tried out: 0.35 M NaCl and 0.35 M NaOH. In both cases, regeneration took place bottom-up at 88 mL/min. Kinetics and recovery capacity were compared.

### 3.3.2.3 Desorption of N: regenerant concentration

After selecting NaOH as the best regenerant of all those tested, several concentrations of NaOH were tested: 0.1 M, 0.2 M, 0.3 M, 0.35 M and 0.4 M. All of them performed were in duplicate. The main goal was to obtain the maximum concentration of  $\text{NH}_4^+\text{-N}$  in the obtained permeate as quickly as possible, in order to use that concentrated permeate in the HFMC recovery system for  $\text{NH}_4^+$  salt production.

### 3.3.3 Lifespan determination

In view of the results seen in adsorption/desorption trials, lifespan determination assay conditions were selected. Several top to bottom adsorptions and bottom-up desorption experiments were carried out at 70 mL/min flow rate for adsorption and 100 mL/min flow rate and 0.35 M NaOH for regeneration. The aim of this test was to determine that the time that  $\text{NH}_4^+\text{-N}$  adsorption capacity of the zeolite, expressed in terms of  $\text{NH}_4^+\text{-N}$  absorbed per g of zeolite is constant.

Tests was considered over when a significant decay of the cation exchange capacity (CEC) was observed.

The amount of zeolite contained in the column during this trial was 2296.4 g and the calculated BV was 0.8 L.

### 3.3.4 HFMC recovery system for $\text{NH}_4^+$ salts production

Hollow-fibre membrane contactors (HFMC) used as shown in Figure 3-2 in section 3.1., were 3M™ Liquid-Cel™ EXF Series polypropylene Membrane Contactors with a unitary membrane surface of 1.4 m<sup>2</sup>. Pumps used were calibrated and several conditions were tested. All the tests were carried out by duplicate.

In Table 3-1 the assays carried out are described. Assays A1 to A4 are done to determine the effect of flow rate on the recovery rate, attending mainly to the possible effect of turbulence over the ammonia transfer. The aim of Test A5 was to determine whether the application of different flow rates on both sides of the membrane has a significant effect on the recovery process. Assays A6 and A7 are focused on the obtention of as much concentrated salt as possible. Because of that, different acid concentrations were applied. Finally, assay A8 maintained the same conditions but the acid concentration varied during the experiments because more acid was added when the acid solution pH was near neutral in order to maximise the nitrogen content of the product.

The last aspect evaluated was the different acid solutions used in order to obtain different salts and, at the same time, observe if this fact has some effect on the membrane performance.



Table 3-1: HFMC assays

Assay	Acid used	Acid concentration (M)	Permeate flow rate (mL/min)	Acid flow rate (mL/min)
A1	H <sub>2</sub> SO <sub>4</sub>	0.096	200	
A2			400	
A3			600	
A4			800	
A5			800	400
A6	HNO <sub>3</sub>	0.096	400	
A7		0.2	400	
A8		Variable	400	

### 3.3.5 PGPB selection and evaluation

The selection of bacterial strains was made according to bibliographic information and the previous experience of CEBAS-CSIC working with Plant Growth Promoting Rhizobacteria (PGPR). The selected bacteria were obtained from the Spanish Type Culture Collection.

Three experiments were carried out in order to determine the optimal mixture of PGPR and ammonium salts. For all three experiments, an inoculum comprising the aforementioned bacteria was prepared with a known optical density.

Three fertilisers (ammonium nitrate salts) with different contraptions and pH were used for the experiments (see Table 3-2). The used fertilisers were the following: Fertiliser 1, Fertiliser 2 and Fertiliser 3.

Table 3-2: Fertilisers obtained in the recovery process

Fertilizer	pH	EC (mS/cm)	NH <sub>4</sub> <sup>+</sup> (mg/L)
1	8.24	166	29100
2	1.31	132	19700
3	0.97	180	23600

The first experiment attempted to directly mix the PGPR with ammonium salts at different dilution rates. The second experiment followed the same logic but included struvite as P source. The last experiment included different fertiliser dilutions, which were amended with the culture medium Luria Bertani LB at two different rates. For all experiments, the optical density was measured after 5-7 days under shaking conditions at room temperature.



## 4. Results and discussion

### 4.1 Feedstock characterisation

As described in D2.8, the WWTP located in Ourense was selected as supplier for the WW for the experiments, mainly due to its higher N content than the other WWTP evaluated. The stream chosen was the anaerobic digestion supernatant. During work package trials, sixteen aleatory samples were taken from Reza WWTP (Ourense) from January 2022 to February 2023, and then characterised in terms described in section 3.2. Results are shown in Table 4-1.

Table 4-1: Feedstock characterisation

		Average	Standard deviation	
pH		7.96	±	0.77
CE	mS/cm	9.24	±	0.83
Alkalinity	mg CaCO <sub>3</sub> /L	6328.00	±	4263.73
COD <sub>t</sub>	mg/L	2192.85	±	596.32
COD <sub>s</sub>		1637.88	±	277.55
P <sub>t</sub>		17.04	±	5.46
PO <sub>4</sub> <sup>-3</sup>		9.91	±	4.32
N <sub>t</sub>		1477.35	±	201.18
NH <sub>4</sub> <sup>+</sup>		1248.88	±	175.54
NO <sub>3</sub> <sup>-</sup>		7.01	±	2.13
SO <sub>4</sub> <sup>-2</sup>		106.90	±	36.78
TSS	g/L	0.64	±	0.13

### 4.2 Pre-treatment selection

The need for pre-treatment was determined based on the post-treatment total suspended solids (TSS) value. Results are shown in Table 4-2.

Table 4-2: TSS content depending on the pre-treatment applied

Sample	TSS (g/L)
Not treated	0.82±0.014
Decanted	0.78±0.014
Filtrated	0.51±0.000





The WW used was characterised for a low decanting capacity (Table 4-2). Decantation for 30 minutes only reduced TSS in WW by 5%, while filtration eliminated 38% of the TSS. Filtration was, thus, selected as the pre-treatment method.



Figure 4-1: V30 tests carried out

### 4.3 Flow-rate screening trials

CEC during 75 (0.071 BV/min), 60 (0.057 BV/min) and 30 (0.028 BV/min) mL/min trials were similar (13.7, 12.81 and 13.47 g  $\text{NH}_4^+\text{-N}$  /g zeolite, respectively), while operating at 135 (0.127 BV/min) mL/min, which reduces the hydraulic retention time (HRT), considerably reduced the adsorption capacity to 8.60 g  $\text{NH}_4^+\text{-N}$ /g zeolite. Given these results, the shorter HRT (135 mL/min flow-rate) was discarded.

Furthermore, Figure 4-2 shows that 0.071 BV/min kinetics reach a high saturation in shorter period of time. This optimises the saturation of the zeolite by using a smaller amount of WW (represented in Figure 4-2 as bed volumes, BV) without compromising the maximum adsorption capacity.

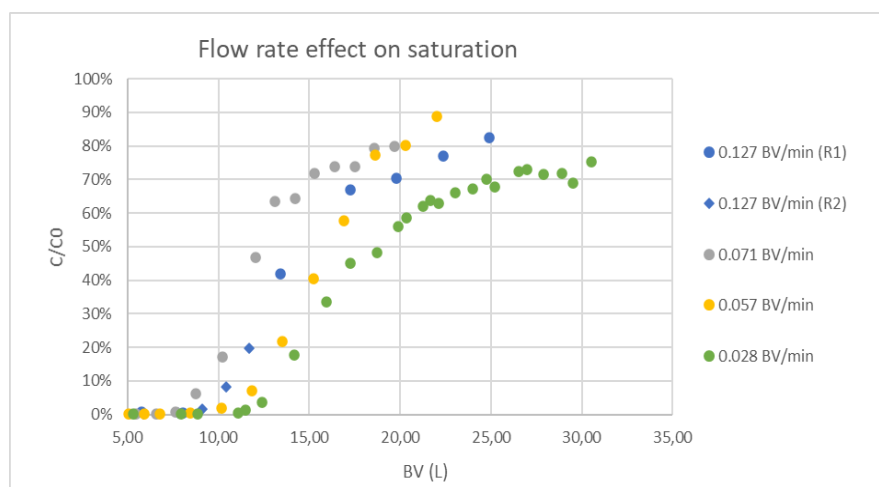


Figure 4-2: Flow rate effect over saturation step





According to 30 mL/min kinetics shown in Figure 4-2, this condition was not cost-effective, as it needed a huge amount of WW volume to achieve saturation of zeolite (where maximum adsorption capacity is ensured). This would translate into considerable  $\text{NH}_4^+\text{-N}$  losses during the adsorption process. What's more, 0.028 BV/min condition needed almost 17 hours to achieve saturation, which is not practicable to perform lifespan assays. For these reasons, 30 mL/min condition was discarded too.

75 mL/min implies a residence time in the column (TRH) of 13 mins. For adsorption technologies, TRHs lower than 10 min are not recommended because this is not enough to retain the compounds of interest. Thus 75 mL/min (0.071 BV/min) was selected as the best condition to recreate in lifespan assays and pilot trials, as it allows to reduce de HRT without compromising adsorption capacity. This flow will be used in the design of the pilot plant.

#### 4.4 Regenerant selection

Figure 4-3 shows recovery kinetics depending on the regenerant used. We can observe how by the time 10 BV of NaCl 0.35 had flowed through the column the maximum recovery capacity was achieved for NaCl, while this capacity continued rising when NaOH 0.35M was used.

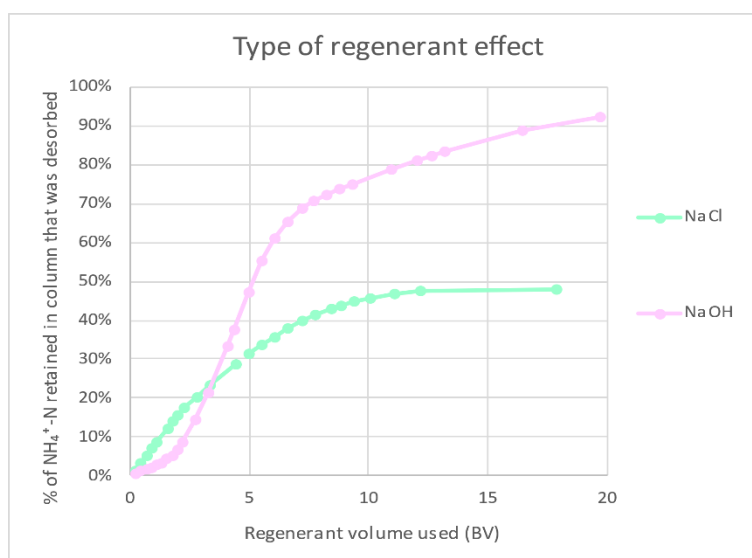


Figure 4-3: Regenerant effect over the regeneration

Maximum recovery capacity achieved by using NaCl as regenerant was 48%, while using NaOH as regenerant recovered 92% of the ammonia retained in the column. NaOH was selected as the regenerant used for subsequent assays.



## 4.5 Regenerant concentration

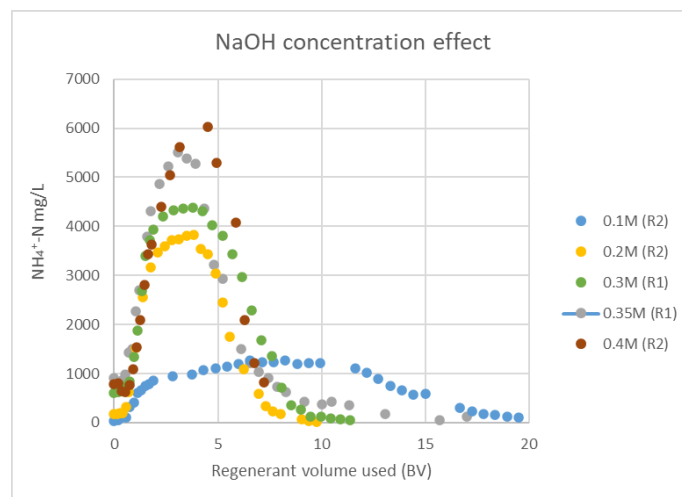


Figure 4-4: NaOH concentration effect

As shown in Figure 4-4, NaOH 0.1M test obtained the flattest curve, which means this leads to a low permeate concentration to be used in HFMC assays. NaOH 0.4M obtained best results, because if we stopped pilot assays by the time 5 BV, we would obtain highest  $\text{NH}_4^+\text{-N}$  concentration in the permeate. However, as this was considered too aggressive for long-term recycling of zeolite, the selected conditions for lifespan trials were 0.35M.

## 4.6 Lifespan assay

Lifespan assays were performed from 08/11/2022 to 07/02/2023 and there was one noteworthy event that could have affected the results: a bed breakup during the sixth regeneration performed. However, results and conclusions deduced from these experiments were large, so section 4.6 will be itemised.

### 4.6.1 Cation exchange capacity evolution

The cation exchange capacity (CEC) was measured as the amount of  $\text{NH}_4^+\text{-N}$  adsorbed per gram of zeolite by the time adsorption-desorption equilibrium was achieved in the experiment. The evolution of CEC is shown in Figure 4-5.

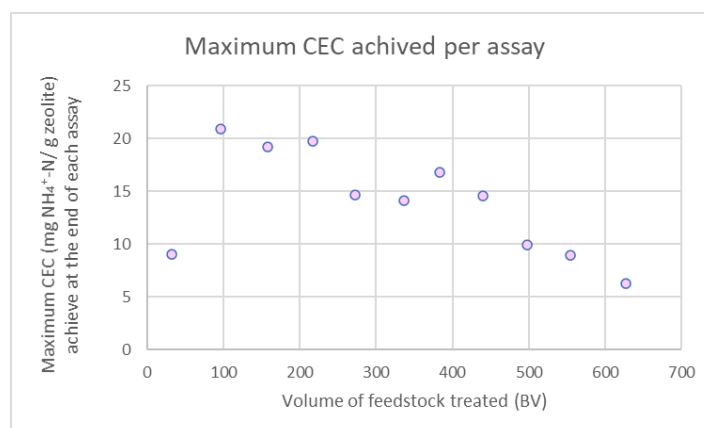


Figure 4-5: Cation Exchange Capacity (CEC) evolution during the time operation in terms of BV



Each point represented in Figure 4-5 corresponds to an adsorption assay. Accumulated BV shows the amount of WW that had flowed through the column when that CEC value was achieved. CEC was expected to be higher in during the first adsorption (S1), but two different reasons might had caused the results obtained:

- Activation of zeolite at the beginning of the assay was only partially ineffective. Soaking of zeolite for its activation took place inside of the column and probably a large amount of zeolite did not get in contact with NaOH during the process. This would be solved after the first regeneration, where non-activated zeolite should have finished activation in contact with NaOH. This will be in compliance with what is seen in Figure 4-6, which shows how first regeneration assay did not recover as much  $\text{NH}_4^+\text{-N}$  as expected. In this case,  $\text{Na}^+$  cations probably bound to non-activated zeolite instead of replacing  $\text{NH}_4^+$  cations in the aluminosilicate structure.
- Washing of zeolite after activation left the adsorbent in alkaline conditions. This did not happen in subsequent assays, where pH was lowered after each regeneration process.

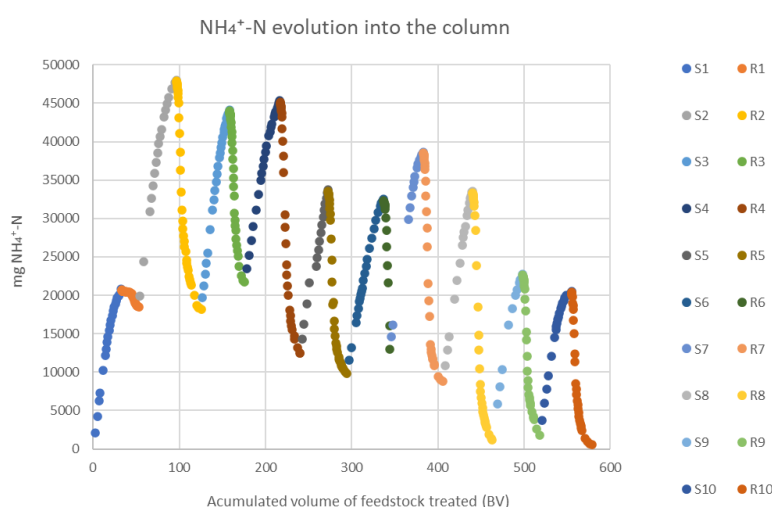


Figure 4-6: Ammonium absorbed in the column evolution showing saturation (S) and regeneration (R) steps

The increase of CEC in assay seven is justified by the fact that the bed breakup during the sixth regeneration. The CEC calculation was done considering the amount of  $\text{NH}_4^+\text{-N}$  already retained in the column at the beginning of each adsorption process, this means that if recovery balance from sixth regeneration was underestimated, CEC from seventh adsorption will be overestimated. This probably happened during the repair of the zeolite bed inside the column, where non-measurable nitrogen losses were expected. These losses underestimated the recovery capacity of the regeneration process and, consequently, overestimated CEC capacity from the seventh adsorption.

Considering CEC from seventh assay (S7) was overestimated, Figure 4-5 and Figure 4-6 show a clear decrease in concurrently accumulated BV, as expected.

#### 4.6.2 Kinetics evolution

On the other hand, adsorption kinetics decrease as adsorption/desorption cycles increase. This can be seen in Figure 4-7, where we can see how adsorption process 2 and 3 (S2 and S3) adsorbed a higher amount of  $\text{NH}_4^+\text{-N}$  and faster than adsorption process 4-6 (S4-S6). Likewise, S10 performed the slowest adsorption process and retained the lowest amount of  $\text{NH}_4^+\text{-N}$  of all the assays done. Kinetics from S1 was not considered because of the probable unsatisfactory zeolite activation process mentioned above (section 4.6.1), that could probably have affected the adsorption process.



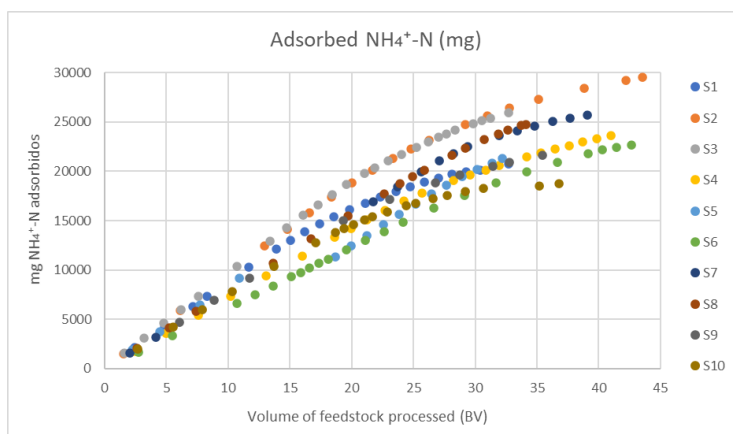


Figure 4-7: Ammonia adsorbed

#### 4.6.3 Cation affinity in zeolite structure

Figure 4-8 shows how the  $\text{NH}_4^+\text{-N}$  recovery process performed according to the whole amount of  $\text{NH}_4^+\text{-N}$  retained in the column. Again, regeneration process one (R1) will not be considered for reasons mentioned in section 4.6.1. Regeneration process 6 (R6) is not shown due to its interruption owing to bed break.

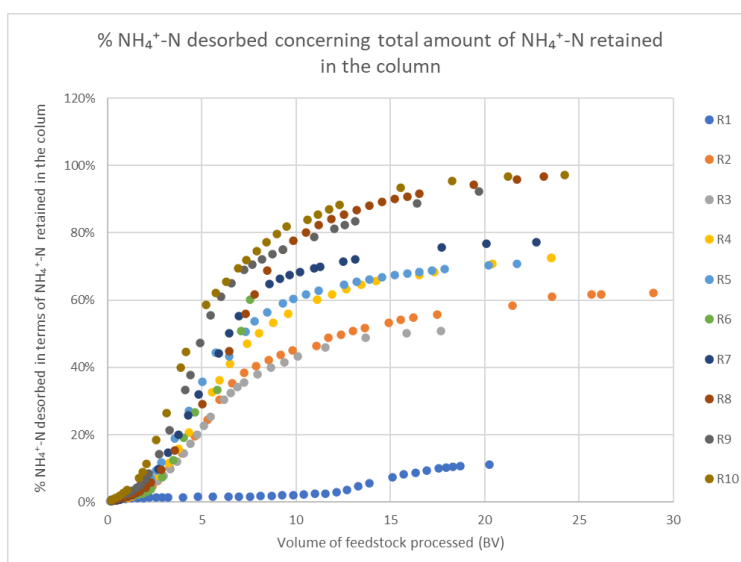


Figure 4-8: Percentage of ammonium desorbed

According to Figure 4-8 we could determine the amount of  $\text{NH}_4^+\text{-N}$  retained in the column after finishing the desorption process performed as shown:  $\text{R2-3} > \text{R4-5} > \text{R6-7} > \text{R8-9} > \text{R10}$ . In every regeneration (desorption) process, the regenerant flow was stopped when achieving a concentration  $< 250 \text{ NH}_4^+\text{-N ppm}$ .

This could guide us to the conclusion that, at the beginning of the trials,  $\text{NH}_4^+$  was retained into the zeolite structure with a higher affinity. This affinity decreased as the adsorption/desorption cycles happened, making it easier to recover  $\text{NH}_4^+$  with the same amount of NaOH used.

#### 4.6.4 Pilot plant operation conclusions

Data collected during lifespan assays was also used to determine some of the pilot plant future operation conditions. Concerning adsorption conditions, it has been already determined that  $70\text{-}75 \text{ mL/min}$  was the optimal flow rate condition, as it allows to reduce the HRT, which will increase the amount of WW potentially treated, without compromising CEC.



In addition, these assays also were useful to determine the BV range where the adsorption process should be stopped. Figure 4-9 normalised the evolution of the zeolite saturation to the amount of  $\text{NH}_4^+\text{-N}$  adsorbed during each individual adsorption process. This allows us to study the saturation performance considering loss of CEC during the assays.

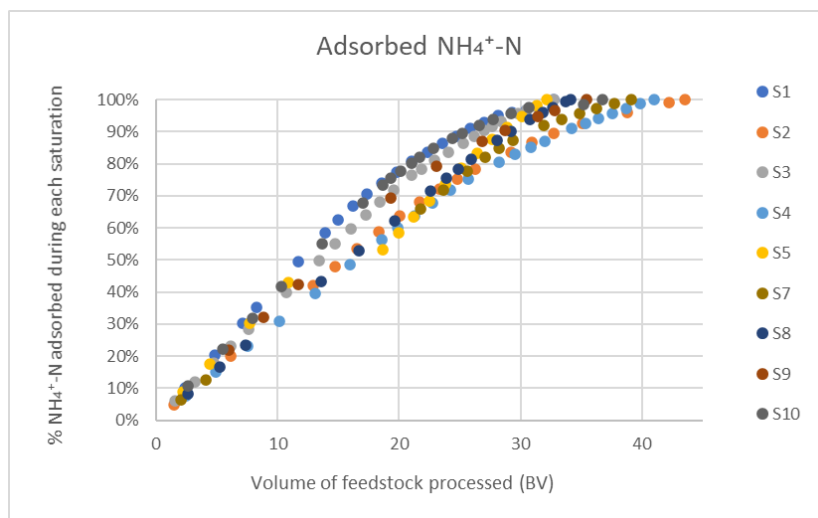


Figure 4-9: Ammonium adsorbed during each saturation

Figure 4-9 shows how in most of the adsorption trials performed, by the time 20BV of WW had flowed through the zeolite, 50% of the total amount of  $\text{NH}_4^+\text{-N}$  that could be adsorbed during the whole process had already been retained in the column. What is more, by the time 20 BV of WW were processed, all of the adsorption trials achieved 50-80% of its zeolite saturation capacity. As shown in Figure 4-2, as the zeolite saturation process happened, the  $\text{NH}_4^+\text{-N}$  lost in rejected water (water that flows out of the column during the adsorption process) increased. After the mentioned 20BV had been processed, the amount of  $\text{NH}_4^+\text{-N}$  lost in the rejected water was considered not-cost-effective. In pilot plant trials, the adsorption process is recommended to be stopped when 20 BV of WW has been treated or at an equivalent  $\text{NH}_4^+\text{-N}$  concentration in the effluent reach values of 250 mg  $\text{NH}_4^+\text{-N/L}$ .

Same conclusions can be drawn by studying the regeneration trials performance, shown in Figure 4-10. The first regeneration (R1) would not be considered as mentioned in section 4.6.1 and subsequent ones. Once again, recovery performance is normalised to the amount of N- recovered in each individual desorption process to observe data unaffected by the loss of affinity mentioned in section 4.6.3.

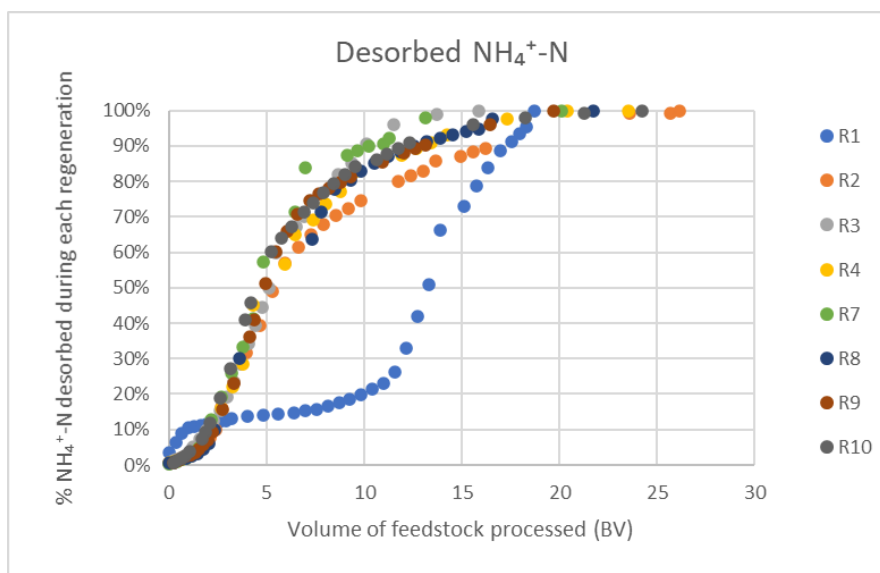


Figure 4-10: Ammonium desorbed

Figure 4-10 shows how, by the time 10 BV of regenerant had flown through the column, 75-90% of the  $\text{NH}_4^+\text{-N}$  recovered in each desorption assay had already been recovered. This means that by stopping the regeneration process after 10 BV of regenerant maximum  $\text{NH}_4^+\text{-N}$  concentration will be ensured in the permeate concentrate obtained, that will be used afterwards in HFMC assays.

#### 4.6.5 Chemical balance

Before the CEC decrease was observed in zeolites used for lifespan assays, 297 BV of WW had been treated. This 297 BV involved 240 g  $\text{NH}_4^+\text{-N}$  adsorbed, of which 96% were recovered. This means that depletion of CEC was observed after 104 mg  $\text{NH}_4^+\text{-N}$  was adsorbed per gram of zeolite.

775.05 mg  $\text{NH}_4^+\text{-N}$  were recovered from each BV treated and for that purpose 58.30 moles of NaOH were used. This means that 3.41 moles of NaOH were needed to recover 1 mol of  $\text{NH}_4^+$ , far away from the theoretical value of 1 mol NaOH/mol  $\text{NH}_4^+$ . This might be due to the presence of another cation in the WW.

Another option that could influence the balance is the creation of preferential paths in the column. This could influence the adsorption capacity, as not all zeolites are in contact with the stream, and the regeneration, preventing the release of the ammonium.

### 4.7 HFMC recovery system for $\text{NH}_4^+$ salts production

#### 4.7.1 Feed flow rate effect

The first tests carried out were relative to the flow rate effect over the recovery process. In Figure 4-11 are shown the assays A1 to A4 in which the feed flow rate varies from 200 mL/min to 800 mL/min.



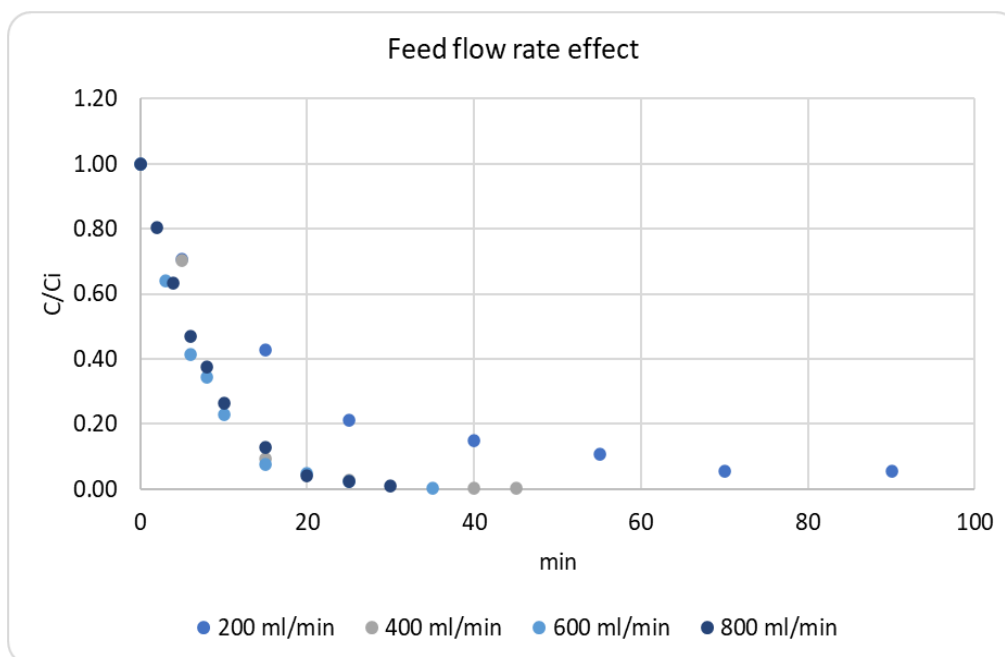


Figure 4-11: Flow rate effect over the membrane performance

The results obtained show that at lower flow rates the recovery rate is slower, needing 90 minutes to remove more than 95% of the ammonium in the feed (for 200 mL/min). However, at higher feed flow rates, the differences are lower. Applying flow rates between 400 mL/min and 800 mL/min, the evolution is similar, and the experiments end around 40 minutes for a flow rate of 400 mL/min and 30 minutes for a feed flow rate of 800 mL/min. This fact could be related to the turbulence created inside the fibre due to the higher flow rate. This turbulence reduces the boundary layer of the fibre reducing its resistance to the pass of molecules from one side to the other. Once the feed flow rate increases, this resistance is reduced until it reaches the minimum value. At this moment, a higher feed flow rate has no influence on the recovery rate. It is important to remark that all tests achieved recovery efficiencies higher than 95% of ammonia nitrogen.

#### 4.7.2 Acid flow rate effect

Once the feed flow rate had been evaluated, the next step was to evaluate the influence of the application of different flow rates to the feed solution and the acid. Figure 4-12 represents A4 and A5. In A4 the same flow rate (800 mL/min) was applied in both streams but, in case A5 a flow rate of 800 mL/min was applied for feed solution and 400 mL/min to the acid one.

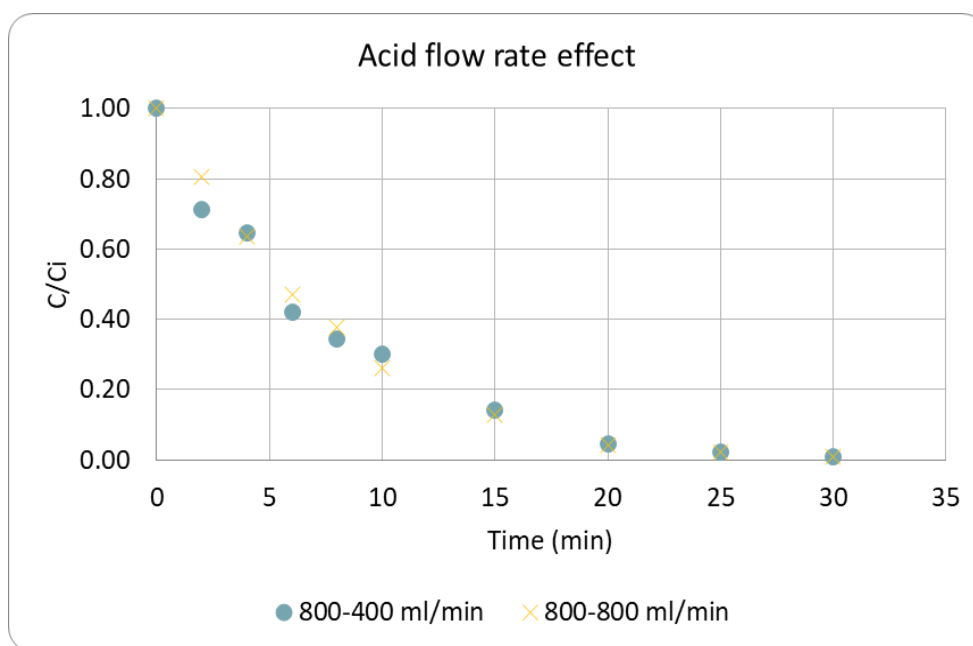


Figure 4-12: Acid flow rate effect on membrane performance

As it can be seen in Figure 4-12, the evolution is similar in both cases, so it can be concluded that the application of different flow rates to each solution has no influence over the recovery rate and the recovery efficiency.

#### 4.7.3 Final product concentration

After analysing the ammonia transfer and the recovery efficiency and rate, the following aspect to study was the product nitrogen content. For that purpose, different acid concentrations were applied. The data are summarised in Table 4-3.

Table 4-3: Fertiliser final concentrations in each assay

Assay	Acid used	Acid concentration (M)	Final product nitrogen concentration (g/l)
A1	H <sub>2</sub> SO <sub>4</sub>	0.096	2.4 g N/l
A2			
A3			
A4			
A5			
A6	HNO <sub>3</sub>	0.096	2.6 g N/l
A7		0.2	6.1 g N/l
A8	HNO <sub>3</sub>	Variable	>19.7 g N/l

In the first tests, carried out with sulphuric acid at a concentration of 0.096 M, the average final ammonia as nitrogen concentration obtained in the acid solution was 2.4 g N/l which is near the stoichiometric value.





Using nitric acid, the final concentration is a bit higher, but it is important to take into account that some of this final nitrogen is introduced in the system by the acid used, so the total amount of nitrogen recovered in this solution is lower than in the sulphuric acid tests.

Finally, assay A8 is a bit different. In this case, a nitric acid addition during the experimentation was implemented in order to obtain a higher concentration. In these tests, concentrations higher than 19.7 g N-NH<sub>4</sub>/l were obtained. The fertiliser obtained in this type of experiments are the ones used for the PGPB selection and evaluation, which results are presented in the following section.

## 4.8 PGPB selection and evaluation

There were two main objectives in this task:

- **Objective 1:** Selection of different bacterial isolates to be used as inoculants in the production of a “smart fertiliser”.
- **Objective 2:** Testing the growth of the selected bacteria in a culture medium based on ammonium salts and struvite to be used as a biofertiliser.

### 4.8.1 Objective 1: Selection of microorganisms.

The selection of bacterial strains was made according to bibliographic information and the previous experience of CEBAS-CSIC working with plant growth promoting PGPR. Four bacteria were selected according to their abilities. The selected bacteria were obtained from the Spanish Type Culture Collection. Table 4-4 shows the selected bacteria.

Table 4-4: PGPB selected

Bacteria	Strain ID	Main characteristics
<i>Pseudomonas putida</i>	ATCC12633	Phosphorus solubilizing bacteria <i>Phytohormone</i> production
<i>Bacillus megaterium</i>	ATCC14581	Alleviation of plant abiotic stress. <i>Phytohormone</i> production
<i>Azospirillum brasilense</i>	ATCC29145	Nitrogen-fixing bacteria <i>Phytohormone</i> production
<i>Pseudomonas aeruginosa</i>	ATCC10145	Biocontrol Agent Phosphorus solubilizing bacteria

### 4.8.2 Objective 2: Testing the growth of the selected bacteria in a culture medium based on ammonium salts and struvite to be used as a biofertiliser.

#### **Experiment 1:**

Each fertiliser was diluted 1:5, 1:10, 1:20, 1:50 and 1:100 with sterilised distilled water, inoculated with the bacteria, and the optical density (OD, measurement of bacterial growth) of the fertilisers was measured at time 0 days and after 1, 3, and 7 days of incubation under shaking condition and at room temperature. The values presented in Table 4-5 are the average of three replicates.



Table 4-5: Experiment 1 results

Fertiliser	Dilution	OD 0d	OD 1d	OD 3d	OD 7d
1	0	0.055	0.045	0.046	0.042
1	1:5	0.064	0.040	0.039	0.035
1	1:10	0.055	0.035	0.041	0.030
1	1:20	0.065	0.045	0.044	0.040
1	1:50	0.053	0.044	0.044	0.044
1	1:100	0.070	0.030	0.020	0.025
2	0	0.059	0.035	0.040	0.025
2	1:5	0.060	0.035	0.035	0.036
2	1:10	0.055	0.031	0.030	0.039
2	1:20	0.060	0.032	0.028	0.028
2	1:50	0.054	0.034	0.039	0.030
2	1:100	0.070	0.033	0.032	0.035
3	0	0.071	0.034	0.036	0.039
3	1:5	0.050	0.045	0.035	0.036
3	1:10	0.054	0.032	0.029	0.033
3	1:20	0.063	0.034	0.038	0.034
3	1:50	0.061	0.042	0.038	0.030
3	1:100	0.061	0.043	0.039	0.040

These results clearly show that bacteria are not able to grow on the ammonium salts at any dilution.

### **Experiment 2:**

The experiment 1 was repeated adding struvite in a relation 1:10 (struvite weight:solution volume) to the different dilutions of the fertilisers. The presented values in

Table 4-6 are the average of three replicates.



Table 4-6: Results of experiment 2

Fertiliser	Dilution	Struvite	OD 0d	OD 3d	OD 7d
1	0	1:10 (w/v)	0.125	0.100	0.105
1	1:10	1:10 (w/v)	0.110	0.099	0.100
1	1:20	1:10 (w/v)	0.105	0.090	0.095
1	1:50	1:10 (w/v)	0.120	0.100	0.115
1	1:100	1:10 (w/v)	0.099	0.100	0.099
2	0	1:10 (w/v)	0.115	0.100	0.100
2	1:10	1:10 (w/v)	0.100	0.099	0.105
2	1:20	1:10 (w/v)	0.105	0.095	0.100
2	1:50	1:10 (w/v)	0.110	0.099	0.115
2	1:100	1:10 (w/v)	0.105	0.100	0.100
3	0	1:10 (w/v)	0.120	0.125	0.120
3	1:10	1:10 (w/v)	0.100	0.105	0.100
3	1:20	1:10 (w/v)	0.105	0.090	0.095
3	1:50	1:10 (w/v)	0.100	0.095	0.090
3	1:100	1:10 (w/v)	0.111	0.099	0.100

The addition of struvite did not allow the complete growth of bacteria in any of the dilutions tested.

### **Experiment 3:**

In this experiment, the different dilutions of the fertilisers were amended with the culture medium Luria Bertani LB at two different rates. The optical density was measured after 5 days under shaking conditions at room temperature. Results are shown in Table 4-7.

Table 4-7: Results of experiment 3 (in bold the best condition for each fertiliser)

Fertiliser	Dilution	Addition of LB culture medium	OD 0d	OD 5d
1	0	1:10 (v:v)	0.065	0.070



1	1:5	1:10 (v:v)	0.045	0.050
1	1:10	1:10 (v:v)	0.050	0.070
1	1:20	1:10 (v:v)	0.055	0.098
1	1:50	1:10 (v:v)	0.050	<b>0.350</b>
1	1:100	1:10 (v:v)	0.055	0.210
2	0	1:10 (v:v)	0.040	0.040
2	1:5	1:10 (v:v)	0.049	0.055
2	1:10	1:10 (v:v)	0.048	0.075
2	1:20	1:10 (v:v)	0.047	0.085
2	1:50	1:10 (v:v)	0.041	0.157
2	1:100	1:10 (v:v)	0.042	<b>0.198</b>
3	0	1:10 (v:v)	0.055	0.055
3	1:5	1:10 (v:v)	0.060	0.060
3	1:10	1:10 (v:v)	0.062	0.056
3	1:20	1:10 (v:v)	0.054	0.091
3	1:50	1:10 (v:v)	0.053	0.151
3	1:100	1:10 (v:v)	0.043	<b>0.200</b>
1	0	1:20 (v:v)	0.056	0.090
1	1:5	1:20 (v:v)	0.058	0.100
1	1:10	1:20 (v:v)	0.060	0.070
1	1:20	1:20 (v:v)	0.043	0.151
1	1:50	1:20 (v:v)	0.045	<b>0.401</b>
1	1:100	1:20 (v:v)	0.060	0.290
Fertiliser	Dilution	Addition of LB culture medium	OD 0d	OD 5d
2	0	1:20 (v:v)	0.054	0.049
2	1:5	1:20 (v:v)	0.046	0.100
2	1:10	1:20 (v:v)	0.056	0.136
2	1:20	1:20 (v:v)	0.065	0.125



2	1:50	1:20 (v:v)	0.054	<b>0.275</b>
2	1:100	1:20 (v:v)	0.052	0.202
3	0	1:20 (v:v)	0.041	0.040
3	1:5	1:20 (v:v)	0.056	0.080
3	1:10	1:20 (v:v)	0.056	0.099
3	1:20	1:20 (v:v)	0.057	0.120
3	1:50	1:20 (v:v)	0.060	0.190
3	1:100	1:20 (v:v)	0.065	<b>0.220</b>

This experiment demonstrated that it is necessary to add a culture medium to the fertiliser to allow bacteria to grow. The bacterial growth was dependent on the type of fertiliser, and higher with an increased concentration of culture medium. In general, bacterial growth was higher in fertiliser 1.1, which had an alkaline pH.



## 5. Next steps

According to the results presented in this deliverable and in D2.6, the main parameters have been studied and selected to design the pilot-scale plant as well as start its operation. The preliminary design will follow the set-up included in Figure 5-1, with an important scale-up, treating 800 L/day.

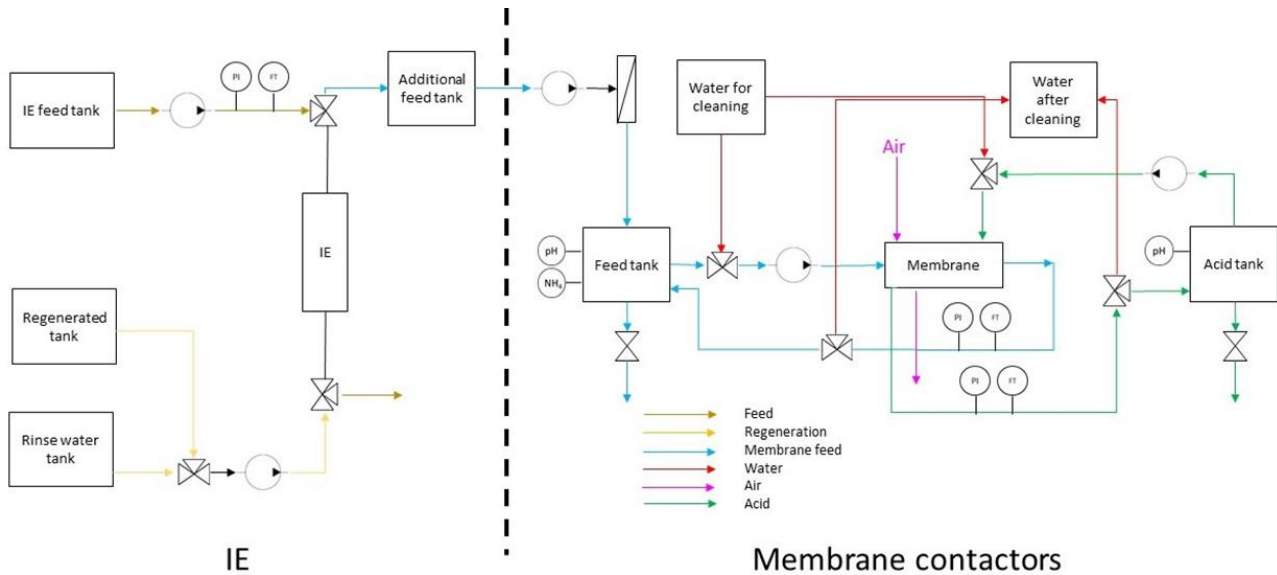


Figure 5-1: Pilot plant layout

The treatment train will be similar to the one used in the laboratory, including a pre-treatment with a filtration system to remove the solids. This pilot will be located in Reza WWTP (WWTP 2) which provides higher flow rates and higher concentration of ammonia favouring the optimal recovery in terms of costs.

Regarding the Smart BBF, we are going to optimise the recipe once we have the bacteria selection. After that, the blending process at pilot scale and the BBF application in crops will be the main goals.



## 6. Conclusions

- Pilot plant will be located in Reza's WWTP, in Ourense, due to the high amount of nitrogen detected in its WW studies.
- A filtration pre-treatment is needed for the optimal operation of the pilot plant.
- 75 mL/min was determined to be the optimal flow rate operation for pilot plant trials.
- NaOH was selected as the optimal regenerant for the desorption process.
- 0.35 M of NaOH was determined as the optimal regenerant concentration for the desorption process.
- CEC depletion occurred after processing almost 300 BV of real WW. This involved 104  $\text{NH}_4^+$ mg/g zeolite.
- Most of the nitrogen adsorbed, 96%, could be recovered by the technology proposed.
- As adsorption/desorption cycles happened, not only a CEC depletion was observed, but also a kinetics deceleration and an increase of the regenerant ease to desorb the  $\text{NH}_4^+$  retained.
- The adsorption process is recommended to be stopped after 20 BV has flown through the adsorbent, in order to minimise the loss of nitrogen in the pilot plant. Then proceed with the regeneration process.
- The regeneration process is recommended to be stopped after 10 BV of NaOH 0.35M had flow through the adsorbent, in order to maximise the  $\text{NH}_4^+$  concentration in the permeate obtained that would later be used in HFMC  $\text{NH}_4^+$ -salt production.
- HFMC shows recovery efficiencies higher than 95% with the feed flow rate having a remarkable effect on the recovery rate. The higher the feed flow rate, the higher the recovery rate.
- The maximum ammonia concentration in the ammonia salt is around 30 g/l as ammonia nitrate.
- The selected PGPB are *Pseudomonas putida*, *Bacillus megaterium*, *Azospirillum brasilense* and *Pseudomonas aeruginosa*.
- It is necessary to add a culture medium to the fertiliser to allow bacteria to grow.



## 7. References

Lubensky, J., Ellersdorfer, M., Stocker, K., (2019). Ammonium recovery from model solutions and sludge liquor with a combined ion exchange and air stripping process. *J. Water Process Eng.* 32, 100909. <https://doi.org/10.1016/j.jwpe.2019.100909>

Noriega-Hevia, G., Serralta, J., Borrás, L., Seco, A., Ferrer, J., (2020). Nitrogen recovery using a membrane contactor: Modelling nitrogen and pH evolution. *J. Environ. Chem. Eng.* 8. <https://doi.org/10.1016/j.jece.2020.103880>

Razon, L.F. (2014) Life cycle analysis of an alternative to the haber-bosch process: Non-renewable energy usage and global warming potential of liquid ammonia from cyanobacteria, *Environ. Prog. Sustain. Energy.* 33 618–624. <https://doi.org/10.1002/ep.11817>.

Vaneeckhaute, C., Lebuf, V., Michels, E., Balia, E., Vanrolleghem, P., Tack, F.M., Meers, E., (2017). Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification. *Waste Biomass Valorization* 8, 21–40. <https://doi.org/10.1007/s12649-016-9642-x>

