

director

Dr. Joan Dosta Parras
*Departament d'Enginyeria Química
i Química Analítica*



Nitrogen recovery from urban wastewater by means of membranes technology

Andreu Serra Toro

June 2020



UNIVERSITAT DE
BARCELONA

Aquesta obra està subjecta a la llicència de:
Reconeixement–NoComercial–SenseObraDerivada



<http://creativecommons.org/licenses/by-nc-nd/3.0/es/>

The proper use of science is not to conquer nature but to live in it.

Barry Commoner

Vull agrair al meu tutor, el doctor Joan Dosta, per totes les aportacions i valoracions que m'ha fet al llarg d'aquests mesos i la immediatesa amb la que m'ha respost sempre que ho he necessitat. També li agraeixo les correccions de l'anglès que no han estat poques.

I agraeixo al doctor Pau Serra, el meu pare, per haver-me guiat en el treball i per haver-hi pogut comptar en tot moment.

CONTENTS

SUMMARY	i
RESUM	iii
1. INTRODUCTION	1
1.1. IMPORTANCE OF AMMONIUM NITROGEN IN ECONOMY	1
1.2. PROBLEMS RELATED TO AMMONIA PRODUCTION	3
1.3. PROBLEMATICS AND OPPORTUNITIES INHERENT TO NH ₄ ⁺ -N IN URBAN WASTEWATER	5
2. OBJECTIVES	5
3. POSSIBLE TREATMENTS OF NITROGEN IN UWW	6
3.1. NITROGEN REMOVAL TECHNIQUES	6
3.1.1. Conventional nitrification/denitrification	6
3.1.2. Partial nitritation / Anammox	9
3.2. NITROGEN RECOVERY TECHNIQUES	11
3.2.1. Chemical and physical processes	12
3.2.1.1. Struvite precipitation	12
3.2.1.2. Stripping ammonia	15
3.2.1.3. Adsorption	17
3.2.2. Membrane technology	18
4. FEASIBILITY ANALYSIS OF SEVERAL NITROGEN TREATMENT STRATEGIES FROM WASTEWATER	20
4.1. CONSIDERED PARAMETERS FOR FEASIBILITY ANALYSIS	21
4.2. NITROGEN REMOVAL AND RECOVERY EFFICIENCIES EVALUATION	28
4.3. ENERGY ANALYSIS OF NITROGEN REMOVAL AND RECOVERY PROCESSES	29
4.4. COST AND BENEFIT ANALYSIS FOR FERTILIZER PRODUCTION OF NITROGEN RECOVERY TECHNIQUES	31
4.5. AGRONOMICAL AND ENVIRONMENTAL CONSIDERATIONS OF FINAL PRODUCTS	32
5. STUDY OF THE OF 2 NITROGEN RECOVERY STRATEGIES IN MUNICIPAL WWTP	35

5.1. NITROGEN BALANCE IN A CONVENTIONAL WWTP WITH ANAEROBIC DIGESTION OF SEWAGE SLUDGE	35
5.2. ANALYSIS OF NITROGEN RECOVERY USING A MEMBRANE CONTACTOR	38
5.2.1. Membrane recovery plant	38
5.2.2. Implementation in Maresme WWTP	39
5.3. ANALYSIS OF STRUVITE PRECIPITATION STRATEGY	41
5.3.1. Struvite recovery plant	41
5.3.2. Implementation in Maresme WWTP	43
5.4. COMPARISON OF THE STUDIED RECOVERY ALTERNATIVES	46
6. CONCLUSIONS	49
7. REFERENCES	51
8. ANNEXES	57

SUMMARY

This study aims to contribute in a small way to the path of circular economy. Therefore, the contamination threat that UWW supposes is explained here as well as its potential as a source for N recovery. This recovery entails two benefits, in one hand, lower concentrations in the effluent discharged into the environment are achieved, and on the other hand, a compound suitable as fertilizer is produced.

A bibliographic research is carried out in order to determine the impact of these problematics as well as existing technologies to face them. The most important treatments used nowadays for WWTPs are explained to know how these plants operate and which N recovery techniques exist.

A feasibility analysis for those techniques involving membranes technology or struvite precipitation is carried out from data obtained in literature. This analysis can be divided in the study of two aspects, technical capability of the technique to be implemented in plant, and economic balance. Technical capability evaluates the similarity between the stream parameters required for each technique and the actual conditions of wastewater in WWTP as well as the efficiency of both N removal and recovery. Only techniques capable to be performed in streams existent in conventional municipal WWTPs as well as to remove enough N to produce a harmless effluent for the environment are considered suitable to implement. Economical balance takes into account benefit produced from final product's sale, energetic costs, operational costs and chemical costs.

Agronomical and environmental considerations of final products are explained since they have a direct repercussion on final fertilizers sale price and its applicability to the soils. Maresme WWTPs characteristics are presented because they are the base for implementation calculation. These plants water line and sludge line are described too.

Once the most suitable techniques are determined, a subsequent and detailed study for Hollow Fibre Membrane Contactors (HFMC) and Struvite Precipitation (SP) is carried out. These processes are explained in depth and various parameters related with each technique's implementation are calculated. Thanks to these calculation, the values of ammonia recovered, product generated, and economic considerations could be taken into account for the case of Maresme plants. Operational advantages and disadvantages for both techniques are presented too considering their implementation in Maresme WWTPs.

By analysing the impact of their implementation in plant, a comparison between both techniques is carried out. It is determined that great amounts of N could be recovered using HFMC and the economic balance would be significantly high. However, this technique would present

operational problems like membrane fouling. SP technique present the advantage of recovering P but its N recovery efficiency is much lower. Despite its economic balance is negative, controlled precipitation of struvite represents a great benefit for those plants affected by uncontrolled crystallisation.

Finally, a combination of both techniques implementation in a sequence of SP and MC is studied since calculation results suggest that this could present synergies. Several benefits could be achieved by operating with this combination: great recoveries would be reached for both N and P, and operational problems as membrane fouling or uncontrolled struvite crystallisation would be solved or sharply reduced while economic balance would be positive.

Keywords: Urban Wastewater, Wastewater Treatment Plant, Nitrogen Recovery, Membrane Technology, Struvite Precipitation

RESUM

Aquest estudi pretén aportar el seu granet de sorra en el desenvolupament cap a una economia circular. Per tant, l'amenaça de contaminació que suposen les aigües residuals així com el seu potencial com a fonts per a la recuperació de nitrogen s'expliquen aquí. La seva recuperació comporta dos grans beneficis, per una banda s'assoleixen baixes concentracions a l'efluent que es descarrega al medi ambient i per l'altra, es produeix un compost útil com a fertilitzant.

S'ha dut a terme una recerca bibliogràfica per tal de determinar l'impacte d'aquestes problemàtiques així com per saber quines són les tecnologies existents per fer-hi front. S'expliquen els tractaments més importants avui en dia usats en EDARs convencionals per saber com operen aquestes plantes i quines són les tècniques de recuperació de nitrogen disponibles.

S'ha dut a terme una anàlisi de viabilitat per aquelles tècniques que involucren tecnologia de membranes o bé la precipitació d'estruvita a partir de dades bibliogràfiques. Aquesta anàlisi es pot dividir en l'estudi de dos aspectes, la capacitat de la tècnica per a ser implementada en planta i el seu balanç econòmic. La capacitat tècnica avalua la semblança entre els paràmetres dels diferents corrents que requereix cada tècnica i les condicions reals dels corrents que té l'EDAR. També es té en compte l'eficiència que proporciona tant per l'eliminació com per la recuperació de nitrogen. Només les tècniques que es poden dur a terme mitjançant els corrents de les plantes del Maresme i d'eliminar prou nitrogen com per produir un efluent inòcua pel medi ambient es consideraran adequades per una posterior implementació. El balanç econòmic té en compte el benefici que proporciona la venda del producte final, els costos energètics, els operacionals i els químics.

Les característiques agronòmiques i mediambientals dels productes finals s'expliquen ja que tenen una repercussió directa en el preu final del fertilitzant i la seva aplicabilitat en sòls. Es presenten també les característiques de les EDAR del Maresme ja que seran la base amb la qual es duran a terme els càlculs d'implementació. En el mateix capítol es descriu la línia d'aigües i la línia de fangs d'aquestes plantes.

Un cop s'ha determinat quines són les tècniques més adequades, es du a terme un estudi detallat per la tecnologia de Contactors de Membrana de Fibra Buida (HFMC) i la Precipitació d'Estruvita (SP). En aquesta secció s'expliquen detalladament aquests processos i es calculen diversos paràmetres característics de cada tècnica. Gràcies a aquesta anàlisi es poden estimar els valors de l'amoni recuperat, el producte generat o el balanç econòmic pel cas concret de les plantes del Maresme. La presentació de les avantatges i desavantatges d'ambdues tècniques s'ha fet tenint en compte que la seva implantació es fa a les plantes del Maresme.

Es du a terme una comparació entre aquestes dues estratègies mitjançant una anàlisi de l'impacte que té la seva implantació. S'ha determinat que grans quantitats de nitrogen poden ser recuperades usant HFMC i que el seu balanç econòmic és notablement alt. Tot i això, aquesta tècnica podria presentar importants contratemps operacionals com l'embrutiment de les membranes. La SP presenta l'avantatge de recuperar fòsfor encara que el rendiment de recuperació de nitrogen és molt baix. Tot i que el seu balanç econòmic és negatiu, la precipitació controlada d'estruvita suposa un gran benefici per aquelles plantes afectades per la seva cristal·lització incontrolada.

Finalment, s'ha estudiat la implantació de les dues tècniques en una seqüència de SP i MC ja que els resultats dels càlculs suggerien que podien existir sinèrgies entre les dues tècniques. L'operació segons aquesta combinació podria comportar diversos beneficis com: alts rendiments de recuperació tant pel nitrogen com pel fòsfor, la minimització de l'impacte de problemes com la cristal·lització incontrolada d'estruvita i dels problemes d'embrutiment de membranes i tot això combinat amb un balanç econòmic positiu.

Paraules clau: Aigua Residual Urbana, Estació Depurador d'Aigües Residuals, Recuperació de Nitrogen, Tecnologia de Membranes, Precipitació d'Estruvita.

1. INTRODUCTION

Nitrogen (N) is an essential element for human and every other form of live development. This N necessity is the reason why a growing population has been always linked to an increase of its production. The fact that N natural cycle is not enough to supply the whole population because it is a slow and difficult process makes even more important to find a way to produce available N for ourselves.

1.1. Importance of ammonium nitrogen ($\text{NH}_4^+\text{-N}$) in economy

In 1913 ammonia was started to be produced in an industrial way from N gas by means of the Haber-Bosch process for the first time. Halfway through XX century this process spreads around the world allowing a sharp increase in population growth. Nowadays, above a 50% of the world's population is fed by an agriculture that uses synthetic fertilizers (Erisman *et al.*, 2008). In Figure 1, an estimation of population sustained with and without the production of Haber-Bosch N is shown. Although this study was made from predictions it has a high reliability because it combines the studies and previsions done by Smil (2002), Stewart (2005) and Erisman (2008).

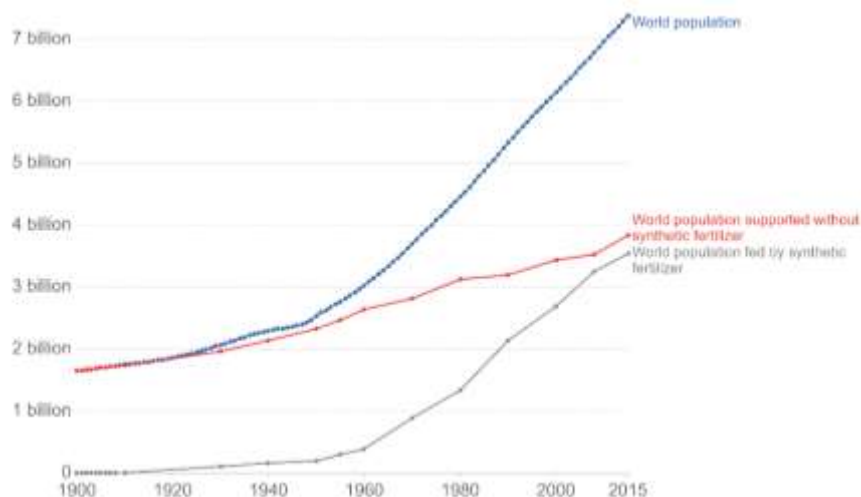


Figure 1.1. World population with and without synthetic nitrogen fertilizers. (Valclav *et al.*, 2009)

1.2. Problems related to ammonia production

Haber-Bosch process has an energetic cost of 35-50 MJ/kg N and supposes a nearly 2% of global CO_2 emissions (Yan *et al.*, 2018). These facts are the reason why it is so important to tend to a circular economy that takes advantage from the Total Ammonium Nitrogen (TAN) contained

in wastewaters instead of converting it into N gas or throw it out to the environment where it could lead to several problems, such as eutrophication.

To produce 1 ton of anhydrous NH_3 fertilizer, which spends an 87% of total energy in the fertilizer industry, there's a request of 949 m^3 of natural gas and 1.6 tons of carbon dioxide are emitted (Beckinghausen, 2020). These environmental impact combined with monetary cost suggest that alternative methods for fertilizer production should be employed from now on. It has to be noted that only 17% of recovered N is finally consumed for humans once it has get through agriculture and ranching industry, the rest of it ends in the waters and the atmosphere (Fowler *et al.*, 2013).

N cycle is a biogeochemical cycle that contains the diverse chemical forms of this element: organic N, ammonia, nitrite, nitrate, and nitrogen gas, among others. This cycle can be considered as a gaseous one because it has the main reserve in the atmosphere where it takes up nearly a 78% of total volume. Its transformation can be carried out by biological and non-biological processes. There are some subprocesses in this cycle and they are N fixation, mineralization and denitrification. Human activities like fossil combustible combustion, artificial nitrogenised fertilizers use and the emission of N in the environment by means of effluent waste had altered its cycle.

The importance of this cycle for all living forms is due to its necessity to assimilate N used for the formation of vital components as proteins or nucleic acids (see Figure 2). Nevertheless, in the process called N fixation, atmospheric nitrogen could not be directly absorbed by organisms, with the exception of some bacteria and plants. These organisms fix unavailable N allowing heterotrophic organisms to obtain it by means of the food chain. Organic rests came back to the soil by putrefaction, then it can be returned to the atmosphere by the action of some specialized bacteria, closing the cycle.

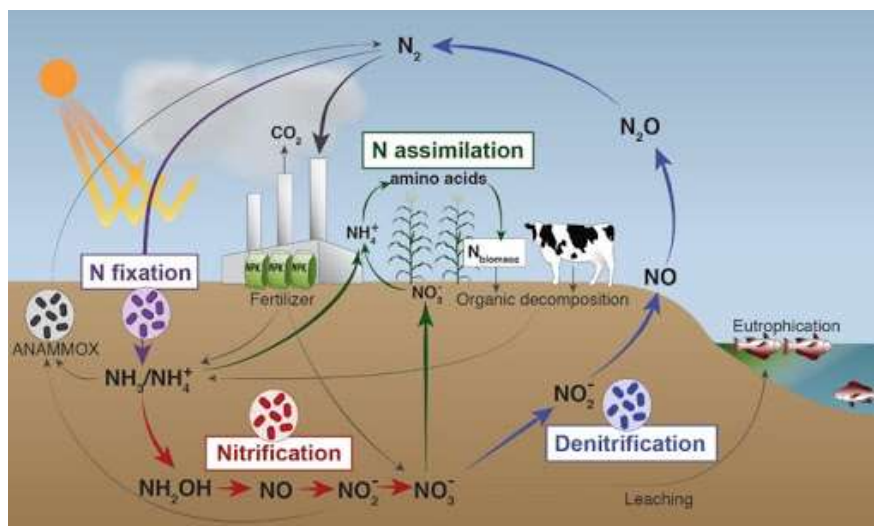


Figure 1.2. Nitrogen cycle diagram. (Arlington, 2016)

There are a few ways to convert N gas into other forms more chemically reactive (usable for living organisms): biological fixation (bacteria, leguminous), fossil combustible combustion (NO_x),

industrial fixation (Haber-Bosch) and other processes like photons or lightning. The recovery of TAN from wastewaters could lead to a non-natural and controlled process to commercialise ammonia with a lower cost and impact than the Haber-Bosch process.

During the last century, the biogeochemical cycle of N (as well as the phosphorus cycle) have been radically changed by humans as a result of many industrial and agricultural processes. While carbon pollution gets all the headlines for its role in climate change, N pollution is a challenging problem too. Somehow we need to produce more food to feed an expanding population while minimising the problems associated with the use of these fertilisers. In Europe alone, the environmental and human health costs of N pollution are estimated to be 70-320 billion euros per year (European Commission Science and Knowledge service, 2016). Its emission such as ammonia, nitrogen oxide (usually bound to the vehicles combustion and industrial processes) and nitrous oxides contribute to particulate matter and acid rain. Nitrogenous gases also play an important role in global climate change. Nitrous oxide is a particularly potent greenhouse gas as it is over 300 times more effective at trapping heat in the atmosphere than carbon dioxide (Lan *et al.*, 2020).

Nowadays certain activities, basically Haber-Bosch process, convert more atmospheric N into reactive forms than all of the Earth's terrestrial processes combined. Much of this new reactive N is emitted to the atmosphere in various forms rather than taken up by crops. When it is rained out, it pollutes waterways and coastal zones or accumulates in the terrestrial biosphere. These can become oxygen-starved as bacteria consume the blooms of algae that grow in response to the high nutrient supply. A significant fraction of the applied N and phosphorus (P) makes its way to the sea, and can push marine and aquatic systems across ecological thresholds of their own. One regional-scale example of this effect is the decrease in the shrimp catch in the Gulf of Mexico's 'dead zone' caused by fertilizer transported in rivers from the US Midwest.

1.3. Problematics and opportunities inherent to UWW nitrogen

N present in urban wastewaters (UWW) has been traditionally removed using biological processes such as nitrification (ammonium is converted into nitrite by ammonium oxidizing microorganisms, followed by transformation into nitrate via nitrite oxidizing microorganisms) and denitrification (nitrate is reduced to molecular N, which is released to the atmosphere). Although its removal from wastewaters avoids the harmful effects of nitrogen contamination of the water bodies (eutrophication, toxicity problems), it do not comply with the aims of circular economy.

On one hand, the industrial Haber-Bosch process for ammonia production is energy-intensive, consuming $6.4 \cdot 10^{12}$ MJ/year of non-renewable energy which is equivalent to 90 million cars in terms of energy usage or almost 80 million people in terms of global warming potential (Yan *et al.*, 2018). However, N removal from wastewaters requires large amounts of energy, where the aeration for nitrification alone occupies between 50 and 70% of total energy

consumption in wastewater treatment plants (WWTPs) (Kirova-Yordanova, 2004). A new sewage treatment paradigm based on the so-called Water Resource Recovery Facility (WRRF) concept has emerged within the scientific community for waste-to-resource recovery (Fowler *et al.*, 2013). Within this paradigm, sewage is no longer considered as a waste but as a source of raw valuable resources, resulting in environmental and economic benefits (Garcia-González and Vanotti, 2015). N is one of these valuable resources present in wastewaters, which are expected to be recovered.

The concentration of $\text{NH}_4^+\text{-N}$ varies from 10 to 200 mg/L in UWW and it can reach 1000 mg/L in industrial wastewater and 5000 mg/L in effluents that come from livestock wastes (Lema and Suarez, 2017). Compared with UWW, effluents with high concentrations of ammonia imply other problematics to keep in mind. As an example of this problems there are metal corrosion, the reduction of the dissolved oxygen concentration, the toxic effects on fish, or the reduction disinfection efficiencies. The traditional way of make use of the livestock waste as fertilizer for agricultural soils is no more a valid option since it has caused the contamination of aquifers and soils. Furthermore, in 2015 the 94% of total ammonia emissions in Europe was caused by the agricultural sector (EEA, 2017). This vast numbers forced the scientific community to find a way to recover N in a sustainable way.

2. OBJECTIVES

The main motivation of this study is to know the problematics inherent to ammonium nitrogen production and disposal, as well as the existing ways to solve or mitigate these problems. This study is focused in urban wastewater, a nitrogen containing source that has to be treated before its return to the environment. By means of recovery techniques usage, both goals of ammonium nitrogen production and contamination prevention can be achieved.

The general objective of this work is to critically study $\text{NH}_4^+\text{-N}$ recovery techniques from urban wastewater, focusing on those that recovers nitrogen as a product with high agronomic value. To meet this general objective, the following goals are planned:

- To review the main $\text{NH}_4^+\text{-N}$ removal and recovery processes from urban wastewater.
- To evaluate which is the most suitable nitrogen recovery technique by means of membrane technology for its implementation in a WWTP.
- To study struvite precipitation in urban WWTPs for combined magnesium, nitrogen and phosphorus recovery.
- To determine the technical feasibility of implementing these techniques in a conventional WWTP, considering nutrient recovery efficiencies, productions and operational requirements.
- To determine the economic feasibility of implementing these techniques in a conventional WWTP, considering the operational cost (energetic cost and chemical cost) and benefits from product sale.
- To compare different techniques and implementation strategies.

3. N-NH₄⁺ REMOVAL OR RECOVERY FROM WASTEWATERS

The presence of nutrients in wastewaters, such as N, has long been recognised as a source of over enrichment of receiving environments, which could lead to explosive plant growth and algae blooms, resulting in eutrophication, fish kills, etc. Therefore, the removal of these nutrients has become indispensable. The recovery of nitrogen helps to close this cycle and save energy in a later N fixation through Haber-Bosch process.

There are two main ways to treat TAN in wastewaters: by removing it and by recovering it. In spite of the fact that elimination is the most usual as of today, in a circular economy approach, it could be more useful to take advantage of ammonia rich waters N as a resource and not as a waste.

3.1. Nitrogen removal techniques

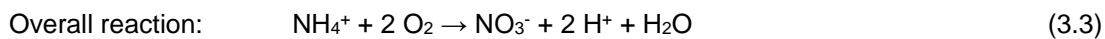
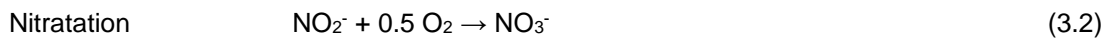
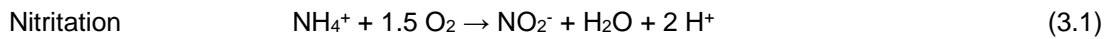
N removal in wastewater treatments has been studied and implemented in full-scale plants from long time ago. The traditional methods used in N removal are nitrification/denitrification (N/DN), deammonification techniques such as anammox and combinations like anammox followed by denitrification or algae treatment. By employing these techniques reactive N is ultimately lost through its biological uptake and its conversion into gas.

While this is the opposite of circular economy, it is by far the most widespread method in wastewater treatment. In fact, there is a big number of WWTP where N is not removed and the plant consists in a sequence of pre-treatment, settlers and biological reactors focused on organic matter removal. This plant configuration must make the effluent enable to be delivered to the environment.

To summarise the application of N removal techniques: they are suitable to use when the purpose is to make the final effluent less contaminant to the environment and N recovery is not needed.

3.1.1. Conventional Nitrification/Denitrification

Nitrification consists in a two-step biological oxidation process: nitritation which converts ammonium N into nitrite (see Equation 1, without considering biomass growth) and nitratation which is the further oxidation of nitrite to nitrate (see Equation 2, without considering biomass growth). The overall reaction (see Equation 3, where biomass growth is not considered) is carried out by means of autotrophic organisms and it requires available dissolved O₂.

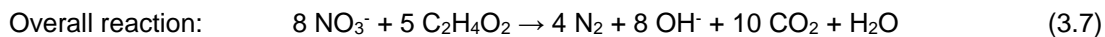
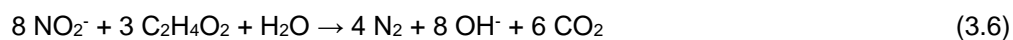
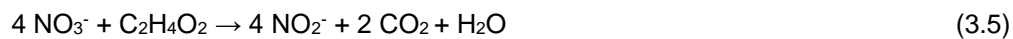


The biomass that performs the first reaction are ammonia-oxidizing bacteria (AOB) and those who carry out the second one are nitrite-oxidizing bacteria (NOB). This oxidation reaction needs inorganic carbon and a certain condition of temperature and pH to take place.

Denitrification is the biological reaction to reduce nitrate to N gas. In Equation 4, N transformations during conventional denitrification are presented. In the conventional denitrification process, the reaction is carried out by means of heterotrophic organisms under anoxic conditions, so it has to take place in total absence of dissolved O_2 .



Denitrification reaction steps when using acetic acid as biodegradable COD to carry out the process are stated in equations 3.5-3.7, without considering biomass growth nor the formation of N_2O .



This reduction reaction needs organic carbon and certain conditions of temperature and pH like it occurs in nitrification.

As the nitrifying bacteria are generally more sensitive than aerobic and anoxic heterotrophic bacteria treating readily biodegradable COD, the nitrification process should be designed as a separate aerobic treatment, after the main biodegradable COD removal process.

Nitrification and denitrification take place in aerobic and anoxic biological reactors, respectively. The most common sequence is an anoxic biological reactor followed by an aerobic one. As shown in Figure 3, an internal recirculation from the aerobic reactor to the anoxic one is usually performed to take nitrates back to the anoxic bioreactor allowing the denitrification to take place.

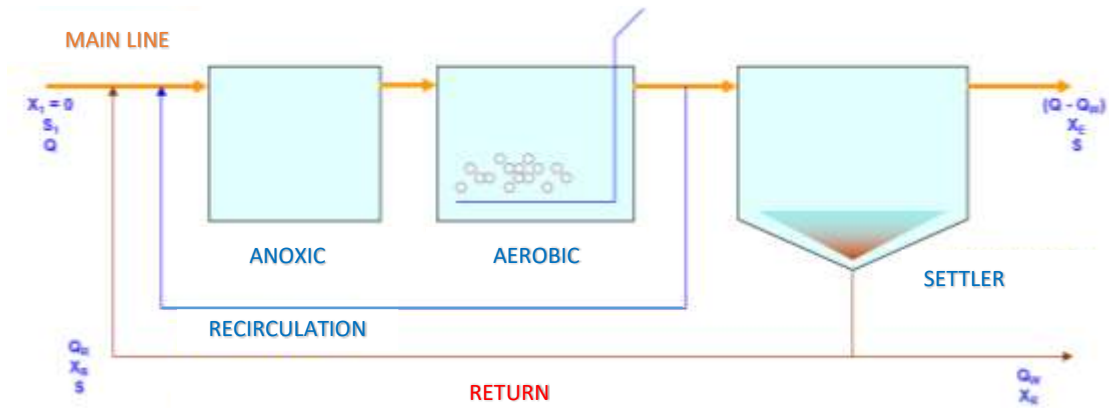


Figure 3.1. Flow diagram of the continuous N/DN treatment usually applied in municipal wastewater treatment plants. (Mata J, "Tecnologies pel medi ambient" class notes)

Membrane Biological Reactor (MBR) systems are specially suitable when a high quality of the effluent is required. In this configuration, the decanter is replaced by a membrane filter that retains particles larger than 0.1-0.4 micrometres. By using these membranes, an effluent exempt of suspended solids (SS) and colloidal matter is obtained. It removes the greater part of bacteria too. While it assures a biomass effective retention inside the reactor, it prevents from bulking problems and a bad separation of sewage in the decantation tank. Figure 3.2 shows a flow diagram of a continuous MBR for municipal wastewater treatment through N/DN.

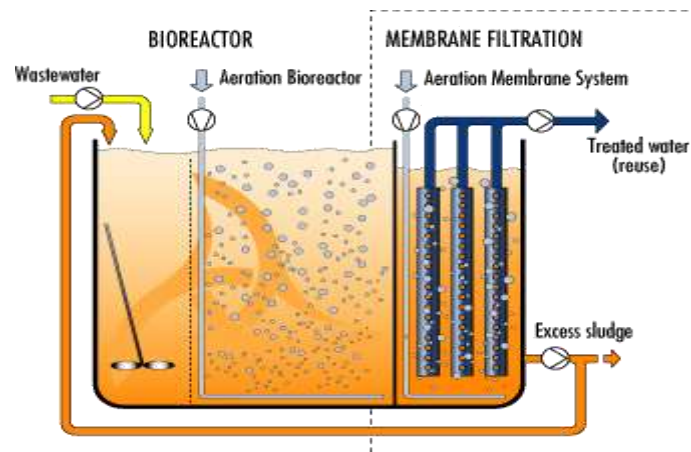


Figure 3.2. Biological Membrane Reactor. (Lenntech, 2010)

There are two main configurations, submerged and tubular membranes. The most interesting aspect for a later comparison of feasibility with other techniques is their energetic cost and the quality of its final effluent. In submerged membranes, this cost varies between 0.6 and 1 kW/m³ while this value varies between 1 and 3 kW/m³ in tubular configuration. For this reason, the submerged MBR technology is the one preferred for municipal wastewater for N/DN treatment, since these plants are characterised by a high influent flowrate.

Membrane filters are usually cleaner than secondary decanters. However, there are some operation condition influencing this process: substrate/biomass ratio, inlet wastewater pretreatment, dirtying problems prevention and membrane cleaning. Additionally, the treated wastewater quality depends on the membranes type, modules, suction pump power or inlet wastewater, among other factors. The experience in several industries put this technique in a high position in the ranking of techniques to treat industrial wastewater. Despite that, in UWW treatment it is still a developing market very linked to the desired destination of the treated wastewater. The MBR systems are able to increase the treatment capacity. However, there are some limitations such as the prevention of membrane fouling, the requirement of membrane cleaning, energetic cost optimization or mechanic forces resistance that make this technique a subject of study.

Other alternative conventional N/DN treatments exist including technologies using a single reactor where:

- (i) Aerated and non-aerated periods are alternated.
- (ii) The fluid moves around between aerated and non-aerated zones.
- (iii) Biofilm or granular biomass is used with a lack of dissolved oxygen supply to promote the presence of aerobic and anoxic zones in the biomass aggregates.
- (iv) Stages of feeding, anaerobic/anoxic/aerobic react, settling and effluent are alternated in operating cycles (Sequencing Batch Reactor or SBR configuration).

3.1.2. Partial nitritation / Anammox process

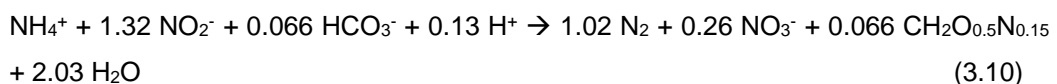
Anammox, an abbreviation for anaerobic ammonium oxidation, is a globally important microbial process of the N cycle. In this biological process, nitrite and ammonium nitrogen are converted directly into diatomic N and water (see Equation 8).



Globally, this process may be responsible for 30-50% of the N₂ gas produced in the oceans (Devol AH, 2015). The application of the Anammox process lies in the removal of ammonium in wastewater treatment and consists in two separate processes. The first step is the nitritation of half of the ammonium to nitrite by ammonia oxidizing bacteria (partial nitritation) as shown in Equation 3.9 where biomass growth were not considered.



The resulting ammonium and nitrite are converted to dinitrogen gas and near to 5% nitrate by anammox bacteria (see Equation 3.10 where biomass has been considered) (Rui *et al.*, 2019).



So the global process without considering the organic matter is stated in Equation 3.11 and Figure 3.3.

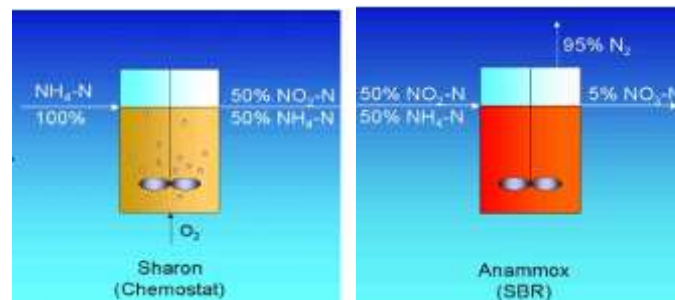
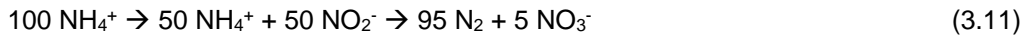


Figure 3.3. Anammox process diagram (Mata J, "Tecnologies pel medi ambient" class notes).

The global process could also take place in one single reactor where two guilds of bacteria form compact granules or biofilms (Cao *et al.*, 2016). For the enrichment of the Anammox organisms, granular biomass or biofilm system seems to be especially suited in which the necessary sludge age of more than 20 days can be ensured. Possible reactors are sequencing batch reactors, fluidised bed reactors or gas-lift-loop reactors. The cost reduction compared to conventional N removal is considerable and the technique is still young but proven in several full-scale installations, especially for the treatment of anaerobic digestion (AnaD) supernatants.

Anammox presents some advantages in comparison with traditional N/DN treatment. Conventional N removal from ammonium-rich wastewater is accomplished in two separate steps: nitrification and denitrification, which reduce nitrate to N_2 with the input of suitable electron donors. Aeration and input of organic substrates (typically methanol) show that these two processes are highly energy consuming, associated with the production of excess sludge and significant amounts of green-house gases such as CO_2 , N_2O and ozone-depleting NO . Since Anammox bacteria convert ammonium and nitrite directly to N_2 anaerobically, this process does not require aeration nor other electron donors. Nevertheless, oxygen is still required for the production of nitrite by ammonia oxidizing bacteria. In partial nitrification/anammox systems, oxygen demand is greatly reduced because only half of the ammonium needs to be oxidized to nitrite instead of full conversion to nitrate.

The autotrophic nature of Anammox bacteria and ammonia oxidizing bacteria guarantee a low yield what means less sludge production. Additionally, Anammox bacteria easily form stable self-aggregated biofilm, allowing reliable operation of compact systems characterized by high biomass concentration and conversion rate up to $5\text{-}10 \text{ kg N/m}^3$. It has been shown that efficient application of the Anammox process in wastewater treatment results in a cost reduction of up to 60% as well as lower CO_2 emissions.

On the other hand, Anammox presents some disadvantages. The doubling time is slow, between 10 days to 2 weeks and this makes it difficult to grow enough sludge for a wastewater

treatment reactor. Also the recovery time after the loss of sludge by accident is longer than in conventional N removal systems. On the other hand, this slow growing rate is an advantage due to the reduction of surplus sludge that needs to be removed and treated. Depending on the exact species, the optimum pH level is 8. Therefore, it can be necessary to adjust the pH of wastewater by adding caustic.

Other biological N removal processes different than conventional N/DN and partial nitrification/Anammox are also available. One example is the nitrification and sulphur-based autotrophic denitrification processes that can be used to remove ammonia from wastewater in an economical way. However, under certain operational conditions, these processes accumulate intermediate compounds, such as elemental sulphur, nitrite and nitrous oxide that are noxious for the environment.

3.2. Nitrogen recovery techniques

N recovery is the next step in the improvement of wastewater treatment process because by utilizing these nutrients for fertiliser the use of energy and petrochemicals could be reduced while achieving a smaller impact on the environment. Nowadays, the greater part of wastewater treatment plants is only focused in N removal and complying with effluent concentration limits. These plants tend to be composed by the water line where the wastewater is treated and the sludge line where the sludge is separated from the water and purged or recycled (Fung and Wibowo, 2013). Recovering N is an opportunity to treat wastewater while obtaining an ammonia product and create a circular economy.

Currently, in most WWTP worldwide, just like it occurs in studied plants in Maresme, N and P are removed from wastewater streams by enhanced biological nutrient removal, which usually is not capable to reach required low levels of total P contained in discharging stream (the limit established by Directive 91/271/CE is 2 mg P/L). Thus, the remaining P content is usually precipitated with iron or aluminium salts resulting in biologically nonprofitable P based minerals due to its low solubility. Moreover, huge amount of sludge is produced, which reported difficulties in its management as well as low reusability. In the last years, several studies have been focused on integrating nutrient recovery processes in these plants working scheme. Several techniques for N recovery already exist but some of them are still being studied so their efficiencies and energy requirements cannot be totally compared.

Barat *et al.* (2009) evaluated the ammonium and phosphate content as well as flow rate and pH value of ten sampling points in a WWTP from Murcia (Spain). Based on their study data, it is concluded that most of the sample points can be potentially used for nutrients recovery depending on the technology used. However, in cases involving membranes, is important to install a filter system in order to reduce the amount of total suspended solids (TSS), which is a critical parameter with a negative influence in nutrient recovery performance.

Moreover, ammonia rich water can be used to grow algae or bacteria that could be used in the creation of biogas or biofuels, as a food source for animals, or as fertilizer. This last use is gaining increasing attention because of the immense demand of the product. However, wastewater cannot be used directly as fertilizer due the potentially elevated concentration of metals and other contaminants (Kern *et al.*, 2008). When studying various N recovery techniques, it is necessary to keep in mind whether the product would be easily used as fertilizer or not in order to determine their economic feasibility.

There are processes of different nature that comprehend the techniques of N recovery. These processes are chemical, physical, and biological (bio-electrochemical) methods through which the elimination and recovery of nutrients is achieved. Their different characteristics are explained in the following sections.

3.2.1. Chemical and physical processes

The principles that determine chemical processes are the separation of N into another usable compounds by means of a chemical reaction. One example of this type of process is the production of struvite, a technique based on accomplishing the specific conditions that make possible the formation of a particular compound. Usually, the correct functioning for these processes lies in knowing the conditions that allow the process to work in its optimal. In struvite case, it is important to operate at narrow pH range between 7.6 and 8.1 (Booker *et al.*, 1999).

In physical process category, membrane technology (Xie *et al.*, 2016), filtration (Gerardo *et al.*, 2013), adsorption and stripping (Ukuwani and Tao, 2016) are included. Zeolite adsorption of ammonium is a good example of feasible technique that has its basis on high cation exchange capacity and high selectivity. In addition, regeneration of loaded zeolite to form rich ammonia concentrates is possible and it can be directly applied to soil as fertilizer (Smith and Smith, 2015). Osmotic systems are included in this group, but some studies have determined that they are preferably used in producing clean water rather than nutrient recuperation (Hancock *et al.*, 2013).

3.2.1.1. Struvite precipitation

P has a similar problematic to N, it is scarcely available in nature while it is essential for human life. Estimations show that the available reserves of clean phosphate rock may be exhausted within the next 50 years (Gilbert, 2009). This problematic is caused because P resources follow a one-way pathway in nature, which is difficult to regenerate, driving to their depletion.

Although this problem is while ago recognized, significant amounts of this resources are not being effectively recycled. P in wastewater can be seen not only as a source of pollution to be reduced, but also as a limited resource to be recovered (Zhou *et al.*, 2017). Thus, excess sludge could be regarded as a potential resource of P (Arakane *et al.*, 2006). However, as stated by

Xialei *et al.* (2018) regarding Llobregat WWTP, it is conventionally removed by adding Fe^{3+} what drives to iron phosphate precipitation in order to obtain a final P concentration below 2 mg P/L, accomplishing EU regulation (Mas-Pla *et al.*, 2006). Figure 3.4 shows the P precipitation process usually carried out in municipal WWTPs to meet standards regulations related to this nutrient.

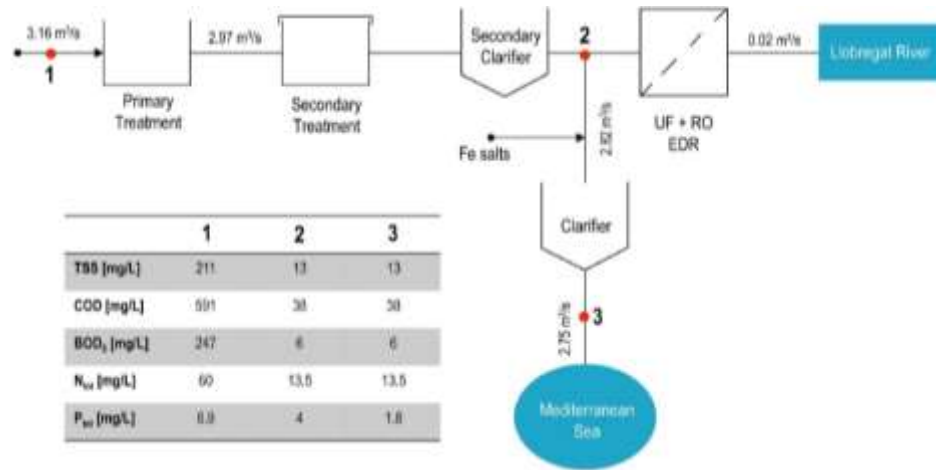


Figure 3.4. P precipitation with Fe in a conventional WWTP. (Xialei *et al.*, 2018)

According to the characteristics of the streams represented in Figure 3.4, a mass balance of P is carried out below to see its final amount contained in sludge and clean:

$$\text{Inlet } P = \text{River spilled } P + \text{Sea spilled } P + \text{Sludge } P;$$

$$\frac{3.16 \text{ m}^3}{\text{s}} \frac{6.9 \text{ g}}{\text{m}^3} = \frac{0.02 \text{ m}^3}{\text{s}} \frac{4 \text{ g}}{\text{m}^3} + \frac{2.75 \text{ m}^3}{\text{s}} \frac{1.8 \text{ g}}{\text{m}^3} + \frac{0.39 \text{ m}^3}{\text{s}} \frac{X \text{ g}}{\text{m}^3} \quad (3.12)$$

Isolating the X, it is found that sludge separated from primary, secondary, and tertiary treatments contains 43 g/m³. The amount of P removed from wastewater by sludge is 16.8 g P/s what equals to a 76.9% of total influent P. This removal starts at the primary and secondary treatment where P is transferred to the sludge, the next step in water line consists in the addition of Fe ion (see Figure 3.4) while in sludge line the sludge produced in previous treatments goes through a thickening, AnaD, thickening, and dewatering. Streams from which struvite precipitation can be performed are those coming after the AnaD (see Figure 3.5).

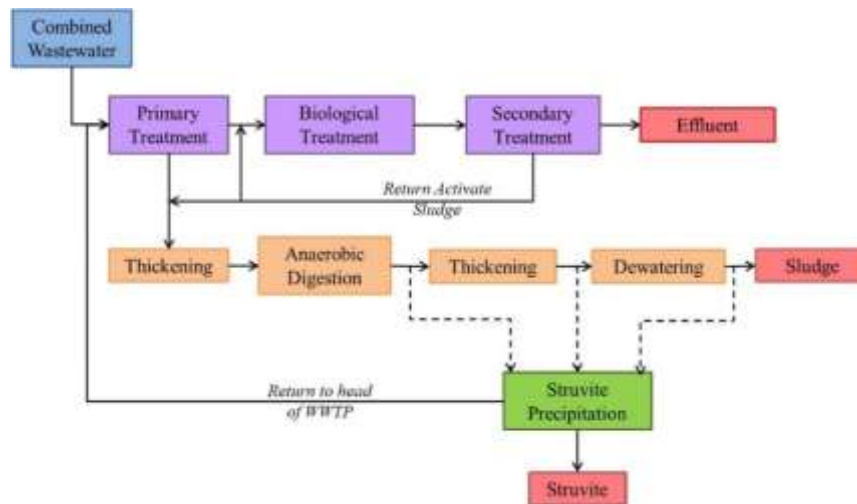


Figure 3.5. Struvite precipitation WWTP flowsheet. (Sena and Hicks, 2018)

By employing struvite crystallization technique it is not only the benefit of P and N recovery what it is achieved, but also the control of uncontrolled struvite formation too, avoiding possible pipes clogging. Magnesium ammonium phosphate known as struvite is a relatively insoluble crystalline precipitate that contains an equal molar ratio of ammonium, phosphate and magnesium ions. Moreover, struvite will be an appropriate fertilizer because it spreads its nutrients slower than other fertilizers, which means that it will not be aggressive to the plant and its effect will last longer. Specific surface area, pore structure, particle size, and environmental compatibility are key parameters to consider for crystallization seeds choose (Duan *et al.*, 2010).

The main operational parameters which affect the formation of P precipitates are pH (in a range between 7 and 11) and molar ratio of participating ions (Peng *et al.*, 2018; Ye *et al.*, 2017). Products of ionic activity Mg^{2+} and PO_4^{3-} must exceed the thermodynamic solubility of the struvite product. The pH value influences on the phosphate concentration, which impacts on crystals average size (Rahman *et al.*, 2014). However, the required addition of Mg is a drawback when using this technique as well as it is recommended to apply a subsequent technique to recover the remaining N.

There is a growing interest in those techniques that involve recovery of TAN and PT through struvite production. The most popular technique to produce it is struvite precipitation, where takes place the following reaction:



Its precipitation as a final product is a specific technique that requires a tight pH range for optimal efficiency and there are different opinions about which is the best pre-treatment preparation or stream to recover struvite from.

Despite struvite precipitation is a technically proven promising technique for both removal and recovery of nutrients, it presents some economical and operational limitations (Hao *et al.*, 2013): large amounts of external Mg and alkali are needed to be added to the wastewater, high purity of struvite is difficult to obtain, and the market for struvite as fertilizer has not been totally established yet. However, nowadays there are other techniques producing struvite different than precipitation. Some of them are: EMNRC, MEC-FO, sludge fermentation, or struvite precipitation by adding LSSA (presented in Table 4.1). These methods present several advantages and disadvantages that make each technique suitable in different conditions.

3.2.1.2. Ammonia stripping

To remove the ammonia out of the wastewater, the air stripping of ammonia-laden water is a proven technology. The ammonia is first stripped from the wastewater in the stripping tower. In this stream ammonium ions exist in equilibrium with ammonia which formula is the next:



According to the acid-base equilibrium of TAN (NH_4^+ and NH_3), below pH 7, TAN will be present in the form of soluble ammonia ions, while above pH 12, all the ammonium ions will be present as a dissolved gas or free ammonia. At any given temperature and pH, we can determine the amount of air or steam (extractor) necessary to provide an adequate ammonia flow. Generally, at higher temperatures, the needed air or steam flow will be lower. Those factors that favour a high efficiency like high pH, high temperature, high air or steam flow, and a greater packed bed depth have to be adjusted before the water enters the stripper.

The equipment used for this stripping process is similar to that of the gas scrubbing technology, an NH_3 stripping tower which is a kind of packed column. Figure 3.6 shows a scheme of an air stripping unit for ammonia recovery. As observed in this Figure, the preheated ammonia-laden water enters the stripper on top. As the water is distributed over the internal packing media, it is broken up into small droplets which brings a big increase of the amount of surface. Air enters the bottom of the tower from a fan and travels upward through the packing. Since the ammonia is partially present as a dissolved gas, some of the ammonia transfer from the water to the air. NaOH is added to obtain a correct pH value, which will allow the ammonia to be dissociated or stripped from the water. The treated water will be collected at the bottom of the stripper; the now ammonia-laden gasses leave the striptower at the top, for further treatment.

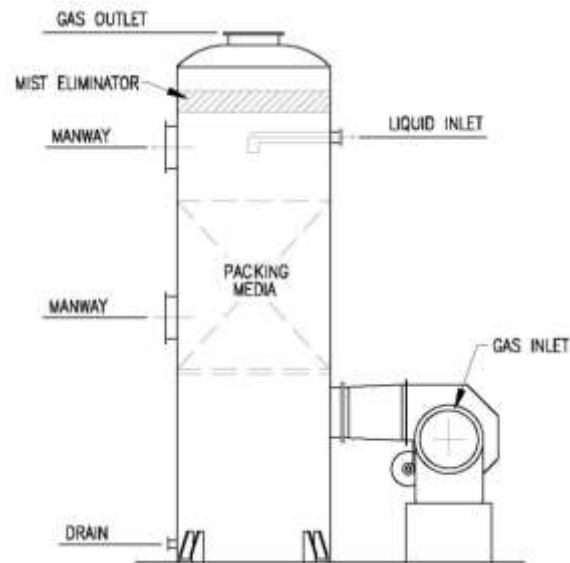


Figure 3.6. Stripping ammonia column.

Once the ammonia is removed from wastewater, there are different methods of treatment such as disposal, air dispersal, concentration as ammonium sulfate, and thermal destruction. The simplest system of air stripper tower involves pH adjustment with air discharged directly to atmosphere. As an advantage we have a low initial cost and operating cost. Nevertheless, removal efficiency is limited by operating temperature and an atmospheric discharge can carry environmental problems.

There are two main ways to operate stripping:

- **Closed loop:** this technique can be used where higher temperatures are preferred to get better efficiency. In the closed loop, the air is sent to an absorber where concentrate ammonium sulphate is formed. The clean air is then recycled back to the stripper. As advantages we have no air emissions and conservation of the energy. As disadvantages, initial and operating cost are higher because of the absorber and must dispose of concentrated ammonia sulfate.
- **Loop coupled with ammonia thermal destruction:** another method is catalytic oxidation system. The air is sent to the catalytic oxidizer where it is heated up to an operating temperature. As the ammonia passes over the catalyst, it is converted to N and water. The exit gas is innocuous and can be released directly to the atmosphere with no difficulty. Strong points of this treatment are that oxidizer will provide control if regulations do not allow release of ammonia and there is no need to deal with concentrated ammonium sulphate. However, it has a high initial and operating cost.

3.2.1.3. Adsorption

Among various ammonium ion removal processes, adsorption is a cost-effective technique that has been widely used in removing ammonium from water and wastewater treatment (Otal *et al.*, 2013; Wang *et al.*, 2014). Waste activated sludge consists mainly of bacterial cells and extracellular polymeric substances with a negative surface charge at certain pH, which are beneficial to the adsorptive removal of positively charged NH_4^+ ions (Nielsen, 1996).

The adsorbed ammonium pollutants on excess sludge can be removed from the eluent upon solid–liquid separation by centrifugation or filtration. However, additional electricity input or equipment configuration like rotators, membranes or filters charge extra operating costs in the separation process. The application of sludge-derived adsorbents in removing contaminants from wastewater has also been investigated in previous studies (Zhang *et al.*, 2013; Guo *et al.*, 2017).

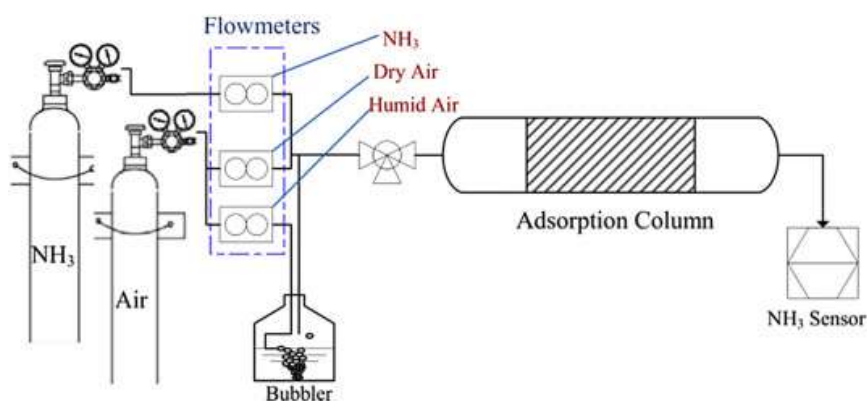


Figure 3.7. Ammonia adsorption system diagram.

Adsorbent selection is the key for a good efficiency. The main materials used to adsorb ammonia N in the present are fly ash, zeolite, sepiolite, limestone, charcoal or activated carbon. However, most of these materials require a secondary treatment, which makes the process cost increase and therefore, it cannot be popularised. The factors that allow to decide which the most adequate adsorbent is, are its dosage, particle size and porous structure because they determine the surface area. There are other properties such as pH, reaction time, concentration of ammonia N in the inlet, the simplicity of the secondary treatment or the effect of activation in adsorbents like carbon or biochar.

Keeping in mind the interest in its effect on the environment, adsorption presents some advantages like the possibility of using the adsorbent in agriculture. This method is used in China where abundant biochar resources are available, which can serve as a good soil conditioner when they are returned to the fields after ammonium N adsorption reaches saturation.

3.2.2. Membrane technology

Membrane systems consist in a selective barrier that allows only some molecules to pass through making possible the separation of this compound from the original mixture. Synthetic membranes are constructed with a determinate purpose and their configuration will vary in porous size, thickness or structure. According to its configuration and driving force there are different types of membranes, physicochemical and bio-electrochemical.

Membrane technology is useful for concentrating nutrients in those streams where some treatment has been previously performed, such as digested effluent, in order to favour the subsequent recovery of these nutrients (Nir *et al.*, 2018). However, it is important to have low levels of TSS since it is a condition for preventing operational issues. Nowadays, forward osmosis (FO), membrane distillation (MD), electrodialysis (ED), and gas permeable membrane (GPM) are the main membrane technologies for ammonia concentration in wastewater (Xie *et al.*, 2016, 2014).

Forward Osmosis. It is a process based on a semipermeable membrane which uses the osmotic pressure difference between the feed and the permeate solution as driving force (Yan *et al.*, 2018). It is capable to concentrate by ten times the nutrient in the original feed solution (Vanotti *et al.*, 2017; Xue *et al.*, 2015). The pH of the solution influence the nutrient retention in the feed side. This occurs due to the mitigation of ammonium ions to the permeate side and the increase in the retention of phosphate ions since the surface of the membrane is negatively charged at alkaline pH (Cartinella *et al.*, 2006).

Membrane distillation. This process driving force is the vapour pressure gradient caused by the heating of the feed solution. Normally, phosphate ions are concentrated in the feed solution because of its extremely low volatility while ammonium ions are accumulated in the permeate side by reacting with the receiving solution (H_2SO_4 or HCl) and producing various products with the form of ammonium salts (Thygesen *et al.*, 2014; Zarebska *et al.*, 2014; Zhao *et al.*, 2013).

Electrodialysis. In the electrodialysis process, a phosphate-rich and ammonium-rich solution can be obtained by a selective separation carried out in both anode and cathode chambers. Efficiencies can be improved by modifying pH or the voltage applied (Tran *et al.*, 2014 and 2015). Traditionally, this kind of processes reported lack of selectivity towards ions while it has a high-energy consumption. Selectivity towards phosphate and ammonium ions specifically has been improved by the integration of ion selective monopolar membranes leading to electrodialysis (Yan *et al.*, 2018). In addition, energy consumption was reduced by integrating electrochemical reactants to the biological process in order to profit the bioelectricity generated from oxidation of organic compounds (Chen *et al.*, 2017; Kelly and He, 2014; Zhang *et al.*, 2014).

Hollow fibre membranes. Hollow fibre membrane contactors (HFMC) are gas-permeable membranes usually made of polypropylene or other polymers. In HFMC, free ammonia is stripped from the feed solution into gas-filled pores of the membrane on the other side where sulphuric

acid absorbs the free ammonia producing ammonium sulphate. The driving force that allows the free ammonia to transfer across the membrane by diffusion is the difference of concentrations between both sides of the membrane.

By means of its implementation, large towers required for ammonia stripping could be replaced with small membrane devices. This methodology offers the prospect of being: selective to ammonia removal, able to operate without the requirement of big amounts of energy input (like air stripping), and suitable for removal of ammonium N to very low levels (Darestani *et al.*, 2017).

The form capable of being transferred across the membrane is ammonia since it is an un-ionized gas. In the original solution, N exists basically as ammonia so that pH will have to be basic enough (values over 8.6) to displace this reaction towards ammonia. This pH regulation can be done either by adding alkali reagent or by aerating and it is essential to maintain the driving force. An acidic solution (usually H_2SO_4) on the other side of the membrane of which pH is beneath 2 dissolves the NH_3 in the form of sulfate ammonium. Regarding aeration as a mechanism to raise pH, the studies of García-González *et al.* (2015), and Vanotti and Szogi (2015) have proposed the use of nitrification inhibitors and introducing low-rate aeration to obtain a higher pH, as schematized in Figure 3.8. That would mean that there is no more need of adding alkaline reagent, which is the main economic drawback from gas-permeable membranes. However, this method improvement can only be carried out with an abundant inorganic carbon supply.

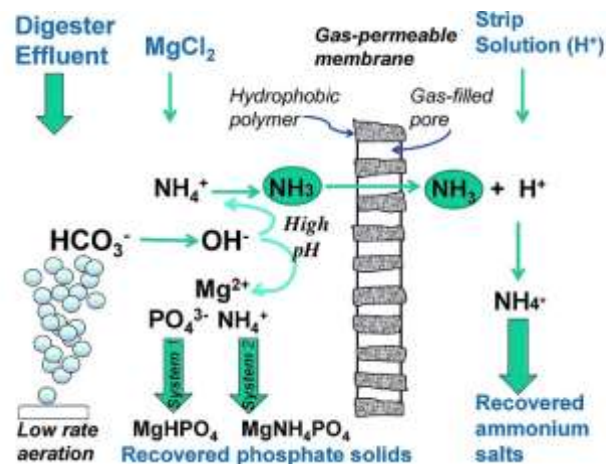


Figure 3.8. HFMC, gas-permeable membrane technique. (Vanotti, 2017)

In Figure 3.8, membrane technology for ammonia recovery is coupled with phosphate solids precipitation. However, a possible threat for membrane technologies is their sensitivity to contaminants, basically SS or other materials that can cause fouling. When existing these contaminants, membrane would likely need to be tuned or combined with previous filters and techniques that allow to achieve a suitable source. Experimental results at pilot scale showed that the application of a struvite pre-treatment would reduce significantly precipitate formation (Ward *et al.*, 2018). Facts like that are essential to know the synergy that diverse techniques could have, and thus verify in pilot scale whether their implementation is worth or not.

4. FEASIBILITY ANALYSIS OF SEVERAL NITROGEN TREATMENT STRATEGIES FROM WASTEWATER

This section is devoted to study the main concepts through which the feasibility of a certain technique to treat urban wastewaters can be determined. These concepts are mainly three:

- The benefit provided by the sale of the product.
- The energetic operating costs.
- The chemicals required costs.

In order to determine the benefit obtained from the product's sale, N removal and recovery efficiencies must be known as well as the form of each technique's final product. Once the application of these parameters to several nitrogen recovery techniques will be explained, a selection of the most feasible techniques will be carried out. Among these techniques, those easiest to implement in a conventional WWTP will be compared in detail.

Before starting with the clarification of the feasibility parameters, there are some matters that will make easier to understand the subsequent subject. Over 50% of standard wastewater treatment energy is spent in aeration to effectively remove N and organics (biodegradable COD). In developed countries plants, nutrient removal processes consume approximately 0.5 kWh/kg O₂ consumed (Benchmarks, 2003). Nutrient removal processes in advanced wastewater treatment consume from 0.4 to 0.5 kWh/m³ (0.43 USA, 0.41 Taiwan, 0.49 New Zealand) and leading this ranking there is Japan with 0.39 kWh/m³ (Gu *et al.*, 2017). This is the reason why most N recovery techniques aim to avoid aeration to make the system economically feasible, so they use different processes and materials to obtain a purified ammonia product.

Since UWW streams are characterised by high volumes but low concentrations, it is essential to pay attention to those internal streams concentrated in N. In WWTP equipped with anaerobic digestion, reject water or centrate (supernatant from anaerobic digestion of sewage sludge) can contribute up to 30% of N loads in the treatment process (Guo *et al.*, 2010). Therefore this stream is an easy target for recovery. As a proposal for the future, a separated source for urine will be helpful since it contributes from 75 to 80% of the total N and above 50% of the total P load in wastewater (Tao *et al.*, 2019). In addition, this source represents only 1% of total mass flow, what means that it is a very concentrated stream suitable for recovery treatments (Tao *et al.*, 2019). Nevertheless, urine streams won't be studied here.

In this section, 3 tables are presented to show the data related with those concepts previously mentioned: nitrogen recovery and removal efficiency (Table 4.1), energy balances (Table 4.2) and the benefit acquired by using each technique (Table 4.3). These tables are an adaptation

from the article of Beckinghausen *et al.* (2020) focused on the evaluation of nitrogen recovery techniques from wastewater. Though these tables have been constructed from the reading of the aforementioned paper, several additions and assumptions have been made in order to represent in a better way what is wanted to show. All modifications and data found in other articles are commented below.

4.1. Considered parameters for feasibility analysis

The clarification of concepts shown in the tables below will be done in this section. Once tables have been presented, the impact of the values of each parameter will be commented.

Percentage of nitrogen removal. N removal efficiencies (see Table 1) represent the removed mass of N divided by the total influent N mass. This parameter is essential to determine the environmental impact this technique would have.

Percentage of nitrogen recovery. N recovery efficiencies are considered to be the recovered mass of N by the total N removed mass, what means that this parameter makes reference to the fraction of N which is recovered as a product and reintroduced in the economy. In other words, recovery efficiency shows the chance to obtain a profitable final product.

$$Eff_{recovery} = \%N_{removal} * \%N_{recovery}$$

Total influent nitrogen. These values are given in two different units, TAN (mg NH₄⁺-N/L) and Total Nitrogen (TN, mg N/L), which includes all the forms of nitrogen (TAN, organic nitrogen, nitrites, nitrates). A comparison between these values and those given by Maresme WWTPs should be carried out in order to determine the possibility to implement each technique in particular as well as the most suitable stream to use.

Form, source and detailed description of the source. This information is especially useful to determine its similarity with UWW and the several streams of municipal WWTPs. However, as stated before, the main way to carry out the comparison between the sources used for these techniques and those from a conventional WWTP will be the levels of N in the inlet (although other parameters could be also necessary to evaluate, such as pH, biodegradable COD, suspended solids or orthophosphates content). In Table 4.1 information about the form of recovered N for each technique is included too.

Energy consumption. This parameter shows the amount of energy (expressed in kWh) needed to recover one kg of N. In order to have all the terms in the same units, the energy was normalized over the amount of nitrogen recovered, so the values are expressed in kWh/kg N.

Energy recovery. It is considered to be the amount of energy (expressed in kWh) generated in the recovery of one kg of N. The form of required energy is always electricity, whereas the form of recovered energy varies among those techniques where energy is generated.

Delta energy. Positive energy balance is related to more energy recovered than required while a negative one means a cost for the plant to cover. This term is based on the form of energy used in each technique, energy quality depends on its form. For example, the MRC-AnOMBR process uses electricity and the energy recovered is in the form of methane. For cases where the process recovers energy in the form of an energy rich gas that also consumes electricity, 40% of the energy of the gas is assumed to be converted into usable electricity (Gong *et al.*, 2017). In the case of recovery of both oxygen and hydrogen, the values considered for energy estimations are 2 kWh/kg O₂ and 33.3 kWh/kg H₂, based on Christiaens *et al.* (2017).

EROI. Energy Return On Investment defines the ratio of the amount of usable energy input from a particular energy resource versus the amount of energy output of a system. In Table 2 it is calculated dividing the value of recovered energy by the required energy (De Luna *et al.*, 2019).

$$EROI = \frac{E_{recovery}}{E_{consumption}}$$

EROI is only applicable for techniques that succeed in generating electricity or heat while they recover N, therefore it is not calculated in techniques where no energy is recovered. The closer its value is to 1, the closer this technique is to supply completely its own energy.

It is important to highlight that even though many different treatment options are mentioned, a great amount of them do not comment on energy requirements regarding their implementation for a full-scale treatment plant.

Table 4.1. Nitrogen recovery technique influent characteristics and results. (adapted from Beckinghausen *et al.*, 2020)

Technique	Substrate	Source	Detailed description of the source	pH	NH ₄ ⁺ -N [mg/L]	TN [mg/L]	N removal [%]	N recovery [%]	Total inlet N recovered [%]	Form of recovered N	Reference
Submersible Microbial Desalination Cell (SMDC)	Digestate	Synthetic	Digestate	7.8	2400		87.9	100	87.90	Amm. sulfate solution	Zhang and Angelidaki, 2015
Struvite Precipitation LSSA (Leachate of Sewage Ash)	Digestate	Agricultural	Anaerobic Digestion swine wastewater	9.5	1727		91.95	100	91.95	Struvite	Kwon et al, 2018
Gas permeable mem. No aeration	Reject from digestate	Agricultural	Digested swine eff.	8.6	1465-2097		92-98	76-95	81.23	Amm. Sulfate solution	Dube et al, 2015
Vacuum mem. Distillation	Reject from digestate	Domestic	AnaD supernatant	7.7	70		85	100	85.00	Amm. Hydroxide solution	Yang et al, 2017
Gas permeable mem.	Reject from digestate	Agricultural	Supernatant from swine wastewater	8.3 6	2350		93-97	92-93	87.88	Amm. Sulfate crystals	Vanotti et al, 2017
Gas permeable mem. Aeration	Reject from digestate	Agricultural	Digested swine eff.	8.6	1465-2097		97-99	96-98	95.06	Amm. Sulfate solution	Dube et al, 2015
ED (Electrodialysis) w stripping	Reject water	Agricultural	Filtered swine manure	8.5		2500	59	6,2	3.66	Ammonia in HNO ₃	Ippersiel et al, 2012
ED w vacuum stripping	Reject water	Agricultural	Filtered swine manure			2500	70	14,5	10.15	Ammonia in HNO ₃	Ippersiel et al, 2012
ED/RO (Reverse Osmosis)	Reject water	Agricultural	Filtered swine manure	8.2 6	4215		75	66,6	49.95	Solution	Mondor et al, 2008
Gas permeable mem. Semicontinuous	Reject water	Agricultural	Centrate from swine manure			3451	56-79	90	60.75	Amm. sulfate solution	Riaño et al, 2019
Microbial electrolysis cells (MEC)	Reject water	Domestic	Urban reject water		1000		72.2	100	72.20	Amm. Chloride	Wu and Modin, 2013
MEC	Reject water	Synthetic	Synthetic reject water		1000		83.6	100	83.60	Amm. Chloride	Wu and Modin, 2013
L-L mem. Contactor	Reject water	Domestic	Zeolite regeneration solution	12. 2	2400		85-98	95-98	88.30	Di-amm. Sulfate solution	Sancho et al, 2017
Bio-electrodialysis	Reject water	Agricultural	Filtered cattle manure	8.1	2150	3270	94	100	94.00	Ammonia in boric acid	Zhang and Angelidaki, 2015
MNRC	Wastewater	Synthetic	Domestic wastewater		23,8		96	24	23.04	Solution	Chen et al, 2015
MPC-IE (Membrane based PreConcentration - Ion Exchange)	Wastewater	Domestic	Raw sewage after solid separation		27,4		74.4	37,5	27.90	Solution	Gong et al, 2017
MEC Aeration	Wastewater	Domestic	Landfill leachate		4540		63.7	53,8	34.27	Amm. Bicarbonate and amm. Fosfate	Qin et al, 2016
MRC - AnOMBR (Microbial Recovery Cell - Anaerobic Osmotic Membrane BioReactor)	Wastewater	Synthetic	Glucose based medium	7.2	21,6		28-45	100	36.50	Solution	Hou et al, 2017

RRMFC (Resource Recovery Microbial Fuel Cell)	Wastewater	Synthetic	Urine containing wastewater		3,89		98	42	41.16	Solution	Lu et al, 2019
Bio-electrodialysis without gas circulation	Wastewater	Domestic	Primary clarifier eff.	7.8	70		85	52	44.20	Ammonia in boric acid	Zhang and Angelidaki, 2015
EMNRC (Enlarged Microbial Nutrient Recovery Cell)	Wastewater	Domestic	Raw domestic wastewater		47,4		80	62	49.60	Struvite	Sun et al, 2018
CapAmm	Wastewater	Domestic	Raw sewage after solids		42,5		62	100	62.00	Amm. sulfate solution	Zhang et al, 2018
Bio-electrodialysis with gas circulation	Wastewater	Domestic	Primary clarifier eff.	7.8	70		90	80	72.00	Ammonia in boric acid	Zhang and Angelidaki, 2015
Struvite Recycling	Wastewater	Agricultural	Swine wastewater	7.7		378	90	91	81.90	Struvite	Huang et al, 2015
Vacuum mem. Distillation	Wastewater	Industrial	Carbonated downstream eff.	6.1	167		96	100	96.00	Amm. Hydroxide solution	Yang et al, 2017
Vacuum mem. Distillation	Wastewater	Industrial	Carbonated downstream eff.	10	167		99.6	100	99.60	Amm. Hydroxide solution	Yang et al, 2017
MEC - FO (Forward Osmosis hybrid)	Wastewater	Synthetic	Synthetic side stream centrate		1000		99.7	100	99.70	Struvite and amm. Sulfate	Zou et al, 2017
TSAHP (Two step alkaline hydrolysis process)	Sludge	Domestic	Sludge from secondary settler	9.7		856	7.78	41,98	3.27	Struvite	Bi et al, 2014
Sludge fermentation	Sludge	Domestic	Centrate from fermented sludge	6.7 3	30		73	75,7	55.26	Struvite	Tong and Chen, 2009
Electrochemical cell (EC) stripping	Urine	Domestic	Domestic urine	9.1 8	5490		87.1	-	-	Amm. sulfate solution	Christiaens et al, 2017
Microbial fuel cells (MFC)	Urine	Domestic	Undiluted urine			4050	-	<1	-	Ammonia in boric acid	Kuntke et al, 2012
EC stripping	Urine	Synthetic	Synthetic urine		5490		59	13,3	7.85	Amm. In HOB medium	Christiaens et al, 2017
MEC - TMCS	Urine	Domestic	Urine	9.1	700		42-51	49	22.79	Amm. sulfate solution	Kuntke et al, 2016
EC - TransMem. ChemiSorption (TMCS)	Urine	Domestic	Urine	9.2	4250		63	56	35.28	Amm. sulfate solution	Rodríguez et al, 2017
EC stripping/absorption	Urine	Domestic	Undiluted urine	8.5	1700		75	57	42.75	Amm. sulfate solution	Luther et al, 2015
Hydrogen Recycling Electrochemical System (HRES) - TMCS	Urine	Domestic	Pretreated human urine	9		3400	73	60	43.80	Amm. sulfate solution	Kuntke et al, 2017
EC stripping/absorption	Urine	Domestic	Undiluted urine	9.2	5100		65-76	53-77	45.83	Amm. sulfate solution	Luther et al, 2015
MEC - TMCS	Urine	Domestic	Urine	9.1	3,4		47	100	47.00	Amm. sulfate solution	Zamora et al, 2017
Capacitive mem. Stripping for Ammonia recovery (CapAmm)	Urine	Synthetic	Synthetic urine		43		58	100	58.00	Amm. sulfate solution	Zhang et al, 2018
Nutrient Separation Microbial Electrolysis Cell (NSMEC)	Urine	Synthetic	10x diluted urine	7.9- 8.5	745	871,4	61	100	61.00	Solution	Tice and Kim, 2014
EC - TMCS	Urine	Synthetic	Synthetic domestic	9.3	4250		92	84	77.28	Amm. sulfate solution	Rodríguez et al, 2017

Table 4.2. Energetic parameters and balances for various techniques. (adapted from Beckinghausen et al., 2020)

Technique	Form	Required Energy [kWh/kg N]	Energy Recovery [kWh/kg N]	Form of Recovered Energy	Delta Energy [kWh/kg N]	EROI	Author
Struvite precipitation LSSA	Digestate	0.90			0.90		Gyutae et al, 2017
SMDC	Digestate	0.90	0.09	Bioelectricity	0.81	0.100	Zhang and Angelidaki, 2015
ED w air stripping	Reject from Digestate	5.95			5.95		Ippersiel et al, 2012
ED w vacuum stripping	Reject from Digestate	4.94			4.94		Ippersiel et al, 2012
Gas permeable mem. Aeration	Reject from Digestate	1.17			1.17		Dube et al, 2015
Gas-permeable mem.	Reject from Digestate	0.97			0.97		Dube et al, 2015
MEC	Reject Water	10.44	4.01	Hydrogen	6.43	0.384	Wu and Modin, 2013
Vacuum mem. Distillation	Reject Water	1.53			1.53		Ukuwani and Tao, 2016
Gas-permeable mem.	Reject Water	1.17			1.17		Vanotti et al, 2017
MEC - FO	Reject Water	1.17	0.34	Hydrogen	0.83	0.291	Zou et al, 2017
MPC - IE	Wastewater	63.34	22.41	Methane	40.93	0.354	Gong et al, 2017
CapAmm	Wastewater	25.10			25.10		Zhang et al, 2018
EMNRC	Wastewater	28.57	4.20	Bioelectricity	24.37	0.147	Sun et al, 2018
MRC - AnOMBR	Wastewater	40.00	28.07	Methane	11.93	0.702	Hou et al, 2017
MEC aeration	Wastewater	8.50	Not reported	Hydrogen*	8.50		Qin et al, 2016
MNRC	Wastewater	6.00	0.96	Bioelectricity	5.04	0.160	Chen et al, 2015
Bio-electrodialysis with recirculation	Wastewater	2.85	2.11	Hydrogen	0.74	0.740	Zhang and Angelidaki, 2015
Bio-electrodialysis without recirculation	Wastewater	2.71	2.35	Hydrogen	0.36	0.867	Zhang and Angelidaki, 2015
Gas-permeable mem.	Wastewater	0.22			0.22		Riaño et al, 2019
Struvite recycling	Wastewater	0.10			0.10		Huang et al, 2015
HRES - TMCS, 50 A/m2	Urine	15.65			15.65		Kuntke et al, 2017
EC stripping	Urine	19.40	5.50	Hydrogen, Oxygen	13.90	0.284	Christiaens et al, 2017
EC - TMCS	Urine	13.59			13.59		Rodríguez et al, 2017
HRES - TMCS, 10 A/m2	Urine	8.48			8.48		Kuntke et al, 2017
CapAmm	Urine	7.80			7.80		Zhang et al, 2018
HRES - TMCS, 20 A/m2	Urine	7.26			7.26		Kuntke et al, 2017
MEC - TMCS	Urine	2.49	Not reported	Hydrogen*	2.49		Kuntke et al, 2012
NSMEC	Urine	1.80			1.80		Tice and Kim, 2014
MFC	Urine	3.05	1.86	Electricity	1.19	0.610	Kuntke et al, 2012

Total benefit. All of the studied techniques produce a pure final product that can be sold commercially or utilized as fertilizer. In Table 4.3 the values for estimated fertilizer monetary benefit are used along with its electrical and chemical costs to determine overall benefit. This analysis appraise the techniques as standalone processes and it has to be mentioned that it does not include potential energy savings due to decreased aeration requirements.

$$Benefit_{Total} = Value_{product} - Cost_{electricity} - Cost_{others}$$

Negative values indicate that this technique would suppose an outlay for the plant, whereas positive values indicate a benefit gained by the sale of the product. The conversion of USD to € used when needed is considered as 0.914 €/USD.

Product value. This parameter is linked with the form of recovered N and shows its monetary value in € per ton of product. The sale values for 1 ton of product are taken as 300 €/ton struvite (Cornel and Schaum, 2009; Dockhorn, 2009; Peng *et al.*, 2018), 476 €/ton ammonium sulfate (Dube *et al.*, 2016), 459 €/ton di-ammonium phosphate (Maaß *et al.*, 2014), and 239 €/ton urea. Nevertheless, the prices of these products are taken from literature referred to USA data, except for struvite which data is referred to EU values.

Electricity cost. Starting at delta energy column it can be finally determined the electricity cost in € per ton of product by knowing the kg of N contained in a ton of product and the monetary value for energy has been calculated using 0.08 € per kWh (value given by plant managers).

Some assumptions have been done for the calculation of Struvite Precipitation LSSA and Vacuum Membrane Distillation techniques because of its lack of data in energy consumption. Electricity cost for LSSA has been calculated as 1.5 times Struvite Recycling's since both techniques are similar but SR have a lower delta energy value. Electricity cost for VMD technique has been found by maintaining the same relation electricity cost-delta energy as GPM technique because of both technologies similarity.

Others cost. Finally, this cost refers to the outlay of buying those needed chemical reagents required for each technique. Usually, these reagents are used to maintain a specific pH or added in order to produce the final product.

In the case of struvite production, this value has been calculated from an average nitrogen concentration in the inlet of 65 mg/L and an operational cost of 0.119 €/m³ (Xialei *et al.*, 2018). The result is a cost of others of 82 €/T product.

Table 4.3. Cost and benefit details for fertilizer production using various techniques. (adapted from Beckinghausen et al., 2020)

Technique	Form	Form of recovered N	Product value [€/ton product]	Delta Energy [kWh/kg N]	Energy [kWh/ton product]	Cost electricity [€/ton product]	Cost other [€/ton product]	Total benefit [€/ton product]	Author
SMDC	Digestate	Amm sulfate solution	476.14	0.81	165.07	13.21	176.72	286.21	Zhang and Angelidaki, 2015
Struvite precipitation LSSA	Digestate	Struvite	300.00	0.90	6718.41	537.47	81.99	-319.46	Gyutae et al, 2017
Gas-permeable mem. With aeration	Reject from Digestate	Amm sulfate solution	476.14	1.17	224.24	17.94	201.84	256.36	Dube et al, 2015
Gas permeable mem. Without aeration	Reject from Digestate	Amm sulfate solution	476.14	0.97	147.63	11.81	176.72	287.61	Dube et al, 2015
MEC aeration	Wastewater	Amm chloride	476.14	6.39	1633.95	130.72	928.67	-583.25	Qin et al, 2016
Struvite recycling	Wastewater	Struvite	300.00	0.10	4478.94	358.32	81.99	-140.31	Huang et al, 2015
CapAmm	Wastewater	Amm sulfate solution	476.14	25.10	4824.96	386.00	176.72	-86.58	Zhang et al, 2018
EMNRC	Wastewater	Struvite	300.00	24.37	807.36	64.59	81.99	153.42	Sun et al, 2018
MEC - FO	Wastewater	Struvite + amm sulfate	300.00	0.86	160.36	12.83	81.99	205.18	Zou et al, 2017
Vacuum membrane distillation	Wastewater	Amm sulfate solution	476.14	1.53	293.24	23.46	176.72	275.96	Ukuwani and Tao, 2016
HRES - TMCS 10 A/m ²	Urine	Amm sulfate solution	476.14	15.72	7291.46	583.32	176.72	-283.90	Kuntke et al, 2017
EC - TMCS	Urine	Amm sulfate solution	476.14	13.59	2613.20	209.06	176.72	90.36	Rodríguez et al, 2017
EC strip/acid, day 1	Urine	Amm sulfate solution	476.14	11.93	2292.79	183.42	176.72	115.99	Luther et al, 2015
EC strip/acid, day 9	Urine	Amm sulfate solution	476.14	9.00	1730.06	138.40	176.72	161.01	Luther et al, 2015
EC - TMCS	Urine	Amm sulfate solution	476.14	8.51	1635.26	130.82	176.72	168.60	Rodríguez et al, 2017
EC strip/acid 20 A/m ²	Urine	Amm sulfate solution	476.14	8.50	1633.95	130.72	176.72	168.70	Christiaens et al, 2017
CapAmm	Urine	Amm sulfate solution	476.14	7.80	1499.39	119.95	176.72	179.47	Zhang et al, 2018
MEC - TMCS	Urine	Amm sulfate solution	476.14	2.49	478.65	38.29	176.72	261.13	Zamora et al, 2017
HRES - TMCS 50 A/m ²	Urine	Amm sulfate solution	476.14	2.27	435.98	34.88	176.72	264.54	Kuntke et al, 2017
MEC - TMCS	Urine	Amm sulfate solution	476.14	1.36	261.85	20.95	176.72	278.47	Kuntke et al, 2016
EC strip/HOB medium 21 A/m ²	Urine	Amm sulfate solution	476.14	0.10	19.22	1.54	176.72	297.88	Christiaens et al, 2017

4.2. Nitrogen removal and recovery efficiencies evaluation

Table 4.1 describes a collection of characteristics and results about those studied technologies where various forms of recovered N were obtained as a product of each technology. In this section a review of this table values has been carried out as well as a selection of the most efficient techniques.

Among the techniques studied here, there are 6 of them that produce struvite as final product. This fact occurs in (i) Struvite Precipitation LSSA, (ii) MEC-FO, (iii) Struvite Recycling, (iv) MNRC, (v) Sludge Fermentation, and (vi) TSAHP. The first three have fairly high N recovery efficiencies (92.0%, 99.7%, 81.9%, respectively). These are relatively high N recoveries because most struvite precipitation techniques have an imbalance of P and N. Nevertheless, these techniques succeed thanks to the addition of a P containing material like KH_2PO_4 in Struvite Recycling or Leachate from Sewage Sludge Ash (LSSA) what may increase the electricity cost or others cost.

Most of the recovery techniques generate ammonia solutions that have the potential for fertilizer applications. The downside of ammonia solutions compared to struvite or other solid products (like loaded zeolite) is the higher cost for storage and transportation of liquid solutions, although their sale value is usually higher than struvite's.

Among all of the N recovery techniques that use membrane technology or generate struvite as final product (see Table 4.1), only those that fulfil some requirements have been taken for a subsequent study. These requirements consist of: (i) a percentage of N recovery above 80%, (ii) to have an inlet source different from urine, and (iii) to be the most efficient technique among those of its kind. First two conditions are related with efficiency and they are included to prevent too low nutrient removal and recovery values. The third requirement exclude those techniques where the main source is urine because the concentrations of $\text{NH}_4^+\text{-N}$ and Total N would not be similar enough to UWW concentrations. Finally, for those techniques with different variations (for example, Gas Permeable Membrane) only the one has been taken according to the highest N recovery efficiency ratios.

As stated in Table 4.1 and summarized in Figure 4.1, the most efficient methods of nitrogen recovery are SMDC (87.9%), Struvite Precipitation with LSSA for digestate (92.0%), Gas Permeable Membrane with aeration (95.1%), Bio-electrodialysis (94.0%), MEC-FO (99.7%), Struvite Recycling (81.9%), and Vacuum Membrane Distillation (99.6%). However, this diagram does not include N recovery for bio-electrodialysis because though it fulfil the requirements, there are not data about its energy balances nor product's (ammonia in boric acid) sale and cost.

On the other hand, the least efficient techniques of N recovery should motivate a further research and optimization to understand their limitations. Furthermore, these methods are still in an experimental stage, mostly tested and analysed in lab-scale. Its move to a pilot scale experiment may show that the techniques have different efficiencies or unexpected operational condition changes.

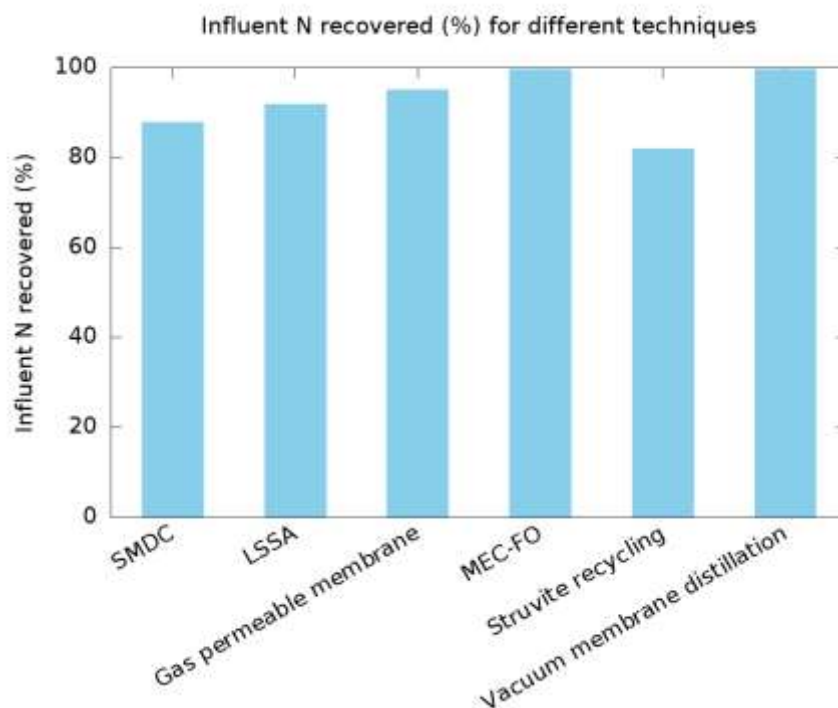


Figure 4.1. Nitrogen recovery (%) of the selected techniques.

As shown in Table 4.1, the main streams used for the analysis are wastewater, reject water, and urine. Wastewater is a popular stream since this term comprehends industrial wastewater, food waste, landfill leachate, and of course, UWW. Techniques explored here incorporate membranes, a technology that is a low energy alternative to traditional water treatment and can be extremely efficient as long as the inlet stream has received a pre-treatment to reduce solid concentrations and fouling contaminants. Reject water has a special interest because of its high concentration of nutrients. In digestate reject water, nutrients released during anaerobic digestion can be recovered in an easier way. Finally, urine is typically used from source-separating systems to prevent the ammonia diluting by other wastewater streams. This kind of stream is not studied here due to its highly different TAN values compared to UWW streams.

4.3. Energy analysis of Nitrogen removal and recovery processes

The energy data summarized in Table 4.2 represent a combination of other studies reported results and estimations from similar techniques. Among the 6 chosen techniques, all the energy requirements are less than the Haber Bosch's (10.3 kWh/kg N), and some of them, like Struvite Recycling, are close to 0. Those techniques with energy requirements beneath Haber-Bosch's are considered energetically favourable because this implies that the energy required to produce

the same fertilizer from Haber-Bosch process is higher. Though their delta energy values are fairly low and some of them even recover energy, any of these techniques is energy positive.

EROI calculation may be helpful for evaluating the effect of these techniques on the final energy requirement of full-scale WWTP and determining the overall energy efficiency of each technology. Most of those techniques that have been analysed do not recover energy. SMDC and MEC-FO have their EROI values at 0.100 and 0.283 respectively, what means that 10.0% and 28.3% of the global energy is recovered. The forms of recovered energy are bioelectricity for SMDC as well as for MEC-FO. The highest EROI value corresponds to MRC-AnOMBR (0.702). Nevertheless, high EROI values are not worth if delta energy is high. One technique can have a high recovery of energy and still not be worth because of a high energy requirement, so in the end, what matters the most is the global energy balance (delta energy).

In Figure 4.2 studied technique's energy requirements referred to kg of N treated are shown as well as its EROI values (red section of the bar). VMD is the most energetically expensive technique and even so it is far below Haber Bosch's requirement (1.53 vs 10.3 kWh/kg N). The most inexpensive technique is Struvite Recycling followed by those where energy has been generated during the process. Nevertheless, recovered energy means a 10 and 28 % of total requirement for SMDC and MEC-FO respectively, which is a relatively low value.

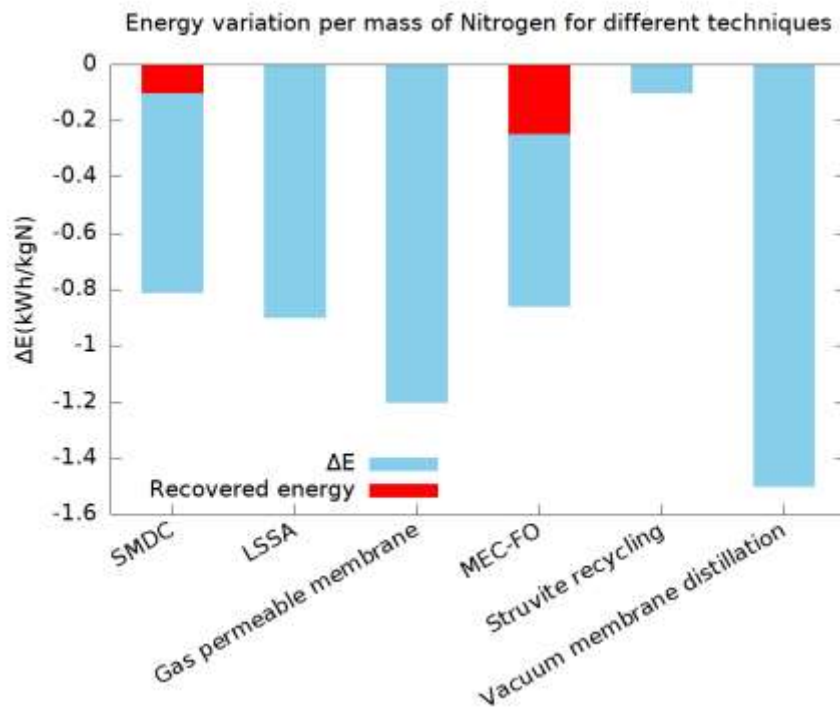


Figure 4.2. Energy variation of the selected techniques.

4.4. Cost and benefit analysis for fertilizer production of nitrogen recovery techniques

Having in mind that one objective of this study is to determine the economic feasibility of the technique's implementation in a full-scale plant, all costs must be identified. The way used here to determine costs is by comparing the cost of the final product generation in terms of electricity costs and chemicals purchasing, with the potential income for its sale. Once this total cost is determined (see Figure 4.3), a comparison between all studied techniques and traditional treatment could be accomplished.

The final products for the studied techniques are mainly ammonium sulfate and struvite, and in the specific case of VMD it is ammonium hydroxide solution. Ammonium sulfate has a higher sale value than struvite (476 €/ton vs 300 €/ton according to Beckinghausen *et al.*, 2020 and Xialei *et al.*, 2019). Struvite's sale value can change due to its purity and the technique with which is produced. However, in this study struvite sale values are considered always the same.

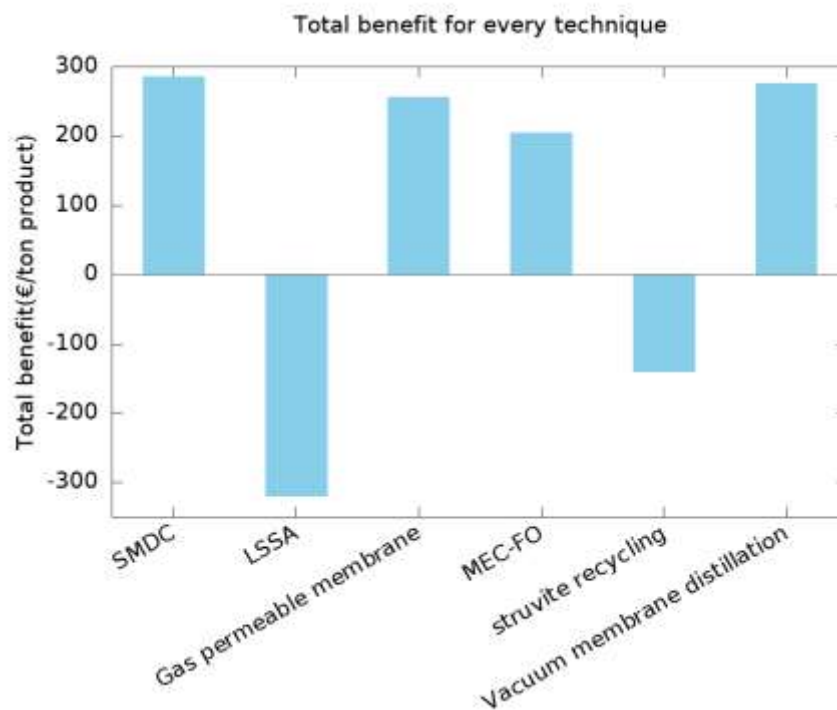


Figure 4.3. Total benefit of the selected techniques.

As stated before, total benefit is the result of product value minus the cost of electricity and others. A positive value means that this technique is supposed to produce a benefit while a negative value means that the plant will have to contribute to treat those wastewaters. Among the techniques considered, the highest benefits will be carried by SMDC, GPM, and VMD with the highest value of 286 € per ton of product.

However, low negative values can be worth to apply in a conventional WWTP considering that nowadays they have to pay to treat wastewater. For example, Struvite Recycle technique have a negative balance of 140 € per ton of product, but, even so, this cost can be lower than conventional cost. And what is more, the elimination of struvite prevents problems of pipe clogging and it is more environmentally favourable since it recovers both N and P.

In the feasibility analysis chapter of this work, some nutrient recovery techniques have been studied and 6 of them have stood out because of their nutrient recovery and characteristics that determine their final cost. 2 techniques among these ones will be taken for a detailed study and especially to determine their capability for a plant implementation:

- Membrane contactors, in which group GPM is included as well as other techniques that may introduce little variations. This technology has been chosen for its high benefit opportunity (256 €/ton product) and its great nitrogen recovery with an efficiency of 95% (data from GPM).
- Struvite Precipitation (SP), with or without recirculation, is the other technique evaluated for a plant implementation since struvite production offers different advantages like the prevention of pipe clogging, the production of a solid fertilizer, and the recovery of both N and P. Although its application entail an outlay for the plant (140 €/ton product), it still may be more inexpensive than nowadays treatment while it offers the benefits mentioned before. Independent of these repercussions, both techniques are clearly an improvement towards circular economy.

4.5. Agronomical and environmental considerations of final products

A brief evaluation of the final products used as fertilizer is carried out here in order to know the advantages and downsides they present. In 2014, 111 tons of N fertilizer were consumed over the world. The 56% of this amount of fertilizer was estimated to be urea-based, followed by 9% of ammonium nitrate and calcium ammonium nitrate (Jones, 2019). Urea production is based on ammonia produced from the Haber-Bosch process, hence it shares the same high energy costs due to the natural gas or coal needed.

In March 2019, the UN Environmental Assembly adopted the resolution titled “Sustainable Nitrogen Management” (UNEP/EA.4/L.16) with the intention of address the root cause of N pollution by active management of these resources. Regarding fertilizer emissions, Pan *et al.* (2016) reported that the problem lies mainly in fertilizer type and farming practices. Its losses on average are about 18% of N applied and can be up to a 64%. Some fertilizers create a high pH zone that can lead to ammonia volatilization, increasing the loss. In order to mitigate it, ammonium nitrate and ammonium phosphate are the most effective non-urea fertilizers that reduced NH_3 emissions by 87.9% and 78.8% respectively. Other alternatives are the addition of zeolite and pyrite to the urea fertilizer that reduce the volatilization by 43.5% and 20.9% respectively.

Furthermore, different forms of fertilizer application like continued stewardship or granules are recommended according to the type of cultivation and its stage.

It has been proved that ammonium sulfate, one of the most obtained final product in this study, increase leaf nitrogen and acidify soils allowing an increased yield of 10%. Ammonium sulfate also provides sulfur to the soil which is lacking in the majority of fertilizers (Chien *et al.*, 2011). Its strong points are that N losses are less compared with urea or ammonium nitrate, and its potential to increase acidity for a subsequent better P and micronutrients uptake by plants.

Struvite, the other main final product here, has the advantage of containing P as well as N, and as said before, P is also a micronutrient vital to plant growth. Nevertheless, the struvite ratio N/P (1:1) is not enough for plant growth. An increase of the application of struvite to reach the necessary N standards will drive the soil to a higher pH which may affect nutrient availability and, what is more, create Mg and P accumulation in the soil (Kataki *et al.*, 2016). From this it can be drawn the conclusion that another N containing fertilizer will have to be applied.

Another concern with struvite's fertilizer is the potential heavy metal contamination depending on the waste stream from which it originates. In regards of soil contamination caused by heavy metals, especially cadmium, several studies have been made. Kern *et al.* (2008) stated that at the moment current organic and mineral fertilizers already contribute to soil heavy metal concentrations. Triple superphosphate (another source of P derived from natural deposits) has a loading for Cd higher by a factor of 10 compared with struvite from activated sludge (Kern *et al.*, 2008). A life cycle analysis carried out in Germany found that substituting mineral P fertilizer, reducing drinking water usage and treating faeces separately a reduction of Cd from 19% to 36% can be achieved in comparison with traditional sludge from wastewater treatment.

Benson (2014) have determined that commercially available fertilizers have an average of 2.59 mg Cd/kg superphosphate fertilizer, and 2.67 mg Cd/kg urea fertilizer. In comparison, there are very different values for Cd concentrations in Switzerland where sewage sludge contains from 0.4 to 1.9 mg Cd/kg dry weight (Franz, 2008). Mosquera-Losada *et al.* (2010) showed variations between composted sludge with an average of 3.76 to 3.89 mg Cd/kg, anaerobic sludge with 4.3 to 15.8 mg Cd/kg, and pelletized sludge with 3.59 mg Cd/kg.

Technologies studied in this work produce a final product which could be used as fertilizer replacing compounds which synthesis relies on Haber-Bosch process. It is not easy to determine which is the most beneficial for agricultural requirements. Membrane technologies produce ammonia concentrated solutions but they are also concentrated with other ions that were present in the used waste source. Therefore, additional steps are required to reach the limit values and make possible to get a valuable product.

To prevent the production of a final product that may not have a viable future in the market, the communication between researchers and users must be taken seriously. Studies continue proving the value of using wastewater products as fertilizers and have confirmed not only benefits

but the lack of contaminant compounds that many have been afraid of (Odlare *et al.*, 2008; 2011; 2014; 2015). Long term studies (more than 40 years) have demonstrated that there was no build-up of heavy metal contamination in the soil or plants in farmlands where sewage sludge has been used (Bergkvist *et al.*, 2003).

Any N recovery technique that aims to supplement the fertilizer market must prove that this technique does not imply contamination risks to the crops. What is more, it must also achieve the same or better performance than mineral options or those derived from Haber Bosch process.

There are some barriers that must be left behind to continue with this research. The focus cannot only be the variation of parameters on a lab stage but the scale up and perform complete energy and economic analyses. In addition, having more pilot scale results and information about the product will help to shape the research in this field. By focusing studies on this issue, the efficiencies of integrating these technologies into existing plant will be proven. Lastly, economic analyses should consider the implementation of incentives and penalties around NO_x emissions like a N tax similar to the already existing carbon tax (Pikaar *et al.*, 2018).

5. STUDY OF THE OF 2 NITROGEN RECOVERY STRATEGIES IN A MUNICIPAL WWTP

To continue with the development of the determination of the best nutrient recovery techniques and its possible implementation to a conventional WWTP, 2 techniques have been selected for a further study. As stated before, the chosen techniques are Struvite Precipitation (SP) and Membrane Contactors (MC).

In the first place, there is an introductory section where the performance of a conventional WWTP is explained. It is mandatory to know how a conventional plant operates, the influent characteristics, such as levels of inlet ammonia and phosphate, as well as the nutrients concentration in different streams.

Once the concepts about WWTP are clear, those selected techniques will be studied in detail in order to determine whether their implementation is feasible or not. At the end, a comparison between both techniques is carried out and it may be interesting to know if these techniques could be applied at the same time obtaining synergies.

5.1. Nitrogen balance in a conventional WWTP with anaerobic digestion of sewage sludge

Wastewater contains many water pollutants and therefore it must be treated before being discharged into the environment. Biological treatment is the most common method for treating wastewater in conventional WWTP, and among the different types of biological treatments, the activated sludge process is the method most often applied as it removes organic matter and nutrients from wastewater (Henze *et al.*, 2009). Anaerobic digestion is the most widely-used biological process for sludge stabilization and energy recovery (Tchobanoglous *et al.*, 2013) though it is usually implemented only in big plants (approximately above 20,000 m³/day or about 200,000 PE).

The data of WWTP streams are composed of wastewater flowrates, levels of TSS, COD, BOD₅, TAN, total Kjeldhal nitrogen (TKN), Total Phosphorus (TP) and their removal efficiencies, as well as other parameters that characterise wastewater (pH, temperature, conductivity, ...). For this study, data from some Maresme WWTPs is used and it has been compared with data from Sur WWTP, a conventional plant located in Madrid (Lizarralde *et al.*, 2018) to make sure internal streams concentrations are similar in magnitude.

There are 11 WWTPs in Maresme that can be divided into different groups according to their size. The water line in small plants consist in a pre-treatment, biological reactor, and secondary settler while its sludge line is composed by a thickener and a dewatering unit. In big plants, the water line goes through a pre-treatment, primary settler, biological reactor, and secondary settler, while sludge line is composed by a thickener, an anaerobic digester and a dewatering unit (see Figure 5.1).

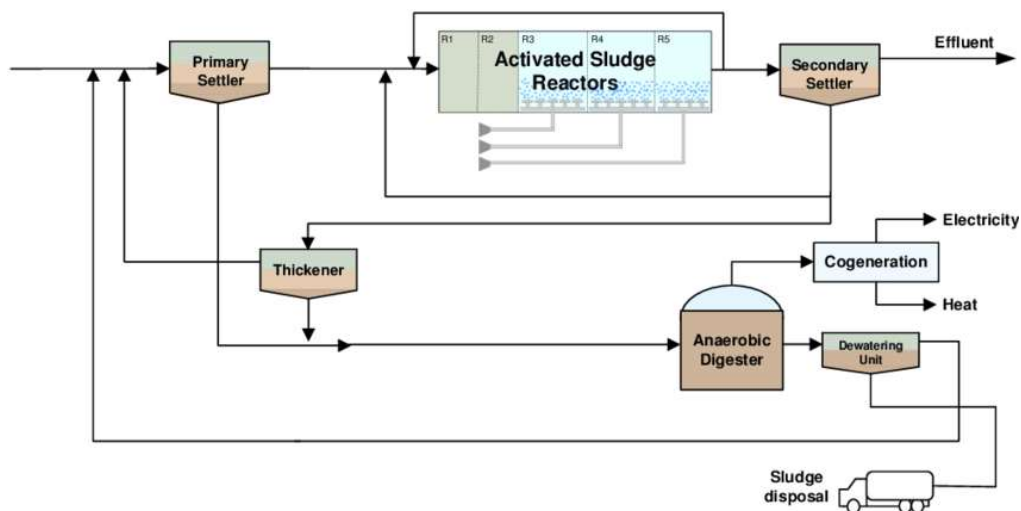


Figure 5.1. Conventional wastewater treatment plant. (Pereira *et al.*, 2012)

In this chapter, 4 WWTPs have been chosen for a subsequent study taking into account the following criteria:

Mataró. Inflow of 25,000 m³/day. There is an anaerobic digestion (AnaD) unit. Its flowsheet is the one mentioned before for big plants (see Figure 5.1).

Pineda. Inflow ranging from 18,000 to 30,000 m³/day. This plant is equipped with AnaD unit. Its flowsheet consists in a pre-treatment, primary settler (DENSEG), and biological filter as bioreactor (BIOFOR) for water line, and thickener, anaerobic digestion, and dewatering for the sludge line.

Teià. Inflow of 14,000 m³/day. This plant does not include AnaD. Its flowsheet is the one mentioned before for small plants with primary settling.

Tordera. Inflow of 2,000 m³/day. This plant does not include AnaD. Its flowsheet is the one mentioned before for small plants. This is the only case in Maresme WWTPs where outflow is not discharged into the sea but in a sensitive aquifer (Tordera river delta). Therefore, nutrient removal is compulsory. N is removed by N/DN process and P is removed by FeCl₃ precipitation.

Table 5.1 summarizes the characteristic parameters of each plant and its data are extracted from Maresme plants manager.

Table 5.1. Inflow and contaminant concentrations.

	Flow	SS			BOD ₅			TN			TP		
	[m ³ /day]	inflow [mg/L]	outflow [mg/L]	efficiency [%]	inflow [mg/L]	outflow [mg/L]	efficiency [%]	inflow [mg/L]	outflow [mg/L]	efficiency [%]	inflow [mg/L]	outflow [mg/L]	efficiency [%]
Mataró WWTP	22628	479	14	96.3	584	16	97.0	75.41	64.43	14.8%	5.06	3.67	27.7%
Pineda WWTP	22273	304	23	91.3	410	23	93.7	63.63	52.47	18.3%	5.39	3.46	38.2%
Teià WWTP	13847	437	16	95.6	518	11	97.6	72.84	34.21	51.8%	10.69	2.26	78.2%
Tordera WWTP	2548	211	12	91.2	318	9	95.6	55.68	11.17	78.7%	8.20	1.42	79.2%

As stated before, Tordera is the only plant designed and operated to remove N and P. This fact can be seen in Table 5.1 in outflow concentration values and removal efficiency. P removal efficiency in Teià plant is higher than standard value due to the presence of polyphosphate-accumulating organisms (PAO), a group of bacteria that, under certain conditions, facilitate its removal.

It is important to highlight that in those plants where N removal is not an objective, a relatively important removal is achieved involuntarily. This fact is linked to the level of saturation of the plant (operation conditions with respect to design conditions). N removal is reached by N/DN. However, involuntary nitrifications occur by over-aeration (regarding the necessity to remove organic carbon) as well as by the presence of dead volumes that cause sludge retention times higher than 10 days (suitable for nitrifying bacteria) despite average time value ranges between 6-8 days. Additionally, denitrifications are caused by the retention of sludge in non-aerated zones (secondary settler) or periods of time where aeration is lower than required.

As stated before, N concentration of the chosen stream for recovery technique implementation is a key factor to determine its feasibility. A more detailed analysis of the plant flowsheet shows some internal streams which characteristics make them especially suitable to obtain high recovery efficiency. These internal streams are:

Decanter centrifuge drain. Sludge dewatering in centrifuges produces a dry sludge while a drain stream is obtained from expelled water. Unfortunately, this stream usually contains high levels of TSS.

Thickener overflow. As thickening settlers concentrate SS in the bottom outflow, a cleaner water stream is overflowed from the top.

Others. Several minor streams across the plant (pre-treatment returns, tanks emptying). These streams are usually very different and variable between plants and depending on several circumstances, such as weather or treated flow charge.

These 3 streams have been analysed in order to determine their concentrations, thus its capability to recover N in an optimal way. In Table 5.2, their concentrations are presented (note that data from Tordera WWTP has not been included because of its lack of internal streams data).

Table 5.2. Flow and nitrogen concentrations in 3 previously mentioned internal streams.

	Mataró (sludge AD: Yes)			Pineda (sludge AD: Yes)			Teià (sludge AD: No)		
	Drain	Overflow	Others	Drain	Overflow	Others	Drain	Overflow	Others
Flowrate [m ³ /day]	216	1406	-	423	-	-	212	1083	-
NH ₄ ⁺ -N [mg/L]	1197	95	205	1002	-	597	123	125	-
NH ₄ ⁺ -N flowrate [kg/day]	259	133	-	424	-	-	26	135	-

Despite these streams charge (kg N/day) is similar in magnitude with water line, internal streams will be more suitable as a source for the recovery since high concentration levels are required. Another basic conclusion drawn from Table 5.2 is that concentration increase significantly in those streams where the sludge has been digested. The responsible of this rise is the cellular disruption of digested microorganisms that takes place in AnaD what release the intracellular material (more available N).

5.2. Analysis of nitrogen recovery using a membrane contactor

In this section the operation and characteristics of a plant with MC is explained, and subsequently, the feasibility of this technique's implementation in Maresme WWTPs is discussed. In order to carry out this analysis, the compiled data of chapter 4 (tables and information about MC) and data from Maresme WWTPs will be used.

5.2.1. Membrane recovery plant

Regarding to wastewater treatment, HFMC technique has been applied with high recovery efficiencies to different N rich streams such as reject water from anaerobic sludge digestion (Seco *et al.*, 2018), swine manure (García-González *et al.*, 2015) and landfill leachate (Li *et al.*, 2014). Its first application in full scale municipal WWTP was recently reported by Ritcher *et al.* (2019). The economic value of the ammonium sulfate produced is not the only benefit since the reduction of the N load entering the biological treatment reduces the energy consumption. It is important to highlight that the N/DN process requires over 5 kWh/kg N, being one of the most energy-demanding process in WWTPs (Wett *et al.*, 2012).

The N rich solution used in the study of Noriega-Hevia *et al.* (2020) is the supernatant from the anaerobic digester of a full scale WWTP located in Valencia (Spain). This stream was treated before carrying out the experiments which consisted in pH adjustment, settling and filtration. Firstly, the pH was increased up to the established value (varying from 9 to 11) (Noriega-Hevia

et al., 2020) by adding a NaOH solution. When the pH of the AnaD supernatant was raised, different compounds (mainly calcium phosphate and calcium carbonate) precipitated which were also susceptible of clogging the membrane. To reduce this risk, the solids were settled during 8 min and the supernatant was passed through a 0.45 μm filter before feeding the HFMC. Table 5.3 shows the main characteristics of the reject water tested in the stated study before and after the pretreatment applied.

Table 5.3. Reject water main characteristics before and after pre-treatment, consisting on pH adjustment, solids settling and filtering, in the experiment of Noriega-Hevia *et al.* (2020).

Parameter	Before Pretreatment	After Pretreatment
COD (mg/L)	1320	620
TSS (mg/L)	5606	(*)
NH ₄ ⁺ -N (mg/L)	820	713
PO ₄ ³⁻ -P (mg/L)	30.5	2.3
pH	8.1	(**)

(*) Under limit of detection.

(**) pH depends on the operating conditions of each experiment.

According to Darestani *et al.* (2017), pH is the main factor affecting N recovery with HFMC technology and it should be maintained over 8. Although according to the membrane manufacturers there are not operational pH requirements for maintaining membrane stability, pH values higher than 11 are not necessary because NH₄⁺-N is already present as free ammonia from pH 8. Furthermore, the higher the pH, the higher the cost of chemical reagents.

Therefore, according to these studies, it is concluded that the industrial implementation must take into account all those operational details that can affect both membrane correct operation and its integrity. In that case, mentioned parameters are SST levels (in order to prevent membrane fouling) and pH.

Unfortunately, those streams where the technique could be applied are not SS free. The equivalent process to MC previous treatment in plant would be dewatering and thickening, and neither of them produce a stream clean enough to be fed. Therefore, for process scale-up a membrane filtration process would be required to protect HFMC modules. What is more, regarding pH regulation, buffer problems can appear because of high complexity in species.

5.2.2. Considerations of its implementation in Maresme WWTP

References recommend concentrations in the inflow from 1465 mg NH₄⁺-N/L (see Table 4.1). In accordance with this concentration, drain stream from Mataró and Pineda are the most suitable streams for HFMC implementation even if their concentrations are slightly lower (see Table 5.2). Teià has no suitable streams since there is no AnaD, so the case would be the same for Tordera.

HFMC recovery efficiency, 95.06% is a pretty high value (see Table 4.1). Regarding Table 5.2 load values and once technique's efficiency is known, the production of ammonia sulfate can be calculated.

All calculation showed below have been carried out for Mataró WWTP case. In Pineda plant case, calculations are carried out following the same way but they are not presented. Results are always presented for both WWTPs.

From a load of 259 kg NH₄⁺-N/day, 89.7 ton NH₄⁺-N/year in form of ammonia sulfate are generated:

$$\frac{216 \text{ m}^3}{\text{day}} \frac{1197 \text{ mg NH}_4^+ \text{ N}}{\text{L}} \frac{10^3 \text{ L}}{\text{m}^3} \frac{\text{kg}}{10^6 \text{ mg}} = 259 \text{ kg NH}_4^+ \text{ N/day}$$

$$\frac{259 \text{ kg NH}_4^+ \text{ N}}{\text{day}} \frac{95.06 \text{ kg NH}_4^+ \text{ N}}{100 \text{ kg NH}_4^+ \text{ N}} \frac{365 \text{ day}}{\text{year}} \frac{\text{ton}}{10^3 \text{ kg}} = 89.7 \text{ ton NH}_4^+ \text{ N/year}$$

Ammonia production will be interesting in order to know the magnitude of crop area feed by its use as fertilizer. However, the final product generated must be determined as well to know which the final cost or benefit for the plant will be.

$$\frac{89.7 \text{ ton NH}_4^+ \text{ N}}{\text{year}} \frac{10^3 \text{ kg}}{\text{ton}} \frac{\text{kmol NH}_4^+ \text{ N}}{18 \text{ kg NH}_4^+ \text{ N}} \frac{\text{kmol AmS}}{2 \text{ kmol NH}_4^+ \text{ N}} \frac{132 \text{ kg AmS}}{\text{kmol AmS}} \frac{\text{ton}}{10^3 \text{ kg}} = 328.9 \text{ ton AmS/year}$$

An economic balance will take into account the income from product's sale while it considers electricity and *other* costs (where required reagent and minor operational costs are included). Ammonium sulfate (AmS) value is 476.1 €/ton product, electricity cost is 17.94 €/ton AmS and others cost is 201.84 €/ton AmS (see Table 4.3).

$$\frac{328.9 \text{ ton AmS}}{\text{year}} \frac{476.1 \text{ €}}{\text{ton AmS}} = 156589 \text{ €/year}$$

$$\frac{328.9 \text{ ton AmS}}{\text{year}} \left(\frac{17.94 \text{ €}}{\text{ton AmS}} + \frac{201.8 \text{ €}}{\text{ton AmS}} \right) = 72286 \text{ €/year}$$

$$156589 \text{ €/year} - 72286 \text{ €/year} = 84303 \text{ €/year}$$

Therefore, in Mataró WWTP, a production of 89.7 ton NH₄⁺-N/year what equals to 328.9 ton AmS/year. Total benefit is 84303 €/year. Moreover, in Pineda WWTP, calculations (carried out following the method shown above) reveal that a production of 147.1 ton NH₄⁺-N/year what equals to 539.4 ton AmS/year would be obtained. Its total benefit is 138280 €/year.

Total benefit would depend on the selling price of the produced AmS, which could contain impurities and is variable based on the place and moment of the sale. Benefit values depend on other costs too so that should be analysed in detail after laboratory experiments with the reject water of the WWTP, since they could differ from other cases considered in literature.

5.3. Analysis of struvite precipitation strategy

The operation and characteristics of a struvite recovery unit are discussed in this section, and an analysis for this technique's implementation is carried out.

Although N is the main element in this study, struvite analysis is carried out from P standpoint, since it is usually more limiting than ammonium to produce struvite.

5.3.1. Struvite recovery plant

In order to study P recovery plants in depth, an industrial scale plant for its recovery by producing struvite, has been taken as an example. This plant, Sur WWTP (Madrid), is sized to treat up to 260 kg of P per day in the form of struvite.

The project was born trying to find a solution of the clogging of pipes caused by uncontrolled struvite precipitation. It generally occurs in the sludge line, downstream from AnaD. As it has been said before, struvite is a crystal made of Mg, ammonium and phosphate and its formula is $\text{NH}_4\text{MgPO}_4 \cdot 6(\text{H}_2\text{O})$. In wastewater, Mg is the limiting reactant to produce struvite so it must be added on purpose in order to make this process industrially feasible. The most common form to provide it is in the form of Mg chloride or Mg oxide. The technology consists on removing a large portion of the dissolved orthophosphate and a small part of ammonium from a liquid stream.

Before the implementation of the struvite reactor, Sur WWTP used to have difficulties with the operation because of the unintended generation of struvite and their precipitation in pipes, elbows and anaerobic digesters. Since the SP unit was set up, struvite formation is controlled and the number of obstruction cases has been dramatically reduced. In addition, this process allows to obtain a high quality product that can be used as fertilizer.

To make struvite able to be picked up, a crystallization reactor with continuous recirculation is implemented. It must be fed with MgCl_2 and caustic soda (to increase pH and reach the optimal conditions for crystallization). The stream feeding the reactor is dewatering overflow, and floatation overflows only in the event that it becomes necessary to supplement P load to bring it up to operational levels. The dewatering overflow is more suitable to feed the reactor because it has a much higher concentrations of ammonium and phosphate than floatation overflows.

The correct functioning lies on the control of struvite precipitation in an upflow bed reactor. Fluidised bed is achieved thanks to the recirculation pumping, the responsible for maintaining a constant upward flux in the reactor. The effluent is removed from a nozzle at the top of the reactor and is returned to the plant. The crystallized particles are extracted by means of the pressure gradient between the top and the floor of the reactor. Pressure differential and pH (regulated by NaOH addition) make possible the determination of the total amount of product in order to know how much of it has to be extracted.

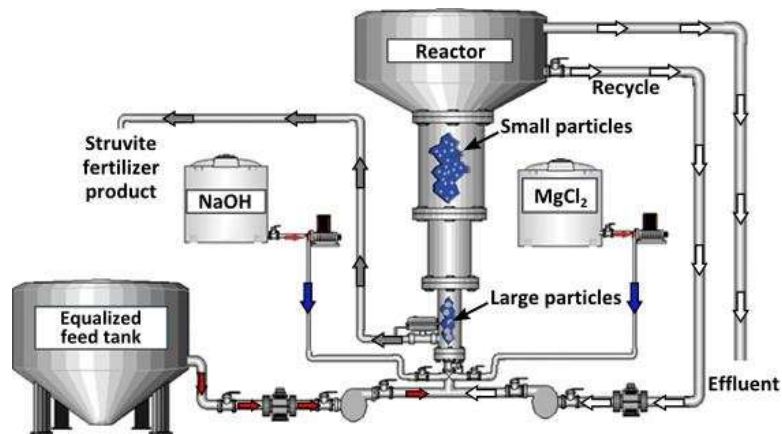


Figure 5.1. Struvite precipitation reactor flowsheet. (Adapted from Hazen and Sawyer, 2010)

Final product's preparation consists in several steps. (i) In the first stage, the extracted product goes through a vibrating screen used for solids-liquid separation. (ii) From this screen, the product is fed into a fluidised bed dryer. The air is fed into the dryer in order to remove the water from the commercial product. (iii) Finally, the particles produced in there are isolated from each other by the pneumatic effect of the turbulence that fluidisation produces.

Struvite crystals have been certified as a pathogen free and extremely pure fertilizer. Furthermore, compared to the standard fertilizer produced in WWTP like urea, ammonia or different nitrates, struvite contains not only N but P too.

Struvite uncontrolled precipitation is a common problem especially in plants located nearby the sea. This fact is due to high levels of salinity what lead to a Mg contribution. Pineda plant has important problems caused by struvite while Mataró has had punctual episodes. An example of big WWTP affected by struvite could be Tarragona. Struvite crystallises basically in digesters exit, elbows, welds, and inside centrifuges or dewatered stream receiving wells.



Figure 5.2. Struvite crystal extracted from a pipe in Pineda WWTP.

In Pineda, an anti-incrustation product is being applied in order to minimise uncontrolled crystallization impact. Moreover, periodically (about 10 days per year) water at high pressure is applied from a hose to strip off incipient crystals. Finally, equipment maintenance must be taken into account.



Figure 5.3. Decanter centrifuge drain pipe completely clogged by struvite crystals in Pineda WWTP.

5.3.2. Implementation in Maresme WWTP

References recommend concentrations in the inflow nearby 378 mg N/L (see Table 4.1), that equals to 486 mg NH₄⁺-N/L:

$$\frac{378 \text{ mg N}}{\text{L}} \frac{1 \text{ mmol N}}{14 \text{ mg N}} \frac{1 \text{ mmol NH}_4^+ \text{ N}}{1 \text{ mmol N}} \frac{18 \text{ mg NH}_4^+ \text{ N}}{1 \text{ mmol NH}_4^+ \text{ N}} = 486 \text{ mg NH}_4^+ \text{ N/L}$$

In order to determine the most suitable stream, Table 5.2 must be evaluated. Drain streams downstream digestion are the best option. *Other* streams are not considered because of their high variability. Therefore, this technique implementation should be studied in both Mataró and Pineda plant but not in Teià and Tordera where there is no AnaD.

Since phosphate and ammonia have a stoichiometric relation of 1:1 and ammonia concentration is further above phosphate's, phosphate will be the limiting reagent in struvite formation. It has been assumed that Mg is added to meet phosphate's demand. Cost associated to its addition are already considered in *others* cost (Table 4.3). Following calculations have been carried out assuming P as limiting reagent.

Table 5.4. P concentrations and flowrate in Mataró, Pineda and Teià WWTP.

	TP influent concentration [mg/L]	TP effluent concentration [mg/L]	TP loading rate in the influent [kg/day]	TP mass rate in the effluent [kg/day]	TP flowrate in the sludge line [kg/day]
Mataró	5.06	3.67	115	83	32
Pineda	5.39	3.46	120	77	43
Teià	10.69	2.26	148	31	117

Total P load rate (kg/day) has been calculated assuming that inflow (m³/day) can be considered the same as outflow (m³/day) since flow in water line almost does not change. All P is considered to be in form of phosphate (PO₄³⁻) since sludge has been digested.

$$\frac{32 \text{ kg P}}{\text{day}} \frac{\text{mol P}}{31 \text{ kg P}} \frac{1 \text{ mol struvite}}{1 \text{ mol P}} \frac{245 \text{ kg struvite}}{\text{mol struvite}} \frac{\text{ton}}{10^3 \text{ kg}} \frac{365 \text{ day}}{\text{year}} = 92.31 \text{ ton struvite/year}$$

As it has been said before, limiting reagent is P, therefore a calculation carried out from N recovery efficiency will not be representative (literature technique achieves the efficiency of 81.90 % by adding bot Mg and phosphate).

To assess the possible benefits of applying this technology, an economic evaluation will take into account the benefit from product's sale while it considers electricity and *other* costs. When the product is struvite, final's product value is 300.0 €/ton product. Electricity cost is 358.32 €/ton as and others cost is 81.99 €/ton as (see Table 4.3).

$$\frac{92.3 \text{ ton struvite}}{\text{year}} \frac{300.0 \text{ €}}{\text{ton struvite}} = 27693 \text{ €/year}$$

$$\frac{92.3 \text{ ton struvite}}{\text{year}} \left(\frac{358.3 \text{ €}}{\text{ton struvite}} + \frac{82.0 \text{ €}}{\text{ton struvite}} \right) = 40644 \text{ €/year}$$

$$27693 \text{ €/year} - 40644 \text{ €/year} = -12951 \text{ €/year}$$

Therefore, in Mataró WWTP a production of 92.3 ton struvite/year could be obtained, with economic losses, if the positive impact to the environment of this solution is not considered, nor the costs that uncontrolled struvite precipitation and pipes clogging. Moreover, in Pineda a production of 124.0 ton struvite/year has been calculated, which would also lead to a negative economic balance.

Pineda operates receiving sludge from Teià WWTP. External sludge is introduced in sludge line at the feeding digesters tank. This fact has no impact in HFMC's calculation because NH₄⁺-N concentration values of internal streams have been taken in situ. However, P concentration used for calculation above is obtained from water inflow and outflow concentrations, thus omitting the P provided by the external sludge. The actual production in Pineda is calculated beneath and takes into account Teià sludge.

$$\frac{117 \text{ kg P}}{\text{day}} \frac{\text{mol P}}{31 \text{ kg P}} \frac{1 \text{ mol struvite}}{1 \text{ mol P}} \frac{245 \text{ kg struvite}}{\text{mol struvite}} \frac{\text{ton}}{10^3 \text{ kg}} \frac{365 \text{ day}}{\text{year}} = 337.5 \text{ ton struvite/year}$$

P loading rate from Teià sludge (117 kg P/day) is much higher than Mataró or Pineda's P loading rates (32 and 43 kg P/day, respectively). This fact is due to 2 characteristics of Teià: (i) the existence of PAOs (which increase P removal efficiency), and (ii) wastewater coming from industry contains high levels of P.

Struvite balance would noticeably change since the amount treated is now near 4 times the considered before.

$$\frac{124.0 + 337.5 \text{ ton struvite}}{\text{year}} \left(\frac{300.0 \text{ €}}{\text{ton struvite}} - \frac{358.3 \text{ €}}{\text{ton struvite}} - \frac{82.0 \text{ €}}{\text{ton struvite}} \right) = -64748 \text{ €/year}$$

Therefore, in Pineda WWTP (considering Teià sludge), a production of 461.5 ton struvite/year could be obtained, leading to a negative economic balance, when considering the aforementioned costs.

Nevertheless, there is an important benefit from the prevention of problems caused by uncontrolled struvite crystallization. Estimation costs for Pineda WWTP are the following ones (data provided by Maresme WWTP managers):

- Anti-incrusting *flospere*: 15000 €/year
- High pressure tank truck: 10 times/year, 900 €/time
- Equipment maintenance average cost: 3000 €/year

$$\frac{15000 \text{ € incr.}}{\text{year}} + \frac{10 \text{ times}}{\text{year}} \frac{900 \text{ € truck}}{\text{time}} + \frac{3000 \text{ € maint.}}{\text{year}} = 27000 \text{ €/year}$$

Taking into account savings involved with controlled struvite crystallization, initial economical loss is reduced from 64748 €/year to 37748 €/year.

After SP, great amount of ammonia still remain in internal streams, hence the application of a subsequent N recovery technique could be interesting. A sequence of struvite crystallization followed by a treatment using MC would allow a better N recovery (overcoming the main SP disadvantage) while producing a lower SS concentration stream feeding the membrane (minimizing fouling risk, the main HFMC disadvantage).

The mass flowrate of the remaining NH_4^+ -N is the difference between drain's N mass flowrate and the N mass flowrate spent in struvite formation.

$$\frac{32 \text{ kg P}}{\text{day}} \frac{1 \text{ kmol P}}{31 \text{ kg P}} \frac{1 \text{ kmol struvite}}{1 \text{ kmol P}} \frac{1 \text{ kmol NH}_4^+ \text{N}}{1 \text{ kmol struvite}} \frac{18 \text{ kg NH}_4^+ \text{N}}{1 \text{ kmol NH}_4^+ \text{N}} = 18.6 \text{ kg NH}_4^+ \text{N/day}$$

$$\frac{259 \text{ kg NH}_4^+ \text{N}}{\text{day}} - \frac{18.6 \text{ kg NH}_4^+ \text{N}}{\text{day}} = 240 \text{ kg NH}_4^+ \text{N/day}$$

Once ammonia loading rate is determined in the drain stream, the same method as the one used in ammonia sulphate's determination (see Section 5.2.2) is used in order to determine both ton of product per year and the result of its economic balance. Final benefit from the combination of SP and HFMC is presented below.

Mataró WWTP. Remaining $\text{NH}_4^+\text{-N}$ is 331 kg/day. Production of 305.3 ton AmS/year. Total benefit is 78260 €/year. Final economic balance after both techniques treatment would represent an income of 65309 €/year.

Pineda WWTP (considering Teià sludge). Remaining $\text{NH}_4^+\text{-N}$ is 394 kg/day. Production of 442.9 ton AmS/year. Total benefit is 113532 €/year. Final economic balance after both techniques treatment would represent an income of 48776 €/year.

5.4. Comparison of the studied recovery alternatives

Table 5.5 summarizes data obtained from chapters 5.2.2 and 5.3.2. It will be necessary to follow the comparison between both techniques carried out below.

Table 5.5. Results compilation from chapter 5.2 and 5.3.

		[ton $\text{NH}_4^+\text{-N}$ /year]	[ton AmS/year]	[ton struvite/year]	Product's sale [€/year]	Operation cost [€/year]	Economic balance [€/year]
Membrane Contactors	Mataró	89.7	328.9	-	156589	72286	84303
	Pineda	147.1	539.4	-	256808	118528	138280
Struvite Precipitation	Mataró	6.8	-	92.3	27693	40664	-12971
	Pineda	26.4	-	461.5	138450	203198	-37748
MC + SP	Mataró	89.7	305.3	92.3	173043	107740	65303
	Pineda	147.1	442.9	461.5	349315	300539	48776

In first place, theoretical N recovery efficiency for MC (95.06 %) is slightly higher than SP's (81.90 %). However, actual N recuperation could be far higher in MC than in SP as it can be seen in Table 5.5. As an example, recovered N mass in Pineda by means of MC is 147.1 ton $\text{NH}_4^+\text{-N}$ /year while N mass obtained by SP is only 26.4.

Within recuperation ambit, determining the production magnitude of what it will be considered as a new N source is indispensable in order to know the study's reach. Data from Eurostat (2018) determine the average quantity of N applied per crop hectare in a year, 50 kg N/ha year. Mataró and Pineda together could feed 4736 ha of crop per year. Knowing total crop surface in Catalonia is 830981 ha (Departament d'Agricultura, Ramaderia, Pesca i Alimentació, Generalitat de Catalunya, 2017) the portion fed by these 2 hypothetical recovery plants means the 0.57 %.

On the other hand, P recovery in MC is non-existent while SP technique recovers almost totally the P present in the sludge line. The presence of both nutrients is the main reason why

struvite is so appreciated as fertilizer. The prevention of uncontrolled struvite crystallization should be emphasised because it is not only the savings benefit what is achieved but the prevention of hours of work to solve the problem, operational risks, and other troubles.

Regarding only the benefit associated to final product's generation, AmS and struvite prices (476.1 €/ton AmS and 300.0 €/ton struvite) must be known to draw conclusions. Benefit achieved by MC is higher because of the product's price and its higher generation (see Table 5.5).

To complete economic comparison, operational costs of both techniques must be calculated. In proportion with generated product, SP production is far more expensive than MC's. At so extend that final balance implies an income for MC technique and an outlay for SP's.

Investment outlay values are not available in this study for either MC or SP technique. Nevertheless, the before mentioned problematic of suspended solids in HFMC would suppose a relatively high installation cost since a previous membrane treatment would be necessary to treat the stream delivered to the HFMC. This is a high flow to be treated by means of membranes, so several equipment should be installed. If SS exceed recommended limits, fouling problems could appear what would decrease HFMC's lifetime. On the other hand, studies estimate SP plant lifetimes nearby 50 years (Bradford-Hartke *et al.*, 2015; Kjerstadius *et al.*, 2017). To summarise, SP have a lower investment outlay than MC but they cannot be known with precision.

An interesting thing to study in detail is the combination of both techniques in a sequence of SP and MC. Nutrient recovery would be maximum since struvite recovers P and the remaining N is recovered as AmS. By means of proposed combination of techniques, for the case of Pineda, a production of 442.9 ton AmS/year and 461.5 ton struvite/year is achieved while in MC and SP alone, only one product is obtained (see Table 5.5). AmS production in MC alone is a bit bigger than in the combined process as some $\text{NH}_4^+\text{-N}$ is spent in struvite crystallization.

Regarding economical side, the higher production mentioned before leads to an income for Pineda of 349000 €/year while the income from product's sale is 257000 €/year for MC and 138000 €/year for SP. Its costs are also higher than techniques operating separately (see Table 5.5). Despite economical balance for SP is negative, the combined process offers the possibility to achieve a positive balance close below MC's.

The combination of SP followed by a treatment using MC would allow a better N recovery (overcoming the main SP disadvantage) while producing a lower SS concentration stream feeding the membrane (minimizing fouling risk, the main HFMC disadvantage). Despite these advantages, investment outlay would be higher than each technique's separately. However, an optimized layout could be found in order to reduce investment outlay. As an example, the MC could treat the effluent of the crystallizer and since both techniques require a high pH, NaOH dispenser could feed both stages (see Figure 5.1).

Finally, an implicit issue that has to be highlighted is that AnaD is absolutely indispensable to reach concentrations suitable to apply the recovery technique. This fact concerns HFMC and SP as well as most of the recovery techniques. Specifying the stream where recuperation is feasible, dewatering centrifuge drain is the only one that fulfil concentration requirements.

6. CONCLUSIONS

This study consists in a bibliographic research of several N removal and recovery techniques regarding its current production problems and the opportunity that UWW represents as a new nutrient source. A feasibility analysis has been carried out regarding both technical and economic feasibility. HFMC and SP have been proposed as the most suitable techniques to implement in a conventional WWTP. A following study from the operational point of view as well as an evaluation of the impact they would have in the specific case of Maresme plants has been carried out in detail. Finally, a comparison between both strategies and a proposal of their combination shows interesting results. The main conclusions drawn from this study are explained below.

N is of vital importance for every form of life. However, its production in a conventional way entails environmental and economic difficulties. A better use of resources in a circular economy strategy would reduce the impact caused by N emissions while its recovery from new resources would save high amounts of energy spent in Haber-Bosch process. From the point of view of UWW as a potential nutrient source, the load of N arriving to WWTPs is significant. Despite conventional plants are capable to remove enough N to make the effluent harmless, in the case of Maresme WWTPs, those discharging in the sea do not perform a N/DN in order to remove N.

Feasibility analysis

Techniques found in literature usually require high inflow N concentrations while offer a wide range of recovery efficiencies. Their products are always ammonium salts or struvite. A great part of these techniques are designed to treat sources providing from swine manure, urine or synthetic streams, which have higher N concentration than UWW. All studied techniques require lower energy than Haber-Bosch's process what means that N production is more energetically inexpensive than conventional way and some of them even generate energy.

The streams of the water line do not have concentrations high enough to feed the recovery units. By sludge treatment with AnaD, high quantities of N and P are freed. This is the cause why suitable streams are found only downstream digestion, mainly in decanter centrifuge drain.

Depending on the characteristics of the studied system (plant location, plant size, stream to be treated, sludge line) a selection of suitable techniques must be carried out. Lots of them are still in a development stage and their data are taken in a lab scale. More work in pilot and real plant must be done in order to obtain reliable data. The sale value of the final product as fertilizer and the price of the reagents also varies according to the place, moment, and regulations. Thus, this analysis is sensitive to price variation.

HFMC and SP implementation

Regarding this study scope, the most suitable techniques for their implementation are HFMC and SP due to their recovery efficiencies, economic balance, and similarity with real plant internal streams. Their study is especially interesting since they are quite different in operational conditions, final products or associated difficulties, what offers a wide variety of opportunities.

HFMC is suitable since it is capable to recover large amounts of $\text{NH}_4^+\text{-N}$ with an efficiency of 95%, what means that high AmS will be produced. Its implementation carries an economic balance highly positive, 256 €/ton of product. Regarding Maresme case, the benefit is close to 84000 and 138000 €/year in Mataró and Pineda respectively. However, this values are not totally accurate since product's sale price can vary. The main drawback for its implementation is that SS concentration in drain stream is excessive for membrane operation what forces a pretreatment. Therefore, investment cost will be high. In the case that pretreatment is not strong enough removing SS, high maintaining costs will be assumed due to membrane fouling.

SP is capable to recover P in yields close to 100% although as N recovery technique it has a much lower efficiency due to the imbalance of N/P rate between struvite molecule and stream compositions. This technique would operate adding Mg in order to assure that limiting reagent is P. In plants nearby the sea where waters are usually rich in Mg, its demand will be lower. Struvite is a valuable fertilizer since it contains both P and N, and release nutrients slowly, although it must be combined with a supplementary N source to reach crop requirements. Economical balance is negative (-140 €/ton). Nevertheless, in those plants where struvite crystallisation is now being an actual problem, its controlled precipitation is crucial. These problems have an appreciable cost (27000 €/year in Pineda) where economical losses would be reduced in a 42% (from 65000 to 38000 €/year). Furthermore, the prevention of operational and working problems (hard to quantify in €/year) is achieved. Pilot plant studies are necessary to obtain more reliable data of energetic costs in SP since it seems to be too high compared with other techniques.

Final proposal

The evaluation of both advantages and disadvantages of each technique suggest that the implementation of a sequence of SP and MC stages could result in an optimal solution since main drawbacks are practically neutralised. An initial SP (where P would be recovered) followed by a treatment using MC would allow a better N recovery (overcoming the main SP disadvantage) while producing a low SS concentrated stream feeding the membrane (minimizing fouling risk, the main HFMC disadvantage). Great nutrient recoveries would be achieved since SP would produce struvite (462 ton/year in Pineda) and the subsequent MC would produce AmS (443 ton/year in Pineda). Economical balance would be positive reaching 70000 €/year in Mataró and 91000 €/year in Pineda. Operational costs may even be reduced since different synergies would appear like in the case of pH control because both techniques need and addition of NaOH. Thus, only one tank will be needed and, what is more, reagent dose could be lower since the effluent from the struvite crystalliser, which in turn represents the MC influent, has already a high pH.

7. REFERENCES

1. Arakane M, Imai T, Murakami S, Takeuchi M, Ukita M, Sekine M, Higuchi T. (2006) Resource recovery from excess sludge by subcritical water combined with magnesium ammonium phosphate process. *Water Science & Technology*, Volume 54, Issue 9, 1 November 2006
2. Beckinghausen A, Odlare M, Thorin E, Schwede S. (2020) From removal to recovery: An evaluation of nitrogen recovery techniques from wastewater. *Applied Energy*, Volume 263, 1 April 2020, Pages 1-12
3. Benson NU. (2014) Trace Metal Levels in Inorganic Fertilizers Commercially Available in Nigeria. *Journal Science Resource Report*, Volume 3, 2014, Pages 610-20
4. Bergkvist P, Jarvis N, Berggren D, Carlgren K. (2003) Long-term effects of sewage sludge application on soil properties, cadmium availability and distribution in arable soil. *Agriculture, Ecosystems and Environment*, Volume 97, Issues 1–3, July 2003, Pages 167-179
5. Bradford-Hartke Z, Lane J, Lant P, Leslie G. (2015) Environmental Benefits and Burdens of Phosphorus Recovery from Municipal Wastewater. *Environmental Science and Technology*, 21 July 2015, 49 14, Pages 8611-8622
6. Cao S, Li B, Du R, Ren N, Peng Y. (2020) Nitrite production in a partial denitrifying upflow sludge bed (USB) reactor equipped with gas automatic circulation (GAC). *Water research [Water Res]*, Volume 173, 15 April 2020, , pp. 115660
7. Chen X, Sun D, Zhang X, Liang P, Huang X. (2015) Novel self-driven microbial nutrient recovery cell with simultaneous wastewater purification. *Scientific Reports*, volume 5, 27 October 2015, Article number: 15744
8. Chien SH, Gearhart MM, Villagarcía S. (2011) Comparison of ammonium sulfate with other nitrogen and sulfur fertilizers in increasing crop production and minimizing environmental impact: a review. *Soil Science*, Volume 176, Issue 7, July 2011, Pages 327-p335
9. Christiaens ME, Gildemyn S, Matassa S, Ysebaert T, De Vrieze J, Rabaey K. Electrochemical ammonia recovery from source-separated urine for microbial protein production. *Environmental Science and Technology*, Volume 51, Issue 22, 21 November 2017, p13143-p13150
10. Cornel P, Schaum C. (2009) Phosphorus recovery from wastewater: needs, technologies and costs. *Water Science and Technology*, Volume 59, 2009, Pages 1069-1076
11. Daguette-Martini S, Vanotti MB, Rodriguez-Pastor M, Rosal A, Moral R. (2018) Nitrogen recovery from wastewater using gas-permeable membranes: impact of inorganic carbon content and natural organic matter. *Water Research*, Volume 137, 15 June 2018, Pages 201-210
12. Darestani M, Haigh V, Couperthwaite SJ, Millar GJ, Nghiem LD. (2017) Hollow fibre membrane contactors for ammonia recovery: Current status and future developments. *Journal of Environmental Chemical Engineering*, Volume 5, Issue 2, April 2017, Pages 1349-1359
13. Departament d'Agricultura, Ramaderia, Pesca i Alimentació, Generalitat de Catalunya. (2017) Evolució de les hectàrees de zona forestal i de conreus, per tipus, a Catalunya
14. Devol AH; School of Oceanography, University of Washington. (2015) Denitrification, Anammox, and N₂ Production in Marine Sediments. *Annu. Rev. Mar. Sci.* 2015.7, Pages 403-423
15. Dockhorn T. (2009) About the economy of phosphorus recovery. *International Conference on Nutrient Recovery from Wastewater Streams*, Vancouver, 2009.

16. Dube PJ, Vanotti MB, Szogi AA, García-González MC. (2016) Enhancing recovery of ammonia from swine manure anaerobic digester effluent using gas-permeable membrane technology. *Waste Management*, Volume 49, March 2016, Pages 372-377
17. Erisman JW, Sutton MA, Galloway J, Klimont Z, Winiwarter W. (2008). *How a century of ammonia synthesis changed the world. Nature Geoscience*, Volume 10, 28 September 2008, Pages 636–639.
18. European Environment Agency (EEA). (2017) Agri-environmental indicator – ammonia emissions
19. European Commission Science and Knowledge service. (2016) New study reveals environmental harm and cost of nitrogen fertilization. 9 August 2016
20. Eurostat Statistics explained. (2018) Agri-environmental indicator - gross nitrogen balance. April 2018.
21. Fowler D, Coyle M, Skiba U, Sutton MA, Cape JN, Reis S, Lucy JS, Alan J, Bruna G, James NG, Peter V, Allison L, Alexander FB, Klaus BB, Frank D, David S, Marcus A, Maren V. (2013) The global nitrogen cycle in the twenty-first century. *Philosophical Transactions: Biological Sciences*, Volume 368, Pages 1-13
22. Franz M. (2008) Phosphate fertilizer from sewage sludge ash (SSA). *Waste Management*, Volume 28, Issue 10, 2008, Pages 1809-1818
23. Fung K.Y and Wivowo C. (2013) Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology. ClearWaterBay Technology, Inc. Design of Industrial Wastewater Treatment Plants: A multi-faced problem. *Current Opinion in Chemical Engineering*, Volume 2, Issue 4, November 2013, Pages 455-460
24. Garcia-González MC, Vanotti MB. (2015) Recovery of ammonia from swine manure using gas-permeable membranes: effect of waste strength and pH. *Waste Management*, Volume 38, April 2015, Pages 455-461
25. Ge Z, Wu L, Zhang F, He Z. (2015) Energy extraction from a large-scale microbial fuel cell system treating municipal wastewater. *Journal of Power Sources*, Volume 297, 30 November 2015, Pages 260-264
26. Gerardo ML, Zacharof MP, Lovitt RW. (2013) Strategies for the recovery of nutrients and metals from anaerobically digested daily farm sludge using cross-flow microfiltration. *Water Research*, Volume 47, Issue 14, 15 September 2013, Pages 4833-4842
27. Gilbert, N. (2009) Environment: The disappearing nutrient. *Nature*, Volume 461, 07 October 2009, Pages 716–718
28. Gong H, Wang Z, Zhang X, Jin Z, Wang C, Zhang L, Wang K. (2017) Organics and nitrogen recovery from sewage via membrane-based pre-concentration combined with ion exchange process. *Chemical Engineering Journal*, Volume 311, 1 March 2017, Pages 13-19
29. Gu Y, Li Y, Li X, Luo P, Wang H, Robinson ZP, Wang X, Wu J, Li F. (2017) The feasibility and challenges of energy self-sufficient wastewater treatment plants. *Applied Energy*, Volume 204, 15 October 2017, Pages 1463-1475
30. Guo CH, Stabnikov V, Ivanov V. (2010) The removal of nitrogen and phosphorus from reject water of municipal wastewater treatment plant using ferric and nitrate bioreductions. *Bioresource Technology*, Volume 101, Issue 11, June 2010, Pages 3992-3999
31. Guo W, Ai Y, Men B, Wang S. (2017) Adsorption of phenanthrene and pyrene by biochar produced from the excess sludge: experimental studies and theoretical analysis. *International Journal of Environmental Science and Technology*; 20 February 2017, Pages 1889-1896

32. Hancock NT, Xu P, Roby MJ, Gomez JD, Cath TY. (2013) Towards direct potable reuse with forward osmosis: Technical assessment of long-term process performance at the pilot scale. *Journal of Membrane Science*, Volume 445, 15 October 2013, Pages 34-46
33. Hao X, Wang C, van Loosdrecht MCM, Hu Y. (2013) Looking beyond struvite for P-recovery. *Environ. Sci. Technol*, Volume 47, 10 April 2013, Pages 4965–4966
34. Henze M, Loosdrecht MCM, Ekama GA, Brdjanovic D. (2008) *Biological Wastewater Treatment Principles: Modeling and Design*. IWA Publishing, London, 1 September 2008, Pages 528
35. Hulsbeek JJ, Kruit J, Roeleveld P, van Loosdrecht M. (2002) A practical protocol for dynamic modelling of activated sludge systems. *Water Science and Technology*, Volume 45, Issue 6, 1 March 2002, Pages 127-136
36. Joan Mata, Ingeniería Química UB, Tecnologías del Medi Ambient, TEMA III 6, p. 9. Search 19/2/20.
37. Jones A. (2019) Sales Drivers and What to Expect for Fertilizer Companies. *Market Realist*, 27 December 2019
38. Katak S, West H, Clarke M, Baruah DC. (2016) Phosphorus recovery as struvite: Recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential. *Resources, Conservation and Recycling*, Volume 107, February 2016, Pages 142-156
39. Kern J, Heinzmann B, Kaufmann AC, Soethe N, Engels C. (2008) Recycling and assessment of struvite phosphorus from sewage sludge. *CIGR eJournal*, Volume 10, 2008
40. Kirova-Yordanova Z. (2004) Exergy analysis of industrial ammonia synthesis. *Energy*, Volume 29, Issues 12–15, October–December 2004, Pages 2373-2384
41. Kjerstadius H, Bernstad Saraiva A, Spångberg J, Davidsson Å. (2017) Carbon footprint of urban source separation for nutrient recovery. *Journal of Environmental Management*, Volume 197, 15 July 2017, Pages 250-257
42. Lan W, Lai P, Wei W, Dongbo W, Bing-Jie N. (2020) Nitrous oxide production from wastewater treatment: The potential as energy resource rather than potent greenhouse gas. *Journal of Hazardous Materials*, Volume 387, 5 April 2020, Pages 121694
43. Lema JM, Suarez S. (2017) *Innovative Wastewater Treatment & Resource Recovery Technologies: Impacts on Energy, Economy and Environment*. IWA Publishing, London, Pages 650
44. Lenntech, Processes, Waste Water Treatment, Membrane Bioreactor, Submerged MBR. Search 20/3/20
45. Li H, Wang W, Zhang Y. (2014) Preparation and characterization of high-selectivity hollow fibre composite nanofiltration membrane by two-way coating technique. *Journal of Applied Polymer Science*, Volume 131, Issue 23, 5 December 2014
46. Lizarralde I, Fernández-Arévalo T, Manas A, Ayesa E, Grau P. (2019) *Water Research*, Volume 153, 15 April 2019, Pages 39-52
47. Lopez-Vazquez CM, Mithaiwala M, Moussa MS, van Loosdrecht MCM, Brdjanovic D. (2013) Coupling ASM3 and ADM1 for wastewater treatment process optimisation and biogas production in a developing country: case-study Surat, India. *Journal of Water, Sanitation and Hygiene for Development*; London Volume 3, Mars 2013, Pages 12-25
48. Maaß O, Grundmann P, von Bock und Polach C. (2014) Added-value from innovative value chains by establishing nutrient cycles via struvite. *Resources, Conservation and Recycling*, Volume 87, June 2014, Pages 126-136

49. Madeline Sena, Andrea Hicks. (2018) Life cycle assessment review of struvite precipitation in wastewater treatment. *Resources, Conservation and Recycling*, Volume 139, December 2018, Pages 194-204
50. Marques AL, Araújo Ofélia QF, Cammarota MC. (2018) Biogas from microalgae: an overview emphasizing pretreatment methods and their energy return on investment (EROI). *Biotechnology Letters*, Volume 41, 01 December 2018, Pages 193–201
51. Mondor M, Ippersiel D, Lamarche F, Masse L. (2009) Fouling characterization of electro dialysis membranes used for the recovery and concentration of ammonia from swine manure. *Bioresource Technology*, Volume 100, Issue 2, January 2009, Pages 566-571
52. Mosquera-Losada MR, Muños-Ferreiro N, Rigueiro-Rodríguez A. (2010) Agronomic characterisation of different types of sewage sludge: Policy implications. *Waste Management*, Volume 30, Issue 3, March 2010, Pages 492-503
53. Nielsen PH. (1996) Adsorption of ammonium to activated sludge. *Water Research*, Volume 30, Issue 3, March 1996, Pages 762-764
54. Nowak O. (2003) Benchmarks for the energy demand of nutrient removal plants. *Water Science and Technology*, Volume 47, Issue 12, 1 June 2003, Pages 125–132
55. Odlare M, Arthurson V, Pell M, Svensson K, Nehrenheim E, Abubaker J. (2011) Land application of organic waste-effects on the soil ecosystem. *Applied Energy*, Volume 88, Issue 6, June 2011, Pages 2210-2218
56. Odlare M, Lindmark J, Ericsson A, Pell M. (2015) Use of organic wastes in agriculture. *Energy Procedia*, Volume 75, August 2015, Pages 2472-2476
57. Odlare M, Pell M, Arthurson JV, Abubaker J, Nehrenheim E. (2014) Combined mineral N and organic waste fertilization-effects on crop growth and soil properties. *Journal of agricultural science*, Volume 152, February 2014, Pages 134-145
58. Odlare M, Pell M, Svensson K. (2008) Changes in soil chemical and microbiological properties during 4 years of application of various organic residues. *Waste Management*, Volume 28, Issue 7, 2008, Pages 1246-1253
59. Otal E, Vilches LF, Luna Y, Poblete R, Garcia-Maya JM, FernandezPereira C. (2013) Ammonium ion adsorption and settleability improvement achieved in a synthetic zeolite-amended activated sludge. *Chinese Journal of Chemical Engineering*, Volume 21, Issue 9, September 2013, Pages 1062-1068
60. Pan B, Lam SK, Mosier A, Luo Y, Chen D. (2016) Ammonia volatilization from synthetic fertilizers and its mitigation strategies: a global synthesis. *Agriculture, Ecosystems and Environment*, Volume 232, 16 September 2016, Pages 283-289
61. Peng L, Dai H, Wu Y, Peng Y, Lu X. (2018) A comprehensive review of phosphorus recovery from wastewater by crystallization processes. *Chemosphere*, Volume 197, April 2018, Pages 768-781
62. Pereira JM, Fernández Arévalo T, Grau P, Ayesa E. (2012) Simulation based analysis of new layouts for eco-efficient Sewage treatment Plants. Conference: 2nd IWA Specialist Conference on EcoTechnologies for Sewage Treatment Plants, June 2012
63. Pikaar I, Matassa S, Rabaey K, Laycock B, Boon N, Verstraete W. The urgent need to re-engineer nitrogen-efficient food production for the planet. *Manag. Waste Resource Management*, Springer International Publishing, 14 April 2018, Pages 35-69

64. Qiu D, Wu Z, Huang SM, Ye WB, Chen X, Luo J, Yang M. (2017) Laminar flow and heat transfer in an internally-cooled hexagonal parallel-plate membrane channel (IHPMC). *Applied Thermal Engineering*, Volume 124, September 2017, Pages 767-780
65. Richter L, M Wichern, M Grömping, U Robecke, J Haberkamp. (2019) Nitrogen recovery from process Water of digested sludge dewatering with membrane contactors. *Water Practice and Technology*, Volume 15, 1 March 2020, Pages 84-91
66. Rosen C, Vrecko D, Gernaey K, Pons MN, Jeppsson U. (2006) Implementing ADM1 for plant-wide benchmark simulations in Matlab/Simulink. *Water Science and Technology*, London, Volume 54, August 2006, Pages 11-19
67. Rui Du, Yong Zhen, Peng Jiantao, Ji Liang, Liang Shi, Rui Tao, Gao Xiang, Chen Li. (2019) Partial denitrification providing nitrite: opportunities of extending application for anammox. *Environment International*, Volume 131, October 2019, 105001
68. Seco A, S Aparicio, J González-Camejo, A Jiménez-Benítez, O Mateo, JF Mora, G Noriega-Hevia, P Sanchis-Perucho, R Serna-García, N Zamorano-López, JB Giménez, A Ruiz-Martínez, D Aguado, R Barat, L Borrás, A Bouzas, N Martí, M Pachés, J Ribes, A Robles, MV Ruano, J Serralta, J Ferrer. (2018) Resource recovery from sulphate-rich sewage through an innovative anaerobic-based water resource recovery facility (WRRF). *Water Science and Technology*, December 2018, 78 9, p1925-p1936
69. Smith D, Smith N. (2015) Nitrogen recovery from onsite wastewater and local recycle. *Proc. Uniting Prog. Natl. Onsite Wastewater Recycl. Assoc. Mega-Conf. Va. Beach Va*
70. Tao W, Bayrakdar A, Wang Y, Agyeman F. (2019) Three-stage treatment for nitrogen and phosphorus recovery from human urine: Hydrolysis, precipitation and vacuum stripping. *Journal of Environmental Management*, Volume 249, 1 November 2019, 109435
71. Tarayre C, De Clercq L, Charlier R, Michels E, Meers E, Camargo-Valero M, Delvigne F. (2016) New perspectives for the design of sustainable bioprocesses for phosphorus recovery from waste. *Bioresource Technology*, Volume 206, April 2016, Pages 264-274
72. The Lenhart Group. (2016) Feeding the world in the 21st century: grand challenges in the nitrogen cycle. National Science Foundation: Arlington, 2016
73. Tchobanoglous G, Stensel H, Tsuchihashi R, Burton F. (2013) *Wastewater Engineering: Treatment and Resource Recovery*, Metcalf & Eddy, McGraw-Hill Education, New York, 2013
74. Ukuwani AT, Tao W. (2016) Developing a vacuum thermal stripping-acid absorption process for ammonia recovery from anaerobic digester effluent. *Water Research*, Volume 106, 1 December 2016, Pages 108-115
75. Valclav Smil. (2009) *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food*. Cambridge MIT Press, 4 July 2009
76. Vanotti MB, Dube PJ, Szoji AA, Gracia-González MC. (2017) Recovery of ammonia and phosphate minerals from swine wastewater using gas-permeable membranes. *Water Research*, Volume 112, 1 April 2017, Pages 137-146
77. Wang XG, Lu SY, Gao CM, Xu XB, Zhang XJ, Bai X, Liu MZ, Wu L. (2014) Highly efficient adsorption of ammonium onto palygorskite nanocomposite and evaluation of its recovery as a multifunctional slow-release fertilizer. *Chemical Engineering Journal*, Volume 252, 15 September 2014, Pages 404-414
78. Wett B, Nyhuis G, Takács I, Murthy S. (2010) Development of enhanced deammonification selector. *Water Environment Federation*, Volume 10, January 2010, Pages 5917-5926

79. Wu X, Modin O. (2013) Ammonium recovery from reject water combined with hydrogen production in a bioelectrochemical reactor. *Bioresource Technology*, Volume 146, October 2013, Pages 530-536
80. Xialei You, César Valderrama, José Luis Cortina. (2019) Nutrients recovery from treated secondary mainstream in an urban wastewater treatment plant: A financial assessment case study. *Science of The Total Environment*, Volume 656, 15 March 2019, Pages 902-909
81. Xiaolei Liu, Anjie Li, Lisha Ma, Zaitao Jing, Jing Yang, Yi Tang, Bin Hu. (2020) A comparison on phosphorus release and struvite recovery from waste activated sludge by different treatment methods. *International Biodeterioration & Biodegradation*, Volume 148, March 2020, 104878
82. Xie M, Shon HK, Gray SR, Elimelech M. (2016) Membrane-based processes for wastewater nutrient recovery: Technology, challenges, and future direction. *Water Research*, Volume 89, 1 February 2016, Pages 210-221
83. Yan T, Ye Y, Ma H, Zhang Y, Guo W, Du B. (2018) A critical review on membrane hybrid System for nutrient recovery from wastewater. *Chemical Engineering Journal*, Volume 348, 15 September 2018, Pages 143-156
84. Younas M, Druon Bocquet S, Sanchez J. (2008) Extraction of aroma compounds in a HFMC: dynamic modelling and simulation. *Journal of Membrane Science*, Volume 323, Issue 2, 15 October 2008, Pages 386-394
85. Zhang W, Zhou Z, An Y, Du S, Ruan D, Zhao C, Ren N, Tian X. (2017) Optimization for zeolite regeneration and nitrogen removal performance of a hypochlorite-chloride regenerant. *Chemosphere*, Volume 178, July 2017, Pages 565-572
86. Zhang WH, Mao SY, Chen H, Huang L, Qiu RL. (2013) Pb(II) and Cr(VI) sorption by biochars pyrolyzed from the municipal wastewater sludge under different heating conditions. *Bioresource Technology*, Volume 147, November 2013, Pages 545-552
87. Zhou K, Barjenbruch M, Kabbe C, Inial G, Remy C. (2017) Phosphorus recovery from municipal and fertilizer wastewater: China's potential and perspective. *Journal of Environmental Sciences*, Volume 52, February 2017, Pages 151-159

8. ANNEXES

Table 8.1. Flows and SST, COD, and BOD5 efficiencies for Mataró WWTP.

Cabals i rendiments (C)		CABAL TRACTAT		SST			DQO			DBO5		
mes	any	m3/dia m3	m3/mes m3	ent mg/l	sort mg/l	rend %	entr mg/l	sort mg/l	rend %	ent mg/l	sort mg/l	rend %
GENER	2019	25.545	791.888	516	23	94,8	1.017	90	90,7	657	26	95,8
FEBRER	2019	24.160	676.468	523	10	97,8	1.006	79	91,8	633	16	97,3
MARÇ	2019	23.903	740.987	566	10	97,9	1.022	72	92,4	659	14	97,8
ABRIL	2019	23.405	702.142	471	9	97,9	903	68	91,9	557	12	97,7
MAIG	2019	24.417	756.928	519	14	96,9	980	78	91,3	605	15	97,3
JUNY	2019	23.934	718.018	474	11	97,5	880	74	91,4	549	14	97,3
JULIOL	2019	25.091	777.811	512	13	96,7	920	79	89,1	559	17	95,2
AGOST	2019	18.636	577.720	426	11	97,3	803	57	92,6	502	10	98,0
SETEMBRE	2019	23.448	703.451	479	7	98,3	860	60	92,3	526	9	98,1
OCTUBRE	2019	24.100	747.090	238	10	95,7	584	68	87,8	372	11	96,9
NOVEMBRE	2019	24.622	738.652	274	17	93,5	641	81	87,1	426	17	96,0
DESEMBRE	2019	23.835	738.882	334	23	92,8	720	85	87,6	458	18	96,0
TOTAL			8.670.037									
<i>mitjana</i>		23.758	722.503	444	13	96,4	861	74	90,5	542	15	96,9
<i>màxim</i>		25.545	791.888	566	23	98,3	1.022	90	92,6	659	26	98,1
<i>mínim</i>		18.636	577.720	238	7	92,8	584	57	87,1	372	9	95,2
Mitjana ANY 2019		23.758	722.503	444	13	96,4	861	74	90,5	542	15	96,9
Mitjana ANY 2018		23.673	719.608	470	11	97,1	885	70	91,3	578	16	97,0
Mitjana ANY 2017		21.501	631.868	505	14	96,5	918	70	91,7	604	17	97,0
Mitjana ANY 2016		23.247	708.453	520	14	96,6	923	72	91,4	597	17	96,8
Mitjana ANY 2015		21.268	646.434	500	15	96,1	916	66	92,2	625	15	97,4
Mitjana ANY 2014		22.323	678.520	432	14	95,3	826	63	91,3	556	14	97,1

Table 8.2. N and P concentrations and efficiencies for Mataró WWTP.

Rendiments (N/P)		N total			P total		
MES	ANY	Entrada <i>mg/l</i>	Sortida <i>mg/l</i>	Rendiment <i>%</i>	Entrada <i>mg/l</i>	Sortida <i>mg/l</i>	Rendiment <i>%</i>
GENER	2019	84,14	72,85	13,4%	4,90	3,83	22,2%
FEBRER	2019	75,14	72,37	3,7%	4,55	3,90	14,3%
MARÇ	2019	79,64	66,93	15,9%	4,55	2,90	36,4%
ABRIL	2019	70,14	66,94	4,4%	5,15	2,90	43,7%
MAIG	2019	78,14	69,52	10,9%	3,85	3,80	3,3%
JUNY	2019	87,64	65,26	25,1%	5,25	5,45	0,0%
JULIOL	2019	75,14	55,57	25,8%	5,57	3,13	37,6%
AGOST	2019	66,64	54,40	18,4%	4,75	2,40	49,2%
SETEMBRE	2019	73,14	65,45	10,6%	4,85	3,95	18,4%
OCTUBRE	2019	50,80	57,10	5,0%	3,25	4,10	0,0%
NOVEMBRE	2019	71,64	72,78	1,8%	4,00	4,90	0,0%
DESEMBRE	2019	78,81	68,02	13,9%	5,10	3,83	24,9%
	<i>mitjana</i>	74,25	65,60	12,4%	4,65	3,76	20,8%
	<i>màxim</i>	87,64	72,85	25,8%	5,57	5,45	49,2%
	<i>mínim</i>	50,80	54,40	1,8%	3,25	2,40	0,0%
Mitjana ANY 2019		74,25	65,60	12,4%	4,65	3,76	20,8%
Mitjana ANY 2018		75,21	63,77	15,6%	4,93	3,49	27,8%
Mitjana ANY 2017		81,26	68,68	15,4%	4,86	3,75	23,1%
Mitjana ANY 2016		72,33	64,41	11,1%	4,96	3,35	33,6%
Mitjana ANY 2015		75,27	63,55	15,7%	5,50	3,78	30,5%
Mitjana ANY 2014		74,14	60,55	18,3%	5,46	3,87	30,0%
Mitjana 2014-2019		75,41	64,43	14,8%	5,06	3,67	27,7%

Table 8.3. Ammonia concentrations in internal streams for Mataró WWTP.

DATA	Amoni lliure mg/l						
	Entrada dec. Primari I.	Aigua entrada integrada	Aigua sortida integrada	Pou buidats vell	Pou buidats nou	Escorregut centrifuga	Retorn de espessidor
6-1-09	74	48	72			1400	124
13-1-09	88	66	65			1379	100
20-1-09	85	61	72			1409	132
26-1-09	10	65	66			781	96
4-2-09	82	25	25			1159	58
10-2-09	86	62	68			1463	93
16-2-09	90	68	78			1410	76
24-2-09	67	54	79			1496	137
Mitjana	73	56	66			1312	102
8-2-10		41	81	124	436	1152	121
16-2-10		56	62	104	293	1124	79
23-2-10		69	63	96	228	1123	106
2-3-10		64	69	104	454	1171	80
8-3-10		44	34	59	252	1118	31
15-3-10		71	77	112	277	1091	117
22-3-10		63	59	67	400	1168	83
29-3-10		58	69	110	271	1168	96
12-4-10		66	72	102	197	735	84
Mitjana		59	65	98	312	1094	89

Table 8.4. Flows and SST, COD, and BOD5 efficiencies for Pineda WWTP.

Cabals i rendiments (C)		CABAL		SST			DQO			DBO5		
mes	any	m3/dia m3	m3/mes m3	ent mg/l	sort mg/l	rend %	ent mg/l	sort mg/l	rend %	ent mg/l	sort mg/l	rend %
GENER	2019	16.949	525.429	342	21	92	756	94	87	519	24	94
FEBRER	2019	17.800	498.395	437	21	95	789	110	85	559	25	95
MARÇ	2019	18.331	568.263	433	21	95	794	98	87	540	21	96
ABRIL	2019	23.765	712.943	343	27	92	729	91	87	498	22	96
MAIG	2019	24.529	760.392	318	27	91	719	99	86	476	23	95
JUNY	2019	26.202	786.051	270	18	93	581	79	86	377	18	95
JULIOL	2019	28.705	889.869	254	23	90	574	85	84	353	19	94
AGOST	2019	27.722	859.396	287	24	92	589	77	87	372	21	94
SETEMBRE	2019	26.246	787.379	259	19	92	548	84	84	325	20	93
OCTUBRE	2019	23.280	721.671	277	21	92	588	98	81	366	20	94
NOVEMBRE	2019	17.971	539.132	281	18	93	564	107	80	334	16	95
DESEMBRE	2019	22.284	690.806	346	13	95	588	103	81	388	10	97
TOTAL			8.339.726									
<i>mitjana</i>		22.815	694.977	320	21	93	652	94	85	426	20	95
<i>màxim</i>		28.705	889.869	437	27	95	794	110	87	559	25	97
<i>mínim</i>		16.949	498.395	254	13	90	548	77	80	325	10	93
Mitjana ANY 2019		22815	694977	320	21	93	652	94	85	426	20	95
Mitjana ANY 2018		22.071	672.184	271	19	92	569	80	85	388	21	94
Mitjana ANY 2017		20.815	633.590	294	20	93	609	79	87	435	20	95
Mitjana ANY 2016		20.630	629.536	289	19	93	603	76	87	425	19	95
Mitjana ANY 2015		20.947	637.671	374	22	93	675	82	86	470	26	94
Mitjana ANY 2014		22.145	673.753	261	26	89	497	86	82	343	29	91
Mitjana ANY 2013		26.490	826.685	316	33	87	608	85	84	385	28	92
Mitjana 2013-2019		22273	681199	304	23	91	602	83	85	410	23	94

Table 8.5. N and P concentrations and efficiencies for Pineda WWTP.

Rendiments (N/P)		N total			P total		
MES	ANY	Entrada	Sortida	Rendiment	Entrada	Sortida	Rendiment
		<i>mg/l</i>	<i>mg/l</i>	<i>%</i>	<i>mg/l</i>	<i>mg/l</i>	<i>%</i>
GENER	2019	85	55	36	6,6	3,7	44
FEBRER	2019	76	69	10	5,8	5,1	12
MARÇ	2019	78	66	15	4,3	8,6	9
ABRIL	2019	71	66	6	5,8	4,9	17
MAIG	2018	84	65	20	5,2	3,3	36
JUNY	2019	49	47	9	3,9	3,3	14
JULIOL	2019	61	58	6	4,9	4,8	4
AGOST	2019	67	59	13	6,2	5,7	8
SETEMBRE	2019	67	62	8	4,8	5,2	0
OCTUBRE	2019	67	55	15	5,1	4,0	22
NOVEMBRE	2019	78	39	50	4,6	1,5	71
DESEMBRE	2019	55	35	31	3,8	1,1	67
	<i>mitjana</i>	70	56	18	5,1	4,2	25
	<i>màxim</i>	85	69	50	6,6	8,6	71
	<i>mínim</i>	49	35	6	3,8	1,1	0
Mitjana ANY 2019		70	56	18	5	4	25
Mitjana ANY 2018		61	52	16	5,0	3,0	42
Mitjana ANY 2017		72	66	11	5,6	3,9	32
Mitjana ANY 2016		71	57	19	5,9	3,5	43
Mitjana ANY 2015		61	47	23	5,7	2,9	49
Mitjana ANY 2014		54	47	14	4,9	3,2	38
Mitjana ANY 2013		56	42	28	5,5	3,5	38
Mitjana 2013-2019		64	52	18	5,39	3,46	38,2

Table 8.6. Ammonia and P concentrations in internal streams for Pineda WWTP.

DATA	Fòsfor Total	Fòsfor Soluble	Nitrogen Amoniacal	Ortofòsats	Magnesi Total	Observacions
	mg P/L	mg P/L	mg/L	µg PO4/L	mg/L	
5-9-16	56,7	43,4	971,0	133370		Escorregut
15-9-16	49,0	29,6	898,0	90750		Escorregut
22-9-16	71,1	41,5	823,0	127300	31,0	Escorregut
22-9-16	>250	321,0	421,0	984450	143,0	Fang Entrada Digestió
22-9-16	>250	281,0	920,0	862900	144,0	Recirculació Digestor A
22-9-16	>250	277,0	1002,0	850025	149,0	Recirculació Digestor B
11-3-18	72,8	33,9	1019	104055	34	Fang Escorregut
13-3-18	>250	302	772	927025	201	Fang Extern
13-3-18	>250	34,5	1203	105845	159	Recirculació Digestor A
13-3-18	>250	41,1	1177	126260	125	Recirculació Digestor B

Table 8.7. Flows and SST, COD, and BOD5 efficiencies for Teià WWTP.

Cabals i rendiments (C)		CABAL TRACTAT		SST			DQO			DBO5		
GENER	2019	14.648	454.095	139	9	92	425	50	88	283	13	95
FEBRER	2019	15.164	424.598	303	6	96	599	43	91	419	8	98
MARÇ	2019	14.537	450.638	343	5	97	626	43	92	426	6	98
ABRIL	2019	14.640	439.198	388	7	97	682	44	92	428	6	98
MAIG	2019	15.619	484.178	483	8	96	789	43	92	542	7	98
JUNY	2019	14.526	435.774	419	8	96	761	45	91	451	8	97
JULIOL	2019	14.705	455.856	634	6	97	985	44	92	608	11	97
AGOST	2019	13.338	413.477	243	5	96	464	40	88	268	9	96
SETEMBRE	2019	15.346	460.387	288	5	97	553	43	90	317	8	97
OCTUBRE	2019	14.492	449.261	308	7	96	610	43	91	358	6	98
NOVEMBRE	2019	14.487	434.619	275	9	94	539	47	90	317	7	98
DESEMBRE	2019	14.584	452.095	502	10	93	810	47	88	509	7	97
<i>TOTAL</i>			5.354.176									
<i>mitjana</i>		14.674	446.181	360	7	96	654	44	90	410	8	97
<i>màxim</i>		15.619	484.178	634	10	97	985	50	92	608	13	98
<i>mínim</i>		13.338	413.477	139	5	92	425	40	88	268	6	95
Mitjana ANY 2019		14674	446181	360	7	96	654	44	90	410	8	97
Mitjana ANY 2018		14.514	441.146	350	9	95	674	45	91	434	9	97
Mitjana ANY 2017		13.031	396.265	532	8	98	926	44	94	587	8	98
Mitjana ANY 2016		12.906	393.441	402	15	96	798	52	93	534	10	98
Mitjana ANY 2015		12.611	383.598	498	19	96	926	57	94	619	14	98
Mitjana ANY 2014		13.721	417.139	459	18	96	833	54	93	539	12	98
Mitjana ANY 2013		14.186	431.252	545	23	96	928	58	94	572	13	98
Mitjana ANY 2012		13.876	423.102	531	20	96	947	58	94	592	11	98
Mitjana ANY 2011		14.208	432.150	387	23	94	739	58	92	466	13	97
Mitjana ANY 2010		14.741	448.425	308	20	93	647	61	90	422	14	97
Mitjana 2010-2019		13847	421270	437	16	96	807	53	93	518	11	98

Table 8.8. N and P concentrations and efficiencies for Mataró WWTP.

Rendiments (N/P)		NTK			P total		
MES	ANY	Entrada <i>mg/l</i>	Sortida <i>mg/l</i>	Rendiment <i>%</i>	Entrada <i>mg/l</i>	Sortida <i>mg/l</i>	Rendiment <i>%</i>
GENER	2019	56	34	39	7,7	3,3	57
FEBRER	2019	53	23	57	7,3	1,3	82
MARÇ	2019	57	28	51	7,5	0,7	91
ABRIL	2019	64	29	55	12,0	2,0	83
MAIG	2019	71	25	65	7,1	1,1	85
JUNY	2019	55	26	53	8,7	1,6	82
JULIOL	2019	88	18	80	11,2	2,5	78
AGOST	2019	47	17	64	7,3	1,5	79
SETEMBRE	2019	55	15	73	5,9	2,0	66
OCTUBRE	2019	29	33		4,9	0,7	87
NOVEMBRE	2019	53	32	40	9,2	1,4	85
DESEMBRE	2019	62	27	56	9,0	0,6	94
	<i>mitjana</i>	58	26	57	8,2	1,6	81
	<i>màxim</i>	88	34	80	12,0	3,3	94
	<i>mínim</i>	29	15	39	4,9	0,6	57
Mitjana ANY 2019		57,5	25,5	57,4	8,2	1,6	80,7
Mitjana ANY 2018		60	22	62	7,5	2,4	67
Mitjana ANY 2017		95	32	59	16,2	2,1	83
Mitjana ANY 2016		73	40	45	11,7	2,8	74
Mitjana ANY 2015		82	38	53	12,2	3,7	83
Mitjana ANY 2014		73	38	49	12,4	1,9	84
Mitjana ANY 2013		77	37	52	11,2	1,5	86
Mitjana ANY 2012		78	31	60	9,9	2,1	78
Mitjana ANY 2011		71	40	43	10,1	2,6	74
Mitjana ANY 2010		62	39	36	7,5	2,0	72
Mitjana 2010-2019		72,8	34,2	51,8	10,7	2,3	78,2

Table 8.9. Ammonia concentrations in internal streams for Teià WWTP.

DATA	NH4+-N mg/l				
	Aigua entrada	Aigua sortida	Sobreeixit espessidor	Escorregut centrifuga	Drenatge integrat
2/12/2008	58	10	136	134	113
9/12/2008	59	30	178	158	134
23/12/2008	64	24	225	329	114
30/12/2008	61	24	165	97	119
6/1/2009	61	25	245	93	105
13/1/2009	51	15	193	78	86
20/1/2009	50	15	56	129	63
27/1/2009	64	10	135	161	97
3/2/2009	24	10	99	91	55
10/2/2009	56	10	99	130	61
17/2/2009	40	24	278	178	84
24/2/2009	55	19	395	125	51
4/3/2009	51	10	37	105	48
10/3/2009	53	10	175	45	60
17/3/2009	55	14	51	45	49
24/3/2009	59	10	99	155	50
2/2/2010	69	60	68	62	70
9/2/2010	15	23	39	94	19
16/2/2010	54	41	63	210	48
23/2/2010	53	51	49	195	58
2/3/2010	57	54	58	65	59
9/3/2010	32	28	22	51	30
16/3/2010	64	57		153	90
23/3/2010	46	42	42	78	47
30/3/2010	55	54	85	109	73
Mitjana	52	27	125	123	71

Table 8.10. Flows and SST, COD, and BOD5 efficiencies for Tordera WWTP.

Cabals i rendiments (C)		CABAL TRACTAT		SST			DQO			DBO5		
MES	ANY	m3/dia m3	m3/mes m3	ent mg/l	sort mg/l	rend %	ent mg/l	sort mg/l	rend %	ent mg/l	sort mg/l	rend %
GENER (*)	2019	2.894	89.700	565	14	97,5	2.990	49	98,4	2.466	12	99,5
FEBRER (*)	2019	2.487	69.625	581	11	98,1	3.206	52	98,4	2.620	12	99,6
MARÇ (*)	2019	2.439	75.603	497	14	97,2	1.818	53	97,1	1.474	10	99,3
ABRIL (*)	2019	2.503	75.092	477	8	97,8	1.725	43	96,3	1.428	7	99,1
MAIG (*)	2019	2.587	80.210	204	7	96,6	449	42	90,7	314	7	97,8
JUNY	2019	2.504	75.110	163	6	96,3	409	40	90,2	257	6	97,7
JULIOL	2019	2.501	77.540	135	11	92,0	361	48	86,6	228	9	96,0
AGOST	2019	2.306	71.473	193	5	97,2	399	41	89,8	243	5	97,8
SETEMBRE	2019	2.525	75.737	233	7	97,2	478	40	91,6	294	5	98,2
OCTUBRE	2019	2.442	75.700	175	6	96,5	391	40	89,8	256	5	98,0
NOVEMBRE	2019	2.420	72.600	279	10	96,2	549	44	92,0	364	7	98,0
DESEMBRE	2019	2.654	82.262	163	12	92,9	319	53	83,5	184	12	93,6
	TOTAL		920.652									
	<i>mitjana</i>	2.522	76.721	305	9	96,3	1.091	45	92,0	844	8	97,9
	<i>màxim</i>	2.894	89.700	581	14	98,1	3.206	53	98,4	2.620	12	99,6
	<i>mínim</i>	2.306	69.625	135	5	92,0	319	40	83,5	184	5	93,6
Mitjana ANY 2019		2522	76721	305	9	96	1091	45	92	844	8	98
Mitjana ANY 2018		3.098	94.159	177	7	96,0	444	41	89,4	325	7	97,5
Mitjana ANY 2017		2.862	86.980	159	7	95,9	325	41	87,1	222	7	97,0
Mitjana ANY 2016		2.518	76.794	175	9	93,9	348	41	86,6	248	7	96,8
Mitjana ANY 2015		2.386	72.574	208	11	92,0	399	45	86,0	290	10	96,0
Mitjana ANY 2014		2.262	68.820	243	13	92,0	448	47	86,0	307	10	97,0
Mitjana ANY 2013		2.262	68.820	243	13	92,0	448	47	86,0	307	10	97,0
Mitjana ANY 2012		2.339	71.115	220	20	87,0	409	51	83,0	279	13	95,0
Mitjana ANY 2011		2.666	81.132	250	14	86,0	335	46	76,0	209	9	93,0
Mitjana ANY 2010		2.568	78.092	129	16	81,0	231	50	71,0	145	11	89,0
Mitjana 2010-2019		2548	77521	211	12	91	448	45	84	318	9	96

Table 8.11. N and P concentrations and efficiencies for Tordera WWTP.

Rendiments (N/P)		N total			P total		
MES	ANY	Entrada	Sortida	Rendiment	Entrada	Sortida	Rendiment
		<i>mg/l</i>	<i>mg/l</i>	<i>%</i>	<i>mg/l</i>	<i>mg/l</i>	<i>%</i>
GENER	2019	92,5	16,0	82,7	14,4	1,0	93,4
FEBRER	2019	105,0	16,7	84,2	24,5	1,2	95,1
MARÇ	2019	85,1	14,8	82,6	12,0	0,7	94,5
ABRIL	2019	76,8	13,4	81,9	11,1	1,1	88,3
MAIG	2019	63,9	13,0	79,1	7,1	1,5	79,1
JUNY	2019	55,9	13,3	75,0	5,4	1,3	76,7
JULIOL	2019	59,6	12,7	78,7	7,2	1,4	80,7
AGOST	2019	53,8	8,9	83,5	5,8	1,4	76,5
SETEMBRE	2019	62,1	11,8	81,0	7,7	0,9	88,1
OCTUBRE	2019	47,1	11,8	74,9	6,1	1,6	73,2
NOVEMBRE	2019	65,0	15,0	76,8	7,7	1,2	84,1
DESEMBRE	2019	50,1	18,0	64,1	7,4	1,1	85,7
	mitjana	68,1	13,8	78,7	9,7	1,2	84,6
	<i>màxim</i>	105,0	18,0	84,2	24,5	1,6	95,1
	<i>mínim</i>	47,1	8,9	64,1	5,4	0,7	73,2
Mitjana ANY 2019		68,1	13,8	78,7	9,7	1,2	84,6
Mitjana ANY 2018		53,3	11,4	78,1	6,8	0,8	88,7
Mitjana ANY 2017		52,5	9,1	82,0	5,8	1,2	78,2
Mitjana ANY 2016		50,6	11,9	76,2	6,5	1,3	76,5
Mitjana ANY 2015		54,7	12,4	77,2	8,6	1,2	84,8
Mitjana ANY 2014		58,8	11,6	74,8	9,4	1,5	79,9
Mitjana ANY 2013		68,6	12,0	82,6	11,5	1,9	81,3
Mitjana ANY 2012		65,6	11,6	81,8	9,6	1,9	77,5
Mitjana ANY 2011		47,3	7,9	82,6	8,1	1,6	74,5
Mitjana ANY 2010		37,4	10,1	72,7	6,0	1,6	66,4
Mitjana 2010-2019		55,7	11,2	78,7	8,2	1,4	79,2