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Deliverable 5.7

Report on the technical results from the implementation of WP5 – input for interrelated WPs

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3	25/05/2022	Revision after PO comments. Added Executive Summary, listed main results in the chapter 5, solved mistake in page 18. Also included a comparison of	Caroline Sielfeld, Maria Kyriazi, Maria Avramidi, Wokke Wijdeveld

[1] **R**=Document, report; **DEM**=Demonstrator, pilot, prototype; **DEC**=website, patent fillings, videos, etc.; **OTHER**=other

[2] **PU**=Public, **CO**=Confidential, only for members of the consortium (including the Commission Services), **CI**=Classified

		ViviCryst with other P recovery methods like struvite precipitation	
4	12/07/2022	Second revision after PO comments. Issue related to the rederence to D5.1 was solved (info was added to D5.1). Reference to D5.8 was included, where further information about energy demand and cost estimations shared with WP8 will be included.	Caroline Sielfeld, Maria Avramidi

Executive Summary

This report presents the technical progress of the WP5 activities. First, the work done by NTUA in CS4 is presented. Regarding CS4, NF and RO membranes were tested performing filtration experiments with bench-scale equipment using synthetic solutions and evaluated trough the WAVE Software. FILMTECH LC HR 4040 and NF 90 4040 showed the highest rejections. These membranes were selected for the pilot, taking into consideration the results of membrane bench scale tests and the outcomes of the WAVE software. The already existing MED unit was refurbished, and the experiments performed with this equipment resulted in water recoveries of up to 92%. Experiments performed with the already existing Crystallization unit showed that NaCl salt from the concentrated stream of the evaporator can be crystallized with purity higher than 98%. For CS5, experimental set-up and preliminary results of the bench-scale experimental phase developed by Eurecat are presented. An UASB AnMBR was operated with flat sheet membranes obtaining a COD removal efficiency of ca. 80% at mainstream conditions and a COD concentration in the permeate of <60 mg/L. A partial nitritation reactor was operated as a sequential batch reactor (SBR) to force biomass granulation. A rapid strategy to start-up the partial nitrification reactor and obtain fast settling granular sludge performing partial nitritation without nitrate accumulation has been developed at 35oC. An Anammox UASB reactor was operated for around 170 days, obtaining a NRR that accounts for a nitrogen removal efficiency (NRE) of 54±10%. A technical issue led to sharp decrease on anammox activity (NRR) and nitrite accumulation. Once NLR and NRR are stable again, temperature decrease will be started (final target is 15ºC). Vivianite crystallization experiments have been performed by Wetsus in a bench-scale crystallizer. The average percentage of P removal obtained in the experiments was approximately 76.5%. A preliminary design of the pilot prototype for CS5 (reactors) has been already developed, and the principal features are presented in this report. BioPhree is a technology developed by Wetsus that will be used for CS4 and CS5. It uses an iron-oxide based adsorbent that can be regenerated and re-used and that selectively adsorbs phosphorus from the water. The pilot unit has been already constructed and first tested on surface water in collaboration with Waterschap Brabantse Delta (Geertruidenberg, Netherlands), a Dutch water board and team member of Wetsus. Then it was transported to Cyrpus where it has been already installed.

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Glossary

AnMBR	Anaerobic membrane bioreactor
AOB	Ammonia-oxidizing bacteria
AOR	Ammonium oxidation rate
BNR	Biological nitrogen removal
BOD_5	Biological oxygen demand after 5 days
COD	Chemical oxygen demand
CIP	Cleaning in place
DO	Dissolved oxygen
EC	Electrical conductivity
EGSB	Expanded granular sludge bed
FA	Free ammonia
LMH	$L/m^2/h$
LTE	Low temperature evaporator
MBR	Membrane bioreactor
MED	Multi-effect distillation
MW	Molecular weight
NF	Nanofiltration
NOB	Nitrite-oxidizing bacteria
NRE	Nitrogen removal efficiency
NLR	Nitrogen loading rate
NRR	Nitrogen removal rate
OLR	Organic loading rate
ppb	Parts per billion

RO	Reverse osmosis
SBR	Sequential batch reactor
SVI_{30}	Sludge volume index at 30 minutes
SVI_5	Sludge volume index at 5 minutes
TMP	Transmembrane pressure
TSS	Total suspended solids
UF	Ultrafiltration
UASB	Up-flow anaerobic sludge blanket
V_s	Superficial velocity
VSS	Volatile suspended solids
WWT	Wastewater
WWTP	Wastewater treatment plant

1. Objectives

The objective of this report is to provide information about the technical results of the implementation of work package 5 (WP5), to ensure smooth implementation of the project and successful flow of information to the other WPs. It comprises the technical results of the implementation of the bench scale operation for case study 4 (CS4) and case study 5 (CS5) for the first year of the project. Both case studies aim to develop improved technical solutions to treat urban wastewater.

2. Introduction

The aim of work package 5 (WP5) is to demonstrate the feasibility to recover phosphorus, water, and energy from urban wastewaters. To achieve this goal, different innovative technologies will be implemented in two demonstration sites: case study (CS) 4 and 5. Both demonstration sites will be implemented in wastewater treatment plants (WWTP). CS4 will be implemented on Larnaca WWTP (located in Cyprus) and CS5 in La Lagosta WWTP (Located in Spain). For the implementation of the prototypes, several bench-scale tests will be performed to design and construct the prototypes for successful implementation of the technologies in a real scenario.

This report is related to the Task 5.5: Coordination of WP5 activities and interrelation with other WPs. Eurecat as WP5 leader is responsible to ensure collection of data generated during the implementation of WP5 and communication of these data to interlinked WPs (WP1, WP2, WP7, WP8, WP9, WP10 and WP11).

The following report contains the technical results obtained in the bench scale pilots so far (M1 - M12) regarding CS4 and CS5, to ensure smooth implementation of the project at Demo Plant Scale and successful flow of information to the other WPs.

3. Technical results of the implementation of CS4

The aim of the large demo system, which will be implemented in CS4 is the treatment of the effluent originating from the WWTP of Larnaca city, Cyprus. This WWTP has a capacity of 100,000 population equivalent per day. Its average inflow is about 18,000 m^3/day while its maximum inflow could reach 27,000 m^3/day. From this unit, 2,500,000 m^3/day of water and 1500 m^3 of sludge are produced per year. Both are used in agriculture.

However, the salinity of the effluent is about 1.5 mg/L. Using water of this level of salinity could cause problems to the cultivation of very sensitive plants, while salt accumulation could cause land problems. Furthermore, water produced by the WWTP has a 0.5 mg/L Phosphorus (P) content. This concentration reinforces algae development in the lagoons, where the effluent stays before passing through the chlorination unit to the water supply system. Algae could also cause problems to the pipes or the watering system components.

The pilot of CS4 is designed to treat this effluent, providing high-quality water which could also be used by industry. Moreover, this pilot design is based on circular economy, which means that the principle of zero discharge should be followed. Thus, NaCl, divalent salts with Ca and Mg, and P produced from the effluent should be recovered in the form of valuable products (salt of high purity for industrial use and P solutions that could be used in fertilizers industry).

CS4 will demonstrate the feasibility of achieving low salinity effluents using a treatment train that will also allow to achieve ultra-low concentrations of P (<0.05 mg/l) in the effluent, and recovering phosphate. Upgrading of water quality will be achieved through the application of suitable membrane technologies. The proposed process will be demonstrated at pilot scale and will be designed to treat an inflow of 24 m^3/day.

The complete treatment train is presented in Figure 1. The first stage of the process is the phosphate removal and recovery with the BioPhree technology. The P concentration in the effluent will be decreased by BioPhree from 0.5 mg/L to 10-40 ppb. At these low levels, phosphorus limits biological growth. This step will also protect the membranes of the next systems from biofouling. Second step will be Nanofiltration (NF). This system will remove calcium and magnesium ions from the effluent. The concentrate from the NF will pass through a low temperature evaporator (LTE), that will remove the divalent ions from water, providing high-quality water. The NF permeate will pass through an RO system, which will produce a high-quality permeate with <100 µS/cm conductivity. The RO concentrate will pass through a Multi-effect distillation evaporator (MED): The MED evaporator will concentrate the brine from RO, also producing high-quality water (condensate). Finally, the brine concentrate from the evaporator will pass through the crystallizer. In the crystallizer, the brine will be further concentrated. The products of the crystallizer will be high-quality water (condensate), and a saturated solution which can be used either in the chlorination unit or for NaCl crystals production (industrial use).

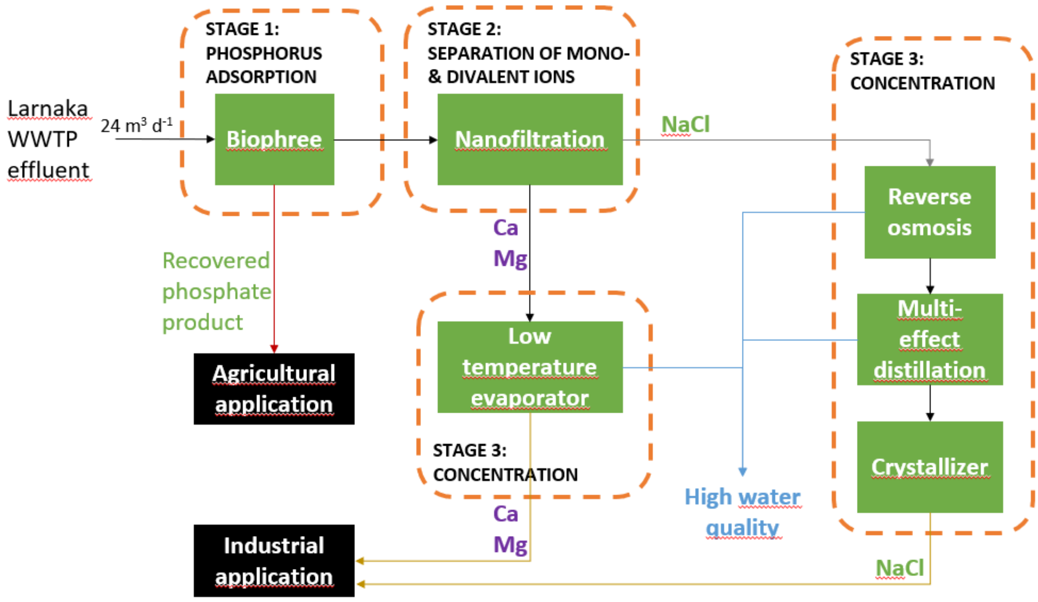


Figure 1.Treatment process diagram for CS4

3.1. Technical results of the implementation of Subtask 5.1.2 “Design & construction of demo plant for CS4”

3.1.1. Design and construction of nanofiltration (NF) and reverse osmosis (RO) units

3.1.1.1. Membrane bioreactor effluent characteristics

The exact analysis of MBR effluent is very crucial for the designing of all the pilot systems. Therefore, at the first two months of the project (M1 and M2), samples from the outlet of MBR of Larnaca WWTP were taken and analyzed by Larnaca, NTUA and external laboratories.

Table 1. Composition of MBR effluent of Larnaca WWTP

Element	Symbol	Unit	Value
Sodium	Na	mg/L	490
Potassium	K	mg/L	43
Magnesium	Mg	mg/L	61
Calcium	Ca	mg/L	149
Boron	B	mg/L	0.67
Chloride	Cl	mg/L	890
Total Phosphorous	P	mg/L	1.52
Total Nitrogen	N	mg/L	10.4
Zinc	Zn	μg/L	42
Copper	Cu	μg/L	14
Lead	Pb	μg/L	<75
Cadmium	Cd	μg/L	<0.5
Mercury	Hg	μg/L	<0.4
Chromium	Cr	μg/L	6.6
Nickel	Ni	μg/L	8.1
Electrical conductivity	EC	mS/cm	4.2
Averaged pH	pH		7.9
Biological oxygen demand (5 days)	BOD_5	mg/L	<1
Chemical oxygen demand	COD	mg/L	20
Total Suspended Solids	TSS	mg/L	7

In Table 1, it is shown that a small amount of organics remains in the effluent. This should be taken into consideration during the membrane choice, as it can create serious functional problems to the membranes. The high amount of TSS, could also be a problem for NF membranes. However, after communication with Larnaca WWTP stuff, NTUA team is informed that is something temporary due to maintenance works on MBR.

Furthermore, from Table 1 it can be concluded that the conductivity of water is mainly due to NaCl (approximately 65%, effluent contains about 1.5 g/L sodium chloride) and that the pilot should treat a slightly basic solution. So, if a high removal of phosphorus, sodium chloride, magnesium and calcium will be achieved, a low salinity water will be produced.

3.1.1.2. Bench scale tests with nanofiltration (NF) and reverse osmosis (RO) units

3.1.1.2.1. Description of RO and NF units

At the first months of the project bench scale tests were conducted by NTUA team using NF and RO units (single module) with capacity of about 0.5 m^3/h and synthetic solutions mimicking the MBR effluent (Table 2). The objectives of the bench scale tests conducted by NTUA in the Labs of Environmental Science and Technology Unit of NTUA were to find:

- the highest recovery of NF and RO membranes
- the efficiency of NF for separating monovalent ions from multivalent
- the quality of permeate and the characteristics of concentrate streams of these membranes

The membrane used in NF unit was a FILMTEC NF270-4040 membrane which is a Polypiperazine Thin-Film Composite membrane, suitable for TOC and medium hardness removal. Low pressure RO membranes FILMTEC LP-2540 delivers high quality water. Figure 2 and Figure 3 presents NF and RO units used for bench scale tests.

Figure 2. NF unit for bench scale tests

Figure 3. RO unit for bench scale tests

3.1.1.2.2. Bench scale tests with NF and RO units

The main goal of the NF experiments is to find under which conditions can be achieved:

- the highest possible divalent ions rejection
- the lowest monovalent ions rejection
- the highest permeate recovery.
-

For the RO experiments is to find under which conditions can be achieved:

- the highest ions rejection
- the highest water recovery

A synthetic solution was prepared in the laboratory of NTUA to simulate the real effluent of MBR. The concentrations of major ions to this solution are according to Table 2.

Table 2. The concentrations of major ions in the brine used for the bench scale tests

Ions	Concentration (mg/L)
K^+	2.5
Na^+	559
Ca^{+2}	228
Mg^{+2}	36
Cl^-	875
SO_4^{-2}	47

In the beginning of each experiment, the system has been run for 10 -15 min to achieve stable operating conditions. The operating conditions, presented Table 3, were maintained throughout all the experiments.

Table 3. Operating conditions of bench scale tests in NF unit

Operating Conditions		Recovery				
		75%	60%	75%	60%	50%
Feed Flow	l/h	400	400	400	400	400
Permeate Flow	l/h	300	240	300	240	200

Concentrate Flow	l/h	100	160	100	160	200
Operating temperature		20	20	20	20	20
pH		7.3	7.3	7.3	7.3	7.3
	l/h	0	0	0	0	0
Recirculation	l/h	200	200	X	X	X
	l/h	300	300	X	X	X
	l/h	400	400	X	X	X
	l/h	500	500	X	X	X

As it is shown in Table 3, combinations of different recovery percentages and different recirculation flows were examined to find the best one in terms of achievement of the three objectives mentioned in paragraph 3.1.1.2.1.

During the experiments, samples of permeate and concentrate were collected. The pH value was corrected between 6 and 6.5, by addition of hydrochloric acid solution, to avoid the use of antiscalant during experiments. Antiscalant is added to almost all desalination processes, using RO and NF membranes, to avoid scaling of salts on the membranes which result in operational problems. The antiscalant does not pass through the membranes so it is rejected to the concentrate stream. However, in this case study we want to recover NaCl of high purity from the concentrate of RO. Thus, antiscalant is avoided through adjustment of pH.

To estimate the efficiency of the processes, in real time, the conductivity of inlet and outlet streams was measured. Furthermore, samples from the inlet and outlet streams are examined with atomic absorption (for cations concentrations) and spectrophotometry (for anions concentrations). The results of the above experiments are summarized in Figure 4, Figure 5, Figure 6 and Figure 7.

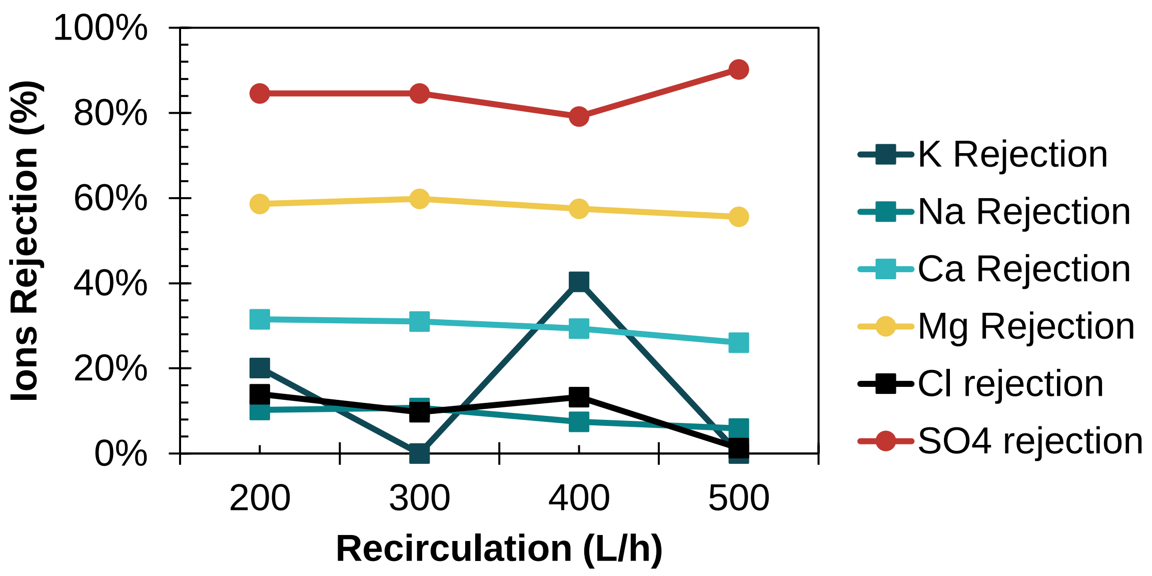


Figure 4. Ions rejection for 75% recovery (pH=7.3) at different recirculation flows

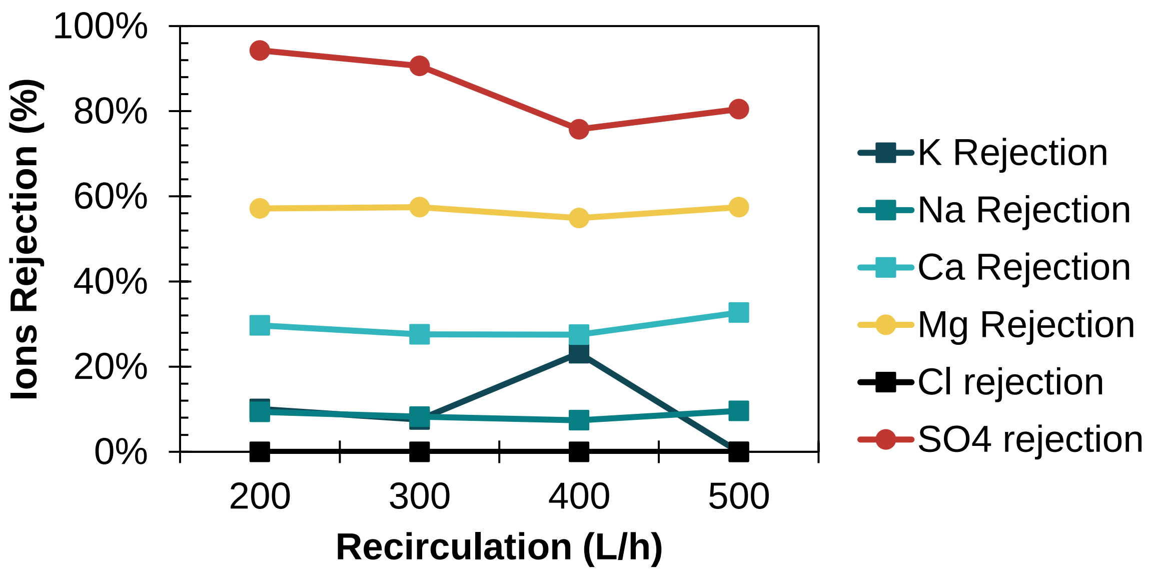


Figure 5. Ions rejection for 60% recovery (pH=7.3) at different recirculation flows

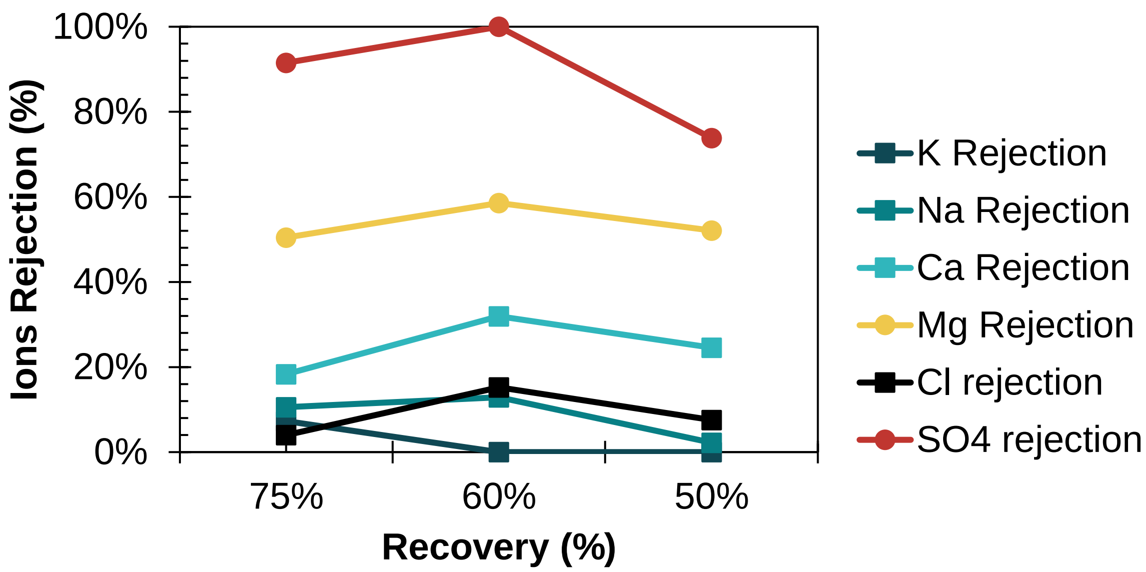


Figure 6. Ions rejection for 50%, 60% and 75% recovery (pH=7.3) without recirculation flow

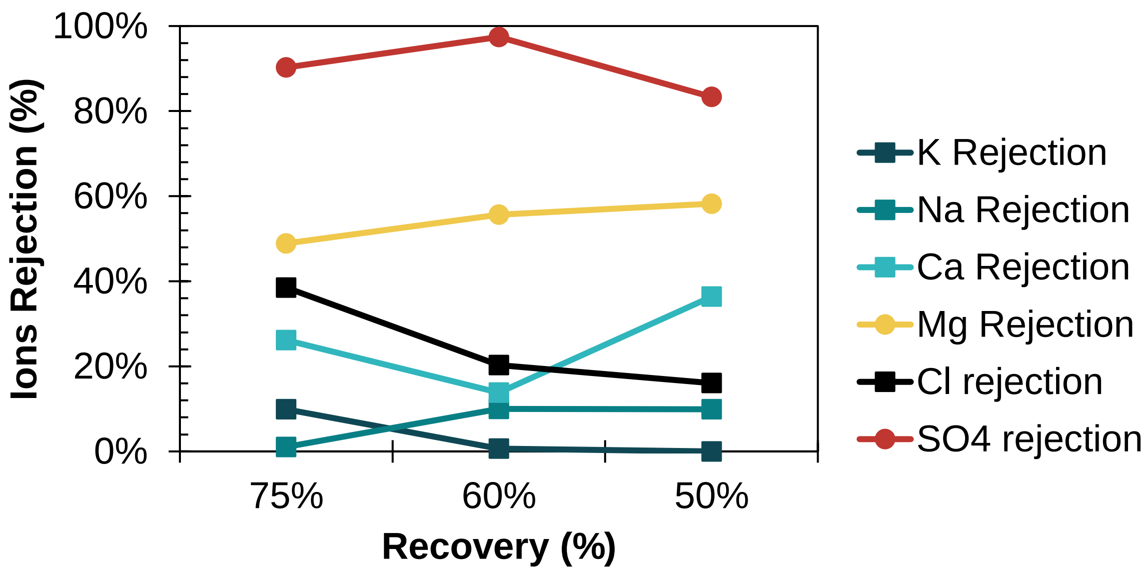


Figure 7. Ions rejection for 50%, 60% and 75% recovery (pH=6) without recirculation flow

It could be observed that NF 270 4040 membrane exhibits low monovalent ions rejection efficiency (about 10 %) which is significantly lower than divalent cations rejection. The highest rejection is observed for sulfate, SO_4^{2-} anions and reaches 90%. Mg^{2+} cations display better rejection characteristics (about 60 %) than Ca^{2+} cations (about 30 %). The rejection efficiencies of all considered ions seem almost independent from concentrate recirculation flow.

Figure 5 presents the rejection factors dependency from concentrate recirculation flow for 60% recovery. It seems that rejection efficiencies of all ions are almost independent of recirculation flow and show the similar values as for higher system recovery (Figure 4). Small decrease in sulfate rejection can be noticed with increase in recirculation. Almost the same results we have to the condition of 0 recirculation.

From the above-mentioned results, it can be concluded that only slight differences exist between 60% and 75% recovery. The highest NF recovery is 75% and can be achieved using re-circulation flows between 30% - 60%. Under these conditions and pH 6 no operational membrane issues are expected. The adjustment of pH using HCl to avoid the addition of antiscalant seems also to have a minor impact to the divalent ions rejection factors. Finally, even though the rejection ions factors for Mg^{+2} and SO_4^{-2} seem satisfactory, the rejection factor for Ca^{+2} ions seems very low. Thus, during the design of the final system more types of membranes were studied and estimated through commercially available simulation software.

The FILMTECH 270-4040 was also tested using the DuPont WAVE software. From the evaluation of WAVE results, it was concluded that the results of bench scale tests are in line with the software outcomes.

WAVE software also gives the opportunity to examine other available membranes. Among them membranes suitable for brackish water, NF 200 4040 and NF 90 4040, were tested. The rejection factors for the major ions and membrane NF 200 4040 were about the same as these observed for membrane NF 270 4040. The rejection factors for NF 90 4040 were about 90% for Ca^{+2} and Mg^{+2}, 96% for SO_4^{-2} and 75% for Na^{+} and Cl^{-}. The permeate of NF from all these experiments was driven to the RO unit. RO unit was based on an XLE 2540 membrane. Two recovery percentages were tested 80%

and 90%. It seems that both tested recoveries can achieve rejection factors of about 90-100% for Mg^{+2}, Ca^{+2}, Cl^{-}, Na^{+}, K^{+} and SO_4^{-2}. No significant differences exist between the rejection factors of anions with 80 and 90% recovery. The XLE 2540 was also tested through WAVE software and the results were similar to the values obtained experimentally. Except of the XLE 2540 membrane, other RO membranes have been tested. The membrane FILMTECH LC HR 4040 presented highest rejection, more than 95%, for all ions so, it was selected as the most suitable membrane for the RO pilot unit.

The pilot has been constructed and will be installed in the Larnaca WWTP station in the first weeks of October. Extended description and results of the pilot will be reported to the D 5.8 (1st update of this deliverable).

3.1.1. Multi-effect distillation (MED) and crystallizer experiments

3.1.1.1. MED evaporator - Experiments

The MED evaporator is made up of two consecutive effects and it operates below atmospheric pressure 0.4 bar at first effect and 0.2 bar at second effect, limiting the boiling temperatures at 70 °C and 60 °C respectively. In each of the MED effects, brine is evaporated resulting in the production of two subsequent streams: (i) a water vapor stream that is then condensed and recovered as fresh water and (ii) a more concentrated brine stream. The vapor stream of the first effect is used to heat the concentrated brine produced in the second effect that is sprayed on top of the bundle, running down from tube to tube by gravity. Therefore, the necessary latent heat for brine vaporization in the second effect is provided by internal heat gain (heating steam from the first effect) and thus energy recovery is achieved. The vapor stream produced by the second effect is used for pre-heating purposes. Specifically, the vapor is passed through a plate heat exchanger where it is condensed, transferring its thermal energy to the brine stream of inlet feed (Figure 8).

The control of the system is accomplished via a PC-based supervisory control and data acquisition (SCADA) interface. Multiple temperature, pressure and flow transmitters are connected in many positions within the system, receiving all the important data for process control. The overall control and monitoring can be achieved using SCADA. All data is collected and controlled using a programmable logic controller (PLC). The aim of the automation system is to display and record information related to the processes, the operation of the equipment etc.

Figure 8. Photo of the containerized system.

Some refurbishments on the system have been made. The vacuum pump was fixed, some electric valves were replaced, a chemical cleaning was performed, and maintenance works were made on the pumps systems.

The concentrated brine from the RO is expected to be between (20 - 40) g/L. For that reason, synthetic brine with NaCl and tap water has been prepared. The tap water had a small concentration of Magnesium and Calcium and the concentration of the inlet brine ranged from 1.4% to 3.9% and the recovery of the system ranged from 83% to 91% (Table 4, Table 5 and Table 6). The condensate vapor at the end of each experiment was a low salinity water (conductivity <30µS) which can be used in several sectors and for irrigation after adjusting the alkalinity.

Table 4. Quality and quantity of the inlet brine solution.

Date	Inlet Brine Volume (L)	Sodium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Inlet brine TDS (mg/L)
25/6/2021	100	8,700	13,428	12	25	22,165
1/7/2021	100	12,700	19,200	15	26	31,941
14/7/2021	100	6,129	9,300	11.3	22	15,462
15/7/2021	100	7,684	11,563	11.6	22	19,280
18/7/2021	100	17,552	2,300	10.4	21	19,884
20/7/2021	100	16,872	2,244	11.3	21	39,338

Table 5. Quality and quantity of the concentrated brine solution.

Date	Concentrated Brine Volume (L)	Sodium (mg/L)	Chloride (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Concentrate TDS (mg/L))
25/6/2021	12	72,340	111,563	104	204.5	184,211
1/7/2021	17	74,892	112,756	87.3	146.7	187,882
14/7/2021	8	76,368	115,511	142	256.3	194,583
15/7/2021	9	96,872	143,765	128	248.6	241,013
18/7/2021	9	195,124	25,388	231.6	238.6	223,129
20/7/2021	9	186,912	24,886	123.7	237.9	214,300

Table 6. System's water recovery for each experiment.

Date	System Recovery (%)
25/6/2021	88
1/7/2021	83
14/7/2021	92
15/7/2021	91
18/7/2021	91
20/7/2021	91

3.1.1.2. Crystallizer – Experiments

The system R 150v3 is an evaporator/crystallizer, from the company called Veolia water, that encompasses the distillation of liquids at low temperature through the combined effect of vacuum technology and the heat pump. The working scheme is as in Figure 9.

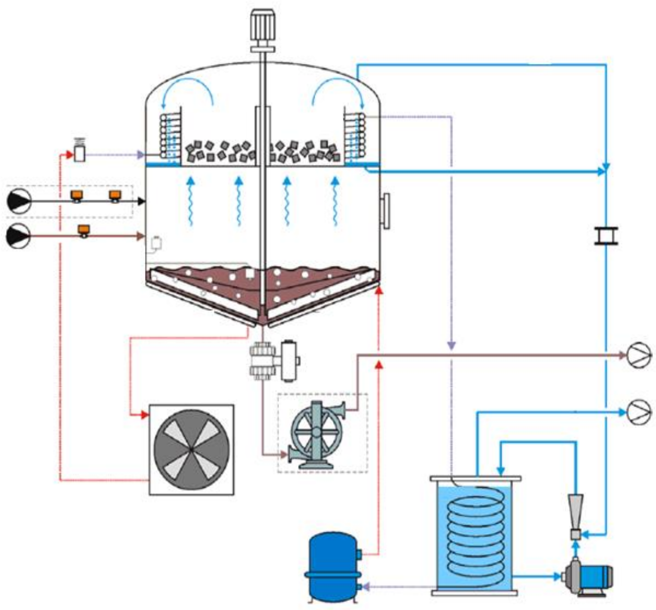


Figure 9. Working scheme of crystallizer.

The NTUA performed six (6) experiments with the crystallizer. At each experiment the recovered brine from the evaporator was used as an inlet to the crystallizer. More specifically, the concentration of the inlet brine to the crystallizer ranged from 18.5% to 21.2%. The goal was to reach the saturation point of the sodium chloride (26%) and recover salt at the end as a product. At the end of the process crystals of salt were produced as it is shown at the following Figure 10. Through these experiments it has been demonstrated that, the NaCl salt from the concentrated stream of evaporator can be crystallized with purity higher than 98%. More data on the composition of the output streams of crystallizer as well as, energy consumption data will be included in the Deliverable 5.1.

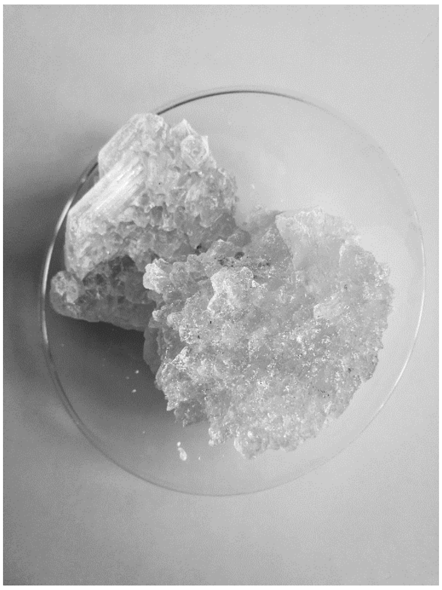


Figure 10. Sodium Chloride crystals.

The designing and construction of the NF and RO units were performed taking into consideration the results of membrane bench scale tests and the outcomes of the WAVE software. More precisely, the NF membrane FILMTECH NF90 4040 presenting the highest divalent ions rejection (approximately 90%) and high permeate recovery, has been selected and installed in the NF pilot unit. Regarding the RO unit, the membrane FILMTECH LC HR 4040 presented the highest rejection of all ions (>95%) and high-water recovery (approximately 90%), has been selected and installed in the RO pilot unit.

After the refurbishment of the MED evaporator and crystallizer a few trial experiments, with simulated RO concentrate, were conducted and it has been shown that the initial objectives can be achieved.

The construction of NF and RO pilot units and the refurbishment of MED evaporator and crystallizer have been completed. The pilot will be installed in Larnaka station to operate in combination with Biophree system which is already installed.

4. Technical results of the implementation of CS5

The CS5 will demonstrate the feasibility of implementing innovative technologies to treat urban wastewater to enhance water reuse, reduce energy consumption and recover energy and phosphorus, contributing to circular economy in the wastewater sector

The proposed process (presented in Figure 11) includes several innovative technologies aiming to (i) produce energy, (ii) reduce energy consumption and (iii) generate by-products for industrial or agricultural purposes. The proposed innovative treatment train will be demonstrated at pilot scale and will be designed to treat an inflow of about 400 L/h (±10m^3/d).

The first stage of the treatment train is an anaerobic digestion process (with granular biomass) coupled to a membrane filtration unit devoted to transform the organic matter into renewable energy (biogas), defined as granular Anaerobic Membrane Bioreactor (AnMBR). Granular AnMBR is a suitable way to reduce energy costs by treating organic matter from urban wastewaters, in comparison to conventional aerobic activated sludge. Under anaerobic conditions, biogas is produced, which is a mixture of methane and carbon dioxide and can be used as energy source. In this way, all the organic matter content in the wastewater can be directly converted into biogas in an efficient manner. Currently, conventional WWTP plants apply activated sludge system (CAS) to remove properly the pollutants; however, they are very intense in terms of energy consumption. As high amounts of sludge are produced as by-product of the performance of the CAS, anaerobic digestion of the sludge can partially recover energy. However, under the innovative approach of using granular sludge in CS5, almost all the organic carbon of the incoming WW is transformed into biogas by the granular AnMBR, and an energy efficient nutrient removal and water recovery technology treatment train is implemented afterwards. Besides, as the proposed innovative treatment train requires less energy than CAS, a neutral or even a positive energy-producing facility can be reached along the demonstration of CS5. Besides the recovery of biogas, the produced sludge (already stabilized) and the permeate can be valorized for agricultural purposes in certain EU countries. This fact is due to the nutrient content, mainly as nitrogen (N) and phosphorus (P), in both effluents.

As N and P are not in demand for the whole year, both can be treated or valorized to obtain water for agricultural or industrial applications. To achieve a suitable reclaimed water for industrial use, nutrients (N and P), salt and solids should be removed. The suitable way to remove N from urban wastewaters is via Biological Nitrogen Removal (BNR) processes. However, conventional nitrogen removal processes (nitrification followed by heterotrophic denitrification) are high energy demanding and technically limited to low loading rates. This CS proposes a two-stage approach to achieve autotrophic BNR, i.e., the removal of ammonium without the need of organic matter. The first stage includes an aerobic granular reactor performing partial nitritation, where half of the incoming ammonium is oxidized to nitrite. The second step consists of granular anaerobic ammonium oxidation bacteria (anammox), where ammonium and nitrite are converted into nitrogen gas. The combination of partial nitritation/anammox (PN/AMX) technologies have been applied successfully at sidestream. However, the implementation of PN/AMX at mainstream still faces some major challenges, that need to be resolved before its full implementation. For instance, low temperature (15ºC to 10ºC in winter season), low nitrogen concentration and NOB outcometition during partial nitritation. The application of PN/AMX approach at mainstream (and sidestream) conditions presents several advantages: (i) 60% of energy reduction related to aeration, in comparison to conventional nitrification process (ii) no organic matter is need for denitrification (all the organic matter can be transformed into biogas in the previous AnMBR) avoiding the injection of additional carbon source and (iii) two-step approach allows for a better optimization of process and operation conditions individually, which eventually will allow for a better control NOB proliferation (in comparison to one-step approach).

The third stage of the innovative proposed treatment train is the removal and recovery of phosphorus with two innovative technologies developed by WETSUS, ViviCryst and BioPhree. The effluent from the anammox reactor will be treated with ViviCryst, a technology based on the chemical precipitation of phosphorus with iron in form of vivianite crystals, which have a potential application as fertilizer. The effluent from ViviCryst will be treated with BioPhree – the same technology proposed in CS4 – an adsorption process that is capable to remove phosphate to ultra-low concentrations.

If high-quality water for industrial application is needed, e.g. for cooling towers, reclaimed water stream from stage 3 will then be treated by reverse osmosis (RO) using regenerated membranes producing high quality water for industrial purposes (Stage 4). Regenerated membranes are obtained from end-of-life RO elements and allow to reduce the environmental impact related to landfill disposal. Regenerated RO membranes also reduce the operational costs of the filtration process, as they require less pressure than new RO elements. Previous P recovery step (stage 3) will avoid biofouling presence on the RO membranes and enhance the RO performance.

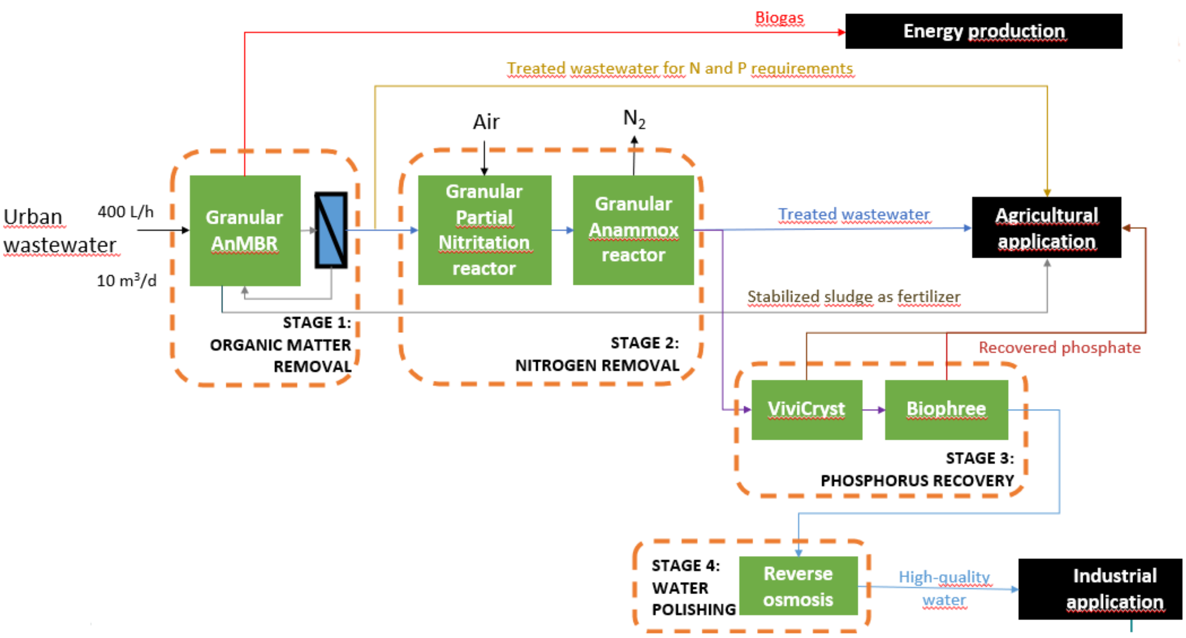


Figure 11. Treatment process diagram for CS5

This deliverable contains the technical results related to the currently ongoing tasks, which are subtask 5.1.1 "Design and construction of bench scale plant for AnMBR, partial nitritation and anammox" and Subtask 5.1.3 "Design and construction of demonstration plant for case study 5". The following sections present the technical results obtained so far in these subtasks.

4.1. Technical results of the implementation of subtask 5.1.1 "Design and construction of bench scale plant for granular AnMBR, partial nitritation and anammox"

The following sections describe the results regarding subtask 5.1.1. Three bench-scale reactors were designed and constructed and are currently in operation in the Eurecat facilities: a UASB granular AnMBR, a bubble column for partial nitritation (PN) reactor, and a granular UASB anammox reactor. Eurecat and Sorigue are working in close collaboration within these 3 reactors, and biweekly meeting are taking place. Wetsus has also constructed a bench-scale crystallizer considering La Llagosta WWTP data to test the ViviCryst technology. The following sections describe the results regarding the operation of the three reactors and the results of the bench-scale experiments of ViviCryst.

4.1.1. Granular AnMBR (UASB reactor)

The following sections describe the experimental set-up and operational results of the granular AnMBR at bench-scale.

4.1.1.1. Reactor experimental set-up

An up-flow anaerobic sludge blanket (UASB) reactor was operated for more than 250 days. The aim was to recover biogas from the organic matter removal from real urban wastewater after primary settler, by an innovative anaerobic digestion process (Figure 12). The reactor working volume was 12 L, with an inner diameter column and height of 0.1 m and 1.32 m, respectively. A gas-liquid-solid separator was installed in the top of the reactor. The reactor had a water jacket which allowed for temperature control with a water bath at 20ºC during the start-up and at 15ºC during the rest of operation (day 56 onwards).

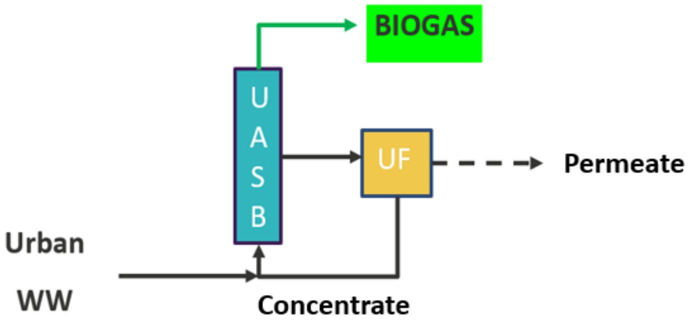


Figure 12. Diagram of the configuration of the granular anaerobic digestion membrane (AnMBR) using a Upflow Anaerobic Sludge Blanket (UASB) reactor

Flat ceramic sheets ultrafiltration (UF) membranes (5 modules) (Chemipol SiCFM-826) were implemented from day 56 of operation. The active membrane area was 0.826 m^2 and the pore size of 0.1 µm (Figure 13). The UF membranes were operated as side configuration and were submerged on the UASB effluent container (ca. 300-400L see Figure 13). Nitrogen gas was continuously injected through a gas diffuser with 2 mm perforations at 0.5 $m^3/m^2/h$, by means of nitrogen generator unit (COMTABE SNG 10) in order to decrease membrane fouling. Permeate was driven through a peristaltic pump (Boyser AMP-16) and the transmembrane pressure (TMP) was monitored through a pressure transducer connected in the suction line. The membrane was operated in cycles of 15 min of filtration and 1 min of relaxation. Every 2 cycles, 2 minutes of backwashing, using produced permeate, took place. Produced concentrate was recirculated to the bottom of the UASB reactor using a peristaltic pump. From day 96 onwards several fouling problems were detected with the membrane. Thus, membrane ceramic plates were cleaned manually twice per week. More harsh cleaning was needed using chemicals every two to three weeks depending on the membrane performance. Cleaning was performed submerging the membrane in hypochlorite (ca. 2000ppm) overnight combined with citric acid (sufficient to achieve pH 2) flushing the following day.

Figure 13. Anaerobic membrane bioreactor experimental set-up

4.1.1.2. Inoculum and wastewater characteristics

The UASB reactor was inoculated with 5 L of granular sludge from a mesophilic anaerobic Internal Circulation reactor treating an industrial wastewater. The biomass was stored for 1 month at 4 °C. Biomass had a good sludge volumetric index of 89 mL/g-TSS.

Urban wastewater after the primary settler of two urban WWTPs were used along the study. The average composition of each urban wastewater is summarized in Table 7. Initially, we used WWT from Manresa for convenience. However, as the pilot demonstration plant will be installed in La Llagosta WWTP, which has a high input of industrial wastewater. It was of vital importance, to test if any influent component could impact the biological process. Furthermore, the use of two different WWTs allowed to assess the robustness of the process.

Table 7. Wastewater characteristics of Manresa and La Llagosta WWTPs after the primary settler. n.d. – not determined. Hyphen indicates that the compound was not detected. 6 samples were used to characterize WW from Manresa and 3 samples for the water from La Llagosta.

	Manresa WW	La Llagosta WW
Total COD (mg/L)	224±91	292±122
Soluble COD (mg/L)	117±39	149±80
Total Nitrogen (mg N/L)	56±8	n.d.
Total phosphorus (mg P/L)	6±1	5.1±0.3
Ammonium (mg $N-NH_4^+$/L)	57±9	47±9
Nitrite (mg $N-NO_2^-$/L)	-	-
Nitrate (mg $N-NO_3^-$/L)	-	-
Phosphate (mg $P-PO_4^{3-}$/L)	4±1	3.9±0.5
Sulfate (mg/L)	175±24	364±156
Conductivity (mS/cm)	1.9±0.2	1.1±0.3
Alkalinity (mg $CaCO_3$/L)	428±45	538±77
pH	7.7±0.3	7.8±0.4
TSS (mg/L)	39±33	19±4
VSS (mg/L)	36±30	20±2
Turbidity (NTU)	88±72	55±22

4.1.1.3. Reactor operation and results

Three operational phases can be distinguished during the granular AnMBR using UASB reactor operation: i) Start-up without membrane, ii) with membrane and urban WW from Manresa WWTP, iii) with membrane and urban WW from La Llagosta WWTP (Figure 14).

A short start-up period using granular anaerobic sludge took place from days 0 to 44. The UASB operation was characterized without membrane and OLR of 0.2 kg/m^3/d was achieved. When trying to increase the OLR to 1.5 kg/m^3/d on day 37, the reactor overloaded. It was aimed to achieve the maximum OLR without reactor overload.

After the membrane installation (from day 44 onwards) permeate effluent quality improved (Figure 14B) from ca. 76 mg-COD/L to 38±16 and 55±11 mg-COD/L with Manresa and La Llagosta WWTP, respectively. Slightly higher permeate COD was detected during the third phase of operation with La Llagosta WW. This was partially expected because of the higher COD content of La Llagosta WW compared to Manresa WW (Table 7). Also, nitrite formation (ca. 12±7 mg-N/L) was detected both in the membrane tank and in the permeate. Consequently, nitrite formation impacted COD measurements, increasing its value while working with La Llagosta WW (Table 8). Theoretical COD equivalent from the nitrite measured in the permeate could account up to 43 mg COD/L. Most likely, nitrite formation was due to the higher temperature during the summer months the long residence time of the water in the UF membrane tank and that being in the open air.

Overall, good effluent quality could be achieved, with a removal efficiency of ca. 80%, independently of the wastewater used. This, led to a maximum theoretical biogas productivity between 0.9-1.1 m^3 biogas/m^3 influent/d (without accounting for putative sulfate reduction). A theoretical value was calculated independently if the biogas was found in the gas or liquid phase was used, because at 15^{o}C most of the biogas is dissolved and did not allow for proper quantification. Nitrogen flushing in the membrane tank also led to biogas stripping. Consequently, the low biogas flow production combined with all the above, did not allow for proper measurement with the available devices, as the biogas flow rate generated was under the measuring ranges.

Membrane operated between 12-22 LMH and reaching maximum transmembrane pressure of 0.7 bar. Every 2-3 weeks intense chemical cleaning was needed. We believe that this intense cleaning needs and the relatively low flux achieved was due to the EPS production in the granular sludge reactor.

After finalizing the characterization of the AnMBR UASB operation, the results obtained with the AnMBR UASB reactor will be compared to an Expanded Granular Sludge Bed (EGSB) AnMBR reactor (running since 23rd of August). Based on the obtained results the best ANMBR technology will be implemented in the demonstration site. Furthermore, a hollow-fiber (HF) membrane long term performance operating in bleeding mode will be assessed. This HF membrane is the lab-scale version of the one that will be implemented in the demonstration site.

*Table 8. Granular AnMBR operational results with Manresa WWT and La Llagosta WWT. *This value is a calculated theoretical value. OLR- Organic loading rate taking into account influent, OLR in-rec – Organic loading rate taking into account influent and recirculation to the reactor.*

	UASB	AnMBR - Manresa	AnMBR - La Llagosta
Operational days (d)	12-35	56 - 174	174-300
Up-flow velocity (m/h)	1.6±0.4	1.5±0.2	1.1±0.1
Temperature (ºC)	20	15	15
OLR (KgCOD/m^3/d)	0.2±0.1	1.6±0.8	1.0±0.4
OLR in+rec (KgCOD/m^3/d)	2.4±0.6	3.8±2.2	3.9±1.3
COD permeate (mg/L)	76±10	38±16	54±11
Removal efficiency (%)	59±11	85±4	77±13
Biogas productivity * **(m^3 biogas/Kg COD influent/d)**	3±1	4±2	4±3

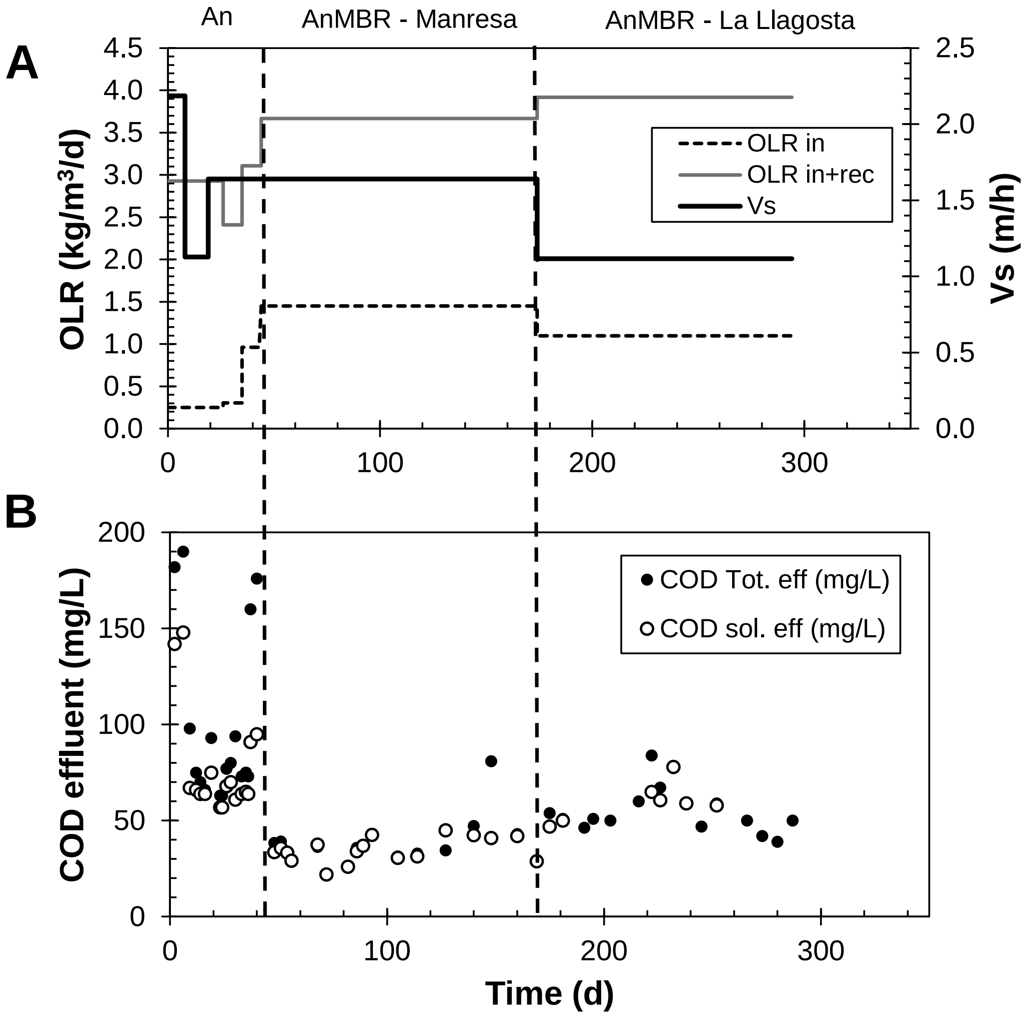


Figure 14. Granular UASB anaerobic membrane bioreactor operational data. Three operational phases are distinguished using dashed lines. An. – anaerobic digestion operation without membrane, AnMBR-Manresa – anaerobic membrane bioreactor operation with membrane implementation and wastewater from Manresa WWTP, AnMBR-La Llagosta – anaerobic membrane bioreactor operation with wastewater from La Llagosta WWTP. A) Organic loading rate (OLR) considering the influent of the system or the influent and recirculation into the reactor and superficial liquid velocity (Vs), B) COD concentration in the UASB effluent or permeate before and after the membrane was implemented.

4.1.2. Partial nitritation reactor

The following sections describe the set-up and the results regarding the operation of the partial nitritation reactor at bench scale.

4.1.2.1. Reactor experimental set-up

A glass bubble column reactor with a 5.1L working volume (Figure 15) was used to achieve partial nitritation. The reactor column length and width were 1.04 m and 0.064 m, respectively. The reactor was operated as a sequential batch reactor (SBR) to force biomass granulation and achieve partial nitritation. Consisting of a filling, reaction, settling and discharge phase (see Figure 16). The discharge volume was set to 3.6 L.

During the reaction phase, ammonium and nitrate concentration were followed online with a sensor (AN-ISE, Hach Lange). The end of the reaction phase was set to finish when the ammonium concentration reached an established set point (50 mg N/L for the start-up). This value was selected to help relive the wastewater preparation efforts while ensuring high FA at the end of the cycle (see next section for further details). When the ammonium/nitrate probe failed (from day 70 onwards) the end of the reaction phase was established by setting the reaction phase time length.

Dissolved oxygen (DO) concentration was measured online with a sensor (5740sc galvanic DO sensor, Hach Lange) and controlled with an on/off air valve to be always below a selected set point (4 mg-O_2/L). Flow rate was set manually with a rotameter and adjusted when needed. pH was measured online with a sensor (differential pHDsc, Hach Lange) and controlled at pH 7.5 or 7.0 (from day 70 onwards) by dosing of 0.5M Na_2CO_3. Temperature was controlled to be around 35^{o}C with a built-in water jacket connected to a thermostatic bath (Digit Cool, P-Selecta).

Data acquisition system was built with an analog input and outputs data acquisition hardware (National instruments). The control and data logger were implemented in a LabVIEW custom program.

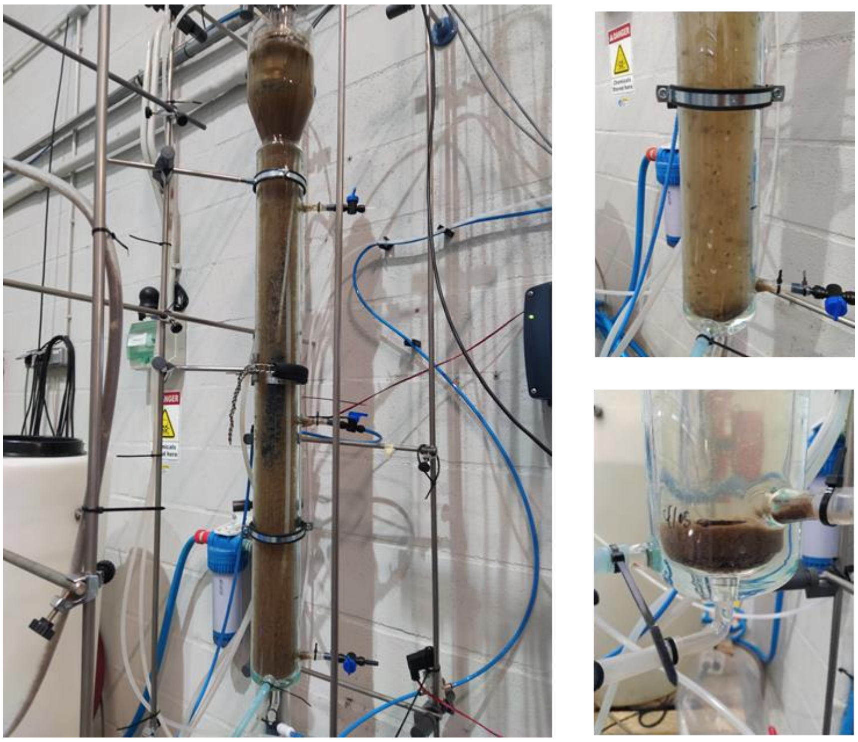


Figure 15. Partial nitritation reactor experimental set-up

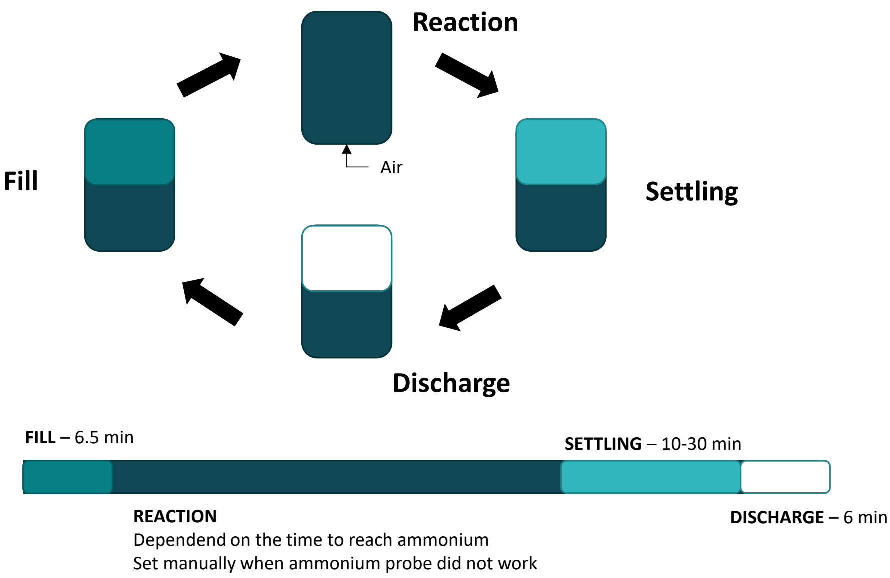


Figure 16. Sequential batch reactor operation (SBR) set-up. Consisting of a filling phase of 6.5 minutes, a reaction phase, settling phase that was decreased during the operational phase to achieve fast settling biomass, and finally a discharge phase.

4.1.2.2. Inoculum and wastewater characteristics

On day 0 and day 70, the reactor was inoculated with 2 L of nitrification biomass (2.7 g-VSS/L and 1.78 SVI_5/SVI_{30} ratio) from Ecoparc2, Montcada i Reixac, that was treating the liquid fraction digestate after anaerobic digestion of organic municipal solid waste.

Reject wastewater from La Llagosta wastewater treatment plant (770 mg-N/L ammonium) was used to feed the partial nitritation reactor. The wastewater was diluted to achieve an influent concentration of ca. 200 mg-N-NH_4^+/L. High ammonium strength wastewater was used (instead of urban wastewater) for the start-up instead of urban wastewater to achieve sufficient free ammonia inhibition for NOB and promote biomass growth.

4.1.2.3. Reactor operation

In general terms the strategy to achieve a fast start-up was based on having sufficient free ammonium (FA) at the start of each cycle for NOB repression, but not for AOB repression. According to Jubany et al. 2008, FA inhibition values are 7 and 1 mg-N/L for AOB and NOB, respectively. To speed up the start-up wastewater was diluted to have 200 mg-N/L, which lead to a fast increase of the number of cycles and a rapid start-up. FA was calculated to be 5-6 mg-N/L at initial of the cycle and ca. 1.5 mg-N/L at the end of the cycle with a set point of 50 mg-N/L (at ca. 32-35 °C and pH 7.7).

Inhibition by FA was combined with an initial DO set point of 4 mg-O_2/L to promote AOB activity. However, oxygen mass transfer resulted in a limiting factor for the reactor operation, as even if trying to increase the air flow rate, the DO in the system remained rather stable and generally below 1 mg-O_2/L (Figure 17)

Nitrogen loading rate (NLR) of 378-740 mg-N/L/d was achieved (Figure 17, Table 9). As the end of the reaction phase was set to finish at 50 mg-N-NH_4^+/L of ammonium, ammonium oxidation rate (AOR) was between 186 – 617 mg-N/L/d (Table 9), close to the NLR. Nitrate concentrations in the effluent was always lower than 1.5 mg-N/L. Thus, partial nitriation was achieved.

Biofilm attachment led to fluctuating biomass concentrations (Figure 17). The top separator was cleaned of biofilm twice a week. SVI_5/SVI_{30} ratio reached 1 in less than 15 days, indicating that fast settling biomass was achieved. Granular-like structure was also observed.

Overall, a rapid strategy to start-up the partial nitrification reactor and obtain fast settling granular sludge performing partial nitritation without nitrate accumulation has been developed at 35°C. Furthermore, due to technical problems two reinoculation events occurred resulting in consistent start-up results with the proposed strategy. Next steps will be focused on decreasing the temperature (final target temperature is 15°C), as well as characterizing NLR and AOR at mainstream conditions (influent ammonium concentrations of ca. 50 mg-N/L). To do so, first temperature will be decreased around 5°C per week. Then, influent concentration will be reduced stepwise until reaching 50 mg-N/L. During the last phase pH will be increased to achieve higher FA concentration in the effluent, while DO will be monitored to achieve concentrations of maximum 1 mgO_2/L.

Table 9. Partial nitritation reactor operational results with diluted reject wastewater from La Llagosta WWTP. NLR – Nitrogen loading rate, AOR – ammonium oxidation rate, DO- dissolved oxygen

Operational days (d)	18-25	26-48	49-69
Temperature (°C)	34.6±0.1	34.7±0.1	33.2±0.9
Settling time	30	20	10
Influent NH_4^+ (mg-N/L)	189±5	173±10	152±11
Influent NO_2^- (mg-N/L)	0	0	0.5±0.7
Influent NO_3^- (mg-N/L)	0.6±0.1	0.5±0.1	0.5±0.1
Effluent NH_4^+ (mg-N/L)	37±10	28±9	74±23
Effluent NO_2^- (mg-N/L)	169±11	205±14	117±49
Effluent NO_3^- (mg-N/L)	1.3±0.1	1.3±0.1	1.0±0.2
pH	7.6±0.1	7.7±0.1	7.6±0.2
DO (mg-O_2/L)	0.5±0.8	0.7±0.5	0.4±0.4
NLR (mg-N/L/d)	524±120	740±129	378±184
AOR (mg-N/L/d)	412±65	617±111	186±114
VSS reactor (mg/L)	429±306	352±228	263±207

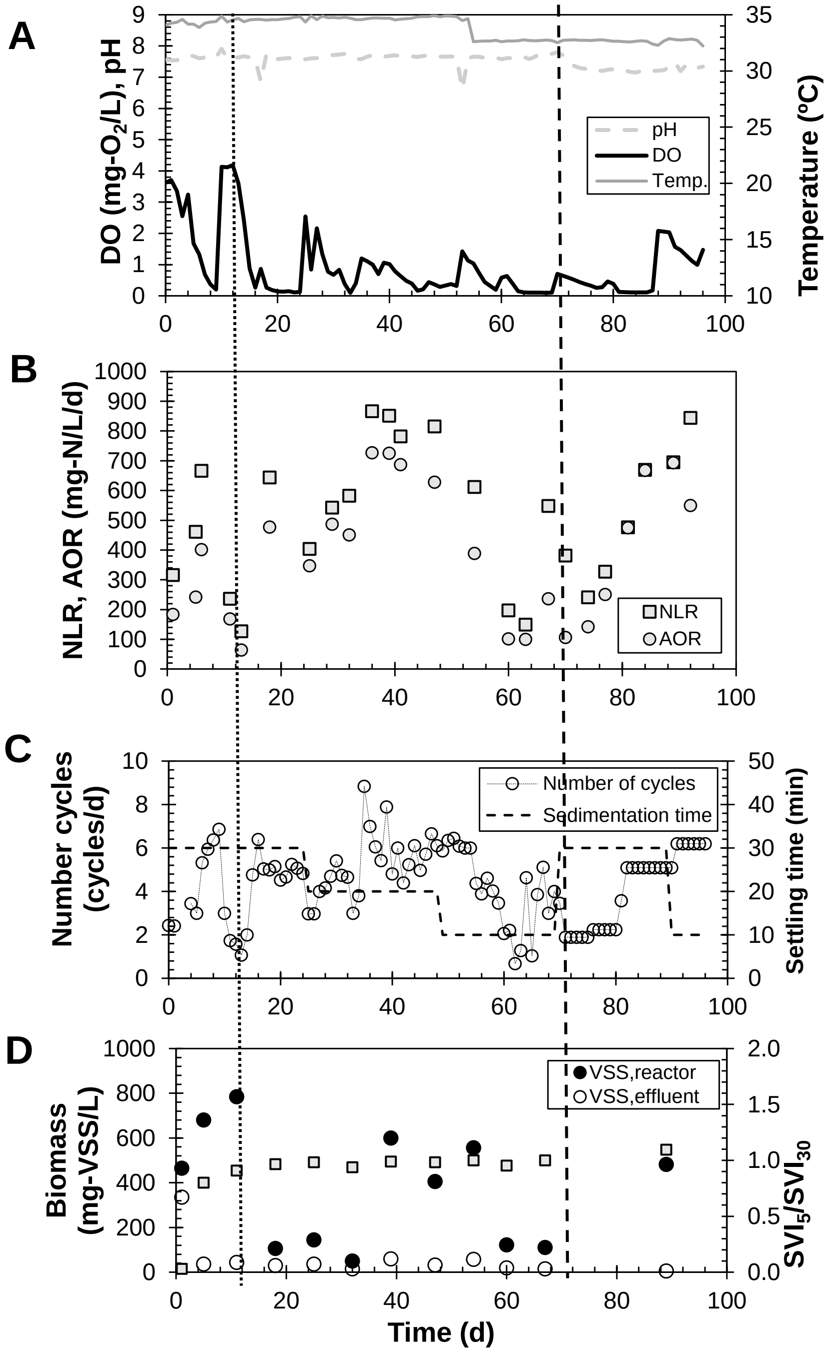


Figure 17. Partial nitritation reactor operation data. A) pH, dissolved oxygen (DO) and Temperature, B) Nitrogen loading rate (NLR) and ammonium oxidation rate (AOR), C) Number of cycles and sedimentation time, D) Biomass and SVI.. First dotted line indicates a technical problem with the discharge valve. The second dashed line indicates a reinoculation and a switch to cycle length control instead of ammonium concentration-based control.

4.1.3. Anammox reactor

The following sections describe the set-up and the results so far regarding the operation of the anammox reactor at bench scale.

4.1.3.1. Reactor experimental set-up

A granular up-flow anaerobic sludge blanket (UASB) reactor of 5 L, 0.08 m inner column and 0.8 m height was operated for more than 170 days (Figure 18 and Figure 19). An external water jacket coupled with a thermostatic water bath (Digit Cool, P-Selecta) was used to control the temperature at 35ºC.

Wastewater was fed from the bottom part of the reactor. Recirculation of the effluent was implemented from day 137 onwards by collecting the effluent in an external tank and recirculating it back to the bottom part of the reactor with a pump.

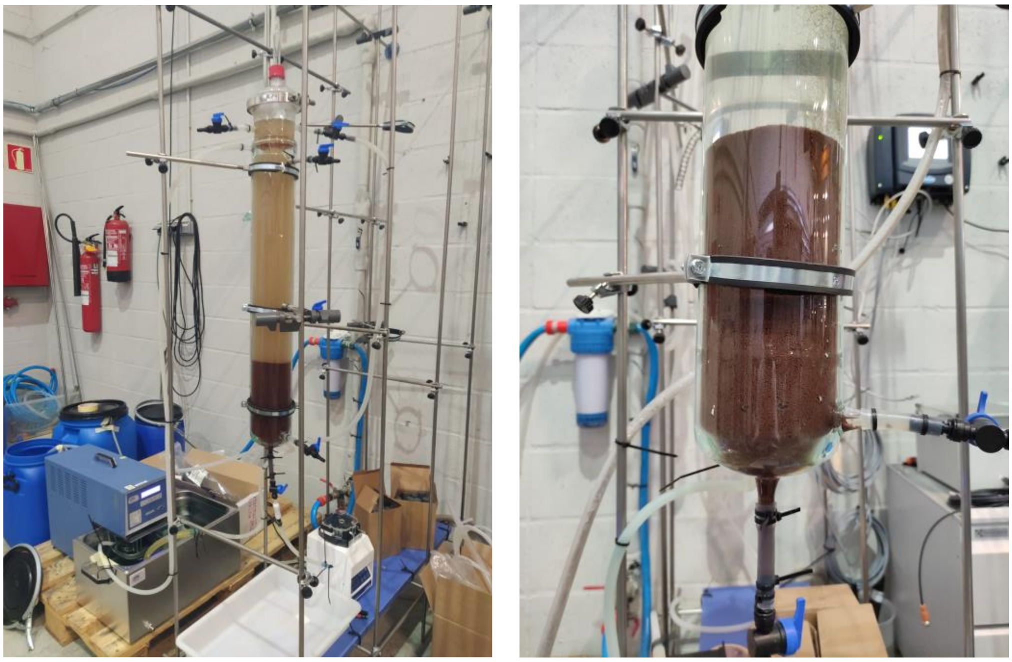


Figure 18. Anammox UASB reactor experimental set-up

4.1.3.2. Inoculum and wastewater characteristics

Diluted reject wastewater obtained from the centrifugation of digestated sludge was used from Manresa or La Llagosta and supplemented with nitrite. For some days (54 to 83) permeate from the AnMBR reactor was used. But due to punctual operational problems with the membranes, it seemed more reliable to used always available wastewater for the start-up.

From day 101, carbonate supplementation of the medium was introduced. Micro and macronutrients (as in Soler-Jofra et al., 2020) supplementation was used from day 12 to ensure no limitation.

Granular anammox inoculum was obtained from TU Delft. 2 L at ca. 50 g-VSS/L concentration were used as inoculum after 3 months in the fridge.

4.1.3.3. Reactor operation

After 20 days of start-up and step wise increase of NLR and nitrogen removal rate (NRR), a rather stable NLR of 462±103 mg-N/L and NRR of 256±80 mg-N/L were obtained from days 22 to 75 (see Table 10). The design targeted NLR was 500 mg-N/L/d. The obtained NRR accounts for a nitrogen removal efficiency (NRE) of 54±10%. The reduced nitrogen removal efficiency was due to two causes: i) nitrate production in the tank (see Figure 19B and Table 10) and ii) the nitrite to ammonium ratio in the influent was around 1, thus some ammonium was left in the effluent.

Nitrate production in the tank was partially reduced but not totally solved by sparging the tank with nitrogen after medium preparation to remove oxygen and partially avoid nitrite transformation to nitrate (see Figure 19B).

On day 76 a technical issue led to air entering the anammox reactor. This led to sharp decrease on anammox activity (NRR) and nitrite accumulation (Figure 19). After several days trying to recover the activity, effluent recirculation was implemented on day 137. Once reactor NLR and NRR are stable, temperature decrease will be started (final target temperature is 15^{o}C).

Table 10. Anammox reactor operational results with. NLR – Nitrogen loading rate, NRR – nitrogen removal rate, DO- dissolved oxygen.

Operational days (d)	22-75
Influent NH_4^+ (mg-N/L)	26±3
Influent NO_2^- (mg-N/L)	21±5
Influent NO_3^- (mg-N/L)	4±4
Effluent NH_4^+ (mg-N/L)	12±3
Effluent NO_2^- (mg-N/L)	1±2
Effluent NO_3^- (mg-N/L)	11±3
pH influent	8.2±0.2
pH effluent	8.3±0.2
NLR (mg-N/L/d)	462±103
NRR (mg-N/L/d)	256±80
NRE (%)	54±10

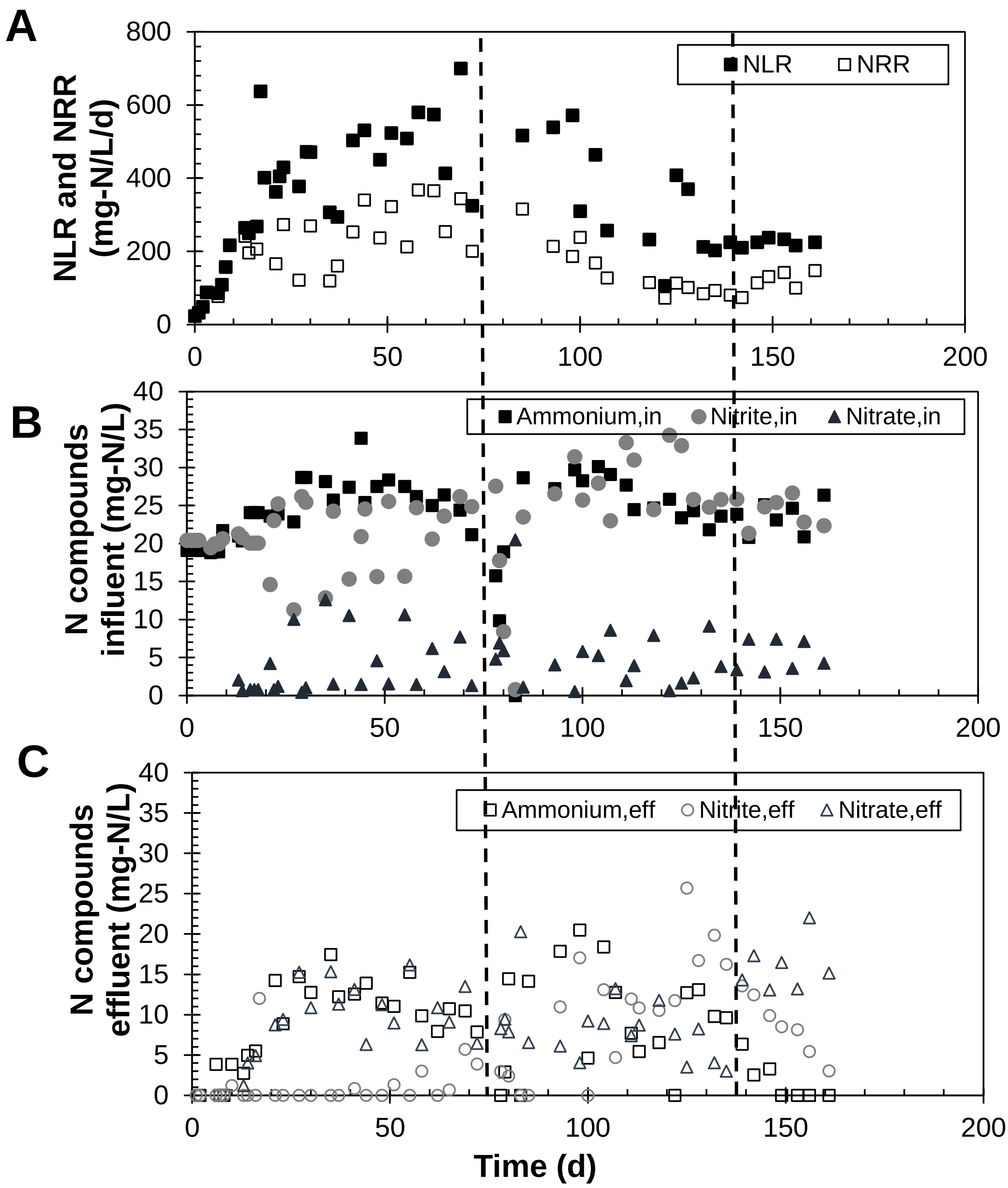


Figure 19. Anammox reactor operation data. First dashed line indicates when air entered the reactor due to a technical issue. Second dashed line indicates recirculation implementation. A) Nitrogen loading rate (NLR) and nitrogen removal rate (NRR). B) Nitrogen compounds concentration in the influent tank, C) Nitrogen compounds concentration in the effluent.

Overall, the data obtained with the AnMBRs PN and anammox reactors will be used to design and operate the demonstration site. Next steps in order to reach such milestones are: i) determine the maximum OLR and ORR of the EGSB reactor and compare it to the UASB reactor, ii) decrease the temperature to 15ºC of both PN and anammox reactors, iii) operate the PN in continuous and mainstream (ca. 50mg-N/L ammonium) conditions, iv) assess the robustness of the three reactors connected.

4.1.4. ViviCryst

Granular AnMBR, Partial nitritation, and Anammox do not remove phosphorus, which allows the selective recovery of phosphorus from a relatively clean water stream. **ViviCryst** is a phosphorus recovery technology which precipitates the crystalline mineral vivianite $(Fe_3(PO_4)_2 \cdot 8H_2O)$ by dosing ferrous (2$^+$) iron under anaerobic conditions.

ViviCryst has advantages compared to other precipitation technologies such as struvite. Due to the low solubility of vivianite (Solubility constant K_{sp} = 10$^{\wedge -35,8}$ at 25 C°), it is suitable for removing P from streams with a relatively low concentration of P in the order of 5-10 mg/L P, such as the effluent stream of wastewater treatment plants that do not remove P.

Struvite, due to its higher solubility (K_{sp} = 10^$^{-13,3}$ at 25 C°), is only applicable on concentrated phosphorus streams with concentration of >100 mg/L P, such as the filtrate or centrate of sewage sludge. Struvite precipitation therefor requires phosphorus removal in the wastewater treatment process, and reaches low overall P recovery efficiencies of only 10-40% (Cornel and Schaum, 2009; Egle et al., 2016; Korving et al., 2019). Vivianite precipitation can recover up to 80% of the total P in a wastewater stream. Furthermore, struvite recovery requires a pH increase (and sometimes first a decrease to release P from sludge), while vivianite recovery can be achieved in the neutral pH range of wastewater effluent.

In short, struvite recovery is not suitable for so called ‘’post-precipitation” in the water treatment line, only from concentrated streams from the sludge line after conventional chemical or biological P-removal.

There are however other post-precipitation technologies being used or developed. These technologies often use aluminium or ferric (3^+) iron to precipitate and recover phosphorus. Using aluminium or ferric iron has an important disadvantage compared to ViviCryst. The disadvantage of these technologies is that the created precipitate is a sludge of very fine particles. This sludge presents difficulties in material handling, and especially dewatering. ViviCryst will have the advantage of creating larger crystal granules, which are relatively easy to dewater and handle.

For Vivicryst, a bench-scale system has been built at the Wetsus laboratory and testing has been going on since March.

4.1.4.1. Description of the bench-scale crystallizer

As presented in Figure 20, the fluidized bed crystallizer (FBC) is composed of a vertical column - where the reaction takes place -, a settler - where any particles eluded from the main column can be gathered and collected -, and three different pumps, used for P dosing, Fe dosing and the reflux pump to control the up-flow velocity.

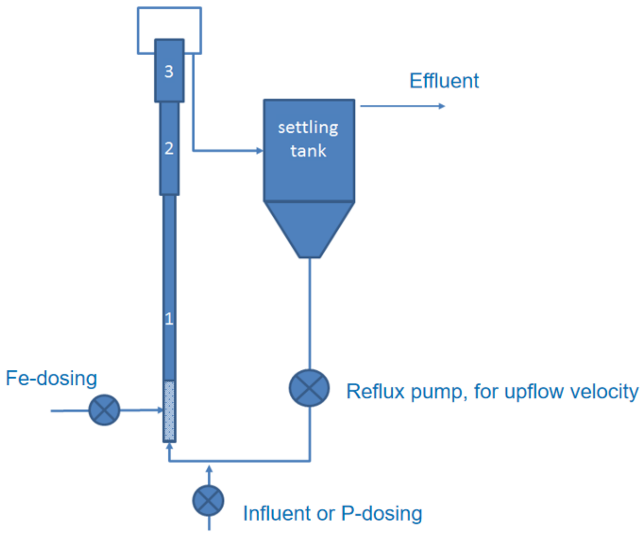
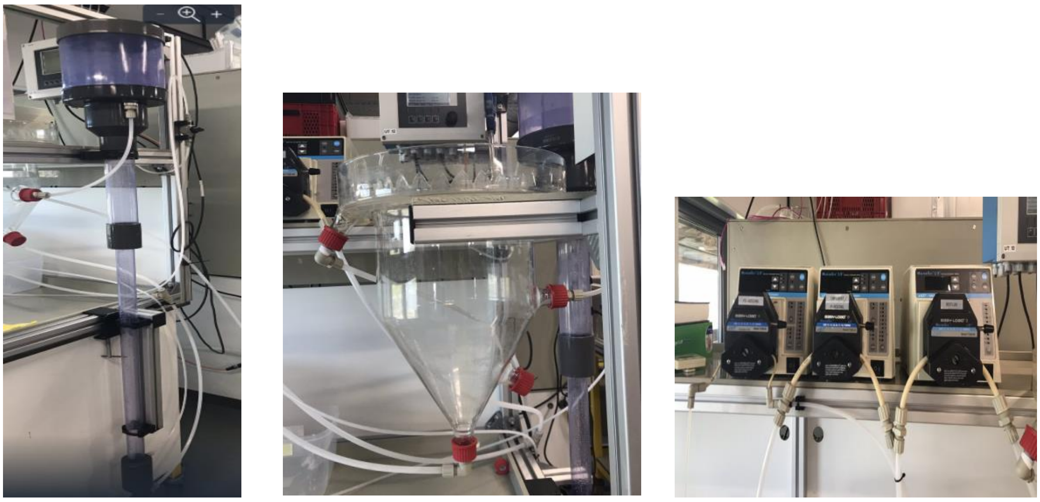


Figure 20. Diagram of the bench-scale crystallizer

The main column of the crystallizer is composed of three different parts that are connected to a sudden enlarged joint. The diameter of each part increases as we move from the bottom to the top. With this expansion of the diameter in each part, the up-flow velocity decreases. Therefore, we keep this format because we want to trap the fines and promote crystal agglomeration.

Additionally, at the lowest part of the main column we place 315 g of sand (approximate height: 15 cm) to create a “sand bed” or “vivianite seed bed”, where all the particles can stick together and form the crystals. Some pictures of the bench-scale crystallizer are presented in Figure 21.



The main column of the crystallizer *The settler* *The three pumps*

Figure 21. Pictures of the bench-scale crystallizer

4.1.4.2. ViviCryst bench-scale testing

To determine the optimal parameters for the operation of the crystallizer three different categories of experiments were conducted. For the first category we used low concentrations of P (5-500 mg/L) and Fe (18-1800 mg/L), in the second one we used intermediate ones, and in the third one we used significantly higher compared to the rest. The experimental conditions and results are provided in Table 11.

Table 11. Bench-scale crystallization experiments

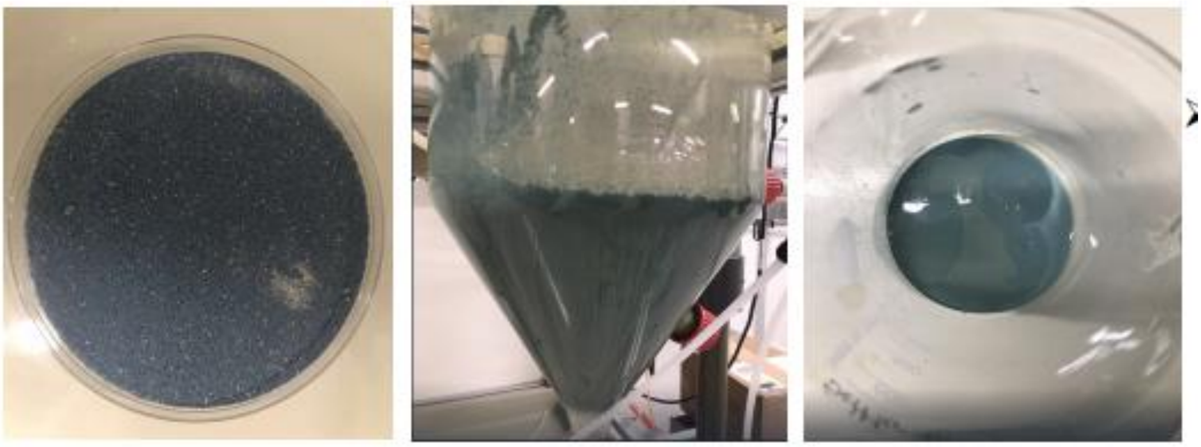
	Experiment with low concentrations of P and Fe	Experiment with intermediate concentrations of P and Fe	Experiment with high concentrations of P and Fe
Fe/P	2.5	2	2
P concentration in influent [mg/L]	5	50	500
Fe concentration in influent [mg/L]	18	180	1800
Reflux pump [mL/min]	500	500	500
Total duration of experiment [h]	4	6.5	8
Average P removal [%]	95	61	77

As presented in the Figure 22, during the experiment with low concentrations there was no vivianite formation observed, but solely a slight change of the color of the solution in the settler (yellowish tone). This can be mainly attributed to the fact that Fe hydroxides that are insoluble at pH 7 were formed. On the other part, the percentage of P removal was good, reaching in average the level of 95%.

Figure 22. Crystallization experiment with low P and Fe concentrations

Regarding the experiment with intermediate concentrations, the average percentage of P removal was not that good, accounting for approximately 61%. Formation of vivianite was observed in the settler, but the particles did not stick together, making it hard to separate and qualify them.

The average percentage of P removal in the experiment with high P and Fe concentrations was sufficient, accounting for approximately 76.5%. There was vivianite formed, as it is presented in the pictures of Figure 23, mostly as fines (at least 50%).



Sand used *Settler during experiment* *Sample from settler after days*

Figure 23. Precipitation of vivianite in the bench-scale crystallization experiment with high amounts of P and Fe

It is worth mentioning that the oxidized vivianite was almost indefinitely stable under the laboratory conditions. Additionally, the magnetic properties of the product were checked and indeed the substance was magnetic. During this experiment the pH dropped very fast (from 7 to 6) due to Fe solution dosing. Therefore, during the next experiments the Fe dosing was set to stop when pH 6.5 and start again at pH 7.

In the next months the aim is to decrease oxygen in the water even further and prevent oxidation of iron to precipitate all P as vivianite and increase the P removal at lower influent P concentrations. Once Wetsus succeeds in forming vivianite at lower concentration, they will focus on improving the agglomeration of the fines into vivianite crystals.

4.2. Technical results of the implementation of Subtask 5.1.3 "Design and construction of demonstration plant for case study 5"

Next sections describe the results so far regarding the design and construction of the prototype for case study 5. The units that are being currently designed and/or constructed are the granular AnMBR, the PN reactor, the Anammox reactor, and the BioPhree unit.

The ViviCryst pilot unit will be designed and constructed in a later phase according to the overall planning.

4.2.1. Design and construction of granular AnMBR, PN reactor and Anammox reactor prototypes

A preliminary prototype concept and design was established based on the results gathered so far regarding Subtask 5.1.1, and it was shared with 3 different engineering companies to ask for quotations. A feeding flowrate of 10 m^3/d was considered for the calculations. Eurecat and Sorigué are organizing several meetings with these companies to further developing and improving the design and finally achieve the construction of the pilot-scale reactors. One of these engineering company will be selected for construction of the prototype to be installed on La Llagosta WWTP.

Selection of the UF technology for the granular AnMBR has been intensively discussed with the engineering companies. This fact is mainly due to the technical feasibility of the implemented UF technology at pilot-scale. The most feasible technology is the hollow fiber membrane. Bench scale tests are required to identify main benefits and limitation of the technology. Besides, in order to complete the design of the prototypes, redefinition of the reaction volume should be performed taking into consideration the bench-scale results. Preliminary design of the reaction volumes were done considering the literature and previous experience of the researchers. A first proposal of the budget has arrived from two of the engineering companies and one quotation is still pending. The final selection of the subcontractor will be based on the cost and experience with the design and construction of similar units. The final design of the prototype will be ready in October-November, using the produced data from bench-scale tests and scientific literature. The procurement of the material and construction will start right after the final design. According to schedule, the pilot will be ready for the start-up in La Llagosta (Barcelona) in February-March 2022.

4.2.1.1. Preliminary design and P&ID of the prototype

The status of the prototype design so far can be seen in the P&ID presented in

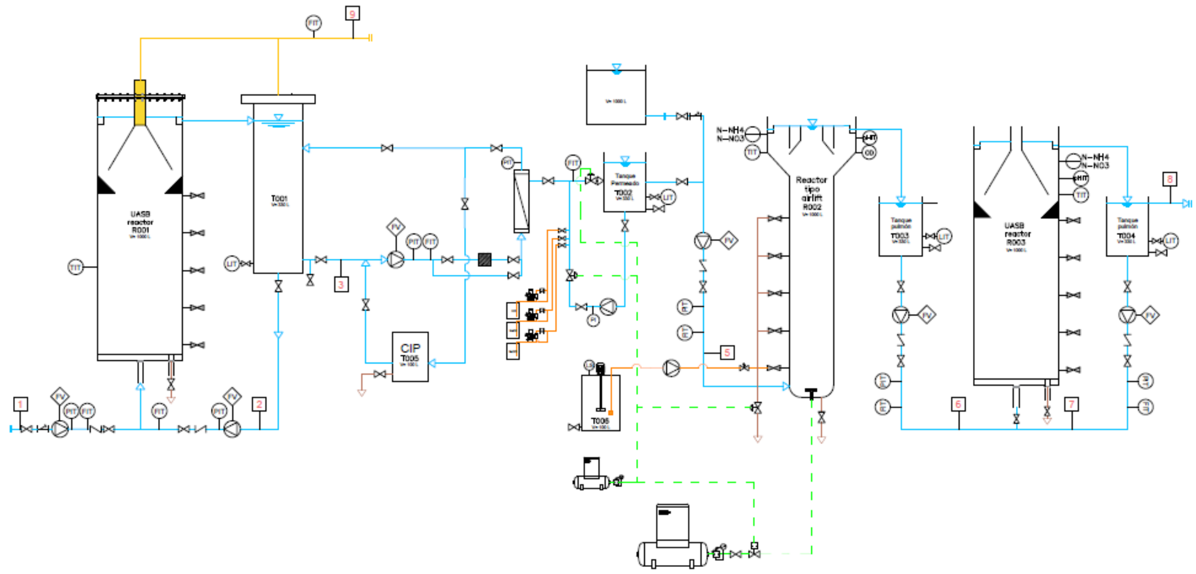


Figure 24.

The principal features/requirements related to the design are the following:

1. Granular anaerobic bioreactor

- One tubular reactor UASB or EGSB type (to be defined) with a volume of 1-4 m^3 (preliminary volume to be recalculated with final data of the bench-scale tests).
- Flow control system required.
- Ultrafiltration (UF) unit connected to the reactor. The concentrate generated by the UF will be recirculated to the reactor and the permeate will be the feed of the partial nitritation reactor. The UF type is not defined yet, Eurecat and Sorigué are discussing 2 options with the engineering companies: tubular or hollow fiber UF membranes.
    - Tubular UF membranes. This kind of membranes were the first option, because they are easily scale-up and successful applied at full-scale. However, these types of membranes have some drawbacks. On one hand, they require high flow rates to

achieve the required cross flow for operation, which implies high recirculation rates that will cause the heating of the water and will interfere with the operational conditions that need to be tested (low temperatures in winter season). Therefore, a cooling system and a large recirculation tank would be required in case of operating with tubular membranes. On the other hand, the membrane surface area needed for the operation would be considerable high (approximately 40 m^2), this implies high equipment cost and high space requirement for the equipment installation.

  - Hollow fiber UF membranes are a good alternative to tubular UF membranes, because a) they do not need a specific cross flow and b) the equipment cost, and space requirements would be significantly lower in comparison to tubular membranes. The main issue related to hollow fiber UF membranes is the production of concentrate; it would be critical to implement an operation configuration that generates the required amount of concentrate needed for the recirculation of the reactor. Besides, hollow fiber membranes are mainly applied to wastewaters with low amount of solids, which is not the case for the expected effluent after UASB/EGSB reactor.
  - Current flat sheet submerged UF membranes are not considered for the CS5, mainly due to the requirement of high nitrogen gas flows, making its operation a non-cost-effective option. Besides, the obtained flux is not so high as was expected, and it technically limited it scale-up for a granular AnMBR.
- System for quantifying the generated biogas is required.

2. Partial nitritation reactor

- One tubular jacketed reactor - heating will be required for the start-up of the prototype – with a volume of 1-2 m^3 (preliminary volume to be recalculated with final data of the bench-scale tests and/or literature review).
- Air bubbling/aeration system at the bottom of the reactor required.
- The reactor must have the option to be operated in SBR and continuous mode
- Flow control system required.

- pH control system required. The HACH sensor that is currently being used at bench-scale could be used also for the prototype.
- Nitrate/Ammonium control required. The HACH sensor that is currently being used at bench-scale could be used also for the prototype.
- Dissolved oxygen control system required (connected to the aeration system). The HACH sensor that is currently being used at bench-scale could be used also for the prototype.
- Temperature control system is required for start-up period.
- The HACH controller/display that is being used currently at bench-scale could be used also for the prototype

3. Anammox reactor

- Tubular UASB reactor, jacketed - heating will be required for the start-up of the prototype - and with a volume of 1-2 m^3 (preliminary volume to be recalculated with final data of the bench-scale tests).
- Flow control system required

4. General

- Chemical cleaning in place (CIP) system for cleaning the membrane is required.
- Programmable Logic Controller (PLC) for the control of all the system.
- Pumps for feeding the reactors.

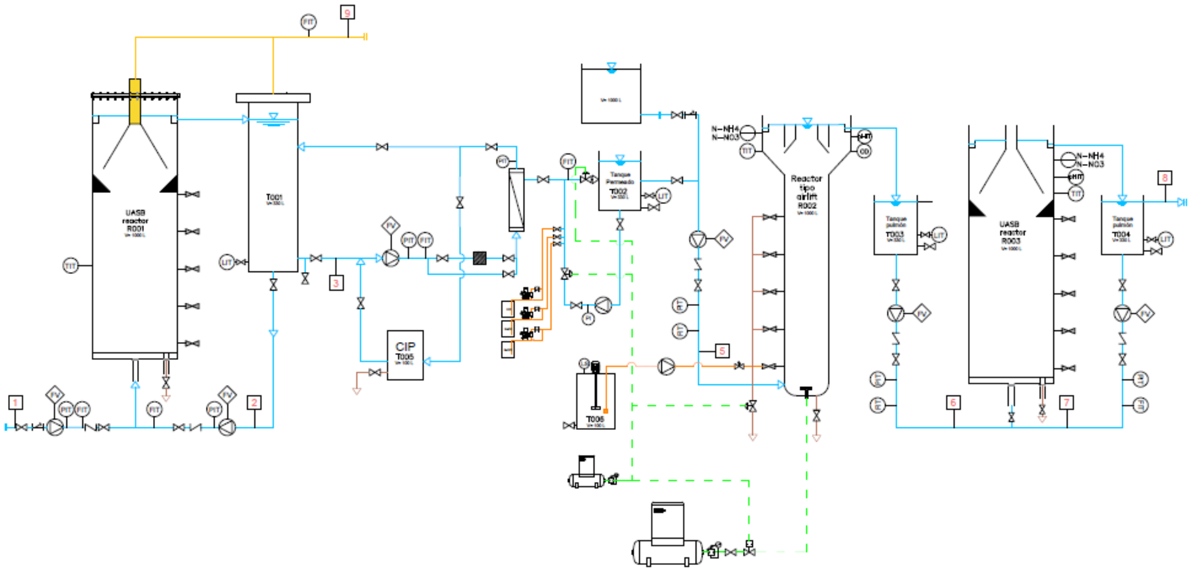


Figure 24. Current status of P&ID for the reactors prototype at pilot scale

4.2.2. Design and construction of the BioPhree prototype

BioPhree is a phosphate adsorption technology to remove soluble phosphate from water streams down to ultra-low levels. Ultra-low means in the range of 10-50 ppb PO_4-P as soluble phosphate (Figure 25). BioPhree can be used to prevent eutrophication in freshwater bodies by treating wastewater effluent or other streams and for remediation of already eutrophied water bodies.

BioPhree uses an iron-oxide based adsorbent that can be regenerated and re-used. Consequently, phosphate can be recovered from the regeneration liquid.

In the BioPhree system, water will first go through a filtration step. Following this, the water will pass through adsorption columns. These columns are filled with an iron-oxide based adsorbent, which selectively adsorbs phosphorus from the water. The contact time of the water with the adsorbent bed is designed so that the effluent will have a phosphorus concentration of 10 ppb PO_4-P. In the pilot system three columns are installed, of which two are used in parallel, and one column is on standby, or being regenerated. In a full-scale installation, more than three columns can be installed with still only one column in standby.

Once the adsorbents get saturated and reach their adsorption capacity, eventually the bed will 'break-through'. This is detected by an online phosphate analyser, which continually monitors the effluent phosphorus concentration.

After a bed has broken through, it needs to be regenerated. This is done by washing the adsorbent with a NaOH solution. The phosphorus is desorbed due to the replacement of the phosphate ion by OH ions. An acid washing step is optional, to remove potential calcium precipitation on the adsorbent. After regeneration, the adsorbent is ready to be used again for adsorption of P.

The NaOH regeneration liquid can be reused many times before being saturated with P and losing its desorption abilities. Phosphorus can be recovered from the regeneration liquid by ultrafiltration.

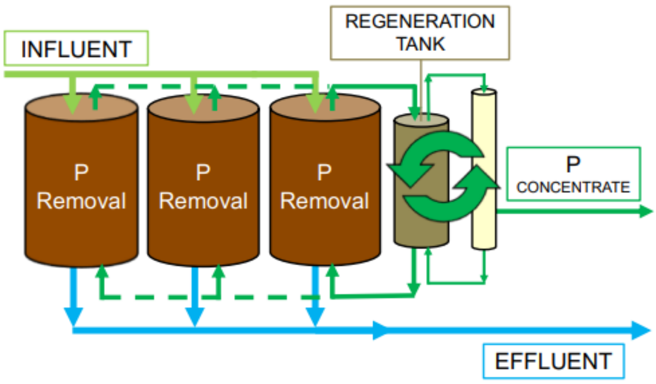


Figure 25. Simplified process scheme of the BioPhree adsorption system (pre-treatment (filtration) not shown)

4.2.2.1. BioPhree pilot design

The principal design considerations for the BioPhree prototype (Figure 26) are the following:

- Be able to treat 1 m^3/h of water in Larnaca and 0.4 m^3/h in Barcelona
- Fully automated. To be controlled and monitored from a distance
- Easy replacement of columns and beds necessary to test different adsorbents.
- Regeneration frequency: aim to have as many as possible for research purposes. With the chosen bed volume, we expect to regenerate every column 9 times per year

- Post-regeneration wash: We use air pressure to push out NaOH of void space to reduce losses.
- Acid dosing on effluent to balance pH with buffer tank for mixing

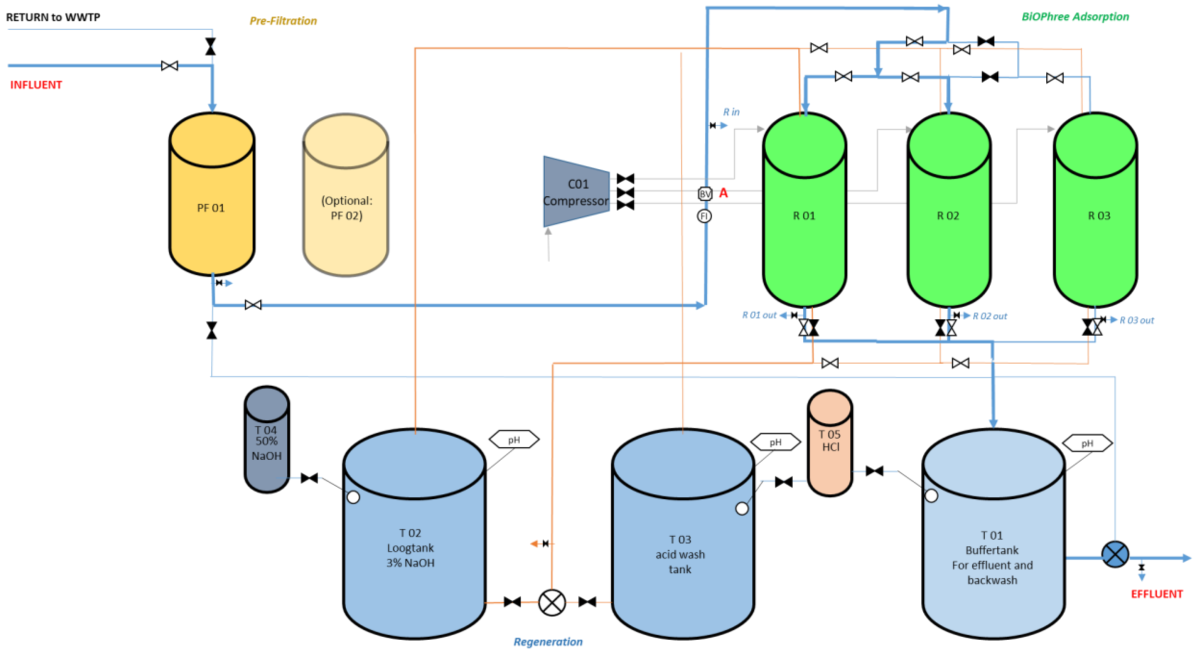


Figure 26. Process flow diagram of the BioPhree pilot

4.2.2.2. Pilot construction, testing and transportation to Larnaca (Cyprus)

The pilot was constructed by Aquacare. Construction was finalized in the week of July 12th with a week of testing and PLC programming. Some pictures of the unit are presented in Figure 27 and Figure 28.

Figure 27. BioPhree filter and adsorption columns

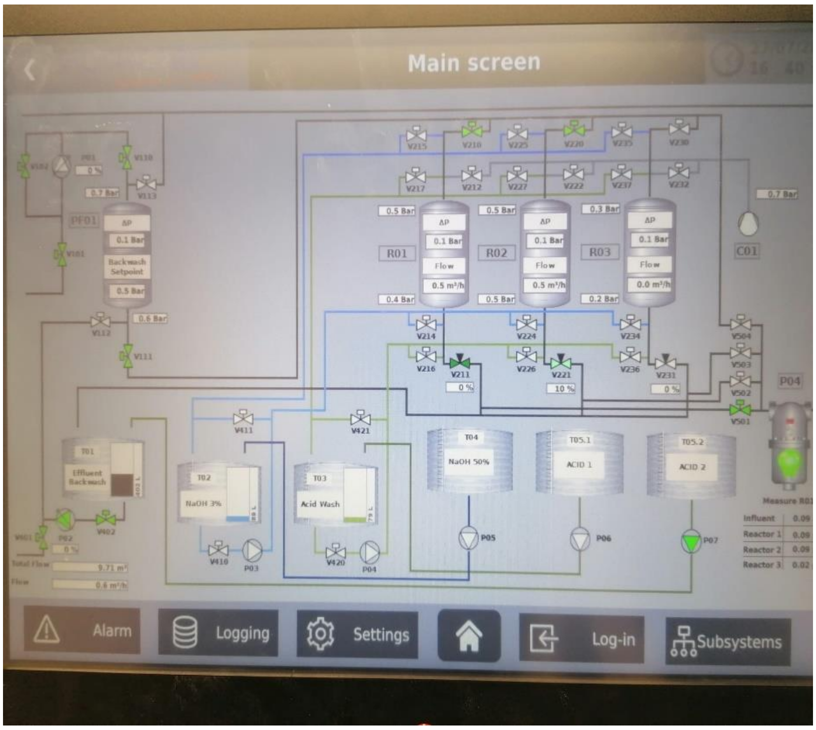


Figure 28. Picture of the process control screen of the BioPhree pilot

Wetsus had the opportunity to test the BioPhree pilot for 3 weeks on surface water in collaboration with Waterschap Brabantse Delta (Geertruidenberg, Netherlands), a Dutch water board and team member of Wetsus. The water board is interested in removing phosphate to deal with (blue) algae blooms.

The pilot container was placed at a small marina and tested for 3 weeks (see Figure 29 and Figure 30). Testing was successful and useful as a pre-test before shipping to Larnaca. For example, Wetsus learned with this test that the influent and effluent pump were over dimensioned and needed to be changed for a good operation. These tests provided valuable experience while the pilot was still close-by before going to Cyprus.

Figure 29. BioPhree pilot container in Geertruidenberg

Figure 30. Influent and effluent intake and discharge points in marina

Influent and effluent concentrations were analysed. In Table 12 the results can be seen in terms of phosphate removal. Phosphate was removed consistently below 0.01 mg/L PO_4-P.

Table 12. BioPhree pilot tests in Geertruidenberg

Date	Influent		Effluent	
	PO_4 (mg/L)	P_{tot} (mg/L)	PO_4 (mg/L)	P_{tot} (mg/L)
27-07-2021	0.07	0.11	<0.01	0.02
29-07-2021	0.09	0.12	<0.01	0.03
02-08-2021	0.07	0.12	<0.01	<0.02

The pilot container has already arrived in Cyprus and is already installed in the WWTP in Larnaca.

5. Conclusions and next steps

This report presented the technical results obtained from month 1 to month 12 of the project regarding the implementation of CS4 and CS5.

NF and RO bench-scale experiments were performed, and membranes FILMTECH LC HR 4040 and NF 90 4040 were selected for operation at pilot scale according to the results obtained. The NF and RO pilot unit was already constructed and will be installed in the Larnaca WWTP station in the first weeks of October. MED and Crystallizer units were refurbished, and first trials with the constructed units show that it is possible to achieve the initial objectives related to sodium chloride recovery. The experiments performed with MED and Crystallizer resulted in water recoveries of up to 92% and NaCl purity higher than 98%. The BioPhree unit for phosphorus recovery has been also designed, constructed, and tested, and has been transported to Larnaca. Next steps will be focused on the installation, start-up and integration of the units.

After the first year of implementation of CS5, 3 bench-scale reactors have been installed and operated for several months. Quite high COD removal efficiency of ca. 80% were obtained at mainstream conditions with an AnMBR in UASB configuration and flat sheet UF membranes. Also, good permeate quality has been obtained by now (<60 mg/L COD). Fast settling granular sludge performing partial nitritation was obtained operating a bubble column as a sequential batch reactor (SBR) to force biomass granulation. Quite good results were obtained during the operation of the Anammox UASB reactor, obtaining a NRR that accounts for a nitrogen removal efficiency (NRE) of 54±10%. The average percentage of P removal obtained in the experiments of Vivianite crystallization was approximately 76.5%, which is a quite good result. Nevertheless, Wetsus must perform further experiments to test lower initial P concentrations (similar to the real effluent to be treated) and enhance the formation of crystals. The preliminary design and P&ID of the reactors prototype at pilot scale (reactors for CS5) has been developed and the main features were presented in this deliverable. The next steps for CS5 are the following:

- AnMBR operation is finalized and the EGSB operation started. The operational results will be compared. This comparison will lead to decision about what type of reactor that should be constructed at pilot scale.
- A hollow-fiber membrane will be tested with EGSB reactor. If the time allows it, also a tubular membrane will be assessed.
- The PN reactor and anammox reactor were stabilized before decreasing the temperature. Temperature was decreased to 15°C for all reactors because the process is meant to operate at mainstream conditions.
- Operate the PN reactor in continuous mode and with 50 mg-N/L in the influent.
- Optimization of vivianite formation at lower P concentrations (5 mg/L) and agglomeration to vivianite crystals.
- Finalize the design of the pilot plant and start construction

Further information about the optimization of the processes at bench-scale and the design of the pilot units will be presented in deliverables D5.1 and D5.2 respectively. Also, this report will be updated at month 24 and at the end of the project. The next update will be submitted in August 2022 (D5.8) and will include technical updates as well as further information related to transversal work packages (for example, the preliminary estimations for energy requirements and costs shared with WP8).

6. References

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