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Evaluation of nutrient recovery from urban wastewater for sustainable fertilizer production

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Evaluation of Nutrient Recovery from Urban Wastewater for Sustainable Fertilizer Production

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All the water that will ever be is, right now.

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Abstract

Climate change and overpopulation have raised significant concerns regarding the security of the food chain. The availability of nutrients is crucial for crop growth and agricultural productivity. In recent years, there has been growing apprehension about the supply of P, upon which Europe heavily relies on external sources. Additionally, the production of reactive nitrogen compounds has had a substantial environmental impact.

This doctoral thesis, titled "Evaluation of Nutrient Recovery from Urban Wastewater for Sustainable Fertilizer Production," focuses on addressing these challenges by developing innovative strategies for the efficient recovery of nutrients from urban wastewater. The research aims to reduce dependence on external P sources and mitigate the environmental impact associated with reactive nitrogen production.

The research aims to develop a technology for the recovery of nitrogen from urban wastewater and its transformation into valuable fertilizers. By reducing the carbon footprint associated with nitrogen production and optimizing P recovery, this study contributes to sustainable water resource management and nutrient cycling.

Through three published articles (Chapter 3-5), this PhD thesis delves into an evaluation of nitrogen flows in Spain, aiming to provide valuable insights and options for enhancing nutrient circularity within the country. Additionally, a novel technology based on ion exchange and liquid-liquid membrane contactors has been implemented and assessed for the recovery and valorization of nitrogen. The evaluation includes a comprehensive analysis of the techno-economic feasibility of the technology, followed by a life cycle assessment of the entire value chain. This encompasses nutrient recovery at wastewater treatment plants (WWTPs) and the subsequent valorization of the recovered nutrients as fertilizers, accompanied by the development of a corresponding business model. The findings from this research shed light on potential pathways for improving nutrient circularity, while considering both the economic viability and environmental sustainability aspects of the value chain.

Contents

List of Figures

List of Tables

List of abbreviations

Abbreviation	Full Form
A_2O	Anaerobic Anoxic Oxic
ACS	American Chemical Society
AD	Anaerobic Digestion
BNF	Biological nitrogen fixation
CAPEX	Capital Expenditure
CAS	Conventional activated sludge
EFA	Elemental Flow Analysis
EU	European Union
GWP	Global Warming Potential
HBNF	Haber-Bosch nitrogen fixation
HRT	Hydraulic Retention time
ISO	International Organization for Standardization
LCA	Life CYCLE ASSESSMENT
LCI	Life Cycle Inventory
LLMC	Liquid-Liquid Membrane Contactor

LNF	Lightning N FIXATION
MKP	Monopotassium Phosphate
NFA	Nitrogen Flow Analysis
NPV	Net Present Value
NS	Nutrient SOLUTION
OPEX	Operating Expenditure
PV	Present Value
SO	Specific OBJECTIVES
T	Plant Lifetime
TEA	Techno-Economic Assessment
TRL	Technology Readiness level
TSS	Total Suspended Solids
WAS	Waste Activated Sludge
WMUs	Water Management Utilities
WWTP	Wastewater Treatment Plant

Chapter 1

1 Chapter 1: Introduction

1.1 Nitrogen flows in Spain

Prior to the 20th century, the nitrogen (N) cycle in natural ecosystems was regulated through biological N fixation (BNF), lightning N fixation (LNF), N deposition, and denitrification [1]. However, the development of the Haber-Bosch nitrogen fixation (HBNF) process has introduced a significant amount of reactive nitrogen (Nr) into terrestrial ecosystems. This increase in Nr has occurred to ensure global food security and meet the demands of approximately 48% of the world's population [2]. Consequently, the N cycles in both terrestrial and marine ecosystems have been heavily disrupted [1]. Furthermore, the inefficient use of fertilizers leads to significant nutrient losses [3]. Approximately 80% of N and 25-75% of phosphorous are lost to the environment through run-off, leaching, and off-gas emissions. These losses contribute to environmental problems such as eutrophication and global warming, while leaving insufficient nutrients in the soil for crop growth [3,4].

Unlike other essential nutrients such as phosphorous (P), N is abundant in the atmosphere as N_2(g). The challenge lies in the fact that the conversion of N_2(g) into reactive forms (Nr) is highly energy-intensive and dependent on fossil fuels [5]. Studies have shown that the Haber-Bosch process, which is used to produce synthetic N fertilizer, accounts for 2.5% of global fossil energy consumption and generates 4-8 tons of CO_2 equivalent per ton of synthesized N fertilizer [6,7].

The impacts of Nr on natural ecosystems (e.g., air, water bodies, and soils), human health, and its correlation with climate change have been extensively reviewed [8]. These studies highlight the cascade of effects caused by Nr; however, more data is needed to quantify the components of this cascade and support effective policy options. Anthropogenic activities, particularly the widespread use of inorganic fertilizers in agriculture, have been identified as the main driving force behind alterations in the natural N cycle [9].

According to the FAOSTAT database on N fertilizers, in 2016, China was leading the market, especially in the production sector [10]. This indicator agrees with the fact that Asia comprises a full 30% of the world's land area with 60% of the world's current population. Other regions such as America and Oceania are more reliant on external sources to meet the internal demand. Africa is an exceptional case. Due to historical, climate and economic reasons, some regions of the continent face scarcity of food and water, which has led to distinct challenges in the agricultural production field [11]. Europe shows particularly high rates of import and export of N fertilizers, although domestic production is sufficient for the agricultural needs of the region [12]. The estimated consumption of mineral N fertilizers in the EU-27 has remained around 10 million tons in the last ten years with fluctuations and a slight upward trend [13]. On the other hand, there is a decreasing trend with a period of stabilization for the gross N balance in agricultural land in EU-28 since 2004 [14]. The countries with the highest N fertilizer consumption are, in order, France and Germany. Following with similar amounts around 1 million tons in 2017 stand Poland, the UK, Turkey and Spain [13].

Spain plays a significant role as an exporter of agricultural products globally, particularly in the European market [15]. However, in the early 1960s, Spain relied mostly on domestic production to meet its food and feed supply needs. By the early 21st century, the country had become a net importer of agricultural products, with the net imports of agricultural products equaling the crop production in terms of N content (650 Gg N y^{-1}) [16]. This demonstrates a heavy dependence on external markets to fulfill the national demand for fertilizers [17]. To address this reliance and reduce the increasing trend of imports, it is essential to identify accumulation points within the N flows and explore options for recovering N based compounds. By recovering N from alternative sources such as wastewater, manure, or food waste, Spain can not only contribute to the circular economy approach on a national level but also reduce external dependency and mitigate the impact of price fluctuations. Additionally, this approach can facilitate N recovery from urban, industrial, and agricultural cycles. Various studies have employed element flow analysis (EFA) to track nutrient flows and manage nutrients at a regional scale [18-21]. Recently, researchers have evaluated nutrient management along the supply chain and introduced a novel method called nutrient footprint, as highlighted by Gronman et al. [22-25]. However, it is worth noting that there is a limited number of studies specifically focused on N, which are listed in Table 1, indicating the need for further research in this area.

Table 1 Summary of the most relevant N Flow Analysis published in the last two decades

Element	Year	Area	Approach	Ref.
N	1998	Huizhou (China)	Urban	[26]
N	2000-2016	Beijing (China)	Urban	[27]

N	2002	Illinois (USA)	Agricultural	[28]
N	2004-2014	France	Agricultural	[29]
N	2015	Scania (Sweden)	Regional	[30]
N	2010	Maeklong river (Thailand)	Regional	[31]
N	2011	Bangkok (Thailand)	Urban	[32]
N	2014	Thailand	Agricultural	[33]
N, P	2004-2007	Finland	National	[34]
N, P	2009	Flanders region (Belgium)	Reginal	[35]
N, P	2014	St. Eustatius (NL)	Agricultural and urban	[36]
P	2012	Spain	National	[37]
N,P,K,Mg	2021	Okanagan (Canada)	Regional	[38]
N,P	2022	Sweden	National	[39]
N	2021	China	Agricultural	[40]
N	2020	Xiamen (China)	Coastal City	[41]
N	2021	Shanghai (China)	Food system	[42]
N	2001	Catalonia (Spain)	Regional	[43]
N	2005	Catalonia (Spain)	Regional	[44]

The utilization of element flow analysis and the introduction of innovative methodologies like the nutrient footprint further enhance our understanding of nutrient flows and enable effective management strategies at a regional scale. However, it is important to recognize the limited number of studies specifically focused on N, underscoring the need for additional research in this area. Further investigations into N mapping and recovery will provide valuable insights and support evidence-based decision-making to optimize nutrient management practices in Spain.

By mapping N flows, embracing nutrient recovery from various sources, and leveraging WWTPs as nutrient hotspots, Spain can take significant strides towards sustainable agriculture, reduce reliance on external markets, and ensure long-term food security while protecting the environment. The following section will review in deeper detail the relevance on nutrient recovery on WWTPs.

1.2 Nutrient Recovery in WWTP

United nations projections estimate that the world's population will reach 8.6 billion in 2030 and 9.8 billion in 2050 [45]. Population and consumption add a huge pressure on food industry to increase its production. To meet this additional demand requires an increase of the intensive agricultural practices, leading to a high land, water, energy, and fertilizers use [46]. Then, a demand growth on plant nutrients is expected. Non-renewable mineral fertilizers, made up of N, P, K and Mg, are the basis of current agricultural system. From an agronomic point of view, crops take up to the 31-49% of the N and 35% of the phosphorus (P) supplied. N is an essential nutrient for all living forms, additionally, it is a key component for fertilizer production, and indeed, it is critical to agriculture uses. A dramatic increase in the production of artificial N fertilizers over the last 50 years lead to an increasing nutrient pollution of water and air [47] . Fertilizer production currently account for about 2-3% of the total global energy consumption being N based-fertilizers responsible for the majority of this consumption [48].

Regarding the wastewater sector, it has been considered a human health concern and environmental hazard for a long time. The actual technologies for wastewater treatment were established in the early 20th century, based on engineering traditions [49]. These technologies were designed to clean the water by removing the organic pollutants and the nutrients, N and phosphorous, but only to meet discharge requirements according to the WW (wastewater) Directive (91/271/EEC) hence the WWTPs (wastewater treatment plants) cannot be considered sustainable.

In recent years there has been a change in mentality in the vision of wastewater treatment plants, which evolves from an end-of-pipe solution to a promising source to recover nutrients for fertilizer purposes. Furthermore, the increasing market value of nutrients due to P scarcity and environmental impact of the production N-based fertilizers [50], are acting as key drivers for resource recovery from WWTP.

Nowadays, resource recovery from waste streams deals with United Nations Sustainable Development Goals 6 and 11 [51]. It is a major goal of interest due to the alarming increase in worldwide pollution levels and raw materials depletion mainly caused by the overuse of fossil fuels and natural resources; hence, current trends are searching for new an alternative source to obtain nutrients: N and P. Although the rationale and necessity to perceive wastewater as a resource has been emphasized, most water management utilities (WMUs) in Europe still focus on wastewater collection and treatment rather than resource recovery. Despite frequent scientific output over a long period on technological solutions to establish a more circular economy-based water sector, the implementation of full-scale resource recovery technologies in the wastewater sector is still very limited [52]. The most common way to recover N and P is thorough anaerobic digestion where the final dried sludge has organic matter, N and P but also heavy metals and pathogens such as viruses and bacteria [53]. The huge amount of sludge generated requires enough greenfield to be applied while causing no harm to the soil that’s why not all the sludge can be used in agriculture which create an inefficient value chain for the nutrients. In Europe, 61% of the sludge goes directly into agriculture, 7.5% goes to landfill, 19.4% goes to incineration and 11.7% is disposed in other way [54].

Since the direct use of sludge is inefficient, A promising way to mitigate the challenges associated to the sustainability of the resource is to produce high-quality Bio-fertilizers by recovering P and N in form of struvite and ammonium salts. Furthermore, latest shift in legal framework coming in forth in 2022 allows P to be recovered from sludge as struvite (phosphate salts). The fertilizer thus obtained can be sold across borders within the EU Single Market.

In terms of application of the struvite as a fertilizer, several studies on struvite agronomic efficiency have been focused on its potential as slow-release fertilizer applied to the soil [55]. Nevertheless, the use of struvite in fertigation as a raw material (liquid fertilizer) for nutrient solution (NS) manufacture has not been studied so far. Hertzberger, et al. [56], developed a review and meta-analysis of the agricultural potential of struvite as a P fertilizer were all the studies tested the struvite as slow-release fertilizer.

These issues have led to a research activity in order to find new technological solutions, focusing on recovery rather than removing nutrients that allow WWTPs to transform from resource consumers to energy recovery facilities and nutrient producers [57].

In conclusion, the projected increase in the world's population, coupled with rising consumption patterns, places tremendous pressure on the food industry to enhance production. To meet this growing demand, intensive agricultural practices relying on land, water, energy, and fertilizers have become prevalent. As a result, there is an expected surge in the demand for plant nutrients, particularly N and P. In this sense, embracing the recovery of nutrients from wastewater not only addresses sustainability challenges but also promotes resource efficiency, circularity, and the transition towards a more sustainable and resilient agricultural system. Future advancements in technology, policy support, and cross-sector collaborations will be crucial in unlocking the full potential of nutrient recovery from wastewater and achieving sustainable resource management in the face of increasing global demands. For this reason, the next section reviews different nutrient recovery technologies focusing on their TRL (Technology Readiness Level) and the different subproducts that can be produced.

1.3 Nutrient recovery technologies

As it has been previously commented, WWTPs have long been seen as a health and environmental concern. Traditional wastewater treatment technologies, established in the early 20th century, were designed to remove organic matter and nutrients like N and P, but are not considered sustainable [57]. For example, regarding N, the main technologies implemented worldwide are biological removal in main line, and in few cases annamox in the sidestream. Both technologies focus on removing N rather than recovering. From the potential recovery in terms of quantity, the major part of the N can be found diluted (around 50 mg N/L without N removal) in the main stream (water line), around 70 -85%. Although it can be recovered there (technically feasible) it is not economic viable due the high flows at low concentrations. This way is economically more feasible to recover N from streams with lower flow and higher concentrations (i.e., side streams; from 600 -1300 mg N-NH_4/L), which more precisely in WWTPs are the anaerobic digestion centrates.

Research activity in recent years has focused on developing technologies able of recovering nutrients from wastewater and valorizing them [58]. These technologies focused on the recovery at the WWTP sidestream, however, some of them could also be applied to other nutrient-rich streams. (i.e., leachates 0.9 -2.6 gN/L [59] or manure (6 -30 kg N /ton) [60])

In general, sidestream (digestate) processing starts with a mechanical separation into a liquid fraction and solid fraction aiming a dewatering [61]. The solid fraction is rich in recalcitrant organic matter, Ca (calcium), Mg, and often P, but offers limited possibilities to recover nutrients, since they are largely organically bound. Soluble N, P, K, organics and mineral salts are present in the liquid fraction. The potential to recover soluble nutrients from the liquid fraction by using extraction techniques is high [62].

The technologies to recover nutrients from WWTPs are summarized in Table 2. Technologies reported in the literature for nutrient recovery from the liquid fraction and currently commercially available or under development are: (1) chemical crystallization [3,63,64], (2) gas stripping and absorption [65-67], (3) acidic air scrubbing [66,68], (4) membrane separation [69-71], (5) ammonia sorption [72-74], and (6) biomass production and harvest [75,76]. [77,78]

Table 2 Main features of the nutrient recovery technologies.

Technology	Main nutrient	Nutrient recovery (%)	Other nutrients	Product	TRL
Crystallization	P	80-90	N,K, Ca, Mg	Struvite	9
Stripping and absorption	N	80-90	-	Amonium sulphate	9
Membrane separation	N	80-85	P	Ammonium salts (N,P,S)	7
Biomass production	N &P	80-98	-	Slow-release fertilizer	7

As it can be seen in table 2, the technologies reviewed are able of achieving high nutrient recovery from reject water. However only a few have reach full scale applications (TRL=9) [77] .

Ammonia stripping and struvite precipitation are the technologies more developed at full scale allowing an average removal and recovery yield of 80-90 % for N and P, respectively [78]. Due to their high degree of development, costs for ammonia stripping and struvite precipitation are relatively low, ranging from 2 to 7 € per kg of nutrient recovered [79]. However, other technologies are rapidly developing and spreading. Pressure-driven membrane technologies (ultrafiltration and reverse osmosis) are emerging as important processes for nutrient recovery, although not selective. N and P removal efficiencies for these technologies are around 75-95 % and 85-99 %, respectively [80,81]. The main drawback of membrane processes is represented by the membrane fouling, which prevents their large diffusion at full scales because of operation challenges. Moreover, the operational cost of this process is higher compared to other available technologies, ranging from 4 to 12 € per m^3 of digestate [82]. Full-scale applications for membrane technologies are available, but still limited, while several studies at laboratory and pilot scale are currently under development [82,83]. Membrane contactors are receiving attention for the possibility to strip ammonia directly in the membrane with high ammonia recovery (over the 95 %). But this technology is currently at the development stage, low TRL, in the EU with several studies at laboratory and pilot scale [84] or even at full scale [85].

Although examples of the application of this technology can be found at full scale, only few works are reported in the scientific literature on nutrients recovery from digestate through membranes technologies. F. Rizzioli et al [77], reported the distribution of the main applications and relative studies on the valorization of digestate by membrane processes in the EU (Figure 1). The color indicates the TRL of the process: Red, Green and Gray stay for high (8-9), medium (5-7) and low (<4) TRL, respectively.

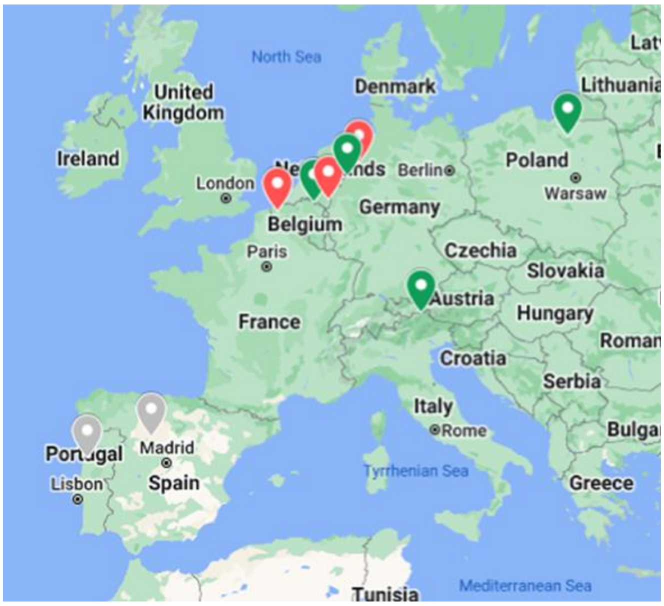

Figure 1 F. Rizzioli et al (2023) examples and TRL of membrane technologies identified in Europe

The environmental factor is equally significant in the development of new technologies, alongside considerations of technical and economic viability. Life Cycle Assessment (LCA) is a comprehensive method to evaluate the potential environmental impacts associated with a product during its entire life cycle. LCA allows assessing the environmental sustainability of wastewater-based resource recovery alternatives and can be combined with other context-specific assessment techniques, such as life cycle costing and risk assessments [86]. This methodology is based on the standardized norm ISO 14040 and 14044 [87,88] and allows evaluating different impact categories, such as global warming potential (GWP), eutrophication, acidification, ozone layer depletion or human toxicity, among others. LCA can be an important screening tool to understand how nutrients recovery implementation can improve the environmental performance when compared with conventional technologies routes for inorganic fertilizers' production.

Some studies have conducted LCAs to evaluate the environmental impacts of recovering nutrients in a WWTP. Amann et al. [89] assessed the environmental impacts of 18 technologies to recover P from different WWTP streams (i.e., liquid streams, sewage sludge and sewage sludge ash) and producing different P-recovered products (i.e., CaP, Struvite, P-rich slag, Phosphoric acid)[89]. Guida et al. [90] conducted an LCA to find the optimum environmental scenarios for ammonium recovery using ion exchange zeolites. Sena et al. [91] evaluated how the implementation of a full-scale struvite crystallizer impacted the overall environmental performance of a WWTP. However, the use of LCA together with other decision-making tools, such as techno-economic assessment (TEA), has been rarely reported in the literature to evaluate nutrient recovery in WWTPs.

In addition, TEA is a methodology based on the calculation of the capital costs, operating costs and revenues associated with a product, technology or process, which allows determining the most important factors influencing its economic feasibility. TEA can be a useful method to understand how the application of novel technologies aimed at recovering valuable resources can influence the economic balance of future WWTPs. Although TEA and LCA are different context-specific assessment techniques, combining them represents a reliable decision-making tool to evaluate different alternatives for nutrient recovery.

Finally, when it comes to the evaluation of these alternatives, it is important to develop a full assessment based on techno economic and environmental aspects. Considering the environmental factors alongside technical and economic aspects is crucial in the development of wastewater-based resource recovery technologies. LCA provides a comprehensive methodology for assessing the environmental sustainability of these alternatives throughout their entire life cycle. It serves as a valuable screening tool to identify opportunities for improving environmental performance alongside with a TEA to evaluate the techno economic feasibility.

1.4 References

1. Luo, Z.; Hu, S.; Chen, D.; Zhu, B. From Production to Consumption: A Coupled Human-Environmental Nitrogen Flow Analysis in China. *Environ Sci Technol* **2018**, *52*, 2025-2035, doi:10.1021/ACS.EST.7B03471.

2. FAO The Future of Food and Agriculture | FAO | Food and Agriculture Organization of the United Nations Available online: http://www.fao.org/publications/fofa/en/ (accessed on 17 August 2021).

3. Sutton, M.A.; Bleeker, A.; de Vries, W.; Bekunda, M.; Reis, S.; Howard, C.M.; Grizzetti, B.; Erisman, J.W.; van Grinsven, H.J.M.; Abrol, Y.P.; et al. Our Nutrient World - The Challenge to Produce More Food and Energy with Less Pollution 2013.

4. Jakrawatana, N.; Ngammuangtueng, P.; Gheewala, S.H. Linking Substance Flow Analysis and Soil and Water Assessment Tool for Nutrient Management. *J Clean Prod* **2017**, *142*, 1158-1168, doi:10.1016/j.jclepro.2016.07.185.

5. Moomaw, W.R. Energy, Industry and Nitrogen: Strategies for Decreasing Reactive Nitrogen Emissions. *Ambio* **2002**, *31*, 184-189.

6. Coppens, J.; Meers, E.; Boon, N.; Buysse, J.; Vlaeminck, S.E. Follow the N and P Road: High-Resolution Nutrient Flow Analysis of the Flanders Region as Precursor for Sustainable Resource Management. *Resour Conserv Recycl* **2016**, *115*, 9-21, doi:10.1016/j.resconrec.2016.08.006.

7. Beckinghausen, A.; Odlare, M.; Thorin, E.; Schwede, S. From Removal to Recovery: An Evaluation of Nitrogen Recovery Techniques from Wastewater. *Appl Energy* **2020**, *263*, 114616, doi:10.1016/j.apenergy.2020.114616.

8. Erisman, J.W.; Galloway, J.N.; Seitzinger, S.; Bleeker, A.; Dise, N.B.; Petrescu, A.M.R.; Leach, A.M.; Vries, W. de Consequences of Human Modification of the Global Nitrogen Cycle. *Philosophical Transactions of the Royal Society B: Biological Sciences* **2013**, *368*, doi:10.1098/RSTB.2013.0116.

9. Vitousek, P.M.; Aber, J.D.; Howarth, R.W.; Likens, G.E.; Matson, P.A.; Schindler, D.W.; Schlesinger, W.H.; Tilman, D.G. Technical Report: Human Alteration of the Global Nitrogen Cycle: Sources and Consequences. *Ecological Applications* **1997**, *7*, 737, doi:10.2307/2269431.

10. Kahrl, F.; Li, Y.; Su, Y.; Tennigkeit, T.; Wilkes, A.; Xu, J. Greenhouse Gas Emissions from Nitrogen Fertilizer Use in China. *Environ Sci Policy* **2010**, *13*, 688-694, doi:10.1016/J.ENVSCI.2010.07.006.

11. Land and Environmental Degradation and Desertification in Africa Available online: http://www.fao.org/3/x5318E/x5318e01.htm (accessed on 17 August 2021).

12. Van Egmond, K.; Bresser, T.; Bouwman, L. The European Nitrogen Case. *Ambio* **2002**, *31*, 72-78, doi:10.1579/0044-7447-31.2.72.

13. Eurostat Available online: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agri-environmental_indicator_-_mineral_fertilizer_consumption (accessed on 18 August 2021).

14. Agri-Environmental Indicator - Gross Nitrogen Balance - Statistics Explained Available online: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agri-environmental_indicator_-_gross_nitrogen_balance (accessed on 18 August 2021).

15. Spanish Agri-Food Exports Increase by 97% in Last Decade Available online: https://www.foodswinesfromspain.com/spanishfoodwine/global/food/news/new-detail/spanish-agri-food-exports-2018.html (accessed on 18 August 2021).

16. Lassaletta, L.; Billen, G.; Romero, E.; Garnier, J.; Aguilera, E. How Changes in Diet and Trade Patterns Have Shaped the N Cycle at the National Scale: Spain (1961-2009). *Regional Environmental Change 2013 14:2* **2013**, *14*, 785-797, doi:10.1007/S10113-013-0536-1.

17. Estadística de Consumo de Fertilizantes En La Agricultura Available online: https://www.mapa.gob.es/es/estadistica/temas/estadisticas-agrarias/agricultura/estadisticas-medios-produccion/fertilizantes.aspx (accessed on 18 August 2021).

18. WangShou, Z.; XuYong, L.; Swaney, D.P.; XinZhong, D. Does Food Demand and Rapid Urbanization Growth Accelerate Regional Nitrogen Inputs? *J Clean Prod* **2016**, *112*, 1401-1409.

19. Cordell, D.; Drangert, J.O.; White, S. The Story of Phosphorus: Global Food Security and Food for Thought. *Global Environmental Change* **2009**, *19*, 292-305, doi:10.1016/J.GLOENVCHA.2008.10.009.

20. Wu, J.; Franzén, D.; Malmström, M.E. Nutrient Flows Following Changes in Source Strengths, Land Use and Climate in an Urban Catchment, Råcksta Träsk in Stockholm, Sweden. *Ecol Modell* **2016**, *338*, 69-77, doi:10.1016/j.ecolmodel.2016.08.001.

21. Baroi, A.R.; Chowdhury, R.B.; Roy, B.B.; Sujauddin, M. Sustainability Assessment of Phosphorus in the Waste Management System of Bangladesh Using Substance Flow Analysis. *J Clean Prod* **2020**, *273*, doi:10.1016/j.jclepro.2020.122865.

22. Grönman, K.; Ypyä, J.; Virtanen, Y.; Kurppa, S.; Soukka, R.; Seuri, P.; Finér, A.; Linnanen, L. Nutrient Footprint as a Tool to Evaluate the Nutrient Balance of a Food Chain. *J Clean Prod* **2016**, *112*, 2429-2440, doi:https://doi.org/10.1016/j.jclepro.2015.09.129.

23. van der Wiel, B.Z.; Weijma, J.; van Middelaar, C.E.; Kleinke, M.; Buisman, C.J.N.; Wichern, F. Restoring Nutrient Circularity: A Review of Nutrient Stock and Flow Analyses of Local Agro-Food-Waste Systems. *Resour Conserv Recycl* **2020**, *160*, doi:10.1016/j.resconrec.2020.104901.

24. Xu, R.; Cai, Y.; Wang, X.; Li, C.; Liu, Q.; Yang, Z. Agricultural Nitrogen Flow in a Reservoir Watershed and Its Implications for Water Pollution Mitigation. *J Clean Prod* **2020**, *267*, doi:10.1016/j.jclepro.2020.122034.

25. Zhang, X.; Zhang, Y.; Wang, Y.; Fath, B.D. Research Progress and Hotspot Analysis for Reactive Nitrogen Flows in Macroscopic Systems Based on a CiteSpace Analysis. *Ecol Modell* **2021**, *443*, doi:10.1016/j.ecolmodel.2021.109456.

26. Ma, X.; Wang, Z.; Yin, Z.; Koenig, A. Nitrogen Flow Analysis in Huizhou, South China. *Environmental Management 2007 41:3* **2007**, *41*, 378-388, doi:10.1007/S00267-007-9053-7.

27. Pan, J.; Ding, N.; Yang, J. Science of the Total Environment Changes of Urban Nitrogen Metabolism in the Beijing Megacity Of. *Science of the Total Environment* **2019**, *666*, 1048-1057, doi:10.1016/j.scitotenv.2019.02.315.

28. Singh, S.; Compton, J.E.; Hawkins, T.R.; Sobota, D.J.; Cooter, E.J. A Nitrogen Physical Input-Output Table (PIOT) Model for Illinois. *Ecol Modell* **2017**, *360*, 194-203, doi:10.1016/J.ECOLMODEL.2017.06.015.

29. Billen, G.; le Noë, J.; Garnier, J. Two Contrasted Future Scenarios for the French Agro-Food System. *Science of The Total Environment* **2018**, *637-638*, 695-705, doi:10.1016/J.SCITOTENV.2018.05.043.

30. Nitrogen Flow in Scania - Epsilon Archive for Student Projects Available online: https://stud.epsilon.slu.se/8129/ (accessed on 9 February 2022).

31. Pharino, C.; Sailamai, N.; Kamphaengthong, P.L. Material Flow Analysis of Nitrogen in Maeklong River Basin in Ratchaburi and Samut Songkhram Province, Thailand. *Water Conservation Science and Engineering* **2016**, *1*, 167-175, doi:10.1007/S41101-016-0011-1.

32. Buathong, T.; Boontanon, S.K.; Boontanon, N.; Surinkul, N.; Harada, H.; Fujii, S. Nitrogen Flow Analysis in Bangkok City, Thailand: Area Zoning and Questionnaire Investigation Approach☆. *undefined* **2013**, *17*, 586-595, doi:10.1016/J.PROENV.2013.02.074.

33. Suesatpanit, T. Substance Flow Analysis of Nitrogen in Food Production and Consumption System of Thailand. *undefined* **2017**.

34. Antikainen, R.; Haapanen, R.; Lemola, R.; Nousiainen, J.I.; Rekolainen, S. Nitrogen and Phosphorus Flows in the Finnish Agricultural and Forest Sectors, 1910-2000. *Water Air Soil Pollut* **2008**, *194*, 163-177, doi:10.1007/S11270-008-9705-0.

35. Coppens, J.; Meers, E.; Boon, N.; Buysse, J.; Vlaeminck, S.E. Follow the N and P Road: High-Resolution Nutrient Flow Analysis of the Flanders Region as Precursor for Sustainable Resource Management. *Resour Conserv Recycl* **2016**, *115*, 9-21, doi:10.1016/J.RESCONREC.2016.08.006.

36. Firmansyah, I.; Spiller, M.; de Ruijter, F.J.; Carsjens, G.J.; Zeeman, G. Assessment of Nitrogen and Phosphorus Flows in Agricultural and Urban Systems in a Small Island under Limited Data Availability. *undefined* **2017**, *574*, 1521-1532, doi:10.1016/J.SCITOTENV.2016.08.159.

37. Álvarez, J.; Roca, M.; Valderrama, C.; Cortina, J.L. A Phosphorous Flow Analysis in Spain. *Science of The Total Environment* **2018**, *612*, 995-1006, doi:10.1016/J.SCITOTENV.2017.08.299.

38. Harder, R.; Giampietro, M.; Mullinix, K.; Smukler, S. Assessing the Circularity of Nutrient Flows Related to the Food System in the Okanagan Bioregion, BC Canada. *Resour Conserv Recycl* **2021**, *174*, doi:10.1016/j.resconrec.2021.105842.

39. Sinha, R.; Thomas, J.B.E.; Strand; Söderqvist, T.; Stadmark, J.; Franzen, F.; Ingmansson, I.; Gröndahl, F.; Hasselström, L. Quantifying Nutrient Recovery by Element Flow Analysis: Harvest and Use of Seven Marine Biomasses to Close N and P Loops. *Resour Conserv Recycl* **2022**, *178*, doi:10.1016/j.resconrec.2021.106031.

40. Jin, X.; Zhang, N.; Zhao, Z.; Bai, Z.; Ma, L. Nitrogen Budgets of Contrasting Crop-Livestock Systems in China. *Environmental Pollution* **2021**, *288*, doi:10.1016/j.envpol.2021.117633.

41. Li, Y.; Cui, S.; Gao, B.; Tang, J.; Huang, W.; Huang, Y. Modeling Nitrogen Flow in a Coastal City–A Case Study of Xiamen in 2015. *Science of the Total Environment* **2020**, *735*, doi:10.1016/j.scitotenv.2020.139294.

42. Liao, C.; Xia, Y.; Wu, D. Nitrogen Flows Associated with Food Production and Consumption System of Shanghai. *Environmental Pollution* **2021**, *279*, doi:10.1016/j.envpol.2021.116906.

43. Bartrolí, J.; Martin, M.J.; Rigola, M. Issues in System Boundary Definition for Substance Flow Analysis: The Case of Nitrogen Cycle Management in Catalonia. *ScientificWorldJournal* 2001, *1 Suppl 2*, 892-897.

44. Bartrolí, J.; Martin, M.J.; Rigola, M. *The Nitrogen Balance for Catalan Agriculture Soils and Livestock Sectors*; 2005; Vol. 4;.

45. World Population Prospects: The 2017 Revision Available online: https://www.un.org/development/desa/publications/world-population-prospects-the-2017-revision.html.

46. Godfray, H.C.J.; Beddington, J.R.; Crute, I.R.; Haddad, L.; Lawrence, D.; Muir, J.F.; Pretty, J.; Robinson, S.; Thomas, S.M.; Toulmin, C. Food Security: The Challenge of Feeding 9 Billion People. *Science (1979)* 2010, *327*, 812-818.

47. Chapter 14: Effects of Airborne Nitrogen Pollutants on Vegetation: Critical Loads.

48. Basosi, R.; Fierro, A.; Jez, S. *Mineral Nitrogen Fertilizers: Environmental Impact of Production and Use*; 2014;

49. Puchongkawarin, C.; Gomez-Mont, C.; Stuckey, D.C.; Chachuat, B. Optimization-Based Methodology for the Development of Wastewater Facilities for Energy and Nutrient Recovery. *Chemosphere* **2015**, *140*, 150-158, doi:10.1016/j.chemosphere.2014.08.061.

50. Basosi, R.; Spinelli, D.; Fierro, A.; Jez, S. Mineral Nitrogen Fertilizers: Environmental Impact of Production and Use. *Fertilizers: Components, Uses in Agriculture and Environmental Impacts* **2014**, 3-43.

51. THE 17 GOALS | Sustainable Development Available online: https://sdgs.un.org/goals (accessed on 31 October 2022).

52. Stanchev, P.; Vasilaki, V.; Dosta, J.; Katsou, E. Measuring The Circular Economy Of Water Sector In The Three-Fold Linkage Of Water, Energy And Materials.

53. Sewage Sludge Available online: https://environment.ec.europa.eu/topics/waste-and-recycling/sewage-sludge_en (accessed on 28 November 2022).

54. European Union Available online: https://water.europa.eu/freshwater/countries/uwwt/european-union (accessed on 28 November 2022).

55. Ryu, H.D.; Lim, C.S.; Kim, Y.K.; Kim, K.Y.; Lee, S.I. Recovery of Struvite Obtained from Semiconductor Wastewater and Reuse as a Slow-Release Fertilizer. *Environ. Eng. Sci.* **2012**,

29, 540-548, doi:10.1089/ees.2011.0207.

56. Hertzberger, A.J.; Cusick, R.D.; Margenot, A.J. A Review and Meta-Analysis of the Agricultural Potential of Struvite as a Phosphorus Fertilizer. *Soil Science Society of America Journal* **2020**, *84*, 653-671, doi:10.1002/SAJ2.20065.

57. Mo, W.; Zhang, Q. Can Municipal Wastewater Treatment Systems Be Carbon Neutral? *J Environ Manage* **2012**, *112*, 360-367, doi:10.1016/j.jenvman.2012.08.014.

58. Vaneeckhaute, C.; Lebuf, V.; Michels, E.; Belia, E.; Vanrolleghem, P.A.; Tack, F.M.G.; Meers, E. Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification. *Waste Biomass Valorization* 2017, *8*, 21-40.

59. Mukherjee, S.; Mukhopadhyay, S.; Hashim, M.A.; Gupta, B. sen Contemporary Environmental Issues of Landfill Leachate: Assessment and Remedies. *Crit Rev Environ Sci Technol* **2015**, *45*, 472-590, doi:10.1080/10643389.2013.876524.

60. Https://Lpelc.Org Available online: https://lpelc.org/category/manure-nutrients/ (accessed on 1 December 2022).

61. Hjorth, M.; Christensen, K. v.; Christensen, M.L.; Sommer, S.G. Solid-Liquid Separation of Animal Slurry in Theory and Practice. A Review. *Agron. Sustain. Dev.* **2010**, *30*, 153-180, doi:10.1051/agro/2009010.

62. Vaneeckhaute, C.; Meers, E.; Michels, E.; Christiaens, P.; Tack, F.M.G. Fate of Macronutrients in Water Treatment of Digestate Using Vibrating Reversed Osmosis. *Water Air Soil Poll.* **2012**, *223*, 1593-1603, doi:10.1007/s11270-011-0967-6.

63. le Corre, K.S.; Valsami-Jones, E.; Hobbs, P.; Parsons, S.A. Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Crit. Rev. Env. Sci. Tec.* **2009**, *39*, 433-477, doi:10.1080/10643380701640573.

64. Uludag-Demirer, S.; Demirer, G.N.; Chen, S. Ammonia Removal from Anaerobically Digested Dairy Manure by Struvite Precipitation. *Process Biochem.* **2005**, *40*, 3667-3674, doi:10.1016/j.procbio.2005.02.028.

65. Bonmatí, A.; Flotats, X. Air Stripping of Ammonia from Pig Slurry: Characterisation and Feasibility as a Pre- or Post-Treatment to Mesophilic Anaerobic Digestion. *Waste Manage.* **2003**, *23*, 261-272, doi:10.1016/s0956-053x(02)00144-7.

66. Guštin, S.; Marinšek-Logar, R. Effect of PH, Temperature and Air Flow Rate on the Continuous Ammonia Stripping of the Anaerobic Digestion Effluent. *Process Saf. Environ.* **2011**, *89*, 61-66, doi:10.1016/j.psep.2010.11.001.

67. Liao, P.H.; Chen, A.; Lo, K. v. Removal of Nitrogen from Swine Manure Wastewaters by Ammonia Stripping. *Bioresour. Technol.* **1995**, *54*, 17-20, doi:10.1016/0960-8524(95)00105-0.

68. Melse, R.W.; Ogink, N.W.M. Air Scrubbing Techniques for Ammonia and Odor Reduction at Livestock Operations: Review of on-Farm Research in the Netherlands. *Trans. ASAE* **2005**, *48*, 2303-2313, doi:10.13031/2013.20094.

69. Kertész, S.; Beszédes, S.; László, Z.; Szabó, G.; Hodúr, C. Nanofiltration and Reverse Osmosis of Pig Manure: Comparison of Results from Vibratory and Classical Modules. *Desalination Water Treat.* **2010**, *14*, 233-238, doi:10.5004/dwt.2010.1076.

70. Ledda, C.; Schievano, A.; Salati, S.; Adani, F. Nitrogen and Water Recovery from Animal Slurries by a New Integrated Ultrafiltration, Reverse Osmosis and Cold Stripping Process: A Case Study. *Water Res.* **2013**, *47*, 6157-6166, doi:10.1016/j.watres.2013.07.037.

71. Waeger, F.; Delhaye, T.; Fuchs, W. The Use of Ceramic Microfiltration and Ultrafiltration Membranes for Particle Removal from Anaerobic Digester Effluents. *Sep. Purif. Technol.* **2010**, *73*, 271-278, doi:10.1016/j.seppur.2010.04.013.

72. Guo, X.; Zeng, L.; Jin, X. Advanced Regeneration and Fixed-Bed Study of Ammonium and Potassium Removal from Anaerobic Digested Wastewater by Natural Zeolite. *J. Environ. Sci.* **2013**, *25*, 954-961, doi:10.1016/s1001-0742(12)60115-6.

73. Nutrient Recovery from Biogas Digestate by Adsorption and Ion-Exchange Using Clinoptilolite | Request PDF Available online: https://www.researchgate.net/publication/258207254_Nutrient_recovery_from_biogas_diges

tate_by_adsorption_and_ion-exchange_using_clinoptilolite (accessed on 6 November 2022).

74. A Review of Enhancement Techniques, Processing Options Andnovel Digestate Products; Report OMK006–002; Waste AndResources Action Plan (WRAP): United Kingdom, 2012 - Buscar Con Google Available online: https://www.google.com/search?q=A+review+of+enhancement+techniques%2C+processing+options+andnovel+digestate+products%3B+Report+OMK006%E2%80%94002%3B+Waste+andResources+Action+Plan+(WRAP)%3A+United+Kingdom%2C+2012&rlz=1C1ONGR_esES950ES950&oq=A+review+of+enhancement+techniques%2C+processing+options+andnovel+digestate+products%3B+Report+OMK006%E2%80%94002%3B+Waste+andResources+Action+Plan+(WRAP)%3A+United+Kingdom%2C+2012&aqs=chrome..69i57j69i64.823j0j7&sourceid=chrome&ie=UTF-8 (accessed on 6 November 2022).

75. González-Fernández, C.; Molinuevo-Salces, B.; García-González, M.C. Nitrogen Transformations under Different Conditions in Open Ponds by Means of Microalgae-Bacteria Consortium Treating Pig Slurry. *Bioresour. Technol.* **2011**, *102*, 960-966, doi:10.1016/j.biortech.2010.09.052.

76. Xu, J.; Shen, G. Growing Duckweed in Swine Wastewater for Nutrient Recovery and Biomass Production. *Bioresour. Technol.* **2011**, *102*, 848-853, doi:10.1016/j.biortech.2010.09.003.

77. Rizzioli, F.; Bertasini, D.; Bolzonella, D.; Frison, N.; Battista, F. A Critical Review on the Techno-Economic Feasibility of Nutrients Recovery from Anaerobic Digestate in the Agricultural Sector. *Sep Purif Technol* **2023**, *306*, 122690, doi:10.1016/j.seppur.2022.122690.

78. Ozturk, I.; Altinbas, M.; Koyuncu, I.; Arikan, O.; Gomec-Yangin, C. Advanced Physico-Chemical Treatment Experiences on Young Municipal Landfill Leachates. *Waste Management* **2003**, *23*, 441-446, doi:10.1016/S0956-053X(03)00061-8.

79. Brienza, C.; Sigurnjak, I.; Meier, T.; Michels, E.; Adani, F.; Schoumans, O.; Vaneeckhaute, C.; Meers, E. Techno-Economic Assessment at Full Scale of a Biogas Refinery Plant Receiving Nitrogen Rich Feedstock and Producing Renewable Energy and Biobased Fertilizers. *J Clean Prod* **2021**, *308*, 127408, doi:10.1016/J.JCLEPRO.2021.127408.

80. Zielińska, M.; Mikucka, W. Membrane Filtration for Valorization of Digestate from the Anaerobitreatment of Distillery Stillage. *Desalination Water Treat* **2021**, *215*, 60-68, doi:10.5004/DWT.2021.26772.

81. Pinelli, D.; Bovina, S.; Rubertelli, G.; Martinelli, A.; Guida, S.; Soares, A.; Frascari, D. Regeneration and Modelling of a Phosphorous Removal and Recovery Hybrid Ion Exchange Resin after Long Term Operation with Municipal Wastewater. *Chemosphere* **2022**, *286*, 131581, doi:10.1016/J.CHEMOSPHERE.2021.131581.

82. Fangueiro, D.; Snauwaert, E.; Provolo, G.; Hidalgo, D.; Adani, F.; Kabbe, C.; Bonmati, A.; Brandsma, J. Available Technologies for Nutrients Recovery from Animal Manure and Digestates.

83. Pinelli, D.; Bovina, S.; Rubertelli, G.; Martinelli, A.; Guida, S.; Soares, A.; Frascari, D. Regeneration and Modelling of a Phosphorous Removal and Recovery Hybrid Ion Exchange Resin after Long Term Operation with Municipal Wastewater. *Chemosphere* **2022**, *286*, 131581, doi:10.1016/J.CHEMOSPHERE.2021.131581.

84. Norddahl, B.; Horn, V.G.; Larsson, M.; du Preez, J.H.; Christensen, K. A Membrane Contactor for Ammonia Stripping, Pilot Scale Experience and Modeling. *Desalination* **2006**, *199*, 172-174, doi:10.1016/J.DESAL.2006.03.037.

85. Chiumenti, A.; da Borso, F.; Teri, F.; Chiumenti, R.; Piaia, B. Full-Scale Membrane Filtration System for the Treatment of Digestate from a Co-Digestion Plant. *Appl Eng Agric* **2013**, *29*, 985-990, doi:10.13031/AEA.29.10117.

86. Corominas, L.; Larsen, H.F.; Flores-Alsina, X.; Vanrolleghem, P.A. Including Life Cycle Assessment for Decision-Making in Controlling Wastewater Nutrient Removal Systems. *J Environ Manage* **2013**, *128*, 759-767, doi:10.1016/j.jenvman.2013.06.002.

87. UNE-EN ISO 14044:2006 Gestión Ambiental. Análisis Del Ciclo De... Available online: https://www.une.org/encuentra-tu-norma/busca-tu-norma/norma?c=N0038059 (accessed on 18 July 2023).

88. UNE-EN ISO 14040:2006 Gestión Ambiental. Análisis Del Ciclo De... Available online:

https://www.une.org/encuentra-tu-norma/busca-tu-norma/norma?c=N0038060 (accessed on 18 July 2023).

89. Amann, A.; Zoboli, O.; Krampe, J.; Rechberger, H.; Zessner, M.; Egle, L. Environmental Impacts of Phosphorus Recovery from Municipal Wastewater. *Resour Conserv Recycl* **2018**, *130*, 127-139, doi:10.1016/j.resconrec.2017.11.002.

90. Guida, S.; Conzelmann, L.; Remy, C.; Vale, P.; Jefferson, B.; Soares, A. Resilience and Life Cycle Assessment of Ion Exchange Process for Ammonium Removal from Municipal Wastewater. *Science of the Total Environment* **2021**, *783*, doi:10.1016/j.scitotenv.2021.146834.

91. Sena, M.; Hicks, A. Life Cycle Assessment Review of Struvite Precipitation in Wastewater Treatment. *Resour Conserv Recycl* **2018**, *139*, 194-204, doi:10.1016/j.resconrec.2018.08.009.

92. Https://Phosphorusplatform.Eu/ Available online: https://phosphorusplatform.eu/scope-in-print/news/359-phosphate-rock-in-eu-critical-raw-materials-list (accessed on 7 December 2022).

93. Mayor, A.; Vecino, X.; Reig, M.; de Arespacochaga, N.; Valderrama, C.; Cortina, J.L. Ammonium Valorization from Urban Wastewater as Liquid Fertilizers by Using Liquid-Liquid Membrane Contactors. *Hollow Fiber Membrane Contactors* **2020**, 225-240, doi:10.1201/9780429398889-20.

94. Licon Bernal, E.E.; Maya, C.; Valderrama, C.; Cortina, J.L. Valorization of Ammonia Concentrates from Treated Urban Wastewater Using Liquid-Liquid Membrane Contactors. *Chemical Engineering Journal* **2016**, *302*, 641-649, doi:10.1016/J.CEJ.2016.05.094.

Chapter 2

2 Chapter 2: Objectives and methodology

2.1 General objective and thesis scope

The general objective of this PhD thesis is to evaluate and compare from a technical and economic point of view a nutrient recovery treatment train based on ion exchange and liquid-liquid membrane contactors applied to municipal wastewater stream to produce cost-effective fertilizers.

There are several specific objectives (SO) to accomplish to achieve the general objective.

SO1 - Critical revision of the state-of-the-art technologies for nutrient recovery technologies in urban wastewater treatment.

SO2 - Assess the mass flows of N in the Spanish country to identify potential spots for recovery and how to improve circularity of nutrients.

SO3 - Experimental evaluation of an innovative system prototype (pilot-scale) integrating Ion exchange and liquid-liquid membrane contactors; and techno-economic comparison with a full-scale conventional treatment scheme configuration (CAS).

SO4 - Operation of the treatment train and achieve recovery rates up to 42% of P (>50% as struvite) up to 11% N from wastewater influent.

SO5 - Achieve 80% reduction of CO_2 eq emissions associated to energy consumption in conventional N-fertilizers production by partial substitution with recovered fertilizers.

SO6 - Use LCA and LCC tools to assess the whole value chain, from the nutrient recovery till its valorization in field.

2.2 PhD thesis organization

In this PhD thesis, novel techniques involving Ion Exchange with zeolites (IX) and Liquid-Liquid Membrane Contactors (LLMC) have been used for the effective utilization of N in fertilization applications. The initial phase of the thesis aimed to comprehensively analyze the N flows within Spanish territory, with a particular emphasis on identifying the main N flows and their potential for recovery (**Publication 1, chapter3**). Based on the findings of the initial publication, it is evident that WWTPs play a crucial role as significant hubs for nutrient recovery. Subsequently, the focus of the thesis shifted towards studying alternatives to recover and valorize nutrients from WWTPs and its valorization as fertilizers by taking into account the whole value chain. (**Publication 2, chapter4**), which is predominantly discharged into water bodies as NH_4^+ and released into the atmosphere as N_2(g), along with a minor fraction as NO_x(g), consequently impacting the environment. In this specific section, the thesis concentrated on a hybrid system that combines zeolites stage and a LLMC for efficient recovery of NH_3 from treated urban wastewater. Prior to LLMC, ion exchange with zeolites was chosen as an advanced pre-treatment and concentration step. The system was tested using the effluent from Vilanova I la Geltrú (VNG) WWTP (mainstream, with 50 mg N-NH_4/L) and anaerobic digestion concentrates (sidestream, ranging from 600-800 mg N-NH_4/L) from Murcia ESTE WWTP. Natural zeolite, primarily clinoptilolite, exhibited remarkable effectiveness in desorbing retained ammonium by utilizing a 2% NaOH solution within a closed-loop configuration. This process resulted in an ammonia-rich brine, enabling the recovery of over 95% NH_3 using polypropylene LLMC. A demonstration plant with a capacity of 1 m^3/h effectively processed both urban wastewaters, which were previously treated via ultrafiltration to eliminate over 90% of suspended solids and 60-65% of COD. The 2% NaOH regeneration brines (with concentrations ranging from 2.4-5.6 g N-NH_4/L) were treated in a closed-loop LLMC pilot system, resulting in the production of 10-15% N streams suitable for utilization as liquid fertilizers. The final section of the thesis (**Publication 3, chapter 5**) encompassed conducting a comprehensive LCA and TEA of the proposed treatment train. The nutrient recovery scheme was implemented within the sludge line of the WWTP and involved struvite crystallization for P recovery and an ion-exchange process combined with a gas-permeable membrane contactor for N recovery. Subsequently, the recovered fertilizers were utilized in agriculture, and their performance was compared to that of a commercial fertilizer solution.

2.3 Methodology

2.3.1 Nitrogen Flow Analysis in Spain

EFA is a widely employed methodology for assessing resource flows, including energy, water, and minerals, at various geographical scales, spanning from global to local.

In this Thesis, the Nitrogen Flow Analysis (NFA) was specifically developed for the Spanish territory, which comprises 16 autonomous communities. It should be noted that the NFA excludes three other communities, namely the Balearic and Canary Islands, as well as the cities of Ceuta and Melilla located on the African continent. The analysis focuses on quantifying the flows of N in various forms and divides the NFA into several subsystems. The agricultural and food production systems receive primary attention since the consumption of N in the form of fertilizers accounts for 43% of the total N imported within the national boundaries. Additionally, the analysis takes into account other industrial uses of N, such as its presence in fertilizers and chemicals. Flows related to the recovery of N from wastewaters and the application of urban and farming bio-solids to agriculture are also considered in the analysis.

The time period chosen for the analysis is the year 2016, as it represents the most recent year for which accurate information regarding the majority of flows is available. During this year, detailed data on N flows and their various forms were gathered and used as the basis for the analysis.

The model utilized in the NFA was developed using Stan 2.6, a software developed by the Technische Universität Wien. Stan allows for the creation of graphical models with predefined components, including processes, flows, system boundaries, and text fields. It also provides the necessary tools for conducting EFA, such as mathematical-statistical techniques like data reconciliation and error propagation. By leveraging these capabilities, the NFA model ensures a robust and rigorous analysis of the N flows within the Spanish territory, enabling a comprehensive understanding of the N dynamics and its implications for resource management and environmental sustainability.

The final system (Figure 2) comprises 29 flows and 7 subsystems, five of which have stocks. Regarding subsystems, the following were considered for calculations: agriculture, air, households, industry, transport, waste management and water bodies. The subsystems with stocks, that is, internal accumulation of N, are agriculture, air, industry, waste management and water bodies.

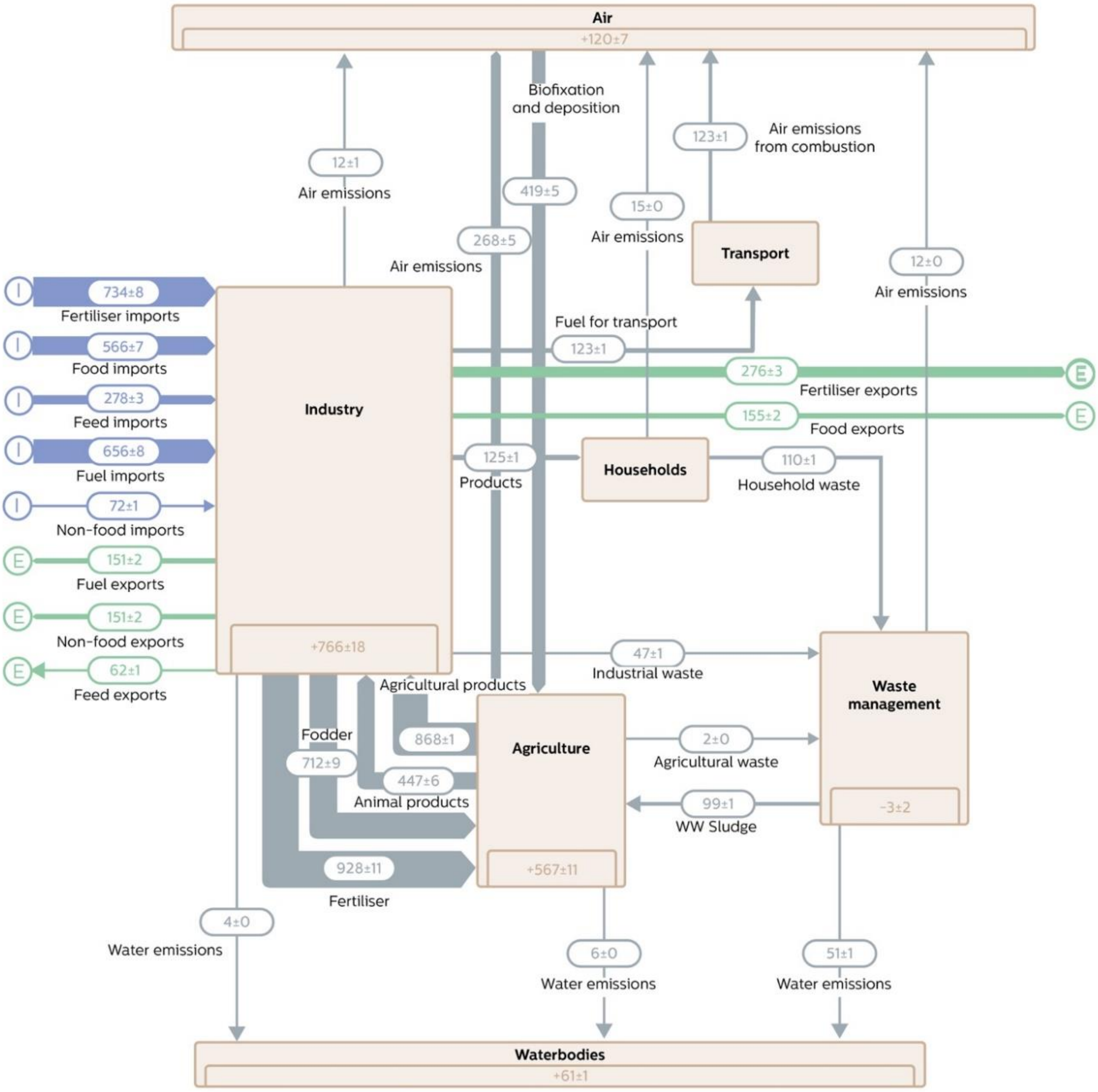

Figure 2 N flows in Spain (2016)

2.3.2 Research platform for nutrients recovery provided by the LIFE ENRICH project

The overall objective of LIFE ENRICH project (LIFE Programme) [46] was to implement the circular economy concept through the demonstration of the whole value chain for nutrient recovery in urban wastewater treatment plants and its further valorization as fertilizing products.

The project aimed to redesign the conventional nutrient value chain, where the N fertilizers are produced via Habber Bosch process, which is energy intensive and P fertilizers are produced from Phosphatic rock, which is a non-renewable source and the EU has declared as critical raw material

[92]. One of the innovative aspects of the project is the integration of different technologies for N and P recovery in a single site.

The N recovery treatment train was based on ion exchange with zeolites as a concentration step previous to a liquid-liquid membrane contactor which allows to produce ammonium salts from anaerobic digestion reject water. The P recovery was based on an elutriation to up concentrate the phosphates previous to the anaerobic digestion to be later recovered as struvite in a crystallization unit.

Murcia Este WWTP (Murcia, Spain) was the experimental site selected to demonstrate this integrated N&P recovery process (Figure 3). First, a large-scale elutriation process was implemented in order to extract and concentrate phosphates before they enter anaerobic digestion. P recovery was tested at pilot scale producing struvite. N recovery was assessed in centrates stream at pilot scale producing ammonium nitrate.

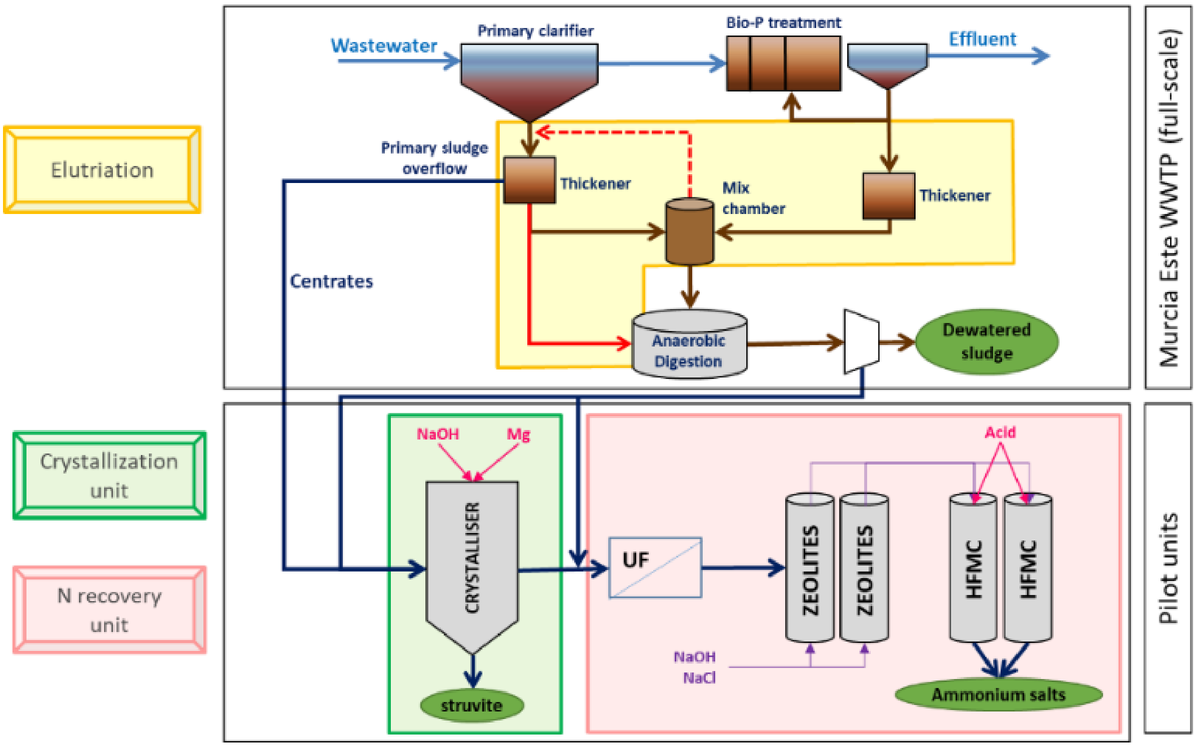

Figure 3 Murcia Este WWTP process configuration

2.3.3 Nutrient recovery in WWTP process streams

The experimental phase comprised two stages: an initial laboratory-scale step to optimize ion exchange, followed by a pilot-scale implementation of the complete treatment train.

For the lab-scale experiments, wastewater samples were obtained from the effluent of the VNG-WWTP, specifically collected from the secondary clarifier. In contrast, the sidestream utilized for the pilot-scale experiments was collected from the Murcia ESTE WWTP. Prior to experimentation, the sidestream was thoroughly characterized in terms of pH, conductivity, total suspended solids (TSS), and dissolved ions.

Natural clinoptilolite zeolites, sourced from ZEOCEM (www.zeocem.com), were employed in the with two different granulometries (from 0.5-1.0 mm to 1.0-2.5 mm). Before commencing the experiments, the zeolites were activated with NaOH 1M.

2.3.3.1 Experimental evaluation of zeolites on ammonium recovery at Lab-scale

The lab-scale experimental setup consisted of two fixed-bed columns, each with dimensions of 18.7 cm in height and 22.6 mm in internal diameter. The columns were then filled with 67 grams of zeolite.

These trials focused on the optimization of operating flows and the regenerating solution with mainstream from VNG effluent (50 mg/L $N\text{-}NH_4$).

Table 3 provides a summary of the experimental conditions used along the operation of the experimental campaign.

Table 3 Sorption - desorption flows used along the experimental campaign

Experiment	Sorption flow (BV/h)	Regeneration flow (BV/h)
4-2	4.1 ± 0.3	2.0 ± 0.2
4-0.8	3.9 ± 0.1	0.8 ± 0.1
10-5	10.1 ± 0.1	5.1 ± 0.3
10-2	9.9 ± 0.1	± 0.2

After that, to investigate the regeneration process, 11 different regenerant solutions were tested. The regenerant solutions consisted of various concentrations of NaOH (0.05, 0.1, and 0.5 mol/L), NaCl (1, 5, 10, and 20 g/L), or a combination of both substances (0.01 mol NaOH/L and 1 g NaCl/L; 0.01 mol

NaOH/L and 20 g NaCl/L; 0.1 mol NaOH/L and 1 g NaCl/L; 0.1 mol NaOH/L and 20 g NaCl/L).

2.3.3.2 Experimental evaluation of zeolites on ammonium recovery at pilot -scale

Based on the results obtained at the lab scale, a pilot plant with a nominal capacity of 1 m^3/h was designed, constructed, and installed at the VNG WWTP. The pilot plant operated for one year at VNG WWTP and was subsequently relocated to the Murcia ESTE WWTP, where it operated for another year. The feed water for the pilot plant consisted of VNG WWTP effluent as the mainstream water source and Murcia Este Centrates as the sidestream water source

The zeolite pilot plant operated continuously for an entire year, testing different streams. The objective was to assess the performance of zeolites in ammonium recovery from both mainstream and sidestream processes of WWTPs. The comparison was based on the adsorption efficiency and capacity of the zeolites under different operating conditions.

A total of four adsorption experiments were conducted for the mainstream process, along with Table 4 provides the details of the experimental design for the zeolites.

Table 4 Zeolites experimental design

	Mainstream	Sidestream
Adsorption - desorption cycles	4	4
Granulometry (mm)	1.0-2.5	0.5-1.0
Adsorption flow (L/h)	400	400
Regeneration flow (L/h)	700	700
Regenerant concentration (NaOH) (M)	0.5	0.2

2.3.3.3 Experimental evaluation of LLMCs on ammonium recovery at pilot -scale

The ammonia recovery system utilizing a LLMC operates in a closed-loop configuration and it is feed with the N rich solution generated in the zeolites regeneration. HNO_3 (0.4 M) was employed as the acid in the stripping solution to produce a N fertilizer, which is a single-nutrient fertilizer. To maintain the desired pH value and optimize mass transfer, a control loop was implemented, wherein HNO_3 (58%) was continuously added over time. The pH set point was established at 3.4. Drying was performed after each experiment at 40ºC for approximately 8 hours with a flow rate of 34 m^3/h.

All the experiments were conducted using the regenerant solution from zeolites treating sidestream, resulting in a regenerant stream with a N-NH_4 concentration of 4-5 g/L. However, the initial regenerant stream had a lower N-NH_4 concentration of 1.3 g/L due to storage at pH 12 for an extended period, resulting in ammonia gas losses.

A summary of the experiments conducted with the LLMCs is presented in Table 5.

Table 5 LLMCs experimental design

	Experiment		
	1	2	3-9
N-NH4 feed concentration (g N-NH4/L)	1.3	4-5	4-5
Feed pH	12	12	12
Acid	HNO3	HNO3	HNO3
Feed flow (L/h)	500	500	500
Acid flow (L/h)	500	500	500
Acid side initial volume (L)	10	10	10
Feed side initial volume (L)	1000	1000	1000
Sampling points	Along the whole experiment	Along the whole experiment	Initial-final

2.3.4 Environmental assessment

LCA methodology was performed according to UNE-EN ISO 14040 and 14044 (ISO, 2006a, 2006b) and was applied to evaluate the potential environmental impacts of recovering ammonium nitrate and struvite for subsequent application as fertilizers using innovative nutrient recovery technologies.

Two scenarios were evaluated in the LCA: (i) the Baseline Scenario, which consists in the application of a commercial solution of conventional fertilizers, and (ii) Scenario 1, which consists in the implementation of the LIFE ENRICH configuration aimed at recovering N and P fertilizers.

The fertilizers used in both scenarios were considered to cover the same fertilized area. For this reason, water supply, crop wastes and energy consumption for crop field application have not been included within the boundaries of the present study since they are expected to be similar for both scenarios.

As a novelty, the present work compared the whole value chain of recovering nutrients from wastewater for crop field application (Scenario 1) with a business-as-usual option for crop field application (Baseline Scenario). For this reason, the selected functional unit was the area of soil fertilized (1 m^2 of fertilized soil).

The life cycle inventory (LCI) input and output data of the nutrient recovery scenario was obtained from the mass and energy balances from Murcia ESTE WWTP after nutrient recovery implementation. The background inventory data for the chemicals and energy were obtained from Ecoinvent v3.6 database.

Chapter 3

3 Chapter 3: Nitrogen Flow Analysis in Spain: perspectives to increase sustainability

3.1 Introduction

The human population has been growing continuously from the industrial revolution to the present time (e.g., an annual growth rate of 1.05%)[1]. Therefore, to meet the growing demand, many agricultural procedures have drastically changed in the past century [2]. In addition, the global trend of concentrating populations in dense urban nodes and the accumulation of livestock in nodes of intensive integration has led to a large flow of nitrogen-containing compounds from anthropogenic activities wasted in the environment in the form of gases, aqueous dissolved species and solid forms [3]. This acceleration of the nitrogen cycle is not only unsustainable at the level of environmental resources but is also very harmful to both natural ecosystems and humans [4]. Harmful effects of excess nitrogen (N) in the environment, i.e., atmosphere, water and soil, are biodiversity reduction, ecosystem degradation, climate change, photochemical smog and groundwater and drinking water pollution, which have been critically reviewed [5].

Before the 20th century, the N cycle regulated itself along with the operation and functioning of natural ecosystems by biological N fixation (BNF), lightning N fixation (LNF), N deposition and denitrification [6]. Since the development of the Haber-Bosch nitrogen fixation (HBNF) process, a considerable amount of reactive nitrogen (N_r), grouping all N species other than N_2, has been incorporated into terrestrial ecosystems (raising its value14 times from 1890 to 2010) to ensure global food security and meet the food demands of approximately 48% of the world's population [7]. Thus, N cycles in terrestrial and marine ecosystems have been greatly altered [6]. In addition, inefficient use of fertilizers causes significant loss of nutrients [8]. Around 80% of N and 25-75% of P are lost to the environment through run-off, leaching and off-gas emissions, causing environmental impacts such as eutrophication and global warming and leaving insufficient nutrients in the soil for crops [8], [9].

In contrast to other essential nutrients such as phosphorous (P), N is abundant in the atmosphere in the form of gas (N_2(g)). The problem lies in the fact that the conversion of inert N gas (N_2(g)) to its reactive forms is extremely energy-intensive and fossil-fuel-dependent [10]. Some studies point out that the Haber-Bosch process used for the production of synthetic N fertilizer entails 2.5% of the global fossil energy usage and implies the production of 4-8 tons of CO_2 eq. per ton of synthesized N fertilizer [11], [12].

The impacts of Nr on natural ecosystems, (e.g., atmosphere, water bodies and soils) human health ecosystems and the correlation between N_r and climate change have been critically reviewed [13]. The study concluded that although there is strong evidence for the cascade of N_r effects, better data are needed to quantify the components of the cascade to best support policy options. When talking about alterations in the natural N cycle due to anthropogenic activities, scientific research points to the popularization of the application of inorganic fertilizers to agricultural soil as the main driver [14].

According to the FAOSTAT database on N fertilizers, in 2016, China was leading the market, especially in the production sector [15]. This indicator agrees with the fact that Asia comprises a full 30% of the world's land area with 60% of the world's current population. Other regions such as America and Oceania are more reliant on external sources to meet the internal demand. Africa is an exceptional case. Due to historical, climate and economic reasons, some regions of the continent face scarcity of food and water, which has led to distinct challenges in the agricultural production field [16]. Europe shows particularly high rates of import and export of N fertilizers, although domestic production is sufficient for the agricultural needs of the region [17]. The estimated consumption of mineral N fertilizers in the EU-27 has remained around 10 million tons in the last ten years with fluctuations and a slight upward trend [18]. On the other hand, there is a decreasing trend with a period of stabilisation for the gross N balance in agricultural land in EU-28 since 2004 [19]. The countries with the highest N fertilizer consumption are, in order, France and Germany. Following on the list, with similar amounts around 1 million tons in 2017, stand Poland, the UK, Turkey and Spain [18].

3.2 Literature review

Spain is an important exporter of agricultural products worldwide, but above all in the European market [20]. In the early 1960s, Spain was almost self-sufficient in terms of food and feed supply. In the first stage of the 21st century, net imports of agricultural products equaled crop production expressed in terms of nitrogen content (650 Gg N y^{-1}) [21].

This demonstrates a great dependence on external markets to satisfy the national demand for fertilizers [22] with accumulation points along the N flows, these N-based compounds could be recovered, thus reducing the rapidly increasing import trend. Recovery of N from alternative sources (i.e., wastewater, manure or food waste) could serve not only as a national approximation to the circular economy approach but also as a way to reduce external dependency in case of price fluctuation and promote N_r recovery options from urban, industrial and agricultural cycles. Element flow analysis (EFA) has been applied to track nutrient flows and manage nutrients in several applications at a regional scale ([23]-[26]). In addition, the management of nutrients along the supply chain has been evaluated and a new method of nutrient footprint has been introduced by Gronman et al. (2016) and (van der Wiel et al., 2020; Xu et al., 2020; Zhang et al., 2021). The review of the state of the art identified a limited number of studies specifically focused on nitrogen, which are listed in Table 6.

Table 6 Summary of the most relevant Nitrogen Flow Analysis published in the last two decades

Element	Year	Area	Approach	Ref.
N	1998	Huizhou (China)	Urban	[31]
N	2000-2016	Beijing (China)	Urban	[32]
N	2002	Illinois (USA)	Agricultural	[33]
N	2004-2014	France	Agricultural	[34]
N	2015	Scania (Sweden)	Regional	[35]
N	2010	Maeklong river (Thailand)	Regional	[36]
N	2011	Bangkok (Thailand)	Urban	[37]
N	2014	Thailand	Agricultural	[38]
N, P	2004-2007	Finland	National	[39]
N, P	2009	Flanders region (Belgium)	Reginal	[40]
N, P	2014	St. Eustatius (NL)	Agricultural and urban	[41]
P	2012	Spain	National	[42]
N,P,K,Mg	2021	Okanagan (Canada)	Regional	[43]
N,P	2022	Sweden	National	[44]
N	2021	China	Agricultural	[45]
N	2020	Xiamen (China)	Coastal City	[46]
N	2021	Shanghai (China)	Food system	[47]
N	2001	Catalonia (Spain)	Regional	[48]
N	2005	Catalonia (Spain)	Regional	[49]
N	2012	Ebro River Basin (Spain)	Regional	[50]
N	2013	Spain	National	[21]

This research aims to perform a Nitrogen Flow Analysis (NFA) to determine the feasibility of i) recovering this element from the several accumulation points within its material flow cycle, or ii) defining actions to promote the reduction of its consumption. The geographic framework is the

Spanish territory contained in the Iberian Peninsula excluding the Balearic and Canary Islands, as well as the Spanish cities in the African continent, Ceuta and Melilla. The year 2016 was selected as the reference year due to it being the latest date on which some of the official sources provided information. Nitrogen input and output data were gathered from public databases. Stan software was used as a tool to develop the NFA and, an uncertainty analysis was also included. N recovery pathways were further discussed as a way to promote the transition to the circular economy approach. The results were compared with the few examples published for cities and regions, including the only two specific regional cases in Catalonia (NE Spain) [48], [49].

3.3 Methodology

Elemental flow analysis (EFA) has been widely used to assess resource flows such as energy, water or minerals at any geographical scale (from global to local) [51] which is useful for providing relevant information to develop regional management strategies [52]. The methodology was established to develop environmental management tools by assessing the technical (Technosphere) and human (anthroposphere) metabolisms. It is based on a) mass balance, which enables a systematic assessment and tracking of flow materials (e.g., N) considering the inputs, transformations and the outputs within the system [53] and b) system analysis, consisting of a three-step procedure:(i) definition of the system, (ii) quantification of the overview of stocks and flows and (iii) interpretation of the results [54]. To determine the unknown data, the algorithm follows a sequence of equations (Eq.1 to Eq.4) [55]:

Balance equation: $\sum inputs = \sum outputs + change\ in\ stock$ Eq. (1)

Transfer coefficient equation: $output_x = transfer\ coef_{to\ output\ x} \cdot \sum inputs$ Eq. (2)

Stock equation: $stock_{Period\ i+1} = stock_{period\ i} + change\ in\ stock_{period\ i}$ Eq. (3)

Concentration equation: $mass_N = mass_{good} \cdot concentration$ Eq. (4)

The entire process is summarized in the general flow chart provided by Mayor.A et al. [56]. The first step is to define the system and its boundaries. Then, all the flows involved need to be identified and quantified using the specific databases as detailed in Mayor.A et al. [56]. The data were extracted from different databases and classified to finally compose the list of all 29 flows characterized for

Spain as summarized in Mayor.A et al. [56]. This dataset is introduced in the model previously defined in STAN as defined by Cencic et al. [55] to obtain the results of the mass balances and according to the definitions of flows, stocks, process, system, etc.

3.3.1 System description and boundaries

The NFA was developed for the Spanish territory, which is organized into 16 autonomous communities and excludes 3 other communities as the Balearic and Canary Islands, as well as two cities on the African continent (e.g., Ceuta and Melilla). The N flows (in ktN) in different forms were targeted and divided the NFA into several subsystems. This was primarily in agriculture and food production systems since N consumption as fertilizer accounts for 43% of the total N imported into the national boundaries [57], but it also considered other industrial uses such as nitrogen in fertilizers and chemicals. The flows associated with the recovery of N from wastewaters and the application of urban and farming bio-solids to agriculture were also considered in the analysis. The time selected was one year, 2016, which was the latest year in which accurate information regarding most flows could be gathered.

The model was developed using Stan 2.6, a software developed by the *Technische Universität Wien* that allows the creation of graphical models with predefined components (processes, flows, system boundary, text fields), as well as the development of Material Flow Analysis through mathematical-statistical tools such as data reconciliation and error propagation [55].

Before the development of an NFA, a good understanding of the element of interest and its behavior in the defined space and boundaries was required. To understand N in a Spanish context, different subsystems and processes were considered. As a starting point, the N cycle in a natural environment without human intervention was reviewed [39], [58]. It is a relevant issue to identify all these compounds because they constitute large flows of N on a national scale. The final resolution of the NFA will be based on the successful determination of these flows regardless of the weight contribution of N in the associated N compounds. Consequently, the main relevant processes to consider to estimate the N flows between systems are a) nitrogen fixation, as conversion from $N_{2(g)}$ in the air into NH_3 or related nitrogenous compounds in the soil; b) ammonification, by which microorganisms in soils, sediments or water produce NH_4^+; c) nitrification by two-step process where NH_3 is first oxidized to NO_2^- which is subsequently oxidized to NO_3^-; d) denitrification, reducing NO_3^- and NO_2^- mainly to

N_2O(g) and N_2(g); and e) lightning, by which N is fixed from the atmosphere to the soil.

3.3.2 Model description

The final system comprises 29 flows and 6 subsystems, three of which have stocks. Regarding subsystems, the following were considered for calculations: agriculture, households, industry, transport, waste management and water bodies. The two most relevant stocks identified within these subsystems are agricultural land and water bodies.

Agriculture is the system with the greatest theoretical relevance in the NFA and comprises crops, livestock, forestry and pasturelands; the most important attribute of this subsystem is that it includes all the soil used for the aforementioned purposes. Air is defined as the part of the troposphere placed just above the territory of study. It should be noted that substances of this subsystem are in constant movement, therefore, it is necessary to approximate the quantification of certain flows. Households represent the majority of end-consumers of goods and services provided by the industrial sector. Consequently, the industry is a general category including all processes performed before the consumption phase except for transport, which builds a subsystem on its own. Waste management is considered as an entity encompassing the largest urban waste management plants but also waste management within industries and agricultural waste management. Lastly, water bodies are all of those contained in the previously defined geographical boundaries, i.e., rivers, lakes, groundwater, etc.

Flows can be divided into those entering and exiting the system and those connecting two subsystems. The former is considered imports/inputs or exports/outputs depending on whether they enter or exit the geographical space; the latter are known as inner flows.

Imports and exports are key parts of the flow definition process. This NFA evaluates five groups of high N content goods: fertilizers, food, feed, fuel and non-food products. These substances are considered to enter or exit the established geographical boundaries.

Non-food comprises listed chemicals in the global trade market containing significant amounts of N, mostly used for production purposes. Inner flows are more numerous and more difficult to classify. Based on their start and end points, they represent many unrelated substances that transport N. The most relevant inner flows in the model are the emissions to the air or water bodies in the specified area.

3.3.2.1 Auxiliary models for agriculture and waste management subsystems

Given the complexity of the flow quantification process, two auxiliary models were developed for agriculture and waste management subsystems to facilitate the build-up of the general model.

3.3.2.2 Agriculture model

The agriculture subsystem comprises three processes: i) crops, ii) livestock and iii) pastureland. Fishing and forestry were not considered due to lack of relevance compared to the three aforementioned processes. The inner flows accounted for are manure and fodder. The former comes from livestock and is applied to crops and pastureland, the latter follows the same path but the other way around. Out of the three processes, only soil (crops and pastureland that are considered a single process) appears as stock due to the fixation of N in the soil. Livestock animals do not appear as stock because, although they retain N in their bodies while they are alive, once they are slaughtered for human consumption, this N is transferred to humans in the form of protein, which appears as meat product leaving the boundaries of the subsystem.

3.3.2.3 Waste management model

The waste management model comprises four end-of-life scenarios: i) WWTP, ii) landfill, iii) waste treatment/composting and iv) incineration. Each scenario acts almost independently of the rest and many external flows, e.g., food waste ends up in end-of-life routes, distributed by fractions according to the waste management strategy defined in Spain. The only inner flow considered in this case is WWTP bio-solids. It appears in WWTP and can be processed via incineration or used in cement industries as a substitute for coke and marginally sent for landfill, although this is banned by the EU regulation. The remaining flows are imports or exports from other subsystems.

3.3.3 Data collection

A key aspect of performing an SFA is the collection of the necessary data to quantify the flows of the system with a certain degree of reliability (Table 7). To fulfil this purpose, several sources of information were consulted (e.g., official statistical databases, published reports, surveys and interviews). The statistical data mainly contained the amounts of N compounds such as N-containing products, chemical fertilizers being applied to the field, crop harvests, milk production, sown crop areas, the number of livestock and the human population.

The availability of data for such a specific element (N) in the Spanish context is a challenge, especially in those systems where N concentration data are not collected or publicly accessible.

3.3.4 Data management and uncertainty assessment

One of the main concerns of SFA is the identification of potential errors and uncertainties. The diverse nature of sources and the varying quality and availability of data makes NFA results inherently uncertain. In this work, the results have been cross-checked by using alternative estimates, comparing with values reported in the literature and making estimates of N mass balance when possible [59]. In some cases, several estimates were made for the same point, and then these N flows were averaged.

Confidence ranges for NFA were obtained by using the HS approach developed by Seyhan [60] and widely used in different EFA studies [60]-[62]. To evaluate the reliability of the results, the information used to quantify each flow was classified into four categories. Hedbrant and Sörme [63] developed a method widely used for the assessment of uncertainty in EFA models. This method involves assigning uncertainty levels to various data sources, such as official statistics or values from the literature and applying an interval to each level [62]. Results, as incorporated into the Stan program, are depicted in Figure 4 along with the 95% confidence limits.

3.3.5 Assessment of N-use efficiency

N-use efficiency (NUE) is widely used as an indicator to assess N management in agriculture (Baligar et al., 2007; Reich et al., 2014). NUE is the ratio of the crop N uptake to the total N fertilizer input. It is also defined as the ratio between the N uptake of crops and the available N in the soil, which would include the N from applied fertilizer plus the residual mineral N in the soil. The Spanish NUE for the reference year was calculated according to European standards using Eq. (5):

$$NUE = \frac{Total\ plant\ N\ uptake}{N\ applied} \cdot 100 \qquad \text{Eq 5}$$

3.4 Results from the model

3.4.1 Main N flows in Spain

This section describes the results obtained for the NFA in Spain for the year 2016, intending to determine areas with an inefficient use of N, identifying the main losses and accumulations and estimating the dependence of Spain on imports of N-based chemicals and N-containing compounds. Figure 4 shows the results of the NFA using the Stan tool.

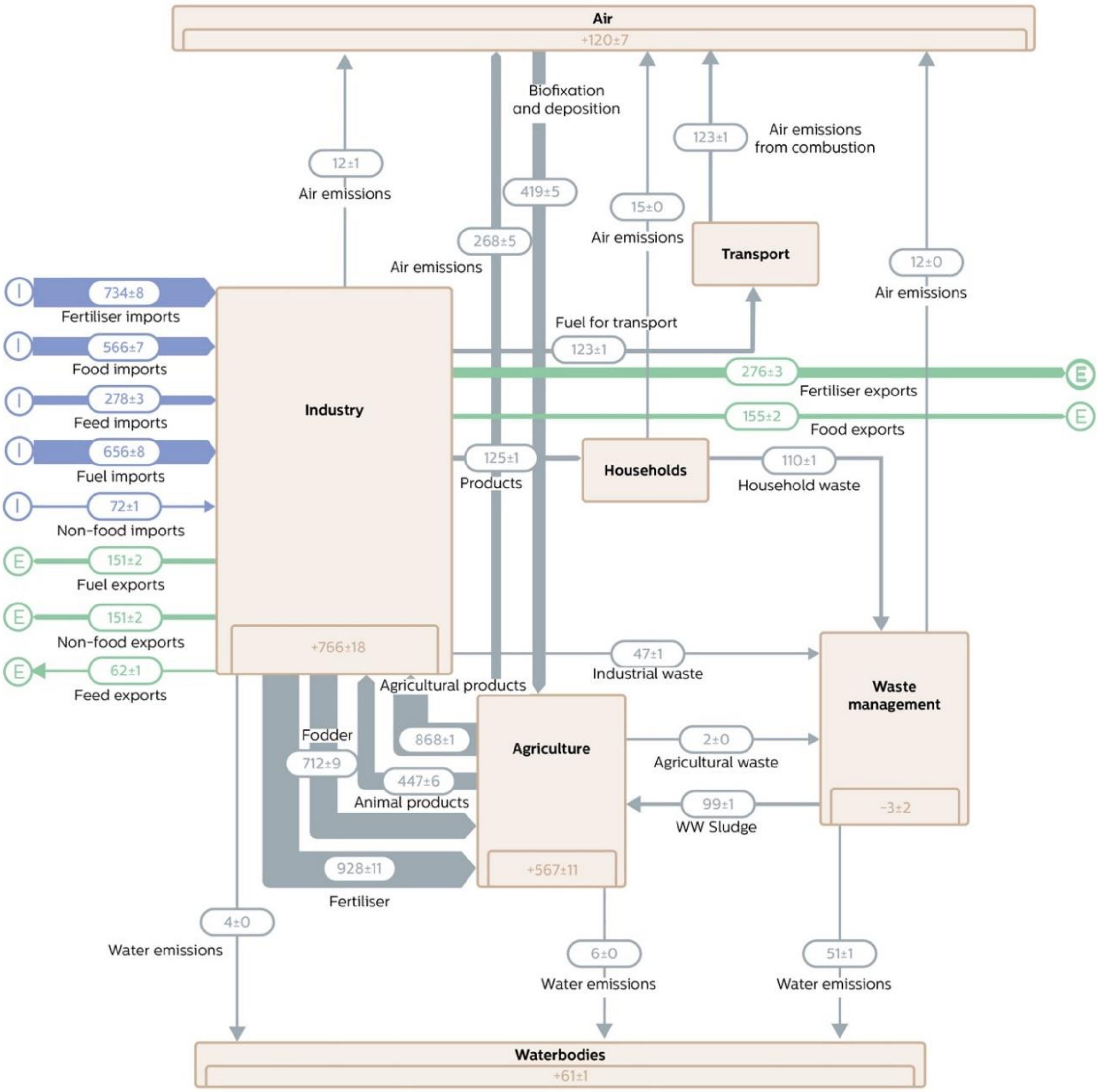

Figure 4 Nitrogen Flow Analysis for Spain with 2016 as the reference year

In Figure 4, the boxes represent the main processes and where stocks involving N are located, while the connecting arrows represent the main N flows. The N flows are presented in the Sankey format, in which the width of the arrow is shown proportional to the size of each flow. The quantity of each N flow (expressed in kt N/y) accompanied by the uncertainty is included in the circle along each arrow. The NFA results point out that Spain in 2016 had a budget of 913 kt N/y (dStock) when only accounting for the accumulation in that year. This accumulation can be found in agriculture (132 kt N/y), water bodies (779 kt N/ y) and dumpsters (2 kt N/y). N accumulates in soil, forests and in groundwater and landfills. There is a clear need for international products with a high N content. Among imports, fertilizer was the largest flow, closely followed by fuels and food. Exports appear to have minimal influence on the national N budget, with the most relevant export flow being that of fertilizer with 284 kt N/y. From Figure4, it can be seen that the greatest interaction between subsystems involves industry and agriculture. Industry is the subsystem with the most linked flows; however, agriculture concentrates the largest flows of N, the flow of fertilizer from industry to agriculture (1191 kt N/y) being one of the most remarkable. Since the amount of fertilizer that the industry produces is higher than the imports, it means that the industry is converting part of the agricultural products into fertilizers. In 2016, 2142 kt N entered the system, while 971 kt N left the geographical boundaries. The strong relationship between the food industry and the anthropogenic intervention in the N cycle is clear, which indicates that fertilizer, food and feed account for 89 % of the annual N flows entering Spain's boundaries. When it comes to exports, the proportions change. The three aforementioned groups of goods represent 62 % of the exported N. The most remarkable distinction between exports and imports is the amount of non-food N that is traded to other countries in comparison to the amount acquired by Spain. This is mainly because Spain exports more than twice the amount of N it imports. When it comes to emissions to the atmosphere the contribution of NO2, NH3 and N2O to the different emissions to the atmosphere are considered. It is noteworthy that the main N emissions to the atmosphere within industry and transport processes exceed 90 % due to NO2 emissions. These emissions come from the N content in the fossil fuels and industrial N2 fixation through high-temperature combustion.

3.4.2 The NFA in the agriculture subsystem

To have a broader understanding of the behaviour of N in the Spanish system, two auxiliary NFA models were developed, one of which focused on agriculture and livestock as a theoretical framework. The review of the state of the art indicates that agriculture could be one of the most important subsystems when evaluating N flows in a given region [59]. However, each territory has different weaknesses and strengths when it comes to nutrient management.

A diagram with the main results of the NFA for the agriculture subsystem is shown in Figure 5. The largest import of N to the system comes from fertilizer applied to agricultural soils.

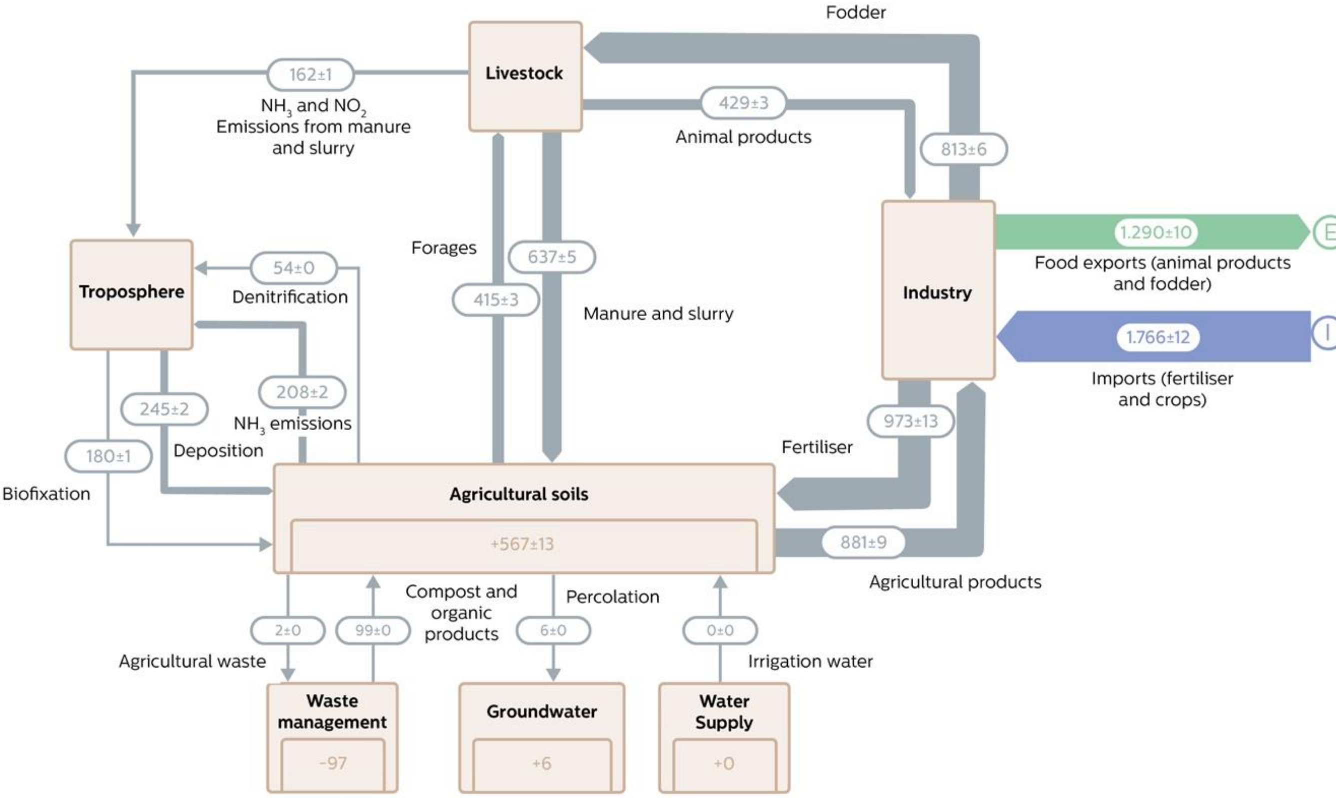

Figure 5 NFA for the agriculture subsystem for Spain with 2016 as the reference year

As can be seen in Figure 5, the imports, which are formed by different types of crops and fertilizers, are sent to their respective processes. The fertilizers go to the agricultural soils to produce forages, which are later combined with the fodder produced by the industry to feed livestock. The value of biofixation by leguminous crops, which accounts for 10% of N imports, is noteworthy.

Regardless, the accumulation is balanced by the fact that plant products accumulate a portion of N and this amount leaves the system once the crop is ready for harvest. Livestock fodder was another major nitrogen import for this subsystem. Livestock was not considered a stock system since once animals are slaughtered for meat production; the accumulated N is transferred to the consumer. A significant flow of N links livestock and cropland, given that manure is used as an organic fertilizer. Pastureland shows a higher stock, mainly attributed to the fact that the values of atmospheric deposition and biological fixation are similar to those assigned to cropland, but the transfer of nutrients from land to plant products is significantly lower when there is no agricultural activity.

As a final balance, in the subsystem defined as agriculture and livestock, imports and exports add up to 1766 ktN and 1290 ktN, respectively. Consequently, the stock of N in agricultural land amounted to 476 ktN in 2016.

3.4.3 The NFA for the Waste Management subsystem

The second subsystem assessed was waste management. It consists of four main processes (end-of-life scenarios) in Spain (Figure 6). Composting seems to be the most widespread waste treatment process with the highest N flows, especially due to the high proportion of food waste in Spain biologically treated for reuse as fertilizer.

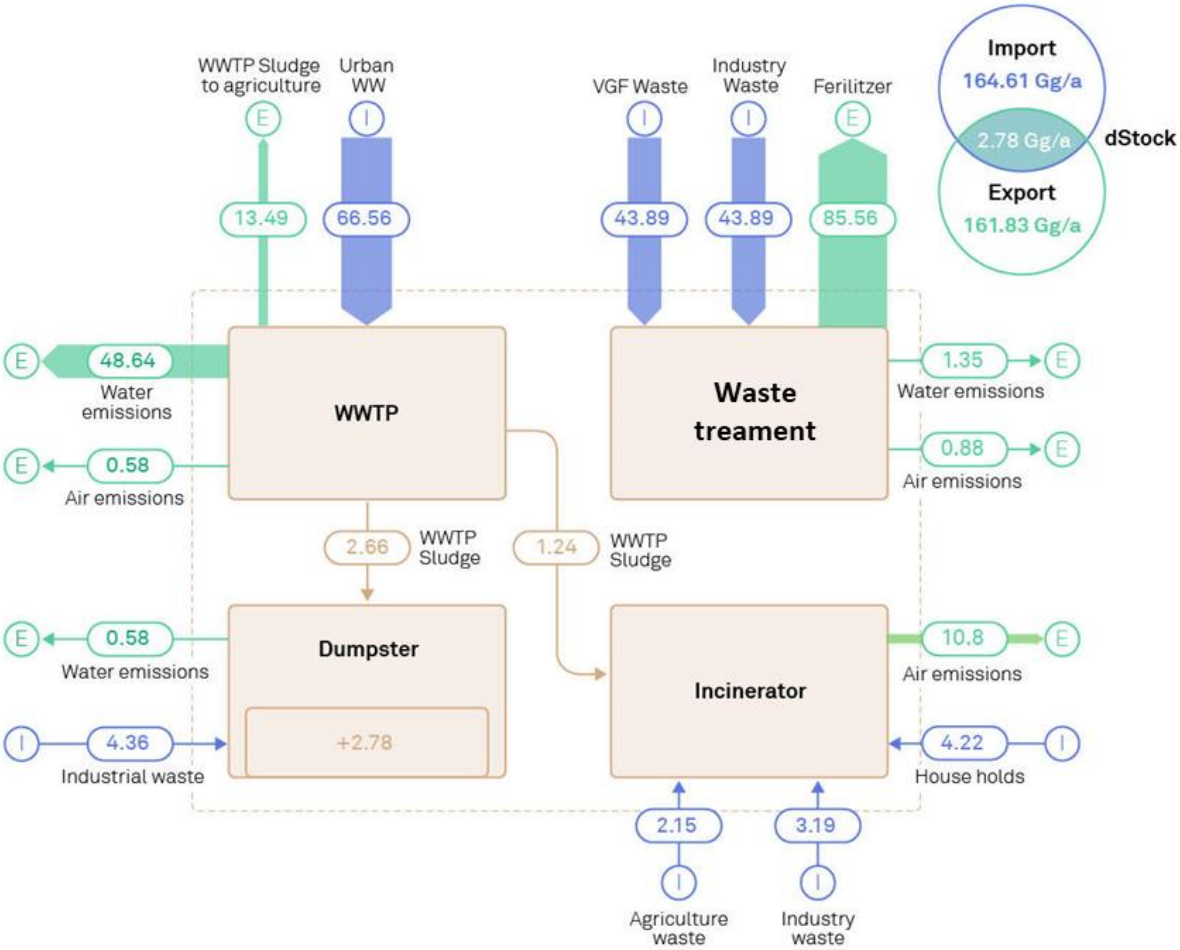

Figure 6 NFA for Waste management subsystem in Spain with 2016 as the reference year

The second most important process is that of WWTPs, which treat urban wastewater and, in some cases, such as in large metropolitan areas, mixes urban and industrial wastewater. These wastewaters usually have high N content, mainly due to the contribution of the human excretion of urea [64]. WWTPs are one of the most recurrent secondary sources identified to implement material recovery strategies, especially for the nutrient cycles (e.g., N and P). WWTP effluents have also shown great potential, which is due to the large volume of treated water that contains a relatively low concentration of total N of approximately 15-60 gN/m^3. Consequently, efforts to reduce the concentration of N in waterworks that already have a tertiary treatment are nowadays a costly management option. In addition, the volume of bio-solids generated is less than the treated water, while the N concentration is up to 6-7 orders of magnitude greater than that of water, about 70-80 g N/Kg. The fact that more than 75% of the bio-solids are valorized in agriculture is having a great positive impact since 86 ktN are recovered as organic fertilizers. However, there are some doubts about the capacity of the crops to use them efficiently, as is the case of agricultural wastes [65] and future options are to promote the recovery of reactive nitrogen as $NH_3(l)$ or liquid fertilizers [66]. Finally, landfills and incineration are widely used waste management options in Spain, but they do not imply particularly high N flows, apart from air emissions derived from waste incineration, which amount to 11 ktN.

It has been difficult to quantify the specific contribution of the agricultural sector to the N cycle, wastewater generated on farms, especially pigs, follows management routes where they are spread on agricultural soils to take benefit the C, N, P and K contents. The continued intensification of livestock farming systems is increasing their total environmental impact, resulting in increased emissions of $NH_3(g)$, greenhouse gases (GHG) and odors that derive from the housing, storage and application of manure and slurry in the field. In a recent study in Europe, it was estimated that animal manure is contributing up to 65% of total anthropogenic NH_3, 40% of N_2O and 10% of CH_4 emissions [67]. Therefore, recovery of NH_3 from agricultural waste will be a priority and an opportunity to reduce Spanish ammonia imports. While the recovery of P from waste water is mandated by regulation in countries such as Germany and Switzerland, regulation is expected to move forward to promote recovery of nitrogen in the form of any reactive type of N. Research efforts are directed at recover ammonium salts to be used as fertilizers and efforts are also directed to recover NH_3 [66].

3.5 Discussion of results

Calculation of the net anthropogenic nitrogen input (NANI) was described by Lassaletta et al. [21] for the agri-food system. The authors reported that the NANI in 2009 for Spain was 1673 kt N/y. In addition, the study provided the evolution of this value since 1961. Thus, taking into account the growth rate for this period and calculating the corresponding value for 2016, which would correspond to the period studied in this work, a NANI of approximately 1835 kt N/y would be expected. In this study, first the total ‘new’ anthropogenic N input to the country, through the application of synthetic fertilizers (1191 kt N/y), net atmospheric inputs (245 kt N/y), BNF by crops (180 kt N/y) and net import of food and feed (479 kt N/y), was estimated, finally representing a NANI of 2095 kt N/y for Spain, 14 % higher than expected by the growth trend of the data reported by Lassaletta et al. [21]. The current results were compared with those reported for other reference cases in Spain. Bartrolí et al. [49] developed a study with the same compartments as defined in the present work, but only for Catalonia. Lassaletta et al. [21] evaluated the agri-food compartment but for the entire Spanish territory. Initially, the main N stocks were compared. Subsequently, the N loss flows (denitrification, NH3 emissions, N discharged to water bodies) were analyzed with respect to the total N inputs reported in these works for one year (426 kt N/y for Bartrolí et al. [49]; 1673 kt N/y for Lassaletta et al. [21]; and 2090 kt N/y in this study). Finally, other relevant flows were compared with total N inputs. All these results are collected in Table 7.[1]

Table 7. Comparison of percentages of stock and flows with studies based on the Spanish territory (Bartrolí et al., [49] and Lassaletta et al., [21])

	This study	Bartrolí et al., (2005)	Lassaletta et al., (2013)[1]
Overall stock	53%	63%	54%
Stock in soils	10%	7%	5%
Stock in water bodies	37%	23%	59%
Denitrification	3%	7%	19%
NH_3 emissions (soil and livestock)	18%	13%	
Water bodies	37%	23%	64%
Food exports	15%	37%	9%
Fertilizer imports to soil	55%	14%	53%
Atmospheric deposition	12%	3%	1%
Biofixation	9%	4%	15%

All these results indicate that overall N stocks within the country have been consistently reported to be around 50-60 % of total N inputs. Furthermore, Lassaletta et al. [21] reported that only 6.5 % of N is transported out of the country through river flows, which allows N stocks to be achieved in soils and water bodies of between 50 and 60 % of total N inputs. Other significant differences that can be found with the previous models are those related to food exports and the contribution of fertilizers. In this case, Bartrolí et al. [49] reported different values but this is due to the fact that their study only considered the autonomous community of Catalonia, which is the fourth in terms of agriculture production [68]. Measures must be taken not only to improve N efficiency at the national level, but also to meet the SDGs in accordance with the 2030 Agenda for Sustainable Development. The areas that can contribute to a considerable reduction of N in the atmosphere are road transport (passenger cars), electricity and heating production, heavy-duty vehicles and buses. Some actions that could reduce these contributions are i) the reduction of NOx emissions with the application of limitation policies aimed at the industry and transport sectors; ii) a paradigm shift in the electricity and heating sector; and iii) a change in the urban mobility model. In this sense, the penetration of electric vehicles in the market in the coming decades could make an important contribution to reduce N emissions.

3.5.1 Linking agriculture and waste subsystems

Analysis of the waste subsystem has shown its potential to produce fertilizers from waste products. In that case, 86 ktN of N is valorized as a biofertilizer from industrial and domestic waste. However, in the case of WWTP, there are no such synergies, although there is the same potential. This is due to several legal barriers that until now do not recognize recovered products like fertilizers, maintaining their status as waste.

Nevertheless, The European Commission has adopted a delegated act to include sewage sludge among the authorized input materials for fertilizer sold across the EU, paving the way for further investment in phosphorus recovery from sludge. The measure extends the Fertilizers Regulation adopted by the Commission in June 2019, which left the issue of sludge-based nutrients open. This was considered a temporary setback by those hoping for a breakthrough in the nutrient recovery market [69].

The provision approving sludge-sourced fertilizers has been added to the regulation, which will come into force in 2022. According to Brussels-based water lobby group EurEau, the new text allows P to be recovered from sludge as struvite (phosphate salts) and from incinerated sludge ash. The fertilizer thus obtained can be sold across borders within the EU Single Market [70].

This procedure has demonstrated the feasibility of obtaining fertilizer status for a recovered product, including struvite within the recovered materials that can be used in agriculture and thereby granting it the CE marking. The same procedure should be followed for other recovered nitrogen-based fertilizers, such as ammonium. In this sense, if struvite and ammonium salts are considered potential alternative sources of N, then WWTP can be considered resource recovery facilities [71]–[74].

Figure 6 shows that each year 49 ktN are discharged into water bodies, which represents 73% of the input flow and could be potentially recovered. In recent years, several technologies have been developed to recover nutrients from wastewater. The most common is the crystallization of struvite, which allows for the recovery of both N and P or even potassium (K-struvite) [75] Stripping and absorption are used to recover ammonia, mainly as ammonium sulphate, but they are not implemented in WWTP facilities due to energy requirements and combinations of ion exchange with membranes to obtain ammonium salts (nitrate, sulphate or phosphate) because of their potential use as fertilizers. However, all these technologies require a high concentration of nutrients to be economically recovered. In a WWTP, these concentrations can only be found in the anaerobic digestion centrates, which can range from 500 to 1500 mg N-NH_4/L. The N present in these streams usually accounts for 10–20 % of the total N in the influent of the WWTP [76]. Considering N losses of 5% in the sludge, there remains a total of 5–10 % of the total N in the influent that could be valorized as fertilizer, which accounts for 3–7 ktN/y of N. Considering the flows represented in Figure 6, the amount of recoverable N from the WWTP represents from 0.2 to 0.5 % of the total N produced as fertilizers in Spain. Although it may not seem huge in terms of global impact, it must be taken into account that this percentage range would allow for a fertilizer-producing company such as Fertiberia (www.fertiberia.es) to manage all the production and distribution of recovered products from WWTPs. In addition, several advantages associated with the use of recycled nutrients should be considered: i) reduction in operating costs for WWTP associated with less maintenance due to uncontrolled precipitation of struvite, ii) lower energy consumption in the aeration of the biologic reactor due to lower nitrogen load, iii) lower cost in sludge transport due to improved sludge dewaterability and iv) reduced carbon footprint compared of recovered fertilizers compared to conventional ones following the Haber-Bosch process [77].

3.5.2 5.2 Assessment of NUE in Spain and actions to increase efficiency

Data from the Agriculture NFA was used to determine the Spanish NUE value. This value considered the N uptake by the plant results from the sum of N in plant products and fodder (1296 ktN) and the applied N is the sum of the application of fertilizer, seeds and manure in crops, as well as N fixed to the soil through BNF or atmospheric deposition (1610 ktN) giving an NUE value of 71%. Regarding agricultural practices, the EU Nitrogen Expert Panel presented the possible objectives for the optimization of N management in the *NUE Indicator Report* (Figure 7).

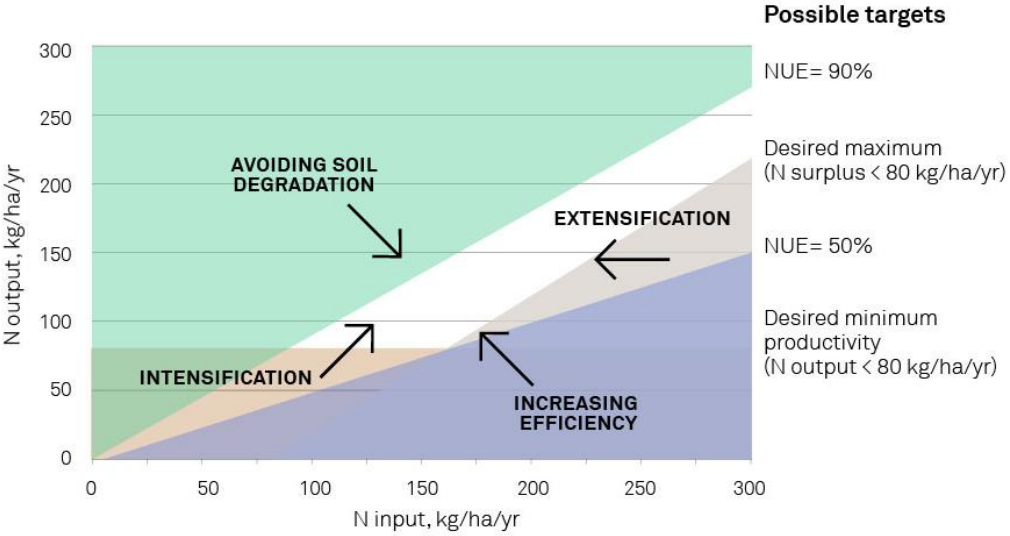

Figure 7 Evaluation of N outputs (kgN/y.ha) as a function of N inputs (kg(ha.h) under potential target indicators as a function of main directions of change in the N use efficiency (Nitrogen Expert Panel, [78])

The most desirable scenario for a country is to have an NUE between 50 and 90% [79]. Lower values indicate inefficient use of N that can lead to externalities. On other hand, NUEs above 90% should be avoided to reduce the risk of soil mining. The Spanish NUE value for 2016 is within the established range; however, being closer to the upper limit indicates that the efficiency could be improved but taking into account the ricks of surpassing the 90% limit.

Although much of the work must be done at the farm scale, important policies need to be implemented at the national and multi-national scales, e.g., facilitating technology transfer and promoting agricultural innovation [80]. Additionally, improving NUE should be adopted as one of the SDGs indicators used alongside crop yield and perhaps other soil health parameters to measure the sustainability of the agricultural sector. Countries should be encouraged to collect data on their N management in crop and livestock production. These data should be used to trace pathways of the three indices of agricultural N pollution, agricultural efficiency and food security targets (N_{sur}, NUE and N_{yield}). In the case of Spain, an Action Plan was presented through the *Integrated National Energy and Climate Plan 2021-2030* published in January 2020 [81], where the Spanish government presented several measures related to N management in the country such as i) introduction of leguminous plants into crop rotation systems to improve N levels in the soil, its structure and fertility. Subsequent crops would require less nitrogenous fertilizer. At the current level leguminous plants apport 245 kt N yearly, which already represents 25% of the N apported by inorganic fertilizers. Further increase in the quantity of N fixed by these crops would result in a lower inorganic requirement, not only contributing to reduce the carbon footprint associated to the use of inorganic fertilizers but also reducing the external dependencies. Also, ii) the production of organic fertilizer using pig and cattle manure in areas with high concentration of livestock was recommended. In addition, there was iii) the National Plan for Emissions Reduction, with the replacement of fossil fuels with renewable energies for electricity production. In this case, if there is a 20% reduction in fuel imports it would directly reduce the industry emissions to atmosphere mainly due to the reduction in NOx production.

3.5.3 NUE in food: a transition towards a sustainable diet

Quantification of the flows in the development of the NFA together with the state of the art indicate that the food industry is an important factor in the N cycle [82]. In the specific case of Spain, food waste is the indicator that places the country behind the rest of the EU member states and that could be key to taking a step forward in terms of the efficiency of N. For instance, according to the European food waste levels reported in 2016 [83], Spain was listed as one of the countries providing data of insufficient quality; therefore, up-to-date information of relevant quality must be collected to identify sources of food loss and act to reduce the waste generated in this sector. It is important to highlight the need to establish policies for the progressive reduction of food waste as well as to promote the recirculation of all those by-products of the food production industry, which could lead to greater efficiency in the use of N.

In terms of livestock production, changes in feed composition can increase N-use efficiency in animals destined for human consumption without affecting the quality of human digestible protein in meat products [84]. The increasing use of synthetic fertilizers, together with other practices of agricultural intensification, has resulted in a considerable increase in agricultural productivity during the decades [85]. However, a large part of the increase in primary agricultural production is used as animal feed [86]. A recent study, *Nitrogen on the table* [87], indicated that current average per capita protein intake in the EU was about 70% higher than that recommended by the World Health Organization (WHO). Spain also stands out as one of the countries with the highest meat consumption in the EU27. This can be seen as an opportunity to experience a notable reduction of N pollution by pursuing a redistribution of the land dedicated to food production by limiting the average meat consumption in the national diet.

Using biophysical models and methods, the large-scale consequences of replacing 25–50% of animal-based foods with plant-based foods on a dietary energy basis were calculated, assuming corresponding changes in production in the EU [88]. The results showed that cutting meat, dairy and eggs in half would achieve a 40% reduction in N emissions, 25–40% reduction in GHG emissions and 23% less per capita use of cropland for food production.

In this sense, a sensitivity analysis was carried out to assess the impact of dietary changes on the overall NFA model.

Assuming a 50% reduction in meat consumption implies a 50% increase in the N consumed through plant-based foods to compensate for the protein consumed through animal products as can be seen in Figure 8.

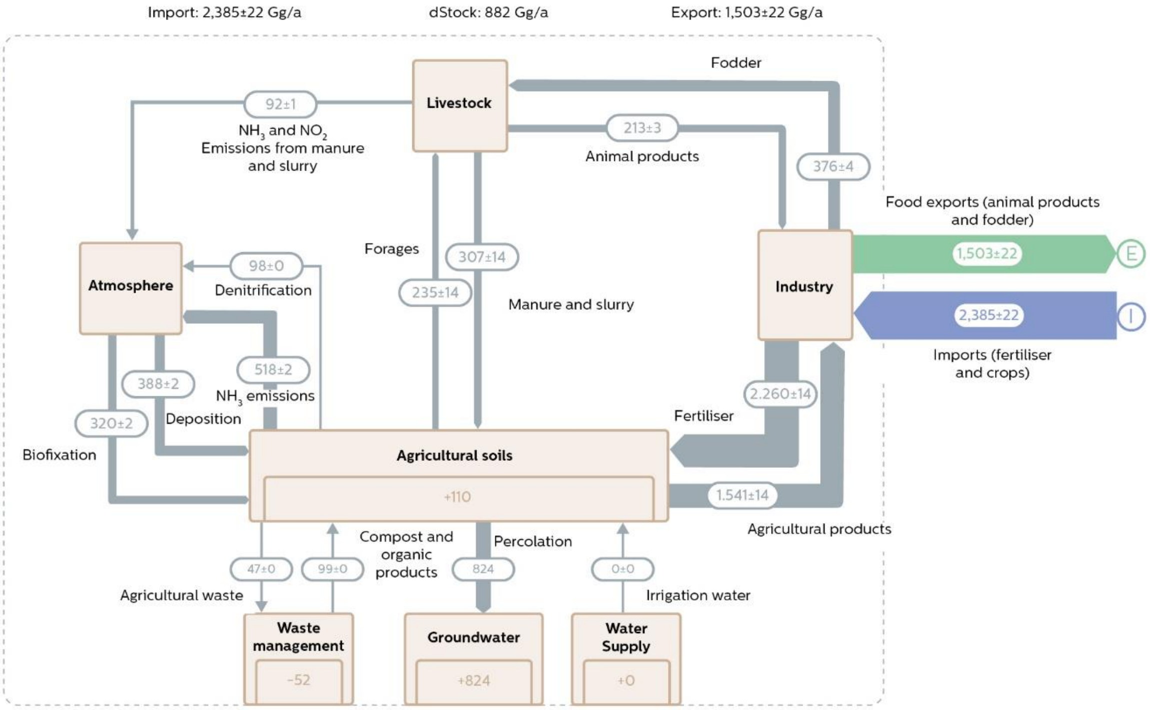

Figure 8 Impact of the hypothesis of 50% reduction in meat consumption on agricultural land

Imports into the system through food would remain constant since no distinction was made in the flow between plant and animal products. Therefore, the study focused on the subsystem of agriculture and livestock. Applying a 50% reduction to all integrated flows in the livestock and a 50% increase in all flows connected to the agriculture, the results indicated that the stock in the agricultural soil would decrease by 22 ktN/y, a reduction of N stock by 16% compared to the current model. Taking into account the increasing trend of NANI reported by Lassaletta et al., (2013), this model could help reduce N imports to the system, and therefore, the accumulation of N in the soils.

A large EU-level initiative to reduce food waste at the individual level is being promoted [89] in addition to other initiatives through the EU Green Deal Action Plan with programs such as Farm to Fork [90]. However, communication is a key aspect to promoting significant changes in the habits of citizens and even more in the change of mentality towards certain aspects of their lifestyle. Nitrogen flows are strongly linked to consumption habits and agricultural practices that must be managed in such a way that the greatest benefit is obtained both for the productivity of the land and to minimize the consequences of the social and environmental problems that arise globally.

3.6 Conclusions

In this study, an NFA has been carried out within the Spanish territory with the data collected in 2016. The Lack of updated data and, in some cases, the variability of the information was the main challenge for the development of this analysis at a national level. Despite the availability of various reliable sources of information for the quantification of N flows related to agriculture, a detailed comparison has been made between the most relevant studies published in the Spanish territory to verify the credibility of the data obtained in this study.

This NFA has been developed taking into account not only the agricultural-related flows but also those linked to industry and waste management, among others. Food consumption habits, heavily linked to the trends in agricultural production, have been proven to be important in the N surplus reduction process.

In this study, the total contribution of anthropogenic N input (NANI) to the country has been estimated, considering the application of synthetic fertilizers (1191 ktN/y), the net atmospheric inputs (245 ktN/y), the N biological fixation by crops (180 ktN/y), and the net food and feed imports (479 ktN/y), which finally represents a NANI of 2095 ktN/y for Spain, 14% higher than expected by trend of growth from the data reported by Lassaletta et al., (2013).

Regarding waste management, prioritizing biological treatment as the main end-of-life scenario for compostable goods would be the best strategy to reduce the wasting of N to the environment, specifically in the atmosphere, water or soil. In this way, avoiding the incineration as an end-of-life scenario, it could be prevented 11 kt N per year from reaching the atmosphere.

According to the results, it is recommended to increase the circular strategy within the territory. This could be achieved by recovering nutrients present in wastewater and transforming them into fertilizers. Taking into account that Spain reports an N stock between 40 % and 60 % (913 kt N/ a), actions should focus on reducing N losses in water bodies in the agricultural sector, which represent 724 kt N per year. Furthermore, considering the agricultural system, there is an annual accumulation of 132 kt N per year in soils that also needs to be addressed. It is important to improve soil N management to increase the organic N in soil and thus maintain the C/N ratio above 10, which is a sign of soil organic matter accumulation. However, it is also important to reduce the risk of nitrate accumulation and leaching, in order to comply with Council Directive 91/676/EEC on the protection of waters against pollution caused by nitrates from agricultural sources. This directive establishes a limit of 170 kg N/ha·y for livestock manure in vulnerable zones. In 2009, the overall value in Spain was 33.14 kg N/ha·y according to Lassaletta et al. [21]. In this study, a value of 41.5 kg N/ha·y was estimated for 2016, which corresponds to an increase of 25 % in only 7 years.

Finally, a revision of dietary patterns in Spain showed that is possible to reduce nitrogen stored in soils by 16 % when considering 50 % less consumption of animal products.

3.7 **References**

[1] FAO, *The state of the world's land and water resources for food and agriculture: Managing systems at risk*. 2013. doi: 10.4324/9780203142837.

[2] F. Brodt and C. Ingels, "Sustainable Agriculture | Learn Science at Scitable," *Environmental science*, vol. 3, no. 10, p. 17, 2011.

[3] W. H. Schlesinger, "On the fate of anthropogenic nitrogen," *Proceedings of the National Academy of Sciences*, vol. 106, no. 1, pp. 203-208, Jan. 2009, doi: 10.1073/PNAS.0810193105.

[4] C. J. Stevens, "Nitrogen in the environment," *Science (1979)*, vol. 363, no. 6427, pp. 578 LP - 580, Feb. 2019, doi: 10.1126/science.aav8215.

[5] J. Pan, N. Ding, and J. Yang, "Changes of urban nitrogen metabolism in the Beijing megacity of China, 2000-2016," *Science of The Total Environment*, vol. 666, pp. 1048-1057, May 2019, doi: 10.1016/J.SCITOTENV.2019.02.315.

[6] Z. Luo, S. Hu, D. Chen, and B. Zhu, "From Production to Consumption: A Coupled Human-Environmental Nitrogen Flow Analysis in China," *Environ Sci Technol*, vol. 52, no. 4, pp. 2025-2035, Feb. 2018, doi: 10.1021/ACS.EST.7B03471.

[7] FAO, "The future of food and agriculture | FAO | Food and Agriculture Organization of the United Nations," 2022. http://www.fao.org/publications/fofa/en/ (accessed Aug. 17, 2021).

[8] M. A. Sutton *et al.*, "Our Nutrient World - The challenge to produce more food and energy with less pollution." ECN, 2013. Accessed: Aug. 17, 2021. [Online]. Available: https://repository.tudelft.nl/islandora/object/uuid%3A49fdfb78-387e-47ac-a4a2-736f7352fb6c

[9] N. Jakrawatana, P. Ngammuangtueng, and S. H. Gheewala, "Linking substance flow analysis and soil and water assessment tool for nutrient management," *J Clean Prod*, vol. 142, pp. 1158-1168, 2017, doi: 10.1016/j.jclepro.2016.07.185.

[10] W. R. Moomaw, "Energy, Industry and Nitrogen: Strategies for Decreasing Reactive Nitrogen Emissions," *Ambio*, vol. 31, no. 2, pp. 184-189, Aug. 2002, [Online]. Available:

http://www.jstor.org.recursos.biblioteca.upc.edu/stable/4315232

[11] J. Coppens, E. Meers, N. Boon, J. Buysse, and S. E. Vlaeminck, “Follow the N and P road: High-resolution nutrient flow analysis of the Flanders region as precursor for sustainable resource management,” *Resour Conserv Recycl*, vol. 115, no. 2016, pp. 9-21, 2016, doi: 10.1016/j.resconrec.2016.08.006.

[12] A. Beckinghausen, M. Odlare, E. Thorin, and S. Schwede, “From removal to recovery: An evaluation of nitrogen recovery techniques from wastewater,” *Appl Energy*, vol. 263, no. February, p. 114616, 2020, doi: 10.1016/j.apenergy.2020.114616.

[13] J. W. Erisman *et al.*, “Consequences of human modification of the global nitrogen cycle,” *Philosophical Transactions of the Royal Society B: Biological Sciences*, vol. 368, no. 1621, Jul. 2013, doi: 10.1098/RSTB.2013.0116.

[14] P. M. Vitousek *et al.*, “Technical Report: Human Alteration of the Global Nitrogen Cycle: Sources and Consequences,” *Ecological Applications*, vol. 7, no. 3, p. 737, Aug. 1997, doi: 10.2307/2269431.

[15] F. Kahrl, Y. Li, Y. Su, T. Tennigkeit, A. Wilkes, and J. Xu, “Greenhouse gas emissions from nitrogen fertilizer use in China,” *Environ Sci Policy*, vol. 13, no. 8, pp. 688-694, Dec. 2010, doi: 10.1016/J.ENVSCI.2010.07.006.

[16] “Land and environmental degradation and desertification in Africa,” 2021. http://www.fao.org/3/x5318E/x5318e01.htm (accessed Aug. 17, 2021).

[17] K. Van Egmond, T. Bresser, and L. Bouwman, “The European nitrogen case,” *Ambio*, vol. 31, no. 2, pp. 72-78, 2002, doi: 10.1579/0044-7447-31.2.72.

[18] “Eurostat,” 2021. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agri-environmental_indicator_-_mineral_fertilizer_consumption (accessed Aug. 18, 2021).

[19] “Eurostat,” 2021. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agri-environmental_indicator_-_gross_nitrogen_balance&oldid=546526 (accessed Aug. 14, 2022).

[20] “Spanish Agri-Food Exports Increase by 97% in Last Decade,” 2019. https://www.foodswinesfromspain.com/spanishfoodwine/global/food/news/new-detail/spanish-agri-

food-exports-2018.html (accessed Aug. 18, 2021).

[21] L. Lassaletta, G. Billen, E. Romero, J. Garnier, and E. Aguilera, “How changes in diet and trade patterns have shaped the N cycle at the national scale: Spain (1961-2009),” *Regional Environmental Change 2013 14:2*, vol. 14, no. 2, pp. 785-797, Oct. 2013, doi: 10.1007/S10113-013-0536-1.

[22] “Estadística de consumo de fertilizantes en la agricultura,” 2021. https://www.mapa.gob.es/es/estadistica/temas/estadisticas-agrarias/agricultura/estadisticas-medios-produccion/fertilizantes.aspx (accessed Aug. 18, 2021).

[23] Z. WangShou, L. XuYong, D. P. Swaney, and D. XinZhong, “Does food demand and rapid urbanization growth accelerate regional nitrogen inputs?,” *J Clean Prod*, vol. 112, no. Part 2, pp. 1401-1409, 2016.

[24] D. Cordell, J. O. Drangert, and S. White, “The story of phosphorus: Global food security and food for thought,” *Global Environmental Change*, vol. 19, no. 2, pp. 292-305, May 2009, doi: 10.1016/J.GLOENVCHA.2008.10.009.

[25] J. Wu, D. Franzén, and M. E. Malmström, “Nutrient flows following changes in source strengths, land use and climate in an urban catchment, Råcksta Träsk in Stockholm, Sweden,” *Ecol Modell*, vol. 338, pp. 69-77, 2016, doi: 10.1016/j.ecolmodel.2016.08.001.

[26] A. R. Baroi, R. B. Chowdhury, B. B. Roy, and M. Sujauddin, “Sustainability assessment of phosphorus in the waste management system of Bangladesh using substance flow analysis,” *J Clean Prod*, vol. 273, 2020, doi: 10.1016/j.jclepro.2020.122865.

[27] K. Grönman *et al.*, “Nutrient footprint as a tool to evaluate the nutrient balance of a food chain,” *J Clean Prod*, vol. 112, pp. 2429-2440, 2016, doi: https://doi.org/10.1016/j.jclepro.2015.09.129.

[28] B. Z. van der Wiel, J. Weijma, C. E. van Middelaar, M. Kleinke, C. J. N. Buisman, and F. Wichern, “Restoring nutrient circularity: A review of nutrient stock and flow analyses of local agro-food-waste systems,” *Resour Conserv Recycl*, vol. 160, no. May, 2020, doi: 10.1016/j.resconrec.2020.104901.

[29] R. Xu, Y. Cai, X. Wang, C. Li, Q. Liu, and Z. Yang, “Agricultural nitrogen flow in a reservoir watershed and its implications for water pollution mitigation,” *J Clean Prod*, vol. 267, 2020, doi:

10.1016/j.jclepro.2020.122034.

[30] X. Zhang, Y. Zhang, Y. Wang, and B. D. Fath, “Research progress and hotspot analysis for reactive nitrogen flows in macroscopic systems based on a CiteSpace analysis,” *Ecol Modell*, vol. 443, no. January, 2021, doi: 10.1016/j.ecolmodel.2021.109456.

[31] X. Ma, Z. Wang, Z. Yin, and A. Koenig, “Nitrogen Flow Analysis in Huizhou, South China,” *Environmental Management 2007 41:3*, vol. 41, no. 3, pp. 378-388, Dec. 2007, doi: 10.1007/S00267-007-9053-7.

[32] J. Pan, N. Ding, and J. Yang, “Science of the Total Environment Changes of urban nitrogen metabolism in the Beijing megacity of,” *Science of the Total Environment*, vol. 666, pp. 1048-1057, 2019, doi: 10.1016/j.scitotenv.2019.02.315.

[33] S. Singh, J. E. Compton, T. R. Hawkins, D. J. Sobota, and E. J. Cooter, “A Nitrogen Physical Input-Output Table (PIOT) model for Illinois,” *Ecol Modell*, vol. 360, pp. 194-203, Sep. 2017, doi: 10.1016/J.ECOLMODEL.2017.06.015.

[34] G. Billen, J. le Noë, and J. Garnier, “Two contrasted future scenarios for the French agro-food system,” *Science of The Total Environment*, vol. 637-638, pp. 695-705, Oct. 2018, doi: 10.1016/J.SCITOTENV.2018.05.043.

[35] “Nitrogen flow in Scania - Epsilon Archive for Student Projects,” 2015. https://stud.epsilon.slu.se/8129/ (accessed Feb. 09, 2022).

[36] C. Pharino, N. Sailamai, and P. L. Kamphaengthong, “Material Flow Analysis of Nitrogen in Maeklong River Basin in Ratchaburi and Samut Songkhram Province, Thailand,” *Water Conservation Science and Engineering*, vol. 1, no. 3, pp. 167-175, Oct. 2016, doi: 10.1007/S41101-016-0011-1.

[37] T. Buathong, S. K. Boontanon, N. Boontanon, N. Surinkul, H. Harada, and S. Fujii, “Nitrogen Flow Analysis in Bangkok City, Thailand: Area Zoning and Questionnaire Investigation Approach☆,” *undefined*, vol. 17, pp. 586-595, 2013, doi: 10.1016/J.PROENV.2013.02.074.

[38] T. Suesatpanit, “Substance Flow Analysis of Nitrogen in Food Production and Consumption System of Thailand,” *undefined*, 2017.

[39] R. Antikainen, R. Haapanen, R. Lemola, J. I. Nousiainen, and S. Rekolainen, “Nitrogen and phosphorus flows in the Finnish agricultural and forest sectors, 1910-2000,” *Water Air Soil Pollut*, vol. 194, no. 1-4, pp. 163-177, Oct. 2008, doi: 10.1007/S11270-008-9705-0.

[40] J. Coppens, E. Meers, N. Boon, J. Buysse, and S. E. Vlaeminck, “Follow the N and P road: High-resolution nutrient flow analysis of the Flanders region as precursor for sustainable resource management,” *Resour Conserv Recycl*, vol. 115, pp. 9-21, Dec. 2016, doi: 10.1016/J.RESCONREC.2016.08.006.

[41] I. Firmansyah, M. Spiller, F. J. de Ruijter, G. J. Carsjens, and G. Zeeman, “Assessment of nitrogen and phosphorus flows in agricultural and urban systems in a small island under limited data availability.,” *undefined*, vol. 574, pp. 1521-1532, Jan. 2017, doi: 10.1016/J.SCITOTENV.2016.08.159.

[42] J. Álvarez, M. Roca, C. Valderrama, and J. L. Cortina, “A Phosphorous Flow Analysis in Spain,” *Science of The Total Environment*, vol. 612, pp. 995-1006, Jan. 2018, doi: 10.1016/J.SCITOTENV.2017.08.299.

[43] R. Harder, M. Giampietro, K. Mullinix, and S. Smukler, “Assessing the circularity of nutrient flows related to the food system in the Okanagan bioregion, BC Canada.,” *Resour Conserv Recycl*, vol. 174, Nov. 2021, doi: 10.1016/j.resconrec.2021.105842.

[44] R. Sinha *et al.*, “Quantifying nutrient recovery by element flow analysis: Harvest and use of seven marine biomasses to close N and P loops,” *Resour Conserv Recycl*, vol. 178, Mar. 2022, doi: 10.1016/j.resconrec.2021.106031.

[45] X. Jin, N. Zhang, Z. Zhao, Z. Bai, and L. Ma, “Nitrogen budgets of contrasting crop-livestock systems in China,” *Environmental Pollution*, vol. 288, Nov. 2021, doi: 10.1016/j.envpol.2021.117633.

[46] Y. Li, S. Cui, B. Gao, J. Tang, W. Huang, and Y. Huang, “Modeling nitrogen flow in a coastal city–A case study of Xiamen in 2015,” *Science of the Total Environment*, vol. 735, Sep. 2020, doi: 10.1016/j.scitotenv.2020.139294.

[47] C. Liao, Y. Xia, and D. Wu, “Nitrogen flows associated with food production and consumption system of Shanghai,” *Environmental Pollution*, vol. 279, Jun. 2021, doi: 10.1016/j.envpol.2021.116906.

[48] J. Bartrolí, M. J. Martin, and M. Rigola, “Issues in system boundary definition for substance flow analysis: the case of nitrogen cycle management in Catalonia.,” *TheScientificWorldJournal*, vol. 1 Suppl 2. pp. 892-897, 2001. doi: 10.1100/tsw.2001.260.

[49] J. Bartrolí, M. J. Martin, and M. Rigola, “The nitrogen balance for Catalan agriculture soils and livestock sectors,” 2005.

[50] L. Lassaletta, E. Romero, G. Billen, J. Garnier, H. García-Gómez, and J. v. Rovira, “Spatialized N budgets in a large agricultural Mediterranean watershed: High loading and low transfer,” *Biogeosciences*, vol. 9, no. 1, pp. 57-70, 2012, doi: 10.5194/BG-9-57-2012.

[51] T. E. Graedel and B. R. Allenby, *Industrial ecology and sustainable engineering*. 2009.

[52] E. van der Voet, “Substance flow analysis methodology,” *A Handbook of Industrial Ecology*, May 2015, doi: 10.4337/9781843765479.00018.

[53] E. van der Voet, R. Kleijn, L. van Oers, R. Heijungs, R. Huele, and P. Mulder, “Substance flows through the economy and environment of a region,” *Environmental Science and Pollution Research 1995 2:2*, vol. 2, no. 2, pp. 90-96, 1995, doi: 10.1007/BF02986723.

[54] P. Baccini and P. H. Brunner, *Metabolism of the Anthroposphere: Analysis, Evaluation, Design*, Second edition., vol. 16, no. 6. Cambridge: John Wiley & Sons, Ltd, 2012. doi: 10.1111/J.1530-9290.2012.00558.X.

[55] O. Cencic and H. Rechberger, “Material flow analysis with Software STAN,” *Journal of Environmental Engineering and Management*, vol. 18, pp. 3-7, 2008.

[56] Á. Mayor, E. Beltran, J. L. Cortina, and C. Valderrama, “Nitrogen flow analysis in Spain: Perspectives to increase sustainability,” *Science of The Total Environment*, vol. 858, p. 160117, Feb. 2023, doi: 10.1016/J.SCITOTENV.2022.160117.

[57] “Productos fertilizantes,” 2021. https://www.mapa.gob.es/es/agricultura/temas/medios-de-produccion/productos-fertilizantes/ (accessed Aug. 19, 2021).

[58] K. Mengel, E. A. Kirby, H. Kosegarten, and T. Appel, “Principales of Plants Nutrition,” p. 849, 2001.

[59] K. Senthilkumar, T. Nesme, A. Mollier, and S. Pellerin, “Regional-scale phosphorus flows and budgets within France: The importance of agricultural production systems,” *Nutr Cycl Agroecosyst*, vol. 92, no. 2, pp. 145-159, Mar. 2012, doi: 10.1007/S10705-011-9478-5.

[60] D. Seyhan, “Country-scale phosphorus balancing as a base for resources conservation,” *Resour Conserv Recycl*, vol. 53, no. 12, pp. 698-709, Oct. 2009, doi: 10.1016/J.RESCONREC.2009.05.001.

[61] E. Asmala and L. Saikku, “Closing a Loop: Substance Flow Analysis of Nitrogen and Phosphorus in the Rainbow Trout Production and Domestic Consumption System in Finland,” *AMBIO 2010 39:2*, vol. 39, no. 2, pp. 126-135, May 2010, doi: 10.1007/S13280-010-0024-5.

[62] J. Cooper and C. Carliell-Marquet, “A substance flow analysis of phosphorus in the UK food production and consumption system,” *Resour Conserv Recycl*, vol. 74, pp. 82-100, May 2013, doi: 10.1016/J.RESCONREC.2013.03.001.

[63] J. Hedbrant and L. Sörme, “Data Vagueness and Uncertainties in Urban Heavy-Metal Data Collection,” *Water, Air and Soil Pollution: Focus 2001 1:3*, vol. 1, no. 3, pp. 43-53, 2001, doi: 10.1023/A:1017591718463.

[64] A. M. Hanson and G. F. Lee, “Forms of Organic Nitrogen in Domestic Wastewater,” *J Water Pollut Control Fed*, vol. 43, no. 11, pp. 2271-2279, Aug. 1971, [Online]. Available: http://www.jstor.org/stable/25037233

[65] L. Loyon, “Overview of manure treatment in France,” *Waste Management*, vol. 61, pp. 516-520, 2017, doi: https://doi.org/10.1016/j.wasman.2016.11.040.

[66] X. Vecino, M. Reig, B. Bhushan, O. Gibert, C. Valderrama, and J. L. Cortina, “Liquid fertilizer production by ammonia recovery from treated ammonia-rich regenerated streams using liquid-liquid membrane contactors,” *Chemical Engineering Journal*, vol. 360, pp. 890-899, 2019, doi: https://doi.org/10.1016/j.cej.2018.12.004.

[67] Y. Hou, G. L. Velthof, J. P. Lesschen, I. G. Staritsky, and O. Oenema, “Nutrient Recovery and Emissions of Ammonia, Nitrous Oxide, and Methane from Animal Manure in Europe: Effects of Manure Treatment Technologies,” *Environ Sci Technol*, vol. 51, no. 1, pp. 375-383, Jan. 2017, doi: 10.1021/acs.est.6b04524.

[68] “Agricultura: valor de la producción por región en España,” 2020. https://es.statista.com/estadisticas/1219154/agricultura-valor-de-la-produccion-en-espana-por-region/ (accessed Aug. 11, 2022).

[69] “European Sustainable Phosphorus Platform - News Archive,” 2022. https://www.phosphorusplatform.eu/scope-in-print/news#_Toc108595806 (accessed Aug. 13, 2022).

[70] “Status of the Regulation (EU),” Feb. 25, 2022. https://www.staphyt.com/2022/02/25/point-sur-la-reglementation-ue-n-2019-1009-relative-aux-matieres-fertilisantes-et-aux-biostimulants/ (accessed Aug. 13, 2022).

[71] D. Bolzonella, F. Fatone, M. Gottardo, and N. Frison, “Nutrients recovery from anaerobic digestate of agro-waste: Techno-economic assessment of full scale applications,” *J Environ Manage*, vol. 216, 2017, doi: 10.1016/j.jenvman.2017.08.026.

[72] V. Lebuf, F. Accoe, C. Vaneeckhaute, E. Meers, E. Michels, and G. Ghekiere, “Nutrient recovery from digestates: techniques and end-products,” *Venice 2012: fourth international symposium on energy from biomass and waste*, no. 1, p. 18, 2012, doi: March 15, 2014.

[73] C. Vaneeckhaute, E. Meers, E. Michels, G. Ghekiere, F. Accoe, and F. M. G. Tack, “Closing the nutrient cycle by using bio-digestion waste derivatives as synthetic fertilizer substitutes: A field experiment,” *Biomass Bioenergy*, vol. 55, pp. 175-189, 2013, doi: 10.1016/j.biombioe.2013.01.032.

[74] W. Verstraete, P. van de Caveye, and V. Diamantis, “Maximum use of resources present in domestic ‘used water,’” *Bioresour Technol*, vol. 100, no. 23, pp. 5537-5545, Dec. 2009, doi: 10.1016/J.BIORTECH.2009.05.047.

[75] C. Vaneeckhaute *et al.*, “Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification,” *Waste and Biomass Valorization*, vol. 8, no. 1. Springer Netherlands, pp. 21-40, Jan. 01, 2017. doi: 10.1007/s12649-016-9642-x.

[76] C. Vaneeckhaute *et al.*, “Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification,” *Waste and Biomass Valorization 2016 8:1*, vol. 8, no. 1, pp. 21-40, Aug. 2016, doi: 10.1007/S12649-016-9642-X.

[77] R. Basosi, A. Fierro, and S. Jez, “Mineral Nitrogen Fertilizers: Environmental Impact of Production and Use,” 2014. [Online]. Available: https://www.researchgate.net/publication/264124538

[78] “Homepage | EU Nitrogen Expert Panel,” 2014. http://www.eunep.com/ (accessed Aug. 23, 2021).

[79] Q. A. Panhwar, A. Ali, U. A. Naher, and M. Y. Memon, “Fertilizer Management Strategies for Enhancing Nutrient Use Efficiency and Sustainable Wheat Production,” *Organic Farming: Global Perspectives and Methods*, pp. 17-39, Jan. 2019, doi: 10.1016/B978-0-12-813272-2.00002-1.

[80] X. Zhang, E. A. Davidson, D. L. Mauzerall, T. D. Searchinger, P. Dumas, and Y. Shen, “Managing nitrogen for sustainable development,” *Nature 2015 528:7580*, vol. 528, no. 7580, pp. 51-59, Nov. 2015, doi: 10.1038/nature15743.

[81] “National energy and climate plans | European Commission,” 2021. https://ec.europa.eu/info/energy-climate-change-environment/implementation-eu-countries/energy-and-climate-governance-and-reporting/national-energy-and-climate-plans_en (accessed Aug. 24, 2021).

[82] R. H. Socolow, “Nitrogen management and the future of food: Lessons from the management of energy and carbon,” *Proc Natl Acad Sci U S A*, vol. 96, no. 11, pp. 6001-6008, May 1999, doi: 10.1073/PNAS.96.11.6001/ASSET/FA4B2334-A807-43C8-8801-3BDEFAE3D148/ASSETS/GRAPHIC/PQ1090896001.JPEG.

[83] “Estimates of European food waste levels | FAO,” 2016. http://www.fao.org/family-farming/detail/es/c/412647/ (accessed Aug. 24, 2021).

[84] E. Cowling *et al.*, “Optimizing Nitrogen Management in Food and Energy Production and Environmental Protection: Summary Statement from the Second International Nitrogen Conference,” *ScientificWorldJournal*, vol. 1, p. 320976, 2001, doi: 10.1100/tsw.2001.481.

[85] D. Tilman, K. G. Cassman, P. A. Matson, R. Naylor, and S. Polasky, “Agricultural sustainability and intensive production practices,” *Nature*, vol. 418, no. 6898, pp. 671-677, 2002, doi: 10.1038/nature01014.

[86] N. Pelletier and P. Tyedmers, “Forecasting potential global environmental costs of livestock production 2000-2050,” *Proc Natl Acad Sci U S A*, vol. 107, pp. 18371-18374, Oct. 2010, doi:

10.1073/pnas.1004659107.

[87] “Nitrogen on the table: the influence of food choices on nitrogen emissions and the European environment | PBL Netherlands Environmental Assessment Agency,” 2016. https://www.pbl.nl/en/publications/nitrogen-on-the-table-the-influence-of-food-choices-on-nitrogen-emissions-and-the-european-environment (accessed Aug. 24, 2021).

[88] H. Westhoek *et al.*, “Food choices, health and environment: Effects of cutting Europe’s meat and dairy intake,” *Global Environmental Change*, vol. 26, no. 1, pp. 196-205, May 2014, doi: 10.1016/J.GLOENVCHA.2014.02.004.

[89] “EU actions against food waste,” 2021. https://ec.europa.eu/food/safety/food-waste/eu-actions-against-food-waste_en (accessed Aug. 24, 2021).

[90] “Farm to Fork Strategy,” 2022. https://ec.europa.eu/food/horizontal-topics/farm-fork-strategy_en (accessed Aug. 24, 2021).

[91] “World Population Prospects: The 2017 Revision,” 2017. https://www.un.org/development/desa/publications/world-population-prospects-the-2017-revision.html

Chapter 4

4 Chapter 4: Advanced hybrid system for ammonium valorization as liquid fertilizer from treated urban waste waters: validation of natural zeolites pretreatment and liquid-liquid membrane contactors at pilot plant scale

4.1 Introduction

United Nations projections predict that the global population will reach 8.6 billion by 2030 and 9.8 billion by 2050 [91]. This growth in population and consumption will put immense pressure on the food industry to increase production, requiring more intensive agricultural practices and higher usage of land, water, energy, and fertilizers [92]. Non-renewable mineral fertilizers, such as N, P, K, and Mg, currently form the basis of modern agriculture. However, crops only absorb 31-49% of supplied N and 35% of supplied P.

Wastewater treatment has long been seen as a health and environmental concern. Traditional wastewater treatment technologies, established in the early 20th century, were designed to remove organic pollutants and nutrients like nitrogen and phosphorus, but are not considered sustainable [93]. Recently, the perspective on wastewater has shifted, transforming from a health concern to a valuable source of nutrients for fertilization. This change has been driven by phosphorus scarcity and the environmental impact of nitrogen-based fertilizer production [94].

As a result, research has been focused on developing new treatments and procedures to turn wastewater treatment plants from energy consumers into energy recovery and nutrient production facilities [95]. Various alternative technologies have been explored for ammonium removal from urban and industrial wastewater, including ion exchange, adsorption, biological technologies, air stripping, chemical precipitation, chemical oxidation, and membrane-based technologies. Each method has its advantages and limitations, including cost, removal rate, sensitivity to pH and temperature, and the introduction of new pollutants [96]. However, when promoting nutrient circularity within urban and industrial water cycles, only certain technologies or combinations of technologies (e.g., hybrid processes) are deemed suitable.

Ion exchange using low-cost sorbents, i.e., natural zeolites [97], and synthetic [98] appear to be a promising option due to the capability to recover ammonium from treated wastewaters after an ion exchange reaction after the exchange of the NH_4^+ in solution by the counter ion (e.g., typically Na^+) of the zeolite. The first removal option is the recovery from the main streams of the conventional activated sludge (CAS) systems or the main streams after a treatment with An-MBR (anaerobic membrane bioreactor) when residual values of NH_4^+ may range between 5 to 60 mg/L. A second option of ammonium recovery is centered in its recovery from the sidestreams generated in the anaerobic digestion of sewage sludge, where ammonium concentrations between 600-900 mg/L NH_4^+ are expected to be treated [99]. Once the zeolites are saturated with NH_4^+ ions, zeolites can be regenerated with NaCl, KCl, NaOH or mixtures of them and then a second stage is needed to recover the N-species (NH_3) present in regeneration brines as a valuable pure by-product (e.g., ammonium salts as fertilizers [100] or ammonia [66]). It has been also reported a wide variety of sorption capacity towards ammonium, ranging from 2- 43.5 mg N-NH_4/L depending on the zeolite properties and the composition of the treated stream (e.g., ammonium concentration and concentration of competing ions) [96], [101]. Besides, the cost of zeolites is much lower than the cost of synthetic zeolites or polymeric sorbents, which provides the potential to be implemented at full scale facilities [96]. However, the application of zeolites at full scale still must face and overcome several challenges. One of the most important is the regeneration stage and the chemicals used (i.e., NaOH, NaCl or KCl) required to maximize nitrogen recovery. In order to achieve recovery efficiencies up to 90-98% doses of NaCl up to 50-80 g/L may be required, which would mean 50-60% of the operational expenditure of the process [102]. Other main issue to be addressed is the presence of competitive ions such as potassium, calcium or magnesium, which are also adsorbed by the zeolites, decreasing the exchange capacity towards ammonium. This effect will be increased treating anaerobic digestion centrates due to concentrations of K, Ca and Mg may reach, on average, values of 350 mg/L, 300 mg/L and 90 mg/L, respectively [103]. Moreover, the lifespan of the zeolites is still one of the key parameters to define the operating cost of this technology and it is also one of the parameters scarcely evaluated in literature. It has been reported that zeolites can be regenerated 12 times with 0.6 M NaCl at pH 10 [104] without losing capacity but it has been also reported a loss of zeolite mass between 2.4 - 5.7 $\%_{weight}$ after 10 cycles of regeneration due to caustic attrition [105].

Once the zeolites are regenerated a N rich solution is produced. This solution must be treated in order to recover and valorize the ammonium. This way liquid-liquid membrane contactors (LLMC) appear as a promising technology to achieve this objective.

The LLMC is a novel and ecofriendly technique where two liquid phases are separated by a membrane and target specie is only transported by diffusion phenomena, due to phases do not mix between them [106]. For that, this technique allows ammonia recovery from wastewater effluents using an acid as stripping solution in several industrial applications [107]. Then, its transformation into ammonium salts is produced and they could be used as liquid fertilizers such as NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$ or $(NH_4)H_2PO_4$, among others [108]-[110].

Licon Bernal et al. and Sancho et al. [111], [112] studied the applicability of hollow-fiber membrane contactors for the recovery of ammonium from a synthetic regenerant solution, which was used as a surrogate for the liquid phase produced during the regeneration of loaded zeolites being applied in tertiary wastewater treatment. Results showed 95% ammonium recovery; therefore, the treated regenerant solution can be reused for zeolite regeneration reducing the operating costs. Garcia-González & Vanotti (2015) investigated the nitrogen recovery from swine manure using hollow-fiber membranes directly submerged into the ammoniacal manure. The investigation of the influence of pH adjustment and aeration rate of swine manure at different ammonium concentrations resulted in ammonium recovery rates up to 94% 47]. Lam e[113].

Investigations with membrane contactor at pilot scale have been conducted at Neugut WWTP (Switzerland). Process water from sludge dewatering deriving from different municipal WWTPs and a digester with codigestion of meat waste processing and containing 700-3,400 mg/l NH_4-N was treated by a pilot plant including three membrane stages in series with 120 m^2 total membrane surface area [114]. Sulphuric acid was recirculated through the lumen side of the hydrophobic hollow-fiber membranes [115]. Boehleret al. (2015) achieved elimination rates between 80% and 99% depending on the adjustment of pH value and temperature (up to pH 10.5 and 54 °C using caustic soda and heat exchange, respectively). A full-scale membrane contactor facility was implemented at Yverdon les Bains WWTP (Switzerland). The facility includes several pretreatment steps (alkali addition, heat exchanger and multiple filtration steps) and membrane modules in series. First operational experiences revealed about 70% nitrogen elimination when the pH value and temperature of the process water were adjusted to pH 9.7 and 40 °C, respectively [116].

The primary objective of this study is to evaluate the technical feasibility of utilizing natural zeolites and LLMCs (liquid-liquid membrane contactors) for recovering and repurposing ammonium from wastewater treatment plants (WWTPs) as a fertilizer. Zeolites were examined as an advanced pretreatment and concentration method prior to implementing LLMCs. Two separate streams were tested: WWTP effluent (diluted stream containing 50 mg N-NH_4/L) and anaerobic digestion centrates (concentrated stream containing 600-800 mg N-NH_4/L).

Initially, a laboratory-scale study was conducted to determine the optimal operating conditions using effluent mainstream wastewater from the Vilanova i la Geltrú (VNG) WWTP and a natural zeolite (ZEOCAT) with a particle size of 1.0-2.5 mm. Subsequently, these conditions were tested at a zeolite pilot plant situated at the VNG-WWTP, operating for one year. Following this, the pilot plant was transported to Murcia ESTE WWTP to operate with anaerobic digestion centrates for another year.

Upon evaluating the zeolites' superior performance in terms of cation capacity and concentration factor, the decision was made to concentrate the valorization efforts within the sidestream, as the lower flow rates and higher nitrogen concentrations would yield better economic performance. The operation of the LLMCs was aimed at producing a high-quality ammonium salt suitable for use as fertilizer, ensuring it is free of heavy metals and organic micropollutants.

4.2 Materials and Methods

4.2.1 Water characterization

Wastewater used at lab experiments was sampled from the effluent of VNG-WWTP. It was collected from the effluent of the secondary clarifier. On the other hand, the sidestream used at pilot scale was collected from Murcia ESTE WWTP. The composition of each sample was characterized measuring pH, conductivity, TSS and dissolved ions. pH and conductivity were measured with Crison pH meter GLP 22 and Crison EC-Meter GLP 31, respectively. Total suspended solids were measured according to the procedures described in the Standard Methods for the Examination of Water and Wastewater [117]. Analysis of cations such as Na+, NH4+, K+, Mg2+ and Ca2+ was carried out by means of cationic chromatograph Thermo Fisher Dionex ICS-1000. Analysis of anions such as anions Cl-, NO3-, PO43- and SO42- was carried out by means of a chromatograph Thermo Fisher Dionex ICS-1100.

4.2.2 Characterization of zeolites

Natural clinoptilolite zeolites were provided by ZEOCEM (www.zeocem.com), with two different granulometries: from 0.5-1.0 mm to 1.0-2.5 mm of mean particle diameter. Morphology and composition of the raw sample and samples after being operated in sorption and desorption cycles were studied by means of Field Emission Scanning Electron Microscope (FESEM) (JEOL JSM-7001F) and X-ray diffraction (XRD).

Prior to experiments, zeolites were washed with distilled water to remove dust and smaller particles. After that, zeolites were submerged in a 1 M NaOH and stirred in an orbital stirrer for 1 h. This process allows to activate the zeolite into its Na+ form, and thus increasing its ammonium exchange capacity. Finally, zeolites were washed out with distilled water to adjust pH to neutral values (7-8) and loaded in the fixed-bed columns.

4.2.3 Column laboratory experimental setup

The lab-scale experimental setup consisted of two fixed-bed columns with 18.7 cm high and 22.6 mm internal diameter, each column had glass wool at the bottom to prevent zeolites from running off. Furthermore, inert sand was added until filling 10% of the column to promote flow distribution. Finally, column was loaded with 67 grams of zeolite.

During the adsorption phase, feed stream entered from the bottom of the column and left the column from the top. When the zeolites were exhausted and a regeneration was required, a first step of counter current (from top to bottom) washing at 4 times feed flow was developed in order to expand the zeolite bed. After that, the regeneration took place from bottom to top (co-current). Finally, once the zeolite was regenerated a last step with Milli-Q water in the same flow conditions as adsorption was carried out in order to adapt the zeolite bed.

In order to determine the porosity of the zeolites column beds once packed, a 10 mL lab cylinder was tared and a certain number of zeolites (W_0) were poured into and the occupied volume was noted ($V_{zeolite}$). Distilled water was then added until the 10 mL level mark. It was then stirred for 1 h in an orbital shaker to compact the zeolites. Finally, excess water was removed until the level matched the level of zeolites, then the cylinder was weighted again (W_1), the difference between both is the weight of water (W_{water}) and thus the volume of water (V_{water}) was estimated. The porosity of the beds was estimated using Eq 6-7:

$$W_0 - W_1 = W_{water} \approx V_{water} \qquad \text{Eq. (6)}$$

$$\frac{V_{water}}{V_{zeolite}} \cdot 100 = porosity \qquad \text{Eq. (7)}$$

Porosity of the columns used in the column experiments were 0.42 for experiments with 2.5 mm zeolite and 0.39 for 0.1 mm zeolite mean diameter, respectively.

4.2.3.1 Experimental design

Mainstream water was used for this first set of experiments at lab-scale. In this case, in order to maximize the nitrogen recovered, different flow rates at the sorption and regeneration steps were evaluated. A total of four experiments, each of which was carried in duplicate, tested different couples of sorption and regeneration flow rates. Each experiment consisted in an adsorption and a regeneration step and between both phases Milli-Q water was circulated counter current for 10 minutes to rinse the column. The experimental conditions for each of the experiments are summarized in Table 8.

Table 8 Sorption – desorption flows for each test.

Experiment	Sorption flow (BV/h)	Regeneration flow (BV/h)
4-2	4.1 ± 0.3	2.0 ± 0.2
4-0.8	3.9 ± 0.1	0.8 ± 0.1
10-5	10.1 ± 0.1	5.1 ± 0.3
10-2	9.9 ± 0.1	± 0.2

In order to achieve optimal regeneration, 11 regenerant solutions were tested al lab-scale, hence a certain amount of zeolite was loaded and saturated using the fixed-bed configuration set-up.

Thus, to study the regeneration process 67 g of zeolite were loaded in a column of 18.7 cm high and 22.6 mm internal diameter. After that, zeolites were fed with VNG-WWTP effluent until saturation was achieved. It was considered that the breakthrough point was reached when the concentration of N-NH$_4$ measured at the effluent was higher than 20% of N-NH4 at the influent (C/C$_0$=0.2). For an influent with 50 mg/L N-NH4, $C/C_0=0.2$ matched 10 mg/L of $N\text{-}NH_4$ in the effluent which was the threshold established by WW Directive (91/271/EEC) for sensitive zones. From the operating point of view, breakthrough point may be surpassed upon reaching $C/C_0=1$ which is the saturation point. The total mass of loaded zeolite was split into 11 fractions of 5.5 g and put into conical flasks, in which 55 mL of regenerant solution was poured (maintaining a ratio of 1:10 $g_{zeolite}$ /mL regenerant). Regenerant solutions were based on NaOH (0.05; 0.1 and 0.5 mol/L), NaCl (1; 5; 10 and 20 g/L) or a mixture of both substances (0.01 mol NaOH/L and 1 g NaCl L; 0.01 mol NaOH/L and 20 g NaCl/L; 0.1 mol NaOH/L and 1 g NaCl/L; 0.1 mol NaOH/L and 20 g NaCL). These conical flasks were shaken for 24 hours, and the supernatant was finally collected and analyzed by ion chromatography.

4.2.4 Zeolites pilot column experimental setup

Considering the results achieved at lab scale, a pilot plant with 1 m3/h of nominal capacity was designed, built and installed in VNG-WWTP to operate for a year and then moved to Murcia ESTE WWTP to operate another year. Feed water for this pilot plant consisted of VNG-WWTP effluent as mainstream water and Murcia Este Centrates, as sidestream water. The feed stream was pre-treated by a filtration system based on a glass filter (0.5-1.0 mm) and an ultrafiltration unit with 50 - 60 kDa size cut-off working in dead-end configuration. Ultrafiltered water was then fed to the zeolite fixed-bed columns as can be seen in Figure 9.

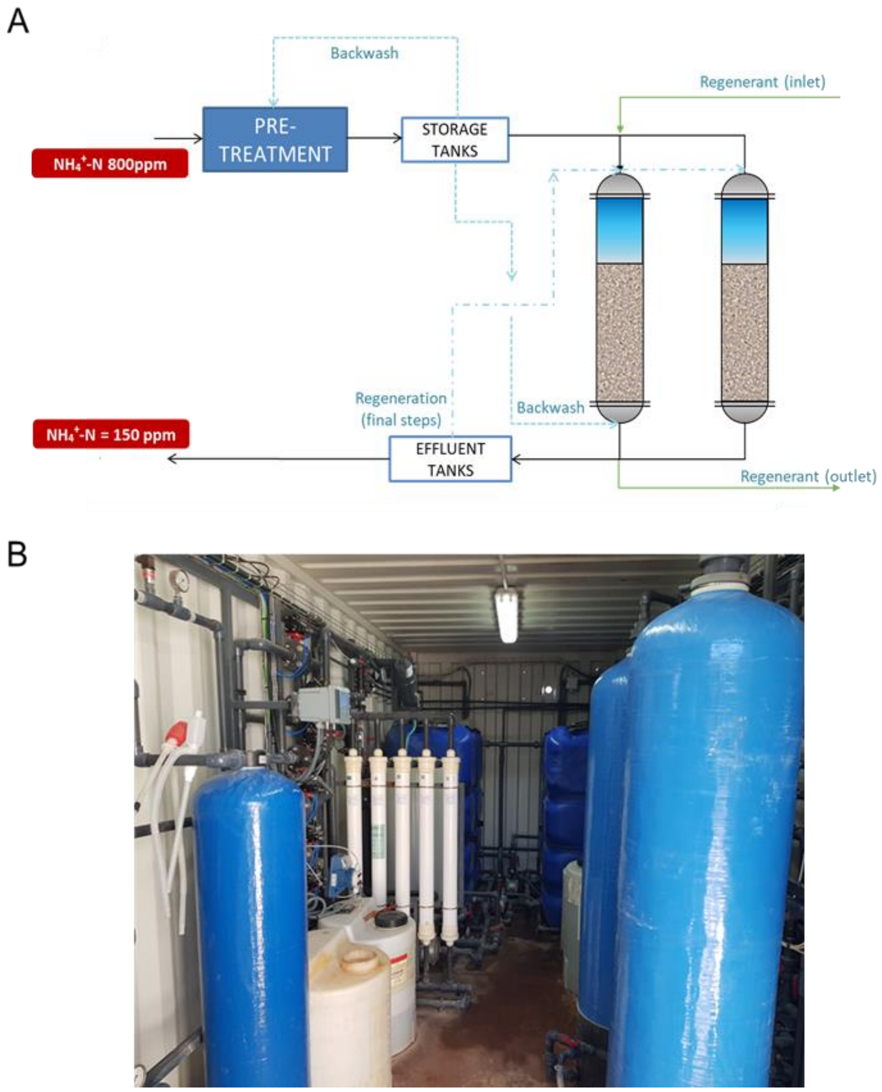

Figure 9 a) schematic flow diagram of the pilot plant; b) Photograph of the pilot plant.

100 kg of zeolites (provided by ZEOCEM with two granulometries 0.5 - 1.0 and 1.0-2.5 mm mean particle diameter) were loaded in each of two columns, which had a capacity of 200 L. It was meant to test both granulometries since the lower the size the higher capacity. However, it can also increase operating problems. These columns were designed to provide maximum operating flexibility. This means that by means of electro valves, it could be operated with columns either in series or parallel or even with only one column.

A 150 L high-density polyethylene tank was used to collect the feed flow and continuously feed the pre-treatment system. Permeate stream from UF unit was then stored in two high-density polyethylene tanks with a total volume of 1500 L and subsequently was pumped to the zeolite columns. Ammonium free water was stored in two high-density polyethylene tanks with a total volume of 1500 L to be used later to prepare the regenerant solution. All reservoir tanks were covered but were vented to maintain atmospheric pressure. A process logic controller (Simatic S7-1200 controller, SIEMENS) was employed to control, operate, and log operational data from the pilot plant.

The zeolites pilot plant was operated continuously for a whole year with each different stream. Each experiment consisted in a sorption until achieving the breakthrough and the consequent regeneration of zeolites. Sorption tests were focused on assessing the cation exchange capacity towards N-NH4, while keeping an effluent with low concentration of N-NH4 (< 1 ppm N-NH4). Once the zeolites surpassed the breakthrough point or reached the saturation point, they were regenerated to recover its ion exchange capacity.

4.2.4.1 Experimental design in mainstream and sidestream

In this study, the performance of zeolite in ammonium recovery from both mainstream and sidestream processes of WWTPs was evaluated. The comparison was based on the adsorption efficiency and capacity of the zeolites under different operating conditions.

A total of four mainstream and four sidestreams adsorption experiments were conducted (Table 9). The operating conditions for each experiment were kept constant in order to assess the stability of the process and assess the decrement of the CEC through different cycles.

Mainstream experiments were conducted by only one column (100 kg zeolites) in order to diminish the experimental time. Zeolites were from ZEOCAT with a particle size of 1.0-2.5 mm and fed at a constant flow of 400 ±50 L/h (8.3 ± 1.01 BV/h) with a centrifuge pump (MS 100/0.55).

Regeneration tests were developed at 700 ± 50 L/h (14.5 ± 1.01 BV/h) and focused on maximizing the ammonium recovery. To do so, the regenerant solution selected was NaOH 0.5 M to guarantee high concentration of sodium and high pH to maximize the recovery. In this experiment, ammonium was measured at the influent and the effluent of the columns as well as during the regeneration process to assess the mass balances for nitrogen.

The regenerant solution was not sampled during the regeneration process. Instead, the whole regenerant solution was stored and analyzed at the end of the process as one homogeneous sample.

Regarding operational conditions with sidestream, flowrate to zeolite columns (ZE) was at 400±50 L/h. Zeolites were from ZEOCAT with a particle size of 0.5-1.0 mm. Regeneration of columns was carried out with 350-500 L of a solution of NaOH 0.2 M. The regenerated stream was stored in a 1 m3 container which was full after 2-3 zeolite experiments. After that an experiment of membrane contactors was carried out.

Table 9 Zeolites experimental design.

	Mainstream	Sidestream
Adsorption - desorption cycles	4	4
Granulometry (mm)	1.0-2.5	0.5-1.0
Adsorption flow (L/h)	400	400
Regeneration flow (L/h)	700	700
Regenerant concentration (NaOH) (M)	0.5	0.2

4.2.5 Liquid-liquid membrane contactors experimental setup

LLMC unit separates two liquid phases by hydrophobic porous hollow fiber membrane (3M). The LLMC system for ammonia recovery, working in a closed-loop configuration, can be described as follows (Figure 10): ammonia-rich wastewater is fed on the feed side (lumen side) while the acid stripping solution is fed on the on the opposite side (shell side). Then, the ammonia recovery process inside the LLMC takes place: ammonia gas diffuses from the feed stream to the feed-membrane interface, volatilizes inside it and then diffuses through the membrane pore of the membrane to reacts with the acid stripping solution on the shell side. In this sense, hydrophobic porous membranes provide a safe technology to assure ammonia recovery from WWTP since the potential organic and inorganic micro-pollutants transport on the generated by-product is avoided [111], [118].

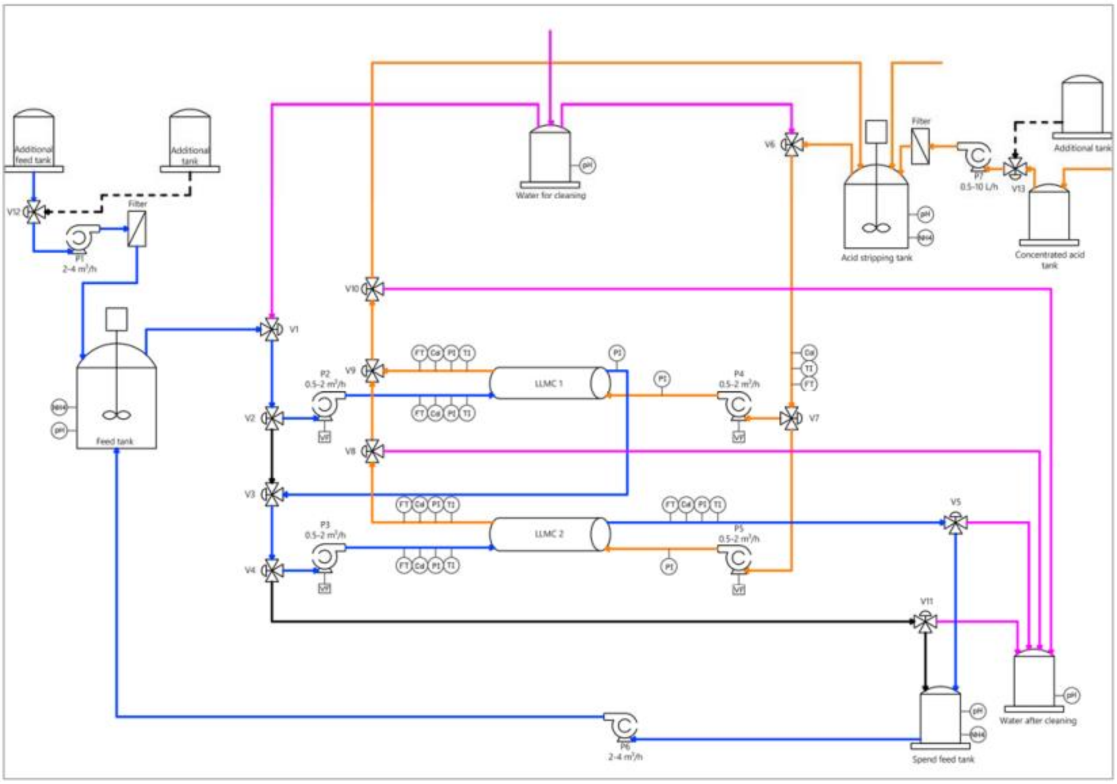

Figure 10 Scheme of the LLMC pilot plant.

The possibility of using different acids allows to produce fertilizers on demand and consequently to increase their potential market penetration. In this case, using HNO_3 (0.4 M), as the acid in the stripping solution, produces a nitrogen fertilizer (which is a single-nutrient fertilizer); whereas when H_3PO_4 is used as a stripping solution, a nitrogen-phosphorous fertilizer (which is a multi-nutrient fertilizer) is obtained. There is a control loop that can maintain the pH at a desired value adding the acid HNO_3 (58%) through the time. In this case, the set point was stablished in order to keep the pH at 3.4 and maximize the mass transfer. On the other hand, an exhausted effluent, free of ammonia is also obtained during the LLMC process. This stream, at high pH, can be reused for the zeolite's regeneration [66], [119].

Since water transport is an unwanted process associated with ammonia transport due to differences in vapor pressure between the feed side and the acid side, drying was performed after conducting an experiment.

The drying time was around 8 hours at 40ºC with a flow rate of 34 m³/h. The maximum gas pressure was 0.70 kg / cm². For this reason, the gas line had pressure, temperature and flow sensors.

Table 10 shows the main parameters considered for the design and operation of the unit.

Table 10 Operation parameters of the membrane contactors unit

Parameter	Value	Units
Feed/ acid volume ratio storage	100	L_{feed}/L_{acid}
Feed and acid flowrates	0.5 – 2	m3/h
Temperature	18 – 25	ºC
Feed pH	>11	
Operating voltage	380	VAC-50 Hz-3F+N
Power	27.7	kW

4.2.5.1 Experimental design

Prior to testing the LLMCs, two fully characterized experiments were conducted to validate their performance. These experiments provided a solid foundation for understanding the capabilities and limitations of the system, enabling further optimization of the process.

All the experiments described in this part were carried out with regenerant solution from zeolites treating sidestream, which produced a regenerant stream with 4-5 g/L N-NH_4. However, the first one only has 1.3 g/L N-NH_4 due to it was stored at pH 12 for a long time before the experiment which led to N loses as ammonia gas.

Following the successful completion of these initial experiments, the system operated in batch mode (producing a total of 9 lots of fertilizer), allowing for analysis only at the beginning and end of each experiment. N-NH_4 concentration was measured using kits during the experiments on the feed side to determine the end of the operation. Kits cannot be used in the acid side due to acidic conditions and high concentrations, requiring distillation and titration. Each experiment started with 10 L of HNO_3 0.4 M in the acid side in order to start the operation, after that, the control loop added HNO_3 (58%) in order to keep the pH at 3.4 and maximize the mass transfer. Full characterizations (N-NH_4, NO_3, ions, heavy metals, and OMPs) were conducted for each batch of fertilizer produced. After each experiment, the membrane underwent a drying procedure to remove any potential water in the pores, preventing pore wetting in subsequent experiments.

Additionally, due to the scale factor, 2 or 3 zeolite experiments were needed to produce 1m3 of N-rich stream required to start the liquid-liquid membrane contactor (LLMC) tests. On the other hand, one of the most critical factors to monitor and avoid is pore wetting. Although the membranes are hydrophobic, pores may become wet during operation. This issue depends on the pressure and the selected acid. If too many pores become wet, constant water transport through the membrane occurs, leading to quality issues in the final product.

The summary of the experiments developed with the LLMCs are displayed in Table 11.

Table 11 LLMCs experimental design

	Experiment		
	1	2	3-9
$N\text{-}NH_4$ feed concentration (g $N\text{-}NH_4$/L)	1.3	4-5	4-5
Feed pH	12	12	12
Acid	HNO_3	HNO_3	HNO_3
Feed flow (L/h)	500	500	500
Acid flow (L/h)	500	500	500
Acid side initial volume (L)	10	10	10
Feed side initial volume (L)	1000	1000	1000
Sampling points	Along the whole experiment	Along the whole experiment	Initial-final

4.2.6 Sampling and analytical methods

The pilot plant was equipped with two real-time ammonium sensors (AN-ISE SC, Hach Lange) - one at the inlet of the columns and another at the outlet - to determine the ammonium uptake of the zeolites by calculating the difference between the two sensors. The PLC (programmable logic controller) was responsible for logging and controlling the measurements of both probes. When the concentration of the effluent matched that of the influent, the PLC initiated the regeneration process. Every day, two samples were taken from the influent and the effluent and sent to IRTA (Institute of Agrifood Research and Technology) for analysis. All samples were analyzed using ion chromatography (IC) to measure the concentration of soluble cations (Ca, Na, K, Mg) and anions ($PO4_3$, Cl, SO_4), as well as distillation and titration to measure $N\text{-}NH_4$. Moreover, heavy metals (Al, Cr, Ni, Cu, Zn, Cd, Hg, Pb) were quantified in each ammonium-rich solution produced during column regeneration using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The content of organic micropollutants in these ammonium-rich streams, including Celestolide, Galaxolide, Tonalide, Ibuprofen, Naproxen, Diclofenac, 4-Octylphenol, 4-Nonylphenol, Bisphenol A, and Triclosan, was analyzed using gas chromatography coupled with mass spectrometry. Additionally, Carbamazepine, Diazepam, Erythromycin, Fluoxetine, Roxithromycin, Sulfamethoxazole, Trimethoprim, Estrone, Estradiol, and Ethinylestradiol were analyzed using liquid chromatography coupled to mass spectrometry.

For the calculation of ammonium uptake, a plot (see Figure 11, a) between the concentrations of the removed ions in the effluent (ordinate) versus the effluent volume (abscissa) was drawn. The breakthrough is defined as the point where the unwanted ions in the effluent appear in appreciable quantities. The extent of breakthrough increases to a point where no more ion exchange occurs, that is, the effluent contains the original concentration of the ions. This point indicates the stage at which the ion exchanger is completely exhausted and must be regenerated or replaced. For the ammonia recovered, a plot (see Figure 11, b) between the concentrations in the effluent (ordinate) versus the effluent volume (abscissa) is drawn.

Other relevant parameters were such as concentration factor and % of recovery, which were calculated as follows:

The concentration factor (CF) was calculated according to the expression indicated according to equation 2:

$$CF = \frac{q_{des} \cdot \frac{m_Z}{V_{reg}}}{C_0} \qquad (3)$$

The recovery percentage ($\%_{recovery}$) was calculated using equation 3:

$$\%_{recovery} = \frac{q_{des}}{\mathrm{CEC}} \cdot 100 \qquad (4)$$

Where C_0 is the initial concentration of the ion in the water (mg/L), m_Z is the mass of zeolite in the column (g), V_{reg} is the volume of regenerating solution needed in the desorption process (L), *CEC* is the adsorption capacity during the adsorption (g N/ $g_{zeolite}$) and q_{des} is the amount of N recovered in the desorption (g N/ $g_{zeolite}$).

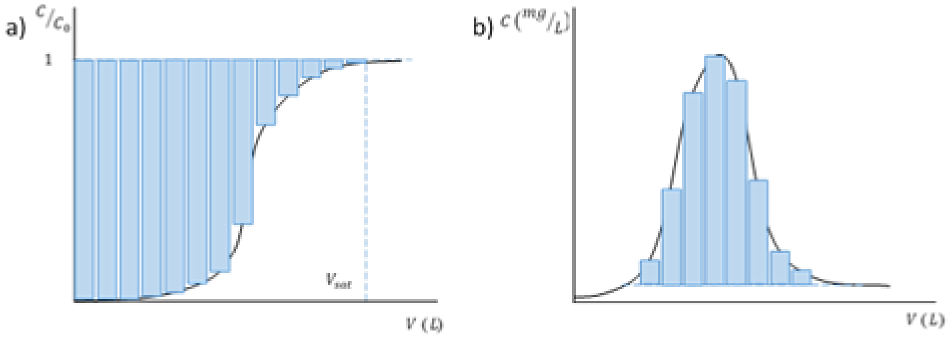

Figure 11 Calculations of N uptake and recovery.

4.3 Results & discussion

4.3.1 Water characterization

Table 12 display the results of the wastewater characterization from mainstream and sidestream.

Table 12 Water characterization

Parameter	Mainstream	Centrates
Conductivity (mS/cm)	2.2	10.1
pH	8.4	8.6
Ca (mg/L)	222	106.5
COD (mg/L)	66	777.3
K (mg/L)	28	545.8
Mg (mg/L)	48	29.0
N-NH_4 (mg N/L)	66	874.3
P-PO_4 (mg P/L)	1	29.0
SO4 (mg/L)	151	168.4
TSS (mg/L)	30	800

4.3.2 Evaluation of the zeolite's regeneration process at lab-scale

4.3.2.1 Optimization of zeolites columns operating conditions at lab-scale

The adsorption results at feed flows of 4 and 10 BV/h, and its corresponding desorption results are displayed in Table 13. Considering these data, mass balances were carried out to assess the recovery effectiveness of the process, the concentration factor (CF) and select the best combination of feed and regeneration flows.

Table 13 Recovery efficiency at lab scale at different flow rates.

	Adsorption		Regeneration			
Experiment	Flow (BV/h)	CEC (mg/gze)	Flow (BV/h)	Nrecovered (mg/gze)	Concentration factor	Recovery (%)
4-2	4.1 ± 0.3	6.4 ± 1.1	2.0 ± 0.0	3.7 ± 0.2	4.8 ± 0.3	59.6 ± 12.7
4-0.8	3.9 ± 0.1	4.4 ± 1.3	0.8 ± 0.0	2.7 ± 0.9	3.4± 1.3	60.2 ± 17.6
10-5	9.8 ± 0.1	5.1 ± 0.2	5.1 ± 0.2	3.1 ± 0.4	2.4 ± 0.2	61.2 ± 10.2
10-2	9.9 ± 0.1	7.6 ± 0.2	1.9 ± 0.1	5.0 ± 0.9	5.3 ± 0.6	66.1 ± 13.8

Considering the efficiency of recovery there was no big difference from one condition to another, except for the adsorption flow of 10 BV/h and a regeneration flow of 2 BV/h which provided approximately 6% higher percentage of recovery. However, there is a direct relation between flowrate and capacity of zeolites [120], [121]. As it is displayed in Table13 selecting a feed flowrate of 10 BV/h allowed to achieve exchange capacities towards the ammonium of 9.8-9.9 mg N-NH4/mg of zeolites which has a direct impact in the operating costs. Thus, for the regeneration, it will always be preferred a flow 5 time higher than the feed to maximize the recovery.

The hydraulic retention time (HRT) influences the operating ammonium exchange capacity when filtering wastewater through a zeolite packed column. Beler-Baykal et al. [122] investigated the effect of the hydraulic retention time within the range 0.5-12 min. They did not recommend a hydraulic retention time of <3 min because the breakthrough would occur too fast, and they eventually selected a retention time of 5 min for their experiments. Beler-Baykal and Guven [123] found that a longer hydraulic retention time (within the interval 3-10 min) delayed the breakthrough but that most ammonium was adsorbed after 5 min. In this work, HRT from 7 to 13 min were tested. It has been assessing that in these ranges there are no significant differences since from 5 minutes onward 80% of the N was extracted. Considering all the experiments, it can be concluded that the mean HRT value is around 10 min which will be the desired value.

4.3.2.2 Optimization of regenerant solution at lab scale

When the zeolite is exhausted, the loading is interrupted and brine is pumped through the column. Both upflow [124], [125] and downflow [126] applications of the brine have been described. Many authors have used sodium chloride with the concentration 0.1-0.6 M NaCl as the regeneration brine [124]-[126]. The time needed for satisfactory regeneration of the exchanger depends on the concentration and pH of the brine. Koon and Kaufmann investigated the impact of pH on the regeneration performance. At pH 11.5 and 2% regeneration brine, 20 BV of regeneration brine were needed, corresponding to 1.3 h of regeneration. Koon and Kaufmann ([124]) found that the regeneration performance was independent of the flow rate within the interval 4-20 BV/h and chose 15 BV/h. Similar results were observed by Semmens and Porter [127], who varied the regeneration flow between 12 and 20 BV/h and continued with the regeneration flow 12 BV/h for 1 h, which is in line with the findings in this work.

When pH was increased to 12 and 12.5, 20 and 10 BV of brine were needed, respectively. In both cases, 1.2% regeneration brine was sufficient. Ødegaard [128] recommended a mixture of sodium chloride and sodium hydroxide as a regeneration brine. This would decrease the need for brine by 90% compared to using only sodium chloride. However, the advantage of using caustic regeneration brine must be put in relation to the disadvantage of possible zeolite attrition [124].

The results obtained from batch desorption tests demonstrated that ammonium recovery can be achieved by providing sodium ions from NaOH, NaCl, or a combination of both. As seen in Figure 12, 90% of N recovery can be achieved with concentrations of NaOH 0.5 M, NaOH 0.1 M, and 20 g NaCl/L. Although NaOH 0.5 M provided more consistent results, possibly due to the pH increase, the optimal regenerant solution was a mixture of NaOH 0.1M and 20 g/L of NaCl, owing to its lower cost: 3 €/kg N recovered with NaOH 0.5 M vs. 1.5 €/kg N recovered with NaOH 0.1M and 20 g/L of NaCl.

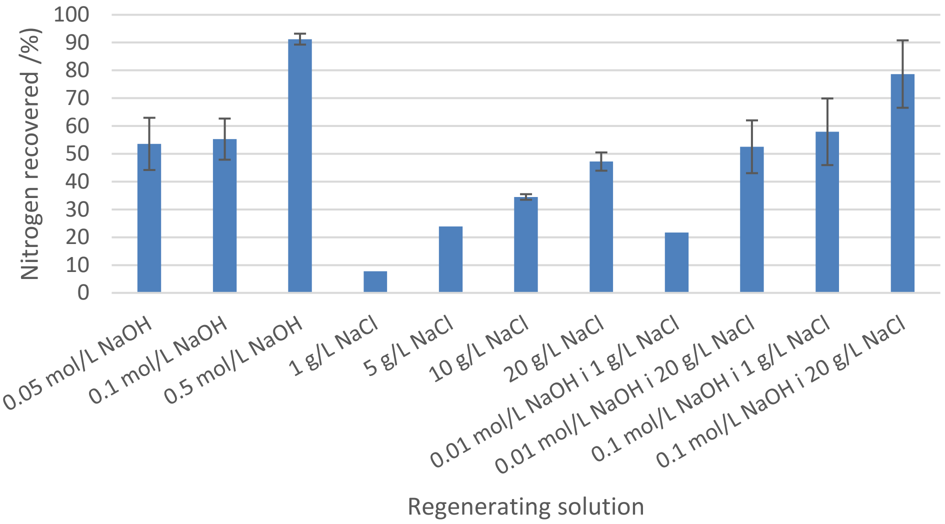

Figure 12 Efficiency of the regenerant solutions (%) using samples from loaded zeolites in column experiments

4.3.3 Zeolites pilot plant performance treating mainstream and sidestream

In this section, the performance of the zeolite at pilot-scale in ammonium recovery from both mainstream and sidestream processes of WWTPs is discussed. The comparison is based on the adsorption efficiency, and capacity of the zeolites under different operating conditions.

The adsorption efficiency of zeolites in mainstream processes was found to be generally lower than in sidestream processes. This is attributed to the low ammonium concentrations. In contrast, sidestream processes typically have higher ammonium concentrations which increase the cation exchange capacity.

Main results for zeolites treating mainstream and sidestream are displayed in Table 14 and 15, respectively.

Table 14 Results from zeolites in mainstream

Mainstream				
Cycles of operation	1	2	3	4
Inlet mean N-NH$_4$ (mg/L)	58,9	66,5	57,9	55,9
CEC (g N-NH$_4$/kg zeo)	5,3	5,3	4,5	3,2
N recovered (g N-NH$_4$/kg zeo)	3,9	3,7	4,1	2,9
Regeneration level (%)	74	70	92	90
CF	15,7	16,3	19,8	13,8

Table 15 Results from zeolites in sidestream

Sidestream				
Cycles of operation	1	2	3	4
Inlet mean N-NH$_4$ (g/L)	0,74	0,68	1,12	0,98
CEC (g N-NH$_4$/kg zeo)	21,1	15,3	11,9	8,9
N recovered (g N-NH$_4$/kg zeo)	8,2	19,4	10,25	10,4
Regeneration level (%)	38,8	126,4	86,1	117,5
CF	6,5	3,0	0,9	1,9

As it can be seen in sidestream there are some points were the N recovered is higher than the N fed in that cycle, in order to understand these results is necessary to assess the overall process efficiency which is depicted in Table 16.

Table 16 Overall process efficiency

	Mainstream				
Cycles	1	2	3	4	total
N fed (mg N-NH$_4$)	526	526	446	324	1823
N recovered (mg N-NH$_4$)	388	367	411	292	1459
Overall recovery (%)					80
	Sidestream				
Cycles	1	2	3	4	total
N fed (mg N-NH$_4$)	2112	1535	1190	885	5722
N recovered (mg N-NH$_4$)	820	1940	1025	1040	4825
Overall recovery (%)					84

As observed, there is a significant impact on the cation exchange capacity (CEC) when treating sidestream compared to mainstream. In sidestream treatment, it was possible to achieve CEC values of around 20 mg N-NH$_4$/g, which is one of the most critical factors to consider when scaling the technology. Meanwhile, for the mainstream the highest value reached is 5.3 mg/g. Shaobin Wang and Yu[129] reviewed different natural zeolites with different treatments and measured the CEC. They reported that the CEC could range from 2 to 30 mg N-NH_4/g. More specifically, they reported data form a similar zeolite which is the NaOH treated zeolite with a CEC from 7.3 to 8.4 mg/g which is in the same range as the mainstream results. Being 30 mg N-NH_4/g the highest value for a zeolite treated with microwaves, it can be considered that the value of 20 mg N-NH_4/g achieved in the sidestream is rather high.

Another essential factor is that in our case the lifespan of these zeolites was 4 cycles using NaOH. For sustainable operation of the process, zeolite's exchange capacity should not be compromised during the regeneration process. It has not been found a concrete number of cycles for the lifespan of the zeolites regenerated with NaOH. However, it has been reported that the electrochemical regeneration of zeolites was investigated by Lei et al. [130]. They pointed out that the synthetic zeolites could be completely regenerated even after the regeneration solution was used for five times, and 96% of the by-product NH_3 was converted into N_2 [130]. An even higher regenerability was observed in the study of Huang et al. [131] where no obvious deterioration tendency was observed for NH_4^+ removal performance of zeolite even after 20 operational cycles.

Liberti et al. [125] investigated the performance of a pilot plant and applied a regeneration brine with the concentration 0.6 M, flow of 24 BV/h, and regeneration period of 40 min. Hlavay et al. [126] found that, if the regeneration flow rate was 5 BV/h, 4 h of regeneration was needed. However, if they increased the flow rate to 7 BV/h, the regeneration period decreased to 1.4 h. Sodium brine with the concentration 0.34 M was used

In mainstream treatment, effluents with less than 1 mg N-NH_4/L can be achieved, which will be crucial if discharge limits become more stringent in the coming years for sensitive zones. Zeolites in sidestream treatment can produce effluents with concentrations lower than 150 mg N-NH_4/L, resulting in a direct reduction in energy consumption for biological removal processes.

Regarding regeneration, the concentration factor was higher in mainstream treatment than in the sidestream. However, since the feed concentration is higher in the sidestream, the final concentration of the regenerant solution is also higher, which favors subsequent valorization processes. In general terms, with a feed concentration of 50 mg N-NH_4/L, a concentration of 1 g N-NH_4/L can be achieved, whereas with a concentration of 800 mg N-NH_4/L, it is possible to achieve concentrations of up to 4000 mg N-NH_4/L.

Concerning the efficiency of recovery, it was possible to achieve recovery rates between 75% and 90% of the fed nitrogen. However, in order to understand the excess of nitrogen found in the regenerations in the sidestream it is necessary to analyze the accumulated N through the different cycles to achieve the final overall value of 80-84% N recovered.

In order to evaluate the quality of the regenerant solution for further treatment, both heavy metals (Table 17) and organic micropollutants (OMP) (Table 18) were analyzed.

Table 17 Heavy metal characterization

	Mainstream			Sidestream		
	Influent ZE	Effluent ZE	Regenerant stream	Influent ZE	Effluent ZE	Regenerant stream
Al (mg/L)	<0,052	0,090	0,283	0,03	0,02	12,75
Cr (mg/L)	<0,005	<0,005	<0,005	0,05	0,05	<0,01
Ni (mg/L)	<0,055	<0,055	<0,055	0,05	0,05	0,02
Cu (mg/L)	<0,052	<0,052	<0,052	0,08	0,05	0,04
Zn (mg/L)	<0,052	<0,052	<0,052	0,03	0,03	0,03
Cd (mg/L)	<0,005	<0,005	<0,005	<0,01	<0,01	<0,01
Hg (mg/L)	<0,003	<0,003	<0,003	<0,003	<0,003	<0,003
Pb (mg/L)	<0,005	<0,005	<0,005	<0,01	<0,01	0,03

As demonstrated in Table 17, heavy metals are not concentrated by the zeolites, and all of them remain below detection levels, with the exception of aluminum. The presence of aluminum at 0.28 mg/L and 12.75 mg/L in the regenerant stream (from the mainstream and side stream, respectively) can be attributed to the partial dissolution of the zeolite caused by the high pH of the regenerant stream. In this case all the parameters comply with current legislation (considering thresholds stablished for sewage sludge and for fertilizers)

Table 18 OMP characterization in mainstream

		Mainstream
OMP (µg/l)	Zeolite influent	Zeolite concentrate
Celestolide	<0,01	0,52
Galaxolide	0,16	<0,01
Tonalide	0,07	<0,01
Carbamazepine	0,15	0,16
Diazepam	0,01	<0,001
Ibuprofen	0,06	0,34
Naproxen	<0,005	<0,005
Diclofenac	2,83	<0,02
4-octylphenol	<0,004	<0,004
4-nonylphenol	<0,004	<0,004
Bisphenol A	<0,005	<0,005
Triclosan	<0,01	<0,01
Erythromycin	0,04	<0,001
Fluoxetine	0,03	0,01
Roxithromycin	<0,004	0,005
Sulfamethoxazole	0,14	0,04
Trimethoprim	0,27	0,07
Citalopram	0,19	<0,003
Estrona	<0,003	<0,002
Estradiol	<0,003	<0,002
Ethinyl estradiol	<0,003	<0,002

For organic micropollutants, the majority were detected below quantification levels in the regenerant for mainstream (table 18) and sidestream (table 24). However, the ion exchange process seemed to concentrate some micropollutants, including Celestolide and Ibuprofen. In contrast, other micropollutants like Sulfamethoxazole, Trimethoprim, and Citalopram were reduced to minimal levels, or even below the quantification threshold. The results for the sidestream can be found in the next section because they were characterized as the LLMC feed.

4.3.4 Zeolite characterization

Zeolites have been extensively characterized, both in their pristine state and after undergoing experiments conducted in sidestream conditions. SEM results are reported in Figure 13. Membranes

2023, 13, x FOR PEER REVIEW 15 of 23 3.4. Zeolite Characterization Zeolites have been extensively characterized, both in their pristine state and after undergoing experiments conducted in sidestream conditions. SEM results are reported in Figure 13.

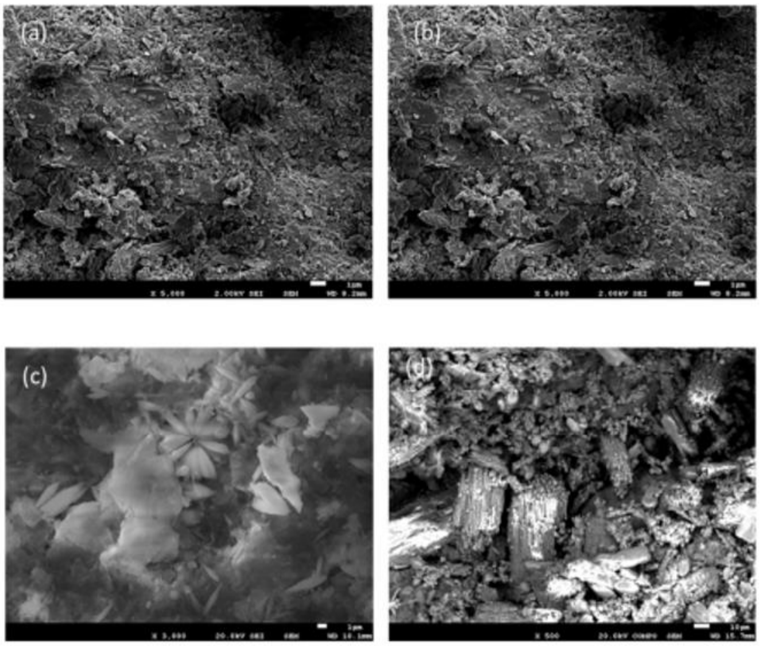

Figure 13 (a) New zeolite (×5000, 2 kV); (b–d) different pictures of zeolites after 4 cycles of operation prior to regeneration (×5000-2 kV, ×3000-20 kV, ×500-20 kV).

As depicted in Figure 13, repeated operation cycles lead to the formation of numerous precipitates on the surface of the zeolites prior to regeneration. These precipitates primarily consist of CaCO3, which has a propensity to precipitate under alkaline conditions that occur during each NaOH-based regeneration process. This observation suggests that incorporating acid washing into the operational protocol after several cycles could be beneficial. Acid washing could help mitigate the formation of precipitates, thereby reducing the risk of bed compaction.

4.3.5 Liquid-liquid membrane contactors performance in sidestream

In this section, the findings from the two fully characterized experiments conducted prior to comprehensive testing of the liquid-liquid membrane contactors (LLMCs) are presented. These initial experiments aimed to validate the performance of the LLMCs and provide insights into the system's capabilities and limitations, laying the groundwork for further optimization of the process.

The results from these preliminary experiments are discussed in detail, highlighting key observations and trends in ammonia removal efficiency. By examining these outcomes, the effectiveness of the LLMCs can be better understood and it is possible to identify areas for potential improvements in the pilot plant setting.

The evolution of N species in feed and fertilizer sides, for the first two experiments are presented in Figures 14 and 15. Moreover, a complete characterization is displayed in Tables 19 and 20.

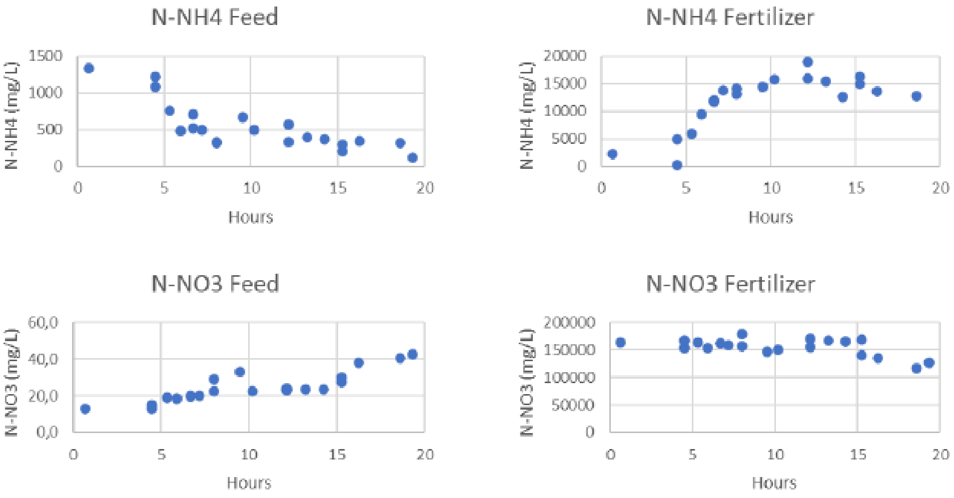

Figure 14 Evolution of N species in feed and fertilizer at 1.3 g N-NH4/L feed

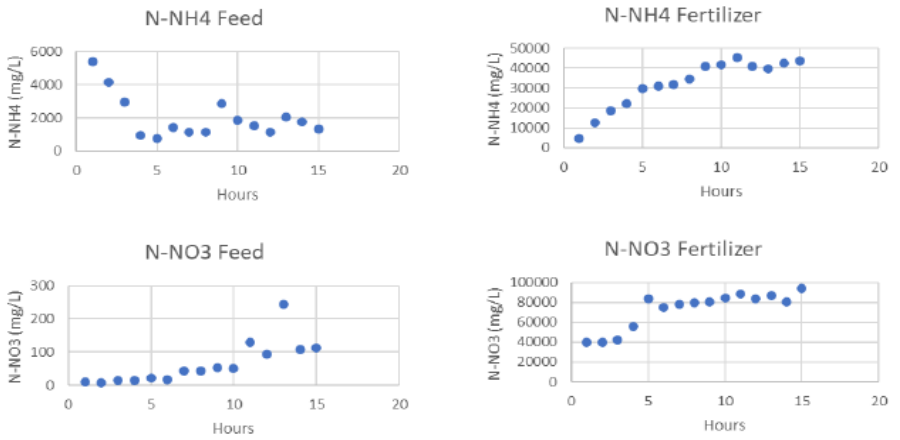

Figure 15 Evolution of N species in feed and fertilizer at 5.4 g N-NH4/L feed

Table 19 First LLMC experiment complete characterization.

	Feed		Fertilizer
Parámetro	Initial	Final	Final
N-NH4 (mg/L)	1341	113	11464
NO3- (mg/L)	58,541	188,4	132155
N-NO3 (mg/L)	13,2	42,5	29841
Al (mg/L)	6,82	5,93	0,58
As (mg/L)	0,02	0,02	<0,01
Be (mg/L)	<0,01	<0,01	<0,01
Bi (mg/L)	<0,01	<0,01	<0,01
B (mg/L)	0,92	0,98	0,1
Ca (mg/L)	1,23	1,31	32,61
Cd (mg/L)	<0,01	<0,01	<0,01
Co (mg/L)	0,01	0,01	0,01
Cr (mg/L)	0,01	0,01	0,63
Cu (mg/L)	0,01	0,01	0,04
Fe (mg/L)	<0,01	<0,01	2,37
K (mg/L)	219,02	216,2	57,13
La (mg/L)	<0,01	<0,01	<0,01
Li (mg/L)	0,03	0,03	0,02
Mg (mg/L)	<0,1	<0,1	11,8
Mn (mg/L)	<0,01	<0,01	0,17
Mo (mg/L)	0,01	0,01	0,02
Na (mg/L)	7078,1	6142,5	1062
Ni (mg/L)	0,02	0,03	0,31
Pb (mg/L)	<0,01	0,01	0,02
P (mg/L)	2,8	2,84	0,72
Rb (mg/L)	0,16	0,17	0,04
Sb (mg/L)	<0,01	<0,01	<0,01
Se (mg/L)	<0,01	0,01	0,1
Si (mg/L)	99,09	121,9	6,02
S (mg/L)	110,2	122	37,23
Sr (mg/L)	0,32	0,29	0,55
Ti (mg/L)	<0,01	<0,01	0,01
Tl (mg/L)	0,01	0,01	<0,01
V (mg/L)	<0,01	<0,01	<0,01
Zn (mg/L)	0,01	0,01	2,58
F- (mg/L)	0,481	0,605	0,333
Cl- (mg/L)	250,1	285,3	105,3

NO2- (mg/L)	<0,1	<0,1	<0,1
Br- (mg/L)	2,552	<0,05	<0,05
PO43- (mg/L)	8,27	8,37	2,13
SO42- (mg/L)	330,60	366,00	111,69

Table 20 Second LLMC experiment complete characterization

	Feed		Fertilizer
Parameter	Initial	Final	Final
N-NH4 (mg/L)	5,41	1,32	43,67
N-NO3 (mg/L)	9	113	93,811
Al (mg/L)	0.01	<0.01	0.49
As (mg/L)	0.01	<0.01	<0.01
Be (mg/L)	<0.01	<0.01	<0.01
Bi (mg/L)	<0.01	<0.01	<0.01
B (mg/L)	0.34	0.37	0.12
Ca (mg/L)	27.14	21.18	31.95
Cd (mg/L)	<0.01	<0.01	<0.01
Co (mg/L)	<0.01	<0.01	0.01
Cr (mg/L)	0.01	0.01	0.29
Cu (mg/L)	0.01	0.01	0.03
Fe (mg/L)	<0.01	<0.01	1.36
K (mg/L)	132.58	141.78	29.96
La (mg/L)	<0.01	<0.01	<0.01
Li (mg/L)	0.07	0.08	0.01
Mg (mg/L)	12.10	1.16	7.13
Mn (mg/L)	0.12	0.01	0.12
Mo (mg/L)	0.01	0.01	0.04
Na (mg/L)	4,979.70	8,190.60	996.80
Ni (mg/L)	0.01	0.01	0.19
Pb (mg/L)	<0.01	<0.01	<0.01
P (mg/L)	0.62	2.00	1.61
Rb (mg/L)	0.07	0.09	0.02
Sb (mg/L)	<0.01	<0.01	<0.01
Se (mg/L)	<0.01	<0.01	0.01
Si (mg/L)	11.23	8.41	3.23
S (mg/L)	150.60	157.80	45.54
Sr (mg/L)	1.12	0.78	0.37
Ti (mg/L)	<0.01	<0.01	0.01
Tl (mg/L)	0.01	<0.01	<0.01

V (mg/L)	<0.01	<0.01	<0.01
Zn (mg/L)	0.06	0.01	4.00
F^- (mg/L)	0.20	<0.02	<0.02
NO_2^- (mg/L)	<0.1	<0.1	<0.1
Br^- (mg/L)	<0.05	<0.05	<0.05
PO_4 (mg/L)	1.81	5.89	4.76
SO_4 (mg/L)	451.80	473.40	136.63

All the experiments in this study were conducted using regenerant solution from zeolites at 4-5 g/L N-NH_4 (sidestream). However, the first experiment had an initial concentration of only 1.3 g/L N-NH_4, as the solution was stored at pH 12 for an extended period, resulting in nitrogen losses due to ammonia gas release. Despite this ammonia loss, the first experiment achieved a removal rate of 91.6%. In the second experiment, with an initial N-NH_4 concentration of 5.4 g/L, the removal rate reached 75.6%. Higher initial concentrations generally result in lower removal rates.

For experiments 3-9, the feed side performance was monitored using kits, with a full characterization of the final product conducted at the end. The evolution of N-NH_4 for these experiments can be seen in Figure 16.

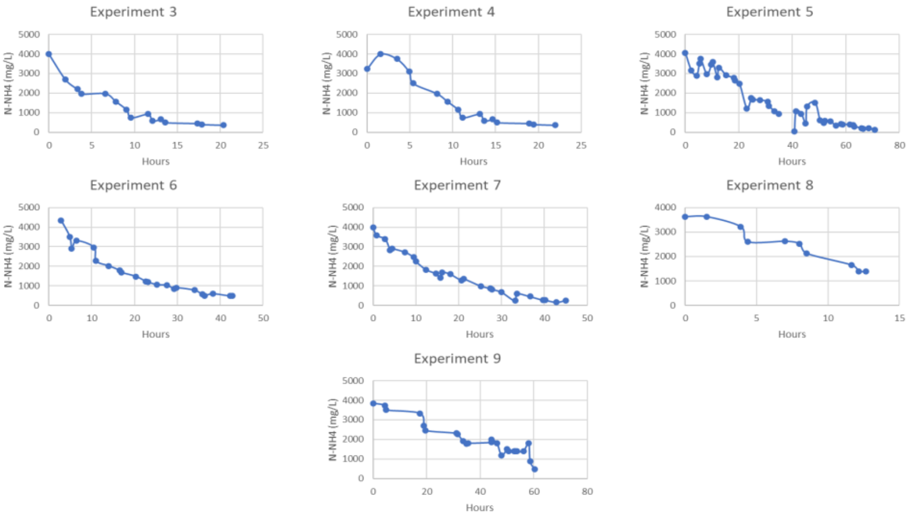

Figure 16 N evolution in the rest of the experiments

Table 21 Characterization for all the fertilizers produced

Experiment	Initial N (mg N-NH4/L)	Final N (mg N-NH4/L)	N removed (%)	Operating time (h)
1	1,34	113	91.6	20
2	5,41	1,320	75.6	15
3	3,99	369	90.8	21
4	3,23	369	88.6	23
5	4,06	138	96.6	70
6	4,34	490	88.7	43
7	4,00	250	93.8	46
8	3,63	1,380	62.0	13
9	3,84	470	87.8	60

As shown in Table 21, ammonia removal reaches values of up to 96.6% of the ammonia in the feed after 70 hours of operation. Table 22 presents the composition of the produced fertilizers in terms of ammonium, nitrate, and total nitrogen content. Lastly, Tables 23 and 24 provide an overview of the ionic composition as well as organic micropollutants (OMPs) characterization of the produced fertilizers, respectively.

Table 22 N composition of each fertilizer produced

	N-NH_4 (g/L)	N-NO3(g/L)	Nt (%)
1	11.5	29.8	4.1
2	43.6	93.8	13.7
3	15.3	95.0	11.0
4	8.2	65.8	7.4
5	12.4	101.4	11.4
6	14.4	140.5	15.5
7	13.2	69.3	8.3
8	18.4	148.0	16.6
9	12.3	127.1	13.9

Table 23 Ionic composition of each fertilizer

HM (mg/L)	Fert 1	Fert 2	Fert 3	Fert 4	Fert 5	Fert 6	Fert 7	Fert 8	Fert 9
Al	0,02	<0,01	1,97	1,67	0,45	0,18	<0,01	0,66	1,96
As	0,02	0,01	0,02	0,02	0,01	0,02	0,02	0,03	0,02
Be	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Bi	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
B	0,05	<0,01	0,02	0,08	0,05	0,04	<0,01	0,03	0,05

Ca	9,79	10,71	8,16	9,75	9,92	24,83	16,61	22,37	29,76
Cd	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Co	<0,01	<0,01	<0,01	<0,01	<0,01	0,01	<0,01	<0,01	<0,01
Cr	<0,01	<0,01	0,09	0,05	0,08	0,15	0,01	0,08	0,05
Cu	0,04	0,1	0,09	0,18	0,29	4,13	0,07	0,26	0,79
Fe	0,05	0,01	1,92	0,3	0,44	3,72	0,05	0,4	0,54
K	51,39	41,36	60,76	67,6	47,68	44,24	46,56	44,99	72,95
La	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Li	0,01	0,01	0,01	0,02	0,02	0,02	0,02	0,02	0,02
Mg	2,09	2,59	2,84	2,93	2,72	7,79	3,57	7,85	6,72
Mn	0,04	0,05	0,04	0,04	0,04	0,15	0,04	0,1	0,1
Mo	0,02	0,09	0,05	0,02	0,02	0,04	0,04	0,01	0,07
Na	3081,8	2462,5	3326,1	3940,9	3592,5	3224,7	3488,3	3391,6	4468,5
Ni	0,03	0,06	0,03	0,03	0,05	0,17	0,02	0,06	0,04
Pb	<0,01	<0,01	0,01	0,05	0,08	0,14	0,01	0,05	0,1
P	0,27	0,16	1,12	2,01	2,14	6,17	2,22	2,27	7,34
Rb	0,04	0,03	0,04	0,05	0,03	0,03	0,03	0,08	0,14
Sb	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Se	<0,01	<0,01	<0,01	<0,01	0,01	<0,01	<0,01	<0,01	0,01
Si	10,93	6,46	13,13	24,3	27,66	18,66	17,76	12,16	30,89
S	35,21	19,54	25,24	39,79	40,83	40,12	31,71	32,86	33,68
Sr	0,16	0,15	0,11	0,16	0,13	0,42	0,32	0,4	0,58
Ti	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Tl	0,01	0,01	<0,01	<0,01	0,01	0,01	0,02	0,01	0,01
V	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Zn	0,18	0,4	0,15	0,54	0,85	3,41	0,11	0,95	1,86

Table 24 OMP composition of each fertilizer

OMP (ng/L)	Zeolite concentarte	Fert 1	Fert 2	Fert 3	Fert 4	Fert 5	Fert 6	Fert 7	Fert 8	Fert 9
Ciprofloxacin	705	44	130	21	34	20	16	46	<1,8	<1,8
Sulfadiazine	4	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	5
Oxytetracycline	697	<2,0	<2,0	<2,0	<2,0	<2,0	<2,0	<2,0	<2,0	<2,0
Sulfamethoxazole	<4,4	<4,4	<4,4	<4,4	<4,4	<4,4	<4,4	<4,4	<4,4	<4,4
Azithromycin	146	<4,0	<4,0	<4,0	<4,0	<4,0	<4,0	<4,0	<4,0	<4,0
Trimethoprim	23	<1,4	<1,4	<1,4	<1,4	<1,4	<1,4	<1,4	<1,4	<1,4
Citalopram	<1,8	9	10	<1,8	<1,8	<1,8	<1,8	11	9	14
Fluoxetine	<35,4	<35,4	<35,4	<10,6	<10,6	<10,6	<10,6	<35,4	<35,4	<35,4
Diazepam	<5,9	<5,9	<5,9	<5,9	<5,9	<5,9	<5,9	<5,9	<5,9	<5,9
Carbamazepine	<6,4	15	<6,4	<6,4	303	<6,4	<6,4	<6,4	<6,4	<6,4

Methiocarb	<11,1	<11,1	<11,1	<11,1	14	<11,1	<11,1	<11,1	<11,1	<11,1

Regarding the membrane performance, the pilot plant was designed with the capability of developing chemical cleanings to the membrane. However, after a whole year of operation, there was no necessity of developing any chemical cleaning. This is due to membranes were fed with clean water (tap water) used for the regeneration of the zeolites thus there was a very low fouling potential. This fact is reinforced by the fact that membranes were not meant to filter the water but only to allow the gas passage which reduce the clogging of the membrane pores. To keep the good performance of the membrane it was identified that the most important is to carry out a drying step between experiments.

Vecino et al. [66] tested the same membranes with a similar initial concentration of 4 g N-NH_4/L with both phosphoric and nitric, achieving 70-76% recovery with both acids in a single step and up to 93% recovery with phosphoric.

Boehler et al. [114] conducted a pilot plant study on the removal of ammoniacal nitrogen from wastewater treatment plant effluent using a membrane contactor unit. The study employed three hollow fiber membrane contactors in series, with a total surface area of 120 m^2, and flow rates ranging from 5 to 12 L/m^2h. To remove ammoniacal nitrogen in the form of ammonium sulfate, a sulfuric acid solution was passed through the lumen side. The pH of the wastewater was adjusted to around 9.5 to convert the ammonium species to ammonia gas, resulting in removal values of 95% or greater when the ammonium-N content was between 700 and 3400 mg/L. The study showed that the inclusion of a CO_2 stripper section reduced the cost associated with addition of sodium hydroxide to elevate solution pH. However, the study also noted that precipitates formed in the stripper sections, which could lead to equipment fouling and clogging.

Norddahl et al. [132] also conducted a pilot plant study using a polypropylene hollow fiber membrane system to remove ammoniacal nitrogen from water. The study used water from either an anaerobic digester which was subsequently filtered by an ultrafiltration unit or a centrifuged sample from a sludge generated by a municipal solid waste treatment plant. The strip solution consisted of 1 wt/wt% sulfuric acid. The study found that pH values of 10 or greater resulted in substantial acceleration of the removal of ammoniacal nitrogen due to the almost total formation of free ammonia.

Ulbricht et al. [133] summarized the results from a commercially operating membrane contactor system located in Wuppertal, Germany. The study employed two membrane contactors in series, which treated between 5 and 10 m^3/h of water containing 500-2000 mg/L ammonia at a temperature of 40-50°C and minimal levels of particulates. The feedwater was pH adjusted to 9 or greater, facilitating ammonia removal values of up to 95%. A common theme from the aforementioned pilot plant studies was the need to raise the feed solution pH to at least 9, and preferably 10, to convert the majority of ammonium ion to ammonia gas.

To summarize, the pilot plant studies showed that membrane contactor technology is effective for the removal of ammoniacal nitrogen from wastewater treatment plant effluent and other sources of water. However, it requires the feed solution pH to be raised to at least 9, and preferably 10, to convert the ammonium species to ammonia gas. Additionally, the inclusion of a CO_2 stripper section can reduce the cost associated with the addition of sodium hydroxide to elevate solution pH, but it can also lead to precipitate formation, which could cause equipment fouling and clogging.

The results demonstrated the potential to achieve high removal rates in the membranes, with values reaching up to 96%. It is evident that dosing acid to maximize mass transfer results in a final product with a high nitrogen content. This product can be directly used as a fertilizer or as a raw material for fertilizer production.

Upon examining the ionic characterization results, the impact of water transport becomes apparent. Each experiment began with 10 L of 0.4 M HNO3 in the acid side to initiate operation, after which the control loop added HNO3 (58%) to maintain a pH of 3.4. The dosed acid ranged from 12 to 15 L. Considering that each experiment produced 50 L of fertilizer, it can be concluded that each experiment experienced water transport of 20-25 L. As it has been reviewed in the literature research this is one of the main aspects in order to control the quality and the concentration of the fertilizer produced [134].

The overall composition of organic micropollutants (OMPs) in the fertilizer remains undetectable despite water transport, ensuring its quality. This is supported by the presence of Ciprofloxacin and Oxytetracycline in the zeolites concentrate, but not in the fertilizer. Heavy metals appear in very low concentrations and are near the detection limit, while nutrient ions such as K, Mg, SO4, and Ca are present in certain concentrations. Sodium is the most significant ion, with concentrations of 3-4 g/L, attributed to the impact of water transport and high concentration of NaOH in the feed side. Spain's fertilizers are regulated under Real Decreto 506/2013, which establishes maximum allowed limits for metals and other elements. When comparing the levels of metals in the provided table, it can be observed that aluminum, arsenic, cadmium, cobalt, chromium, copper, nickel, lead, and zinc in all fertilizers are below the maximum allowed limits.

Considering these findings, it would be worthwhile to explore the use of alternative acids, such as sulfuric acid, to evaluate whether water transport can be reduced. Additionally, adjusting the pH from 3 to 7 could potentially result in neutral solutions with the same molar concentrations of N-NH4 and N-NO3. Lastly, it would be interesting to consider lowering the NaOH concentration in the zeolites to reduce the sodium concentration in the LLMC feed solution, thus minimizing its passage with water. This approach could also decrease NaOH consumption and the NH3 losses associated with high pH.

4.4 **Conclusions**

This study has demonstrated the potential of using zeolites for ammonium recovery in both mainstream and sidestream processes of wastewater treatment plants (WWTPs). The adsorption efficiency and capacity of the zeolites were compared under different operating conditions, revealing that sidestream treatment yielded better results due to higher ammonium concentrations.

The pilot plant experiments showed that the cation exchange capacity (CEC) was significantly higher for sidestream treatment compared to mainstream treatment. With sidestream treatment, CEC values of around 20 mg N-NH_4/g were achievable, while the lifespan of the zeolites was 4 cycles. Mainstream treatment, on the other hand, could produce effluents with less than 1 mg N-NH_4/L, which is important considering the possibility of more stringent discharge limits in the future.

Regeneration efficiency was found to be between 75% and 80% of the fed nitrogen, with the concentration factor being higher in mainstream treatment. However, due to the higher feed concentration in sidestream treatment, the final concentration of its regenerant solution was also higher, favoring subsequent valorization processes.

The quality of the regenerant solution was assessed by analyzing heavy metals and organic micropollutants. Most heavy metals remained below detection levels, except for aluminum, which was attributed to partial dissolution of the zeolite due to the high pH of the regenerant stream. Organic micropollutants were generally detected below quantification levels, although some, like Celestolide and Ibuprofen, were concentrated during the ion exchange process.

Integration of zeolite regeneration with the LLMC system for fertilizer production appears to be a promising approach for wastewater treatment. The zeolite regeneration process effectively captures ammonia, producing a regenerant solution that can then be used as feed for the LLMC system to produce fertilizers.

The preliminary experiments on the LLMC system show removal rates of up to 96.6% of the ammonia in the feed after 70 hours of operation. The produced fertilizers exhibit varied concentrations of ammonium, nitrate, and total nitrogen content, and also show varying levels of heavy metals and other contaminants.

By combining the zeolite regeneration process with the LLMC system, an integrated approach for advanced wastewater treatment can be established. This approach can result in the production of valuable fertilizers, while simultaneously treating wastewater and reducing environmental pollution. Further research and optimization are needed to improve the efficiency and cost-effectiveness of this integrated system, but the initial results demonstrate its potential for application in wastewater treatment and resource recovery.

4.5 **References**

[91] "World Population Prospects: The 2017 Revision," 2017. https://www.un.org/development/desa/publications/world-population-prospects-the-2017-revision.html

[92] H. C. J. Godfray *et al.*, "Food security: The challenge of feeding 9 billion people," *Science*, vol. 327, no. 5967. American Association for the Advancement of Science, pp. 812-818, Feb. 12, 2010. doi: 10.1126/science.1185383.

[93] C. Puchongkawarin, C. Gomez-Mont, D. C. Stuckey, and B. Chachuat, "Optimization-based methodology for the development of wastewater facilities for energy and nutrient recovery," *Chemosphere*, vol. 140, pp. 150-158, 2015, doi: 10.1016/j.chemosphere.2014.08.061.

[94] R. Basosi, D. Spinelli, A. Fierro, and S. Jez, "Mineral nitrogen fertilizers: Environmental impact of production and use," *Fertilizers: Components, Uses in Agriculture and Environmental Impacts*, no. July, pp. 3-43, 2014.

[95] W. Mo and Q. Zhang, "Can municipal wastewater treatment systems be carbon neutral?," *J Environ Manage*, vol. 112, pp. 360-367, 2012, doi: 10.1016/j.jenvman.2012.08.014.

[96] J. Huang, N. R. Kankanamge, C. Chow, D. T. Welsh, T. Li, and P. R. Teasdale, "Removing ammonium from water and wastewater using cost-effective adsorbents: A review," *J Environ Sci (China)*, vol. 63, pp. 174-197, 2018, doi: 10.1016/j.jes.2017.09.009.

[97] A. Mosa, A. El-Ghamry, and M. Tolba, "Biochar-supported natural zeolite composite for recovery and reuse of aqueous phosphate and humate: Batch sorption-desorption and bioassay investigations," *Environ Technol Innov*, vol. 19, 2020, doi: 10.1016/j.eti.2020.100807.

[98] N. Jiang, R. Shang, S. G. J. Heijman, and L. C. Rietveld, "High-silica zeolites for adsorption of organic micro-pollutants in water treatment: A review," *Water Research*, vol. 144. pp. 145-161, 2018. doi: 10.1016/j.watres.2018.07.017.

[99] F. Mazloomi and M. Jalali, "Ammonium removal from aqueous solutions by natural Iranian zeolite in

the presence of organic acids, cations and anions," *J Environ Chem Eng*, vol. 4, no. 2, pp. 1664-1673, 2016, doi: 10.1016/j.jece.2015.11.031.

[100] X. Guo, L. Zeng, and X. Jin, "Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater by natural zeolite," *J Environ Sci (China)*, vol. 25, no. 5, pp. 954-961, 2013, doi: 10.1016/S1001-0742(12)60115-6.

[101] A. Thornton, P. Pearce, and S. A. Parsons, "Ammonium removal from digested sludge liquors using ion exchange," *Water Res*, vol. 41, no. 2, pp. 433-439, 2007, doi: 10.1016/j.watres.2006.10.021.

[102] M. Li, X. Zhu, F. Zhu, G. Ren, G. Cao, and L. Song, "Application of modified zeolite for ammonium removal from drinking water," *Desalination*, vol. 271, no. 1-3, pp. 295-300, 2011, doi: 10.1016/j.desal.2010.12.047.

[103] C. Vaneeckhaute *et al.*, "Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification," *Waste Biomass Valorization*, vol. 8, no. 1, pp. 21-40, 2017, doi: 10.1007/s12649-016-9642-x.

[104] E. L. Cooney, N. A. Booker, D. C. Shallcross, and G. W. Stevens, "Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process," *Sep Sci Technol*, vol. 34, no. 14, pp. 2741-2760, 1999, doi: 10.1081/SS-100100802.

[105] J. H. Koon and W. J. Kaufman, "Ammonia removal from municipal wastewaters by ion exchange," *Journal of the Water Pollution Control Federation*, vol. 47, no. 3 (I), pp. 448-465, 1975.

[106] E. Drioli, Enrico; Criscuoli, Alessandra; Curcio, *Membrane Contactors: Fundamentals, Applications and Potentialitie*, Volume 11. 1st Edition, Elsevier Science, 2006.

[107] M. Darestani, V. Haigh, S. J. Couperthwaite, G. J. Millar, and L. D. Nghiem, "Hollow fibre membrane contactors for ammonia recovery: Current status and future developments," *J Environ Chem Eng*, vol. 5, no. 2, pp. 1349-1359, 2017, doi: 10.1016/j.jece.2017.02.016.

[108] E. E. Licon Bernal, C. Maya, C. Valderrama, and J. L. Cortina, "Valorization of ammonia concentrates from treated urban wastewater using liquid-liquid membrane contactors," *Chemical Engineering Journal*, vol. 302, pp. 641-649, 2016, doi: 10.1016/j.cej.2016.05.094.

[109] I. Sancho, E. Licon, C. Valderrama, N. de Arespacochaga, S. Lopez-Palau, and J. L. Cortina, “Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre membrane contactors,” *Science of the Total Environment*, vol. 584-585, pp. 244-251, 2017, doi: 10.1016/j.scitotenv.2017.01.123.

[110] M. A. Boehler, A. Heisele, A. Seyfried, M. Grömping, and H. Siegrist, “(NH4)2SO4 recovery from liquid side streams,” *Environmental Science and Pollution Research*, vol. 22, no. 10, pp. 7295-7305, 2015, doi: 10.1007/s11356-014-3392-8.

[111] E. E. Licon Bernal, C. Maya, C. Valderrama, and J. L. Cortina, “Valorization of ammonia concentrates from treated urban wastewater using liquid-liquid membrane contactors,” *Chemical Engineering Journal*, vol. 302, pp. 641-649, Oct. 2016, doi: 10.1016/J.CEJ.2016.05.094.

[112] I. Sancho, E. Licon, C. Valderrama, N. de Arespacochaga, S. López-Palau, and J. L. Cortina, “Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre membrane contactors,” *Science of the Total Environment*, vol. 584-585, pp. 244-251, Apr. 2017, doi: 10.1016/j.scitotenv.2017.01.123.

[113] M. C. Garcia-González and M. B. Vanotti, “Recovery of ammonia from swine manure using gas-permeable membranes: Effect of waste strength and pH,” *Waste Management*, vol. 38, no. 1, pp. 455-461, 2015, doi: 10.1016/j.wasman.2015.01.021.

[114] M. A. Boehler, A. Heisele, A. Seyfried, M. Grömping, and H. Siegrist, “(NH4)2SO4 recovery from liquid side streams,” *Environmental Science and Pollution Research*, vol. 22, no. 10, pp. 7295-7305, May 2015, doi: 10.1007/S11356-014-3392-8/METRICS.

[115] M. Darestani, V. Haigh, S. J. Couperthwaite, G. J. Millar, and L. D. Nghiem, “Hollow fi bre membrane contactors for ammonia recovery: Current status and future developments,” vol. 5, pp. 1349-1359, 2017.

[116] “WP4-Nitrogen management in side stream D 4.3: Operation and optimization of membrane ammonia stripping”, Accessed: Feb. 03, 2023. [Online]. Available: www.powerstep.eu

[117] Water Environment and APHA, *Standard Methods for the Examination of Water and Wastewater*. 2005.

[118] A. Mayor, X. Vecino, M. Reig, N. de Arespacochaga, C. Valderrama, and J. L. Cortina, “Ammonium Valorization from Urban Wastewater as Liquid Fertilizers by Using Liquid-Liquid Membrane Contactors,” *Hollow Fiber Membrane Contactors*, pp. 225-240, Nov. 2020, doi: 10.1201/9780429398889-20.

[119] M. Reig, X. Vecino, O. Gibert, C. Valderrama, and J. L. Cortina, “Study of the operational parameters in the hollow fibre liquid-liquid membrane contactors process for ammonia valorisation as liquid fertilizer,” *Sep Purif Technol*, vol. 255, p. 117768, Jan. 2021, doi: 10.1016/J.SEPPUR.2020.117768.

[120] Q. Du, S. Liu, Z. Cao, and Y. Wang, “Ammonia removal from aqueous solution using natural Chinese clinoptilolite,” *Sep Purif Technol*, vol. 44, no. 3, pp. 229-234, 2005, doi: 10.1016/j.seppur.2004.04.011.

[121] X. Guo, L. Zeng, and X. Jin, “Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater by natural zeolite,” *J Environ Sci (China)*, vol. 25, no. 5, pp. 954-961, 2013, doi: 10.1016/S1001-0742(12)60115-6.

[122] B. Beler-Baykal, M. Oldenburg, and I. Sekoulov, “The use of Ion Exchange in Ammonia Removal under Constant and Variable Loads,” *http://dx.doi.org/10.1080/09593331708616438*, vol. 17, no. 7, pp. 717-726, Jul. 2010, doi: 10.1080/09593331708616438.

[123] B. B. Baykal and D. A. Guven, “Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater,” *Water Science and Technology*, vol. 35, no. 7, pp. 47-54, Apr. 1997, doi: 10.2166/WST.1997.0259.

[124] J. H. Koon and W. J. Kaufman, “Ammonia Removal from Municipal Wastewaters by Ion Exchange,” 1975. [Online]. Available: http://about.jstor.org/terms

[125] G. B. R. P. L Liberti, “Advanced wastewater treatment by ion exchange,” *Effluent Water Treat.*, vol. 22, no. 7, pp. 253-257, 1982.

[126] J. Hlavay, G. Y. Vigh, V. Olaszi, and J. Inczédy, “Investigations on natural Hungarian zeolite for ammonia removal,” *Water Res*, vol. 16, no. 4, pp. 417-420, Jan. 1982, doi: 10.1016/0043-1354(82)90165-8.

[127] M. J. Semmens and P. Porter, “Ammonium removal by ion exchange: Using biologically restored

regenerant," *J Water Pollut Control Fed*, vol. 51, pp. 2928-2940, Dec. 1979.

[128] A. Hedström, "Ion Exchange of Ammonium in Zeolites: A Literature Review," *Journal of Environmental Engineering*, vol. 127, no. 8, pp. 673-681, Aug. 2001, doi: 10.1061/(ASCE)0733-9372(2001)127:8(673).

[129] S. Wang and Y. Peng, "Natural zeolites as effective adsorbents in water and wastewater treatment," *Chemical Engineering Journal*, vol. 156, no. 1, pp. 11-24, Jan. 2010, doi: 10.1016/J.CEJ.2009.10.029.

[130] X. Lei, M. Li, Z. Zhang, C. Feng, W. Bai, and N. Sugiura, "Electrochemical regeneration of zeolites and the removal of ammonia," *J Hazard Mater*, vol. 169, no. 1-3, pp. 746-750, Sep. 2009, doi: 10.1016/J.JHAZMAT.2009.04.012.

[131] H. Huang, L. Yang, Q. Xue, J. Liu, L. Hou, and L. Ding, "Removal of ammonium from swine wastewater by zeolite combined with chlorination for regeneration," *J Environ Manage*, vol. 160, pp. 333-341, Sep. 2015, doi: 10.1016/J.JENVMAN.2015.06.039.

[132] B. Norddahl, V. G. Horn, M. Larsson, J. H. Preez, and K. Christensen, "A membrane contactor for ammonia stripping , pilot scale experience and modeling," vol. 199, no. September, pp. 172-174, 2006, doi: 10.1016/j.desal.2006.03.037.

[133] M. Ulbricht, J. Schneider, M. Stasiak, and A. Sengupta, "Ammonia recovery from industrial wastewater by transMembranechemiSorption," *Chem Ing Tech*, vol. 85, no. 8, pp. 1259-1262, 2013, doi: 10.1002/cite.201200237.

[134] S. Guida *et al.*, "Ammonia recovery from brines originating from a municipal wastewater ion exchange process and valorization of recovered nitrogen into microbial protein," *Chemical Engineering Journal*, vol. 427, p. 130896, Jan. 2022, doi: 10.1016/J.CEJ.2021.130896.

[135] A. R. Sheik, E. E. L. Muller, P. Wilmes, K. B. Clark, and X. Zhang, "A hundred years of activated sludge: time for a rethink," 2014, doi: 10.3389/fmicb.2014.00047.

[136] A. Kogler, M. Farmer, J. A. Simon, S. Tilmans, G. F. Wells, and W. A. Tarpeh, "Systematic Evaluation of Emerging Wastewater Nutrient Removal and Recovery Technologies to Inform Practice and Advance Resource Efficiency," *ACS ES&T Engineering*, vol. 1, no. 4, pp. 662-684, Apr. 2021, doi:

10.1021/ACSESTENGG.0C00253.

[137] Á. Robles *et al.*, "New frontiers from removal to recycling of nitrogen and phosphorus from wastewater in the Circular Economy," *Bioresour Technol*, vol. 300, Mar. 2020, doi: 10.1016/j.biortech.2019.122673.

[138] A. Bouzas, N. Martí, S. Grau, R. Barat, D. Mangin, and L. Pastor, "Implementation of a global P-recovery system in urban wastewater treatment plants," *J Clean Prod*, vol. 227, pp. 130-140, Aug. 2019, doi: 10.1016/j.jclepro.2019.04.126.

[139] R. A. Al-Juboori, J. Uzkurt Kaljunen, I. Righetto, and A. Mikola, "Membrane contactor onsite piloting for nutrient recovery from mesophilic digester reject water: The effect of process conditions and pre-treatment options," *Sep Purif Technol*, vol. 303, Dec. 2022, doi: 10.1016/j.seppur.2022.122250.

[140] C. Wan *et al.*, "Simultaneous recovery of nitrogen and phosphorus from sludge fermentation liquid by zeolite adsorption: Mechanism and application," *Sep Purif Technol*, vol. 180, pp. 1-12, 2017, doi: 10.1016/j.seppur.2017.02.031.

[141] R. W. Holloway, A. E. Childress, K. E. Dennett, and T. Y. Cath, "Forward osmosis for concentration of anaerobic digester centrate," *Water Res*, vol. 41, no. 17, pp. 4005-4014, 2007, doi: 10.1016/j.watres.2007.05.054.

[142] M. A. Boehler, A. Heisele, A. Seyfried, M. Grömping, and H. Siegrist, "(NH4)2SO4 recovery from liquid side streams," *Environmental Science and Pollution Research*, vol. 22, no. 10, pp. 7295-7305, May 2015, doi: 10.1007/S11356-014-3392-8.

[143] L. Corominas *et al.*, "The application of life cycle assessment (LCA) to wastewater treatment: A best practice guide and critical review," *Water Res*, vol. 184, Oct. 2020, doi: 10.1016/j.watres.2020.116058.

[144] "UNE-EN ISO 14044:2006.," 2023. https://www.une.org/encuentra-tu-norma/busca-tu-norma/norma?c=N0038059 (accessed Jul. 18, 2023).

[145] "UNE-EN ISO 14040:2006.," 2023. https://www.une.org/encuentra-tu-norma/busca-tu-norma/norma?c=N0038060 (accessed Jul. 18, 2023).

[146] A. Amann, O. Zoboli, J. Krampe, H. Rechberger, M. Zessner, and L. Egle, "Environmental impacts of

phosphorus recovery from municipal wastewater," *Resour Conserv Recycl*, vol. 130, pp. 127-139, Mar. 2018, doi: 10.1016/j.resconrec.2017.11.002.

[147] S. Guida, L. Conzelmann, C. Remy, P. Vale, B. Jefferson, and A. Soares, "Resilience and life cycle assessment of ion exchange process for ammonium removal from municipal wastewater," *Science of the Total Environment*, vol. 783, Aug. 2021, doi: 10.1016/j.scitotenv.2021.146834.

[148] M. Sena, M. Seib, D. R. Noguera, and A. Hicks, "Environmental impacts of phosphorus recovery through struvite precipitation in wastewater treatment," *J Clean Prod*, vol. 280, Jan. 2021, doi: 10.1016/j.jclepro.2020.124222.

[149] Y. Cortes-Peña, D. Kumar, V. Singh, and J. S. Guest, "BioSTEAM: A Fast and Flexible Platform for the Design, Simulation, and Techno-Economic Analysis of Biorefineries under Uncertainty," *ACS Sustain Chem Eng*, vol. 8, no. 8, pp. 3302-3310, Mar. 2020, doi: 10.1021/ACSSUSCHEMENG.9B07040.

[150] M. Roldán, A. Bouzas, A. Seco, E. Mena, Mayor, and R. Barat, "An integral approach to sludge handling in a WWTP operated for EBPR aiming phosphorus recovery: Simulation of alternatives, LCA and LCC analyses," *Water Res*, vol. 175, May 2020, doi: 10.1016/j.watres.2020.115647.

[151] M. Carreras-sempere, R. Caceres, M. Viñas, and C. Biel, "Use of recovered struvite and ammonium nitrate in fertigation in tomato (Lycopersicum esculentum) production for boosting circular and sustainable horticulture," *Agriculture (Switzerland)*, vol. 11, no. 11, Nov. 2021, doi: 10.3390/AGRICULTURE11111063.

[152] Á. Mayor, S. Vinardell, K. Ganesan, C. Bacardí, J. L. Cortina, and C. Valderrama, "Life-cycle assessment and techno-economic evaluation of the value chain in nutrient recovery from wastewater treatment plants for agricultural application," *Science of The Total Environment*, vol. 892, p. 164452, Sep. 2023, doi: 10.1016/J.SCITOTENV.2023.164452.

[153] M. Rufí-Salís *et al.*, "Increasing resource circularity in wastewater treatment: Environmental implications of technological upgrades," *Science of the Total Environment*, vol. 838, Sep. 2022, doi: 10.1016/j.scitotenv.2022.156422.

[154] A. R. Ravishankara, J. S. Daniel, and R. W. Portmann, "Nitrous oxide (N2O): The dominant ozone-

depleting substance emitted in the 21st century," *Science (1979)*, vol. 326, no. 5949, pp. 123-125, 2009, doi: 10.1126/SCIENCE.1176985.

[155] S. Högstrand *et al.*, "Incorporation of main line impact into life cycle assessment of nutrient recovery from reject water using novel membrane contactor technology," *J Clean Prod*, vol. 408, Jul. 2023, doi: 10.1016/j.jclepro.2023.137227.

[156] G. Noriega-Hevia, J. Serralta, A. Seco, and J. Ferrer, "Economic analysis of the scale-up and implantation of a hollow fibre membrane contactor plant for nitrogen recovery in a full-scale wastewater treatment plant," *Sep Purif Technol*, vol. 275, Nov. 2021, doi: 10.1016/j.seppur.2021.119128.

[157] P. Ochs, B. Martin, E. Germain-Cripps, T. Stephenson, M. van Loosdrecht, and A. Soares, "Techno-economic analysis of sidestream ammonia removal technologies: Biological options versus thermal stripping," *Environmental Science and Ecotechnology*, vol. 13, Jan. 2023, doi: 10.1016/j.ese.2022.100220.

[158] "European Comission," 2014. https://ec.europa.eu/commission/presscorner/detail/en/IP_14_599 (accessed Oct. 31, 2022).

[159] M. C. Tomei, G. Bertanza, M. Canato, S. Heimersson, G. Laera, and M. Svanström, "Techno-economic and environmental assessment of upgrading alternatives for sludge stabilization in municipal wastewater treatment plants," *J Clean Prod*, vol. 112, pp. 3106-3115, Jan. 2016, doi: 10.1016/j.jclepro.2015.10.017.

[160] S. Vinardell, S. Astals, K. Koch, J. Mata-Alvarez, and J. Dosta, "Co-digestion of sewage sludge and food waste in a wastewater treatment plant based on mainstream anaerobic membrane bioreactor technology: A techno-economic evaluation," *Bioresour Technol*, vol. 330, Jun. 2021, doi: 10.1016/j.biortech.2021.124978.

[161] G. Rodriguez-Garcia *et al.*, "Life cycle assessment of nutrient removal technologies for the treatment of anaerobic digestion supernatant and its integration in a wastewater treatment plant," *Science of the Total Environment*, vol. 490, pp. 871-879, Aug. 2014, doi: 10.1016/j.scitotenv.2014.05.077.

[162] C. Sembera, C. Macintosh, S. Astals, and K. Koch, "Benefits and drawbacks of food and dairy waste

co-digestion at a high organic loading rate: A Moosburg WWTP case study," *Waste Management*, vol. 95, pp. 217-226, Jul. 2019, doi: 10.1016/j.wasman.2019.06.008.

[163] M. Aguilar-Moreno, S. Vinardell, M. Reig, X. Vecino, C. Valderrama, and J. L. Cortina, "Impact of Sidestream Pre-Treatment on Ammonia Recovery by Membrane Contactors: Experimental and Economic Evaluation," *Membranes (Basel)*, vol. 12, no. 12, Dec. 2022, doi: 10.3390/MEMBRANES12121251.

[164] E. Panos and M. Densing, "The future developments of the electricity prices in view of the implementation of the Paris Agreements: Will the current trends prevail, or a reversal is ahead?," *Energy Econ*, vol. 84, Oct. 2019, doi: 10.1016/j.eneco.2019.104476.

Chapter 5

5 Chapter 5: Life-cycle assessment and techno-economic evaluation of the value chain in nutrient recovery from wastewater treatment plants for agricultural application.

5.1 Introduction

Wastewater treatment plants (WWTPs) typically consume large amounts of energy and chemicals to remove nitrogen and phosphorus from wastewater [135]. However, the removal of nutrients does not fit with the current context of sustainable development established by the United Nations. For this reason, novel technologies are being developed to maximize nutrient recovery and reduce the dependency to raw materials and fossil fuels needed for their production. Nutrient recovery would reduce the amount of natural gas needed for the production of nitrogen-based fertilizers through the conventional Haber-Bosch process and the dependency of non-renewable resources (e.g., phosphate rock) for their production [136]. In this regard, nutrient recovery technologies are expected to be pivotal processes to promote the conversion of WWTPs into biorefineries within a circular economy paradigm [137].

Nutrient recovery technologies are usually implemented in the sludge line of the WWTP, where higher concentrations of nitrogen and phosphorus can be found. Several technologies have been tested to recover nutrients from the sludge line, such as struvite crystallization [138], gas permeable membrane contactors [139], ion exchange [140], or membrane concentration processes [141]. For example, Bouzas et al. [138] recovered more than 85% of phosphorus in the form of struvite in a pilot-scale crystallizer. Boehler et al. [142] evaluated a pilot-scale membrane contactor system and reported ammonia recovery efficiencies above 90%. Wan et al. [140] adsorbed up to 94.1 and 98.3% of ammonium and phosphate, respectively, in a lab-scale ion exchange system. These studies show that these technologies can effectively recover nutrients and promote circular economy in WWTPs. However, further pilot-scale studies at higher Technology Readiness Level (TRL) and for the entire value chain are still necessary to evaluate the environmental and economic feasibility of implementing these novel technologies in a WWTP.

Life Cycle Assessment (LCA) is a comprehensive method to evaluate the potential environmental impacts associated with a product during its entire life cycle. LCA allows assessing the environmental sustainability of wastewater-based resource recovery alternatives and can be combined with other context-specific assessment techniques, such as life cycle costing and risk assessments [143]. This methodology is based on the standardized norm ISO 14040 and 14044 [144], [145] and allows evaluating different impact categories, such as global warming potential (GWP), eutrophication, acidification, ozone layer depletion or human toxicity, among others. LCA can be an important screening tool to understand how nutrients recovery implementation can improve the environmental prospect when compared with conventional technologies for fertilizers' production.

Some studies have conducted LCAs to evaluate the environmental impacts of recovering nutrients in a WWTP. Amann et al. [146] assessed the environmental impacts of 18 technologies to recover phosphorus from different WWTP streams (i.e., liquid streams, sewage sludge and sewage sludge ash) and producing different P-recovered products (i.e., CaP, Struvite, P-rich slag, Phosphoric acid). Guida et al. [147] conducted an LCA to find the optimum environmental scenarios for ammonium recovery using ion exchange zeolites. Sena et al. [148] evaluated how the implementation of a full-scale struvite crystallizer impacted the overall environmental performance of a WWTP. However, the use of LCA together with other decision-making tools, such as techno-economic assessment (TEA), has been rarely reported in the literature to evaluate nutrient recovery in WWTPs, especially at TRL higher than 4.

TEA is a methodology based on the calculation of the capital costs, operating costs and revenues associated with a product, technology or process, which allows determining the most important factors influencing its economic feasibility. TEA can be a useful method to understand how the application of novel technologies aimed at recovering valuable resources can influence the economic balance of future WWTPs [149]. Although TEA and LCA are different context-specific assessment techniques, combining them represents a reliable decision-making tool to evaluate different alternatives for nutrient recovery.

The aim of this study is to evaluate the economic and environmental implications of implementing innovative technologies to recover nitrogen and phosphorus in a WWTP. In this context, the LIFE ENRICH project (LIFE Program) is proposed to implement the concept of circular economy through the demonstration of the entire value chain for the recovery of nutrients in urban wastewater treatment plants and the validation of their agricultural performance in a real case study (end user). To this end, the LCA and TEA of a pilot-scale plant developed within the LIFE ENRICH project were conducted including the crop field application of the recovered fertilizers. The innovative pilot plant for nutrient recovery consisted in (i) struvite crystallization for phosphorus recovery and (ii) ion-exchange process combined with hollow fiber membrane contactor (HFMC) for nitrogen recovery. Additionally, the recovered fertilizers were used in agriculture and the real data obtained during their application were included in the evaluation. To the best of the authors' knowledge, this is the first study in which both the environmental and economic implications of recovering nutrients using struvite crystallization, ion-exchange and HFMC technologies for subsequent agricultural application is evaluated using real pilot-scale data. Overall, this novel study provides a better understanding of the whole value chain of recovering nitrogen and phosphorus in WWTPs from a sustainability perspective.

5.2 Methodology

5.2.1 Case study selection and description

The nutrient recovery technologies proposed by the LIFE ENRICH process were implemented in the Murcia-Este WWTP (Figure 17). The initial configuration of this WWTP consists of (i) primary settling, (ii) biological removal of phosphorus, nitrogen and organic matter using an anaerobic-anoxic-oxic configuration (A2O), (iii) secondary settler and (iv) sludge line. The waste activated sludge (WAS), which is rich in P, is thickened and mixed with the primary sludge in a mixing chamber. The mixed sludge is introduced into the anaerobic digester, where the organic matter is bioxidized into methane-rich biogas. Finally, polyelectrolyte is added and the digested sludge is dewatered to reach a final TSS concentration between 20 and 25% [150] . Further information about this WWTP can be found in Roldán et al. [150].

Pilot-scale prototypes were implemented in the Murcia-Este WWTP to evaluate the feasibility of recovering nitrogen and phosphorus in this WWTP (Figure 17). The nutrient recovery train is based on the implementation of a sludge line configuration, which allows the elutriation process of phosphorus. During the elutriation process, a liquid stream concentrated in phosphate is obtained, whereas the amount of phosphorus in the mixed sludge is reduced [150]. This allows reducing the uncontrolled precipitation of struvite in the anaerobic digester. The phosphate concentrated stream is merged with the anaerobic digester centrates and this flux is treated in a struvite crystallizer, where sodium hydroxide and magnesium chloride are added to adjust the pH and precipitate phosphorus as struvite crystals. The struvite crystals obtained could be applied either directly on the crop field or as precursors to produce other fertilizers.

The struvite crystallizer effluent is fed to an ionic exchange process using zeolites, where sodium hydroxide is used to regenerate the exhausted zeolites (Figure 17). This process concentrates the ammonium into a highly basic stream, which is introduced into a HFMC. In the HFMC, ammonia gas diffuses from the feed solution to an acidic HNO_3 solution, thus generating an ammonium nitrate solution suitable to be valorized as a fertilizer.

The recovered struvite and ammonium nitrate were characterized to meet the legislative requirements for new fertilizing materials (EU 2019/1009). The recovered fertilizers were used as raw material for the manufacture of the optimal nutrient solution for fertigation (injection of water-soluble fertilizers into the irrigation system) of three species of horticultural crops. For this analysis, the tomato crop has been taken as a reference. The crop field application was carried out for tomato cultivation in a 200 m^2 passively ventilated greenhouse located in Cabrils (Barcelona, Spain). Further information on the crop field set-up and the data collected can be found in Carreras-Sempere et al. [151].

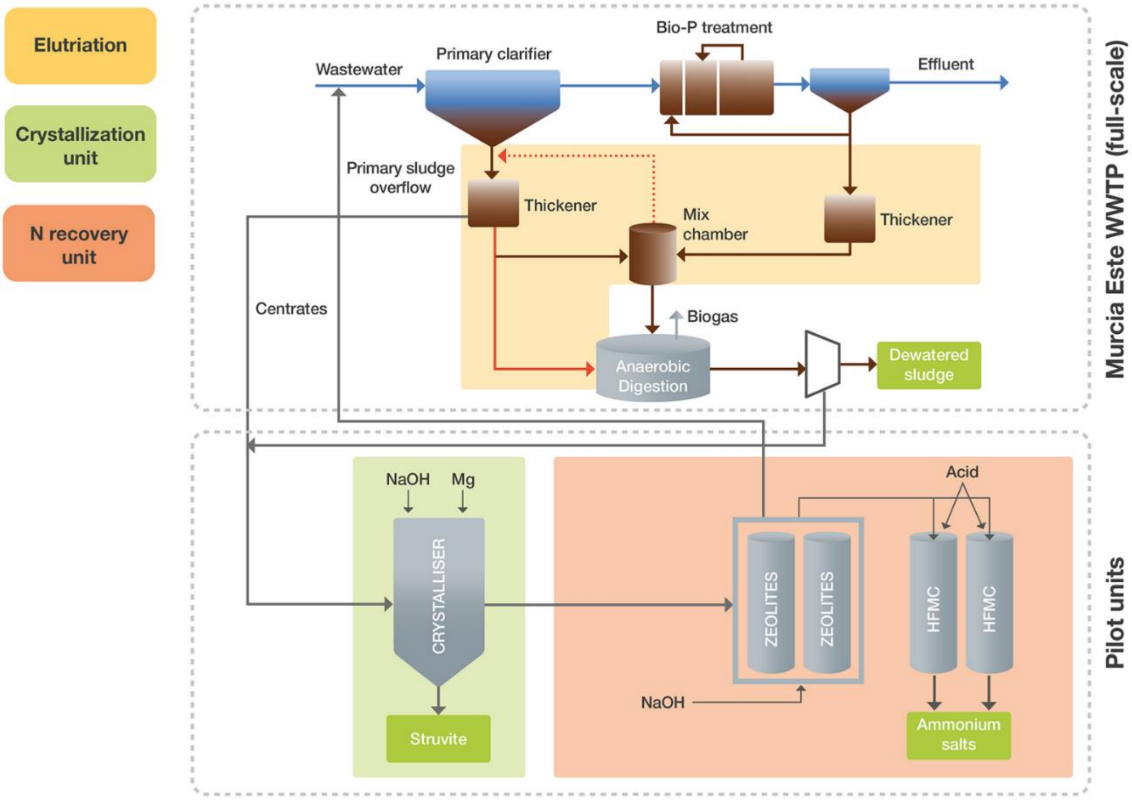

Figure 17 Murcia-Este WWTP process configuration integrating struvite crystallisation, ion exchange and membrane contactor scheme for nitrogen and phosphorus recovery. HFMC: hollow fibre membrane contactor.

5.2.2 Life cycle assessment

LCA methodology was performed according to UNE-EN ISO 14040 and 14044 [144], [145] and was applied to evaluate the potential environmental impacts of recovering ammonium nitrate and struvite for subsequent application as fertilizers using innovative nutrient recovery technologies. The following sections describe the goal and scope, the life cycle inventory (LCI), and the life cycle impact assessment tools and methods used in the LCA.

5.2.2.1 Goal and scope definition

The main objective of the LCA is to evaluate the environmental performance of using a fertilizer solution containing the recovered ammonium nitrate and struvite when compared with the use of a conventional inorganic fertilizer solution. In this section, the scenarios, system boundaries and the functional unit (FU) considered for the LCA are described.

Two scenarios were evaluated in the LCA: (i) the Baseline Scenario, which consists in the application of a commercial solution of conventional fertilizers, and (ii) Scenario 1, which consists in the implementation of the LIFE ENRICH configuration aimed at recovering nitrogen and phosphorus fertilizers. Figure 18 shows the system boundaries and flows included in the Baseline Scenario and Scenario 1.

Baseline Scenario: The Baseline Scenario considers the factors related to the agricultural crop application of a commercial solution based on monopotassium phosphate (MKP), potassium sulphate (K_2SO_4), nitric acid (HNO_3) and calcium nitrate ($Ca(NO_3)_2$) (Figure 18). In this scenario, the system boundaries refer to the whole production process of these fertilizers, including the phosphate rock extraction in the case of P-based fertilizers, and the Haber-Bosch process for the production of N-based fertilizers.

Scenario 1: Scenario 1 considers the sludge line of the Murcia-Este WWTP after implementing nitrogen and phosphorus recovery technologies. The process for nutrients recovery and agricultural application involves five units, whose energy consumption and chemicals' consumption were considered in the LCA (Figure 18). Detailed description of the sludge line, where the nutrient recovery technologies are implemented, can be found in Section 2.1. The struvite and ammonium nitrate recovered in the WWTP were applied in the crop field together with K_2SO_4 and $Ca(NO_3)_2$. The industrial processes to produce these fertilizers were included. Unlike the Baseline Scenario, MKP and HNO_3 were not required for crop field application. In this scenario, the system boundaries included the processes that are related to the sludge line of the WWTP and the agricultural application of the recovered nutrients as fertilizers. Therefore, the water treatment line of the WWTP has been excluded out of the scope of this LCA. It is worth mentioning that the anaerobic digestion centrates would also be treated in the water line of the WWTP regardless of the nutrient recovery implementation. Finally, the electricity produced through the biogas generated in the anaerobic digester was considered to substitute the respective amount of energy needed from the grid.

The fertilizers used in both scenarios were considered to cover the same fertilized area. For this reason, water supply, crop wastes and energy consumption for crop field application have not been included within the boundaries of the present study since they are expected to be similar for both scenarios.

The FU has a large impact on the results of the LCA [148]Calculation of the net a reviewed 65 LCA studies, which considered the recovery of nutrients from wastewater for agricultural application. In the reviewed studies, the amount of wastewater treated, the amount of sludge disposed and the amount of nutrient recycled/removed were the three most common FUs. As a novelty, the present work compared the whole value chain of recovering nutrients from wastewater for crop field application (Scenario 1) with a business-as-usual option for crop field application (Baseline Scenario). For this reason, the selected FU was the area of soil fertilized (1 m^2 of fertilized soil).

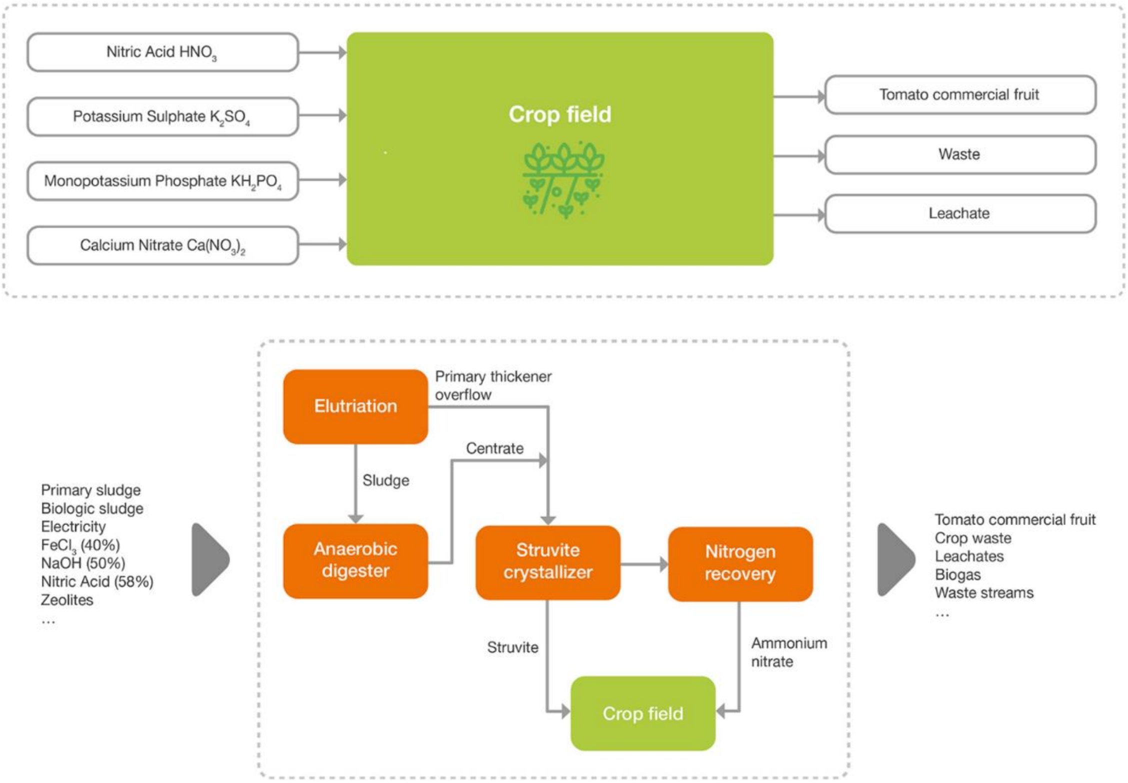

Figure 18 Boundaries of the system for (top) baseline scenario and (bottom) Enrich scenario.

5.2.2.2 *Life cycle inventory*

The life cycle inventory (LCI) input and output data of the nutrient recovery scenario was obtained from the mass and energy balances from Murcia-Este WWTP after nutrient recovery implementation. Table 25 shows the LCI data for both Baseline Scenario and Scenario 1. Detailed information regarding the internal fluxes between processes can be found in Mayor et al. [152]. The background inventory data for the chemicals and energy were obtained from Ecoinvent v3.6 database.

Table 25 Life cycle inventory (LCI) regarding chemicals, electricity, zeolites, fertilizers, waste and recovered products considered for each scenario.

				Baseline Scenario	Scenario 1
Inputs	Electricity	AD+centrifuges	kWh/m2	-	2.5×10-1
		Struvite crystallisation	kWh/m2	-	1.1×10-1
		Nitrogen recovery	kWh/m2	-	1.1×10-1
	Chemicals	FeCl3 40%	kg/m2	-	3.4×10-2
		Nitric acid 58%	kg/m2	-	1.7×10-1
		NaOH 50%	kg/m2	-	1.2×10-1
		Antifouling agent	kg/m2	-	9.5×10-5
		Polyelectrolyte	kg/m2	-	1.0×10-2
		MgCl2	kg/m2	-	8.6×10-3
	Zeolites	Zeolite crystals	kg/m2	-	1.5×10-1
	Fertilizers	Calcium nitrate	kg/m2	9.0×10-2	6.0×10-2
		Monopotassium phosphate	kg/m2	1.1×10-1	-
		Nitric acid 58%	kg/m2	2.8×10-1	-
		Potassium sulfate	kg/m2	1.7×10-1	1.9×10-1
		Struvite	kg/m2	-	1.5×10-1
		Ammonium nitrate	kg N/m2	-	5.4×10-2
Outputs	Waste	Zeolite effluent	kg/m2	-	1.5×10-1
	Energy and fertilizer recovery	Electricity from biogas	kWh/m2	-	1.1×100
		Struvite	kg/m2	-	1.5×10-1
		Ammonium nitrate	kg N/m2	-	5.4×10-2

5.2.2.3 Life cycle impact assessment

The classification and characterization stages of the life cycle impact assessment (LCIA) were conducted using the ReCIPe 2016 Midpoint Hierarchist (H) method and the OpenLCA v1.10.2 software. The mid-point categories included in the LCIA were freshwater eutrophication (kg P_{eq}), freshwater eco-toxicity (kg 1,4-DCB), stratospheric ozone depletion (kg $CFC11_{eq}$), mineral resource scarcity (kg CU_{eq}), global warming (kg CO_{2eq}), fossil resource scarcity (kg oil_{eq}), terrestrial eco-toxicity (kg 1,4-DCB), terrestrial acidification (kg SO_{2eq}), human carcinogenic toxicity (kg 1,4-DCB), land use (m^2a $crop_{eq}$) and water consumption (m^3).

5.2.3 Techno-economic assessment

The TEA was conducted considering two different perspectives. On the one hand, the economic feasibility of implementing the nutrient recovery technologies developed within the LIFE Enrich project were evaluated from the WWTP's perspective. On the other hand, the economic potential of using into agriculture the recovered fertilizers (in comparison with traditional fertilizers) were analyzed from the farmer's perspective.

The capital expenditures (CAPEX), operating expenditures (OPEX) and revenues influenced by the implementation of elutriation and nutrient recovery technologies were considered when evaluating WWTP's economic perspective. The CAPEX comprised the construction and equipment costs concerning the elutriation, struvite crystallization and ammonium recovery processes, whereas the OPEX comprised the electricity consumption, chemicals' consumption, zeolites' consumption, sludge disposal and labor in the sludge line of the WWTP. The revenues comprised the struvite, ammonium nitrate and biogas produced in the WWTP. Detailed information on the CAPEX, OPEX and revenues used for this economic evaluation can be found in Mayor et al. [152].

The fertilizers needed for crop field application were considered when evaluating farmer's economic perspective. Specifically, two different alternatives were compared: (i) Alternative A, where a commercial fertilizer composed of MKP, K_2SO_4, HNO_3 and $Ca(NO_3)_2$ was applied to the crop field and (ii) Alternative B, where the recovered struvite and ammonium nitrate were applied to the crop field together with K_2SO_4 and $Ca(NO_3)_2$.

The present value (PV) of the gross cost and revenues was calculated according to Eq. (8) and (9), respectively. Subsequently, the net present value (NPV) was calculated by using Eq. (10).

$$\mathrm{PV_{GC}} = \mathrm{CAPEX} + \sum_{t=1}^{T} \frac{\mathrm{OPEX_t}}{(1+i)^t} \qquad \text{Eq. (8)}$$

$$\mathrm{PV_R} = \sum_{t=1}^{T} \frac{\mathrm{R_t}}{(1+i)^t} \qquad \text{Eq. (9)}$$

$$\mathrm{NPV} = \sum_{t=1}^{T} \frac{\mathrm{R_t} - \mathrm{OPEX_t}}{(1+i)^t} - \mathrm{CAPEX} \qquad \text{Eq. (10)}$$

where PV_{GC} is the PV of the gross cost (€), PV_R is the PV of the revenues (€), NPV is the net present value (€), CAPEX is the capital expenditure (€), $OPEX_t$ is the operating expenditure at year t (€), R_t is the revenue at year t (€), T is the plant lifetime (20 years) and i is the discount rate (5%).

5.3 Results and discussion

In this section, the environmental and economic results of recovering nutrients in a WWTP for subsequent agricultural application are shown and discussed. Firstly, the results between the comparison of the Baseline and Scenario 1 are presented in terms of LCA analysis. Second, an economic analysis is carried out to evaluate the economic feasibility of implementing the nutrient recovery technologies and using the recovered fertilizers into agriculture.

5.3.1 Environmental performance of applying the recovered nutrients in agriculture

The results of the midpoint impact categories for both scenarios (Baseline Scenario vs Scenario 1) are summarized in Table 26. The results show that Scenario 1 featured a lower environmental impact compared with the Baseline Scenario in most of the categories, such as stratospheric ozone depletion (39%), freshwater eutrophication (12%), global warming (24%), land use (41%), and water consumption (14%), among others. The lower impact can be attributed to the high consumption of chemical reagents (e.g., nitric acid) used in the Baseline Scenario to produce and manufacture the fertilizers. Accordingly, it is conceivable to state that using the recovered fertilizers (i.e. struvite and ammonium nitrate) for crop field application improves the environmental prospect when compared with the use of a commercial nutrient solution. These results agree with other studies, which reported improved environmental implications after implementing technologies for nutrient recovery [147], [153]. For example, Rufí-Salís et al. [153] observed that recovering struvite in the sludge line of a

WWTP using mainstream biological phosphorus removal had the potential to substantially reduce the net environmental in five of the six evaluated impact categories. Conversely, Scenario 1 featured a higher environmental impact in some categories, such as mineral resource scarcity (-34%), human carcinogenic toxicity (-17%) and freshwater ecotoxicity (-4%). The increase in the impact related to mineral resource scarcity can be attributed to the high consumption of chemicals needed in the ion exchange and HFMC systems to recover nitrogen in the sludge line of the WWTP. Freshwater ecotoxicity and human carcinogenic toxicity also feature higher impacts for Scenario 1 than the Baseline Scenario because of the higher consumption of nitric acid for nitrogen recovery and the impact associated with zeolite slurry disposal.

Table 26 Midpoint impact categories evaluated for the Baseline Scenario and Scenario 1. The environmental impacts are referred to the FU (1 m2 of fertilized soil).

Category	Baseline Scenario	Scenario 1	Unit	Comparison (% savings from Scenario 1 to Baseline Scenario)
Freshwater eutrophication	3.3×10^{-4}	2.9×10^{-4}	kg P eq	+12 %
Freshwater Eco-toxicity	7.6×10^{-2}	7.9×10^{-2}	kg 1,4-DCB	-4%
Stratospheric ozone depletion	2.7×10^{-5}	1.6×10^{-5}	kg CFC11 eq	+39%
Mineral resource scarcity	9.5×10^{-3}	1.3×10^{-2}	kg Cu eq	-34%
Global warming	1.5×10^{0}	1.1×10^{0}	kg CO_2 eq	+24%
Fossil resource scarcity	2.5×10^{-1}	2.1×10^{-1}	kg oil eq	+15%
Terrestrial Eco-toxicity	2.6×10^{0}	2.4×10^{0}	kg 1,4-DCB	+6%
Terrestrial Acidification	1.0×10^{-2}	4.5×10^{-3}	kg SO_2 eq	+56%
Human carcinogenic toxicity	1.6×10^{-1}	1.8×10^{-1}	kg 1,4-DCB	-17%
Land use	4.4×10^{-2}	2.6×10^{-2}	m^2a crop eq	+41%
Water consumption	2.2×10^{-2}	1.9×10^{-2}	m^3	+14%

Figure 19 illustrates the midpoint impact categories contribution (in relative terms) for the two scenarios under study. Regarding the Baseline Scenario, monopotassium phosphate and nitric acid were the most important environmental contributors in most of the evaluated categories. This highlights that using commercial nitrogen- and phosphorus-based fertilizers represents an important impact on the environment due to the high consumption of chemical reagents and energy needed for their production. Interestingly, nitric acid accounted for 97% and 65% of the stratospheric ozone depletion and global warning impact categories, respectively. This can be attributed to potential emissions of nitrous oxide (N_2O) during its production, which is a powerful greenhouse and ozone-depleting gas [154]. Regarding Scenario 1, ammonium nitrate production (nitrogen recovery) represented the most important environmental contributor in nine of the evaluated categories (Figure 19). The high environmental impact related to using the recovered ammonium nitrate in agriculture is caused by (i) the high consumption of chemical reagents (i.e., nitric acid and sodium hydroxide) needed in the ion exchange and HFMC stages and (ii) the relatively high energy consumption needed in the nitrogen recovery train. Similar to the outputs obtained by Högstrand et al.[155], these results highlight that the optimization in both energy and chemicals' consumption is important to further improve the environmental prospect of the membrane contactor system.

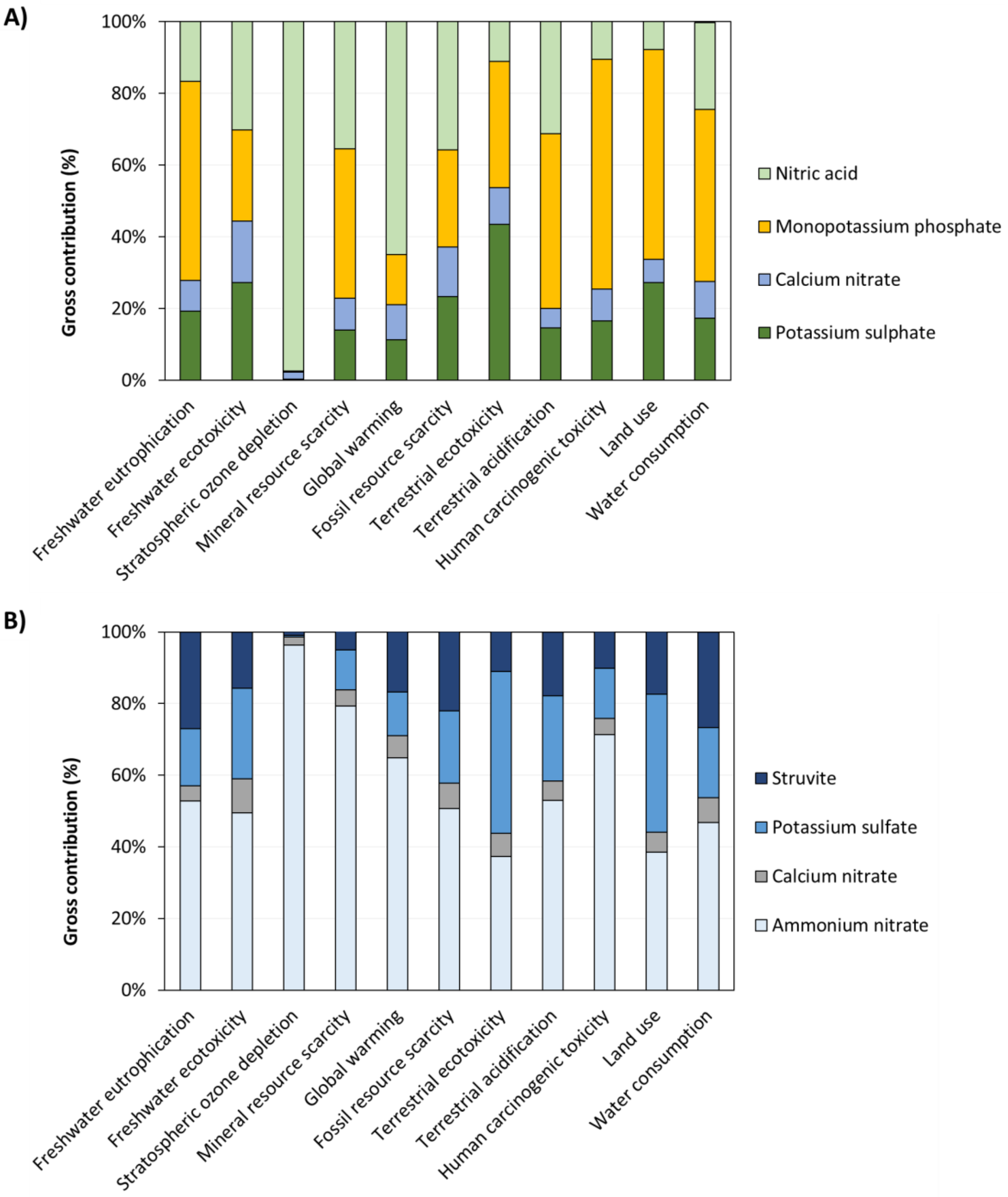

Figure 19 Gross contribution of the midpoint impact categories (in relative terms) for the (A) Baseline Scenario and (B) Scenario 1. The contribution of the electricity produced from the biogas has not been included in the Figure.

5.3.2 Techno-economic assessment

5.3.2.1 Economic balance of nutrient recovery and crop field application

Figure 20A shows the economic balance of implementing elutriation, struvite crystallization and ion exchange + HFMC to recover nutrients in the sludge line of the WWTP. The implementation of these novel technologies allowed achieving a revenue from the value-added fertilizers produced (i.e. ammonium nitrate and struvite), which is an important implication to promote resource recovery and circular economy in future WWTPs. However, these revenues did not compensate the CAPEX and OPEX associated with their implementation, making the process economically unfavorable (negative NPV). This points out that the implementation of these nutrient recovery technologies would increase the treatment cost of the WWTP and, therefore, further improvements are needed to increase the efficiency of these technologies to reach a positive economic balance. It should be noted that this is a demonstrative study carried out within a European project on a pilot scale. If these technologies were scaled-up to an industrial level, the economic balance and environmental impacts would be lower than those obtained in this study. For example, the energy efficiency of the system would be better on an industrial scale, which would reduce the contribution of the electricity (12.9%) to the total cost of the system (see Figure 21A). Furthermore, the application of these nutrient recovery technologies has the potential to reduce the consumption of energy and chemicals in the water line of the WWTP, which could improve the economic balance of implementing these technologies [155]-[157]. Finally, it is worth mentioning that Figure 20A results did not include the economic implications of applying the recovered nutrients as fertilizers. For this reason, it is important to evaluate how the use of a fertilizer solution containing struvite and ammonium nitrate would influence the economics of crop field application (Figure 20B).

The results showed that Alternative B featured a slightly lower gross cost than Alternative A for crop field application (Figure 20B). This implies that using a fertilizer solution containing struvite and ammonium nitrate is less costly than using a typical commercial solution. From these results, it is conceivable to state that the WWTP could have margin to increase the selling price of struvite and ammonium nitrate to improve its economic balance (see Section 3.2.3). Besides economic considerations, the recovery of phosphorus from wastewater is crucial to reduce the dependency of non-renewable phosphate rock, which is considered a Critical Raw Material by the European Commission [158]

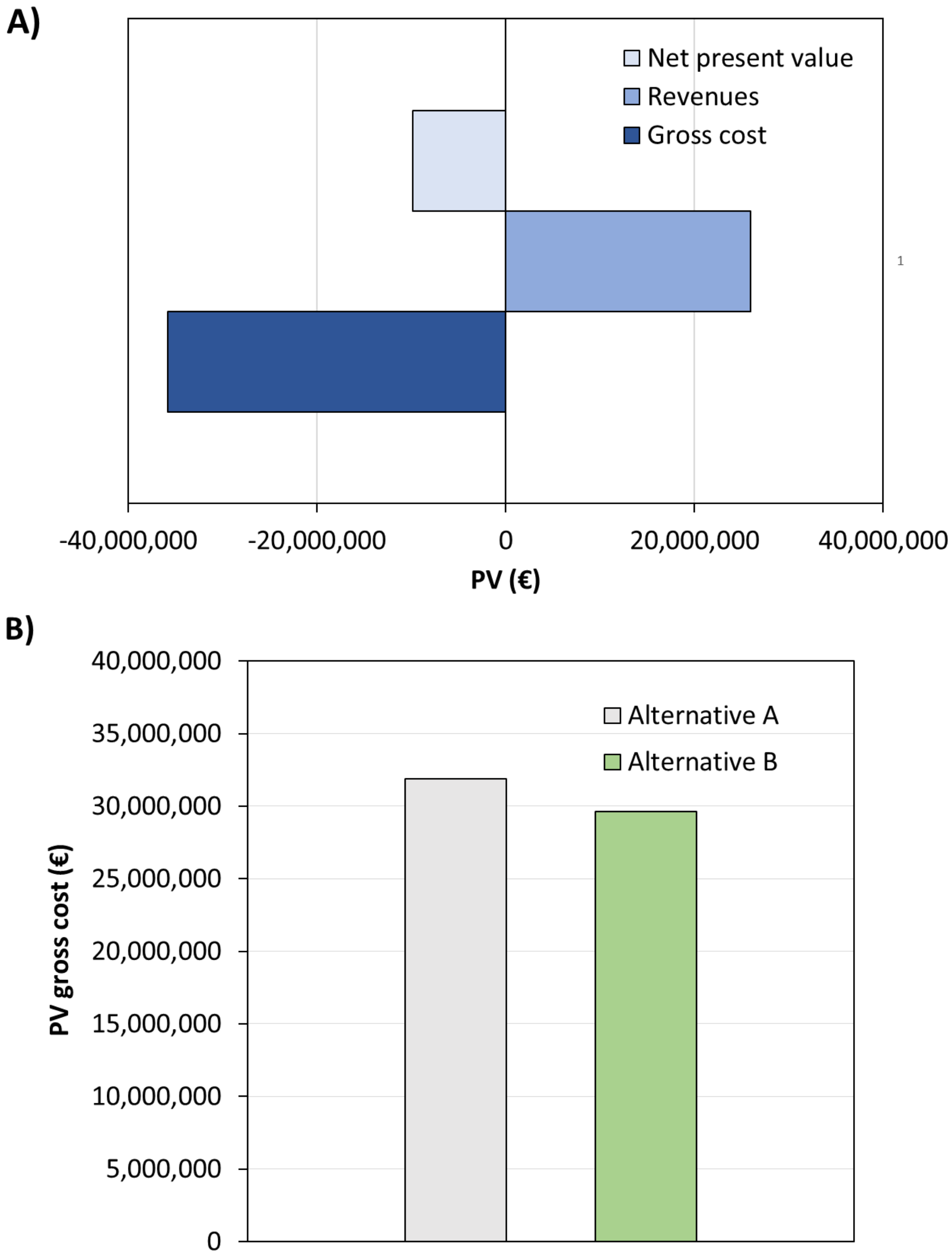

Figure 20 (A) Net present value, present value of the revenues and present value of the gross cost for the sludge line of the WWTP after implementing elutration, struvite recovery and ammonium nitrate recovery (WWTP's perspective). (B) Present value of the gross.

5.3.2.2 *Gross cost contribution*

Figure 21 shows the gross cost distribution of the WWTP after implementing elutration and nutrient recovery technologies. The consumption of chemicals accounted for 30 % of the gross cost and was the most important cost contributor (Figure 21A). The high consumption of chemicals is mainly attributed to (i) the nitric acid needed to recover nitrogen through HFMC, (ii) the sodium hydroxide needed for pH adjustment and zeolites regeneration and (iii) the polyelectrolyte required to improve digested sludge dewaterability. Sludge disposal also featured an important impact on the economic balance since this accounted for 20 % of the gross cost. This agrees with previous publications, which reported that sludge disposal represents a high fraction of the sludge line treatment costs [159], [160]. Finally, it is worth mentioning that the total capital costs (struvite crystalliser, zeolites, HFMC and elutriation tanks) did not account for more than 25 % of the gross cost (Figure 21A). This points out that the operating costs have a larger influence on the implementation of these technologies in the sludge line of the WWTP.

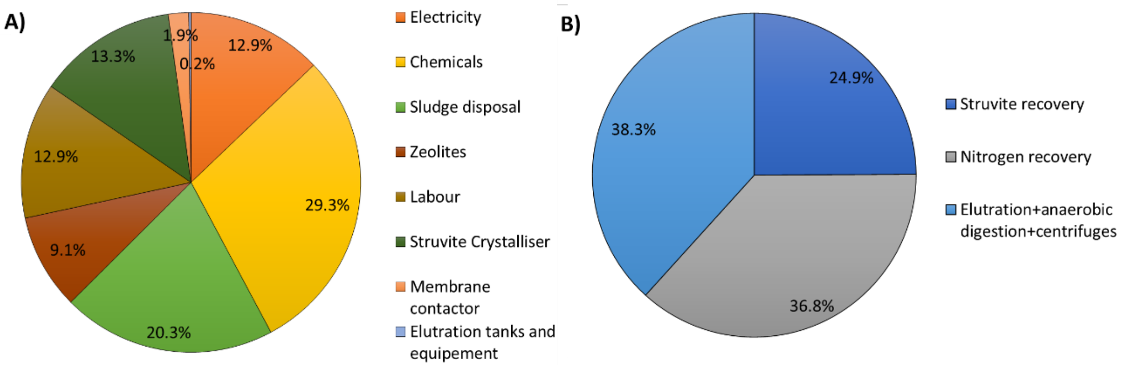

Figure 21 Gross cost distribution of the WWTP after implementing elutration, struvite recovery and ammonium nitrate recovery for (A) the different capital and operating costs and (B) processes.

Nutrient recovery technologies (struvite recovery + nitrogen recovery) represented a higher gross cost contribution (61.7 %) than the other processes of the sludge treatment line (38.3 %). These results highlight that their implementation in a WWTP can substantially increase the gross cost of the sludge line. However, the implementation of these technologies has the potential (i) to generate a revenue from the added-value fertilizer produced, (ii) to reduce the backload of nutrients in the water line and (ii) to reduce the nitrogen and phosphorus concentration in the WWTP effluent [157], [161], [162].

Interestingly, the gross cost contribution of nitrogen recovery (37%) was higher than struvite recovery (25%). This can be mainly attributed to: (i) the high consumption of sodium hydroxide and zeolites for the ion exchange system, (ii) the high consumption of nitric acid and sodium hydroxide in the HFMC system and (iii) the low consumption of $MgCl_2$ needed for struvite crystallization due to the high initial magnesium concentration (c.a. 80 mg/L) in the crystallizer influent. Nevertheless, the amount of ammonium nitrate recovered (c.a. 5300 kg/d) was higher than the amount of struvite recovered (c.a. 3015 kg/d), which leads to an improved profitability for the nitrogen recovery stage.

5.3.2.3 Sensitivity analysis

Figure 22A shows the sensitivity analysis for a ± 30% variation of the most relevant input parameters of the economic analysis. The chemical cost variation was the most sensitive economic parameter to recover nutrients in the WWTP. This output reinforces the idea that optimizing the consumption of chemicals is crucial to improve the economic prospect of implementing ion exchange + HFMC and struvite crystallization for nutrients recovery. The revenue achieved from ammonium nitrate commercialization was the second most sensitive economic parameter. This is an important implication because it demonstrates that future increments in the fertilizer cost can make the implementation of nutrient recovery technologies economically feasible. For this reason, an additional sensitivity analysis was conducted to understand how the potential increase in the cost of the recovered fertilizers could affect the economic prospect of both WWTP and crop field application (Figure 22B).

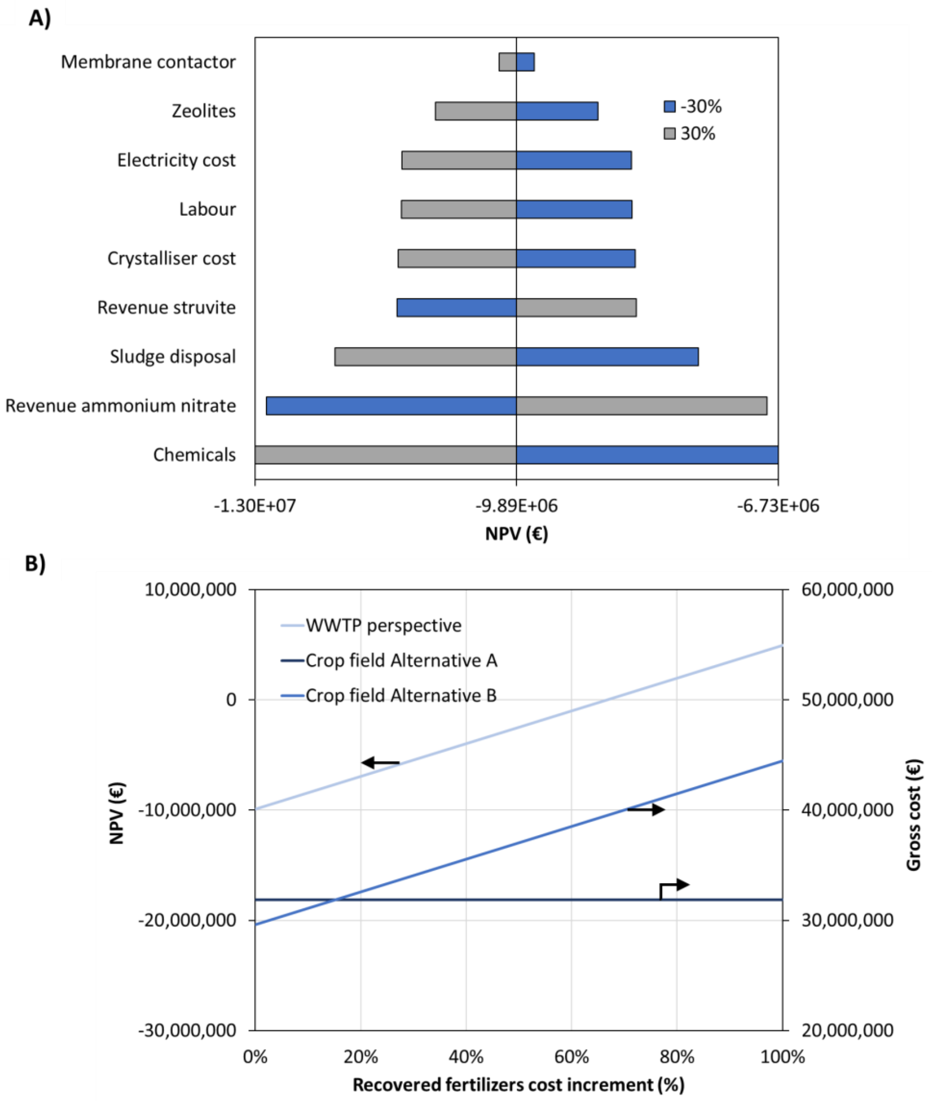

Figure 22 (A) Sensitivity analysis for a ± 30% variation of the most relevant parameters to implement elutration, struvite recovery and ammonium nitrate recovery in the WWTP. (B) Sensitivity analysis for an increase of the recovered fertilizer cost (i.e. struvite and ammonium nitrate costs) for both WWTP and crop field application. The arrows indicate the y-axis corresponding to each data series of the Figure. WWTP: wastewater treatment plant; NPV: net present value.

The NPV of the nutrient recovery system increased from -10,000,000 to +5,000,000 € as the cost increment of fertilizers (ammonium nitrate + struvite) increased from 0 to 100%, respectively (light blue line). The results also illustrate that the implementation of elutriation, struvite recovery and ammonium nitrate recovery in a WWTP would be economically feasible (positive NPV) if the cost of fertilizers increases 66%. This means that the ammonium nitrate and struvite costs should increase up to 0.68

and 0.58 €/kg, respectively. In this regard, it is conceivable to consider that the cost of fertilizers could increase in the future as a result of the progressive increase in the electricity prices[163], [164]. Accordingly, these results would demonstrate that implementing nutrient recovery technologies has the potential to improve the economic balance of the WWTP. However, increasing 66% the cost of fertilizers would make the gross cost of Alternative B (blue line) higher than Alternative A (dark blue line) for crop field application. These results show that future increments in the cost of conventional fertilizers and further optimization of the nutrient recovery scheme would be needed to make the resource recovery configuration economically feasible from both WWTP and farmer points of view.

5.4 **Conclusions**

The present research investigated the economic and environmental implications of recovering nitrogen (ammonium nitrate) and phosphorus (struvite) in a WWTP for their subsequent application in agriculture using real pilot-scale data. The LCA results showed that using a fertilizer solution containing the nutrients recovered in the WWTP was environmentally better than using a synthetic fertilizer solution in most of the evaluated impact categories. These results highlight that using recovered fertilizers features a lower environmental impact than conventional nitrogen-and phosphorus-based fertilizers. Ammonium nitrate represented the most important environmental contributor, which can be mainly attributed to the high consumption of nitric acid and sodium hydroxide in the ion exchange and HFMC stages needed for its production. The TEA illustrated that the revenues achieved from the commercialization of the recovered fertilizers did not offset the extra costs for their implementation. This can be attributed to the high consumption of chemicals, which represented 30% of the gross cost. However, the sensitivity analysis revealed that future increments of 66% in the selling price of ammonium nitrate and struvite could make the implementation of the nutrient recovery scheme economically feasible in a WWTP. Overall, the results of this study results demonstrate that future full-scale application of struvite crystallization, ion exchange and LLMC has the potential to be an economically and environmentally attractive option for nutrient recovery.

5.5 References

[135] A. R. Sheik, E. E. L. Muller, P. Wilmes, K. B. Clark, and X. Zhang, “A hundred years of activated sludge: time for a rethink,” 2014, doi: 10.3389/fmicb.2014.00047.

[136] A. Kogler, M. Farmer, J. A. Simon, S. Tilmans, G. F. Wells, and W. A. Tarpeh, “Systematic Evaluation of Emerging Wastewater Nutrient Removal and Recovery Technologies to Inform Practice and Advance Resource Efficiency,” *ACS ES&T Engineering*, vol. 1, no. 4, pp. 662-684, Apr. 2021, doi: 10.1021/ACSESTENGG.0C00253.

[137] Á. Robles *et al.*, “New frontiers from removal to recycling of nitrogen and phosphorus from wastewater in the Circular Economy,” *Bioresour Technol*, vol. 300, Mar. 2020, doi: 10.1016/j.biortech.2019.122673.

[138] A. Bouzas, N. Martí, S. Grau, R. Barat, D. Mangin, and L. Pastor, “Implementation of a global P-recovery system in urban wastewater treatment plants,” *J Clean Prod*, vol. 227, pp. 130-140, Aug. 2019, doi: 10.1016/j.jclepro.2019.04.126.

[139] R. A. Al-Juboori, J. Uzkurt Kaljunen, I. Righetto, and A. Mikola, “Membrane contactor onsite piloting for nutrient recovery from mesophilic digester reject water: The effect of process conditions and pre-treatment options,” *Sep Purif Technol*, vol. 303, Dec. 2022, doi: 10.1016/j.seppur.2022.122250.

[140] C. Wan *et al.*, “Simultaneous recovery of nitrogen and phosphorus from sludge fermentation liquid by zeolite adsorption: Mechanism and application,” *Sep Purif Technol*, vol. 180, pp. 1-12, 2017, doi: 10.1016/j.seppur.2017.02.031.

[141] R. W. Holloway, A. E. Childress, K. E. Dennett, and T. Y. Cath, “Forward osmosis for concentration of anaerobic digester centrate,” *Water Res*, vol. 41, no. 17, pp. 4005-4014, 2007, doi: 10.1016/j.watres.2007.05.054.

[142] M. A. Boehler, A. Heisele, A. Seyfried, M. Grömping, and H. Siegrist, “(NH4)2SO4 recovery from liquid side streams,” *Environmental Science and Pollution Research*, vol. 22, no. 10, pp. 7295-7305, May 2015, doi: 10.1007/S11356-014-3392-8.

[143] L. Corominas *et al.*, “The application of life cycle assessment (LCA) to wastewater treatment: A best practice guide and critical review,” *Water Res*, vol. 184, Oct. 2020, doi: 10.1016/j.watres.2020.116058.

[144] “UNE-EN ISO 14044:2006.,” 2023. https://www.une.org/encuentra-tu-norma/busca-tu-norma/norma?c=N0038059 (accessed Jul. 18, 2023).

[145] “UNE-EN ISO 14040:2006.,” 2023. https://www.une.org/encuentra-tu-norma/busca-tu-norma/norma?c=N0038060 (accessed Jul. 18, 2023).

[146] A. Amann, O. Zoboli, J. Krampe, H. Rechberger, M. Zessner, and L. Egle, “Environmental impacts of phosphorus recovery from municipal wastewater,” *Resour Conserv Recycl*, vol. 130, pp. 127-139, Mar. 2018, doi: 10.1016/j.resconrec.2017.11.002.

[147] S. Guida, L. Conzelmann, C. Remy, P. Vale, B. Jefferson, and A. Soares, “Resilience and life cycle assessment of ion exchange process for ammonium removal from municipal wastewater,” *Science of the Total Environment*, vol. 783, Aug. 2021, doi: 10.1016/j.scitotenv.2021.146834.

[148] M. Sena, M. Seib, D. R. Noguera, and A. Hicks, “Environmental impacts of phosphorus recovery through struvite precipitation in wastewater treatment,” *J Clean Prod*, vol. 280, Jan. 2021, doi: 10.1016/j.jclepro.2020.124222.

[149] Y. Cortes-Peña, D. Kumar, V. Singh, and J. S. Guest, “BioSTEAM: A Fast and Flexible Platform for the Design, Simulation, and Techno-Economic Analysis of Biorefineries under Uncertainty,” *ACS Sustain Chem Eng*, vol. 8, no. 8, pp. 3302-3310, Mar. 2020, doi: 10.1021/ACSSUSCHEMENG.9B07040.

[150] M. Roldán, A. Bouzas, A. Seco, E. Mena, Mayor, and R. Barat, “An integral approach to sludge handling in a WWTP operated for EBPR aiming phosphorus recovery: Simulation of alternatives, LCA and LCC analyses,” *Water Res*, vol. 175, May 2020, doi: 10.1016/j.watres.2020.115647.

[151] M. Carreras-sempere, R. Caceres, M. Viñas, and C. Biel, “Use of recovered struvite and ammonium nitrate in fertigation in tomato (Lycopersicum esculentum) production for boosting circular and sustainable horticulture,” *Agriculture (Switzerland)*, vol. 11, no. 11, Nov. 2021, doi: 10.3390/AGRICULTURE11111063.

[152] Á. Mayor, S. Vinardell, K. Ganesan, C. Bacardí, J. L. Cortina, and C. Valderrama, "Life-cycle assessment and techno-economic evaluation of the value chain in nutrient recovery from wastewater treatment plants for agricultural application," *Science of The Total Environment*, vol. 892, p. 164452, Sep. 2023, doi: 10.1016/J.SCITOTENV.2023.164452.

[153] M. Rufí-Salís *et al.*, "Increasing resource circularity in wastewater treatment: Environmental implications of technological upgrades," *Science of the Total Environment*, vol. 838, Sep. 2022, doi: 10.1016/j.scitotenv.2022.156422.

[154] A. R. Ravishankara, J. S. Daniel, and R. W. Portmann, "Nitrous oxide (N2O): The dominant ozone-depleting substance emitted in the 21st century," *Science (1979)*, vol. 326, no. 5949, pp. 123-125, 2009, doi: 10.1126/SCIENCE.1176985.

[155] S. Högstrand *et al.*, "Incorporation of main line impact into life cycle assessment of nutrient recovery from reject water using novel membrane contactor technology," *J Clean Prod*, vol. 408, Jul. 2023, doi: 10.1016/j.jclepro.2023.137227.

[156] G. Noriega-Hevia, J. Serralta, A. Seco, and J. Ferrer, "Economic analysis of the scale-up and implantation of a hollow fibre membrane contactor plant for nitrogen recovery in a full-scale wastewater treatment plant," *Sep Purif Technol*, vol. 275, Nov. 2021, doi: 10.1016/j.seppur.2021.119128.

[157] P. Ochs, B. Martin, E. Germain-Cripps, T. Stephenson, M. van Loosdrecht, and A. Soares, "Techno-economic analysis of sidestream ammonia removal technologies: Biological options versus thermal stripping," *Environmental Science and Ecotechnology*, vol. 13, Jan. 2023, doi: 10.1016/j.ese.2022.100220.

[158] "European Comission," 2014. https://ec.europa.eu/commission/presscorner/detail/en/IP_14_599 (accessed Oct. 31, 2022).

[159] M. C. Tomei, G. Bertanza, M. Canato, S. Heimersson, G. Laera, and M. Svanström, "Techno-economic and environmental assessment of upgrading alternatives for sludge stabilization in municipal wastewater treatment plants," *J Clean Prod*, vol. 112, pp. 3106-3115, Jan. 2016, doi: 10.1016/j.jclepro.2015.10.017.

[160] S. Vinardell, S. Astals, K. Koch, J. Mata-Alvarez, and J. Dosta, "Co-digestion of sewage sludge and food waste in a wastewater treatment plant based on mainstream anaerobic membrane bioreactor technology: A techno-economic evaluation," *Bioresour Technol*, vol. 330, Jun. 2021, doi: 10.1016/j.biortech.2021.124978.

[161] G. Rodriguez-Garcia *et al.*, "Life cycle assessment of nutrient removal technologies for the treatment of anaerobic digestion supernatant and its integration in a wastewater treatment plant," *Science of the Total Environment*, vol. 490, pp. 871-879, Aug. 2014, doi: 10.1016/j.scitotenv.2014.05.077.

[162] C. Sembera, C. Macintosh, S. Astals, and K. Koch, "Benefits and drawbacks of food and dairy waste co-digestion at a high organic loading rate: A Moosburg WWTP case study," *Waste Management*, vol. 95, pp. 217-226, Jul. 2019, doi: 10.1016/j.wasman.2019.06.008.

[163] M. Aguilar-Moreno, S. Vinardell, M. Reig, X. Vecino, C. Valderrama, and J. L. Cortina, "Impact of Sidestream Pre-Treatment on Ammonia Recovery by Membrane Contactors: Experimental and Economic Evaluation," *Membranes (Basel)*, vol. 12, no. 12, Dec. 2022, doi: 10.3390/MEMBRANES12121251.

[164] E. Panos and M. Densing, "The future developments of the electricity prices in view of the implementation of the Paris Agreements: Will the current trends prevail, or a reversal is ahead?," *Energy Econ*, vol. 84, Oct. 2019, doi: 10.1016/j.eneco.2019.104476.

Chapter 6

6 Chapter 6: Discussion of the results

The novelty and the scientific and technological outcomes of this thesis relies in its contribution to the demonstration at industrial pilot scale of advanced N recovery schemes and its economic assessment. The work developed aids to promote new routs of N valorization rather than its current removal routes and contributing to unlock technical and economic barriers in its full-scale implementation.

Taking these aspects into consideration, this thesis aimed to conduct a comprehensive analysis of the N flows in Spain (Chapter 3), with a particular focus on WWTPs. Within this context, a new innovative treatment method was proposed and tested at a pilot scale (Chapter 4) to explore novel pathways for N recovery and valorization. Presently, the N is removed and lost as N_2, leading to a significant loss of potential.

Notably, this research goes beyond evaluating the technical performance of the alternative treatment approach; it also considers the entire value chain associated with the process. To achieve this, LCC and LCA tools were employed (Chapter 5).

The comprehensive investigation of the integrated process and the value chain has shed light on valuable insights and conclusions, which are detailed in the subsequent sections of this thesis along with a final outlook. These findings hold great significance in terms of identifying more sustainable and efficient approaches for N management in Spain, contributing to the broader field of environmental science and sustainable resource utilization.

6.1 National management of N flows

Overall, the NFA results provide valuable insights into Spain's N balance, emphasizing the need for sustainable N management strategies to mitigate environmental impacts and ensure resource efficiency. In 2016, a total of 2142 ktN entered the system within Spain's geographical boundaries, while 971 ktN left the country. Fertilizers, food, and feed account for 89% of the annual N flows entering Spain. The largest proportion of N losses was associated with air emissions from agriculture and industry. Results highlight the dependence on products with high N content from third markets. Regarding subsystems, the following were considered for calculations: agriculture, households, industry, transport, waste management, and water bodies. The two most relevant stocks identified within these subsystems are agricultural land and water bodies.

The NFA reveals that in 2016, Spain had a N budget of 913 kt N/y (dStock) when considering only the accumulation for that specific year. This N accumulation can be attributed to various sectors, including agriculture (132 kt N/y), water bodies (779 kt N/y), and dumpsters (2 kt N/y). It is important to note that N also accumulates in soil, forests, groundwater, and landfills. Given the high N accumulation, there is a clear dependence on international products with a significant N content.

Among the imports, fertilizers were the largest flow, followed closely by fuels and food. The import of fertilizers plays a critical role in meeting the N demand in Spain. On the other hand, exports have a minimal influence on the national N budget, with the most significant export flow being fertilizers with 284 kt N/y. This suggests that Spain is primarily a net importer of N related products.

Understanding the N budget and the flow of N within the country is essential for effective N management and addressing potential environmental impacts. By analyzing these flows, policymakers and stakeholders can identify areas where improvements can be made, such as promoting more sustainable agricultural practices and reducing reliance on N intensive imports.

However, the proportions change when it comes to exports. Among the exported goods, the three aforementioned categories still represent a significant portion, accounting for 62% of the exported N. One noteworthy distinction between exports and imports is the amount of non-food N traded to other countries compared to the amount acquired by Spain. Spain exports more than twice the amount of N it imports, indicating a net exporter of non-food N.

These findings highlight the importance of the food industry and agricultural practices in Spain's N flows. It emphasizes the need for sustainable N management strategies to minimize environmental impacts and ensure resource efficiency in the food production and agricultural sectors.

Understanding the balance between N imports and exports is crucial for assessing Spain's N self-sufficiency and its role in the global N cycle. It provides valuable insights into the country's reliance on N intensive products and the potential environmental consequences associated with N-related trade.

Regarding the waste management system, WWTPs play a significant role in the management of urban wastewater, including the treatment of both urban and industrial wastewater, particularly in large metropolitan areas. This wastewater is known to have a high N content, primarily due to the contribution of urea from human excretion. WWTPs are commonly identified as secondary sources with great potential for implementing material recovery strategies, particularly for nutrient cycles such as N and P.

The effluents from WWTPs also hold considerable potential for resource recovery due to their large volume and relatively low concentration of total N, ranging from approximately 15 to 60 g N/m^3. Consequently, reducing the N concentration in WWTP effluents, especially for water treatment plants already employing tertiary treatment, can be a costly management option. Additionally, the volume of generated biosolids is typically smaller than that of the treated water, but they have a significantly higher N concentration, around 6 to 7 times greater than the water, averaging about 70 to 80 g N/kg. The agricultural valorization of more than 75% of these biosolids has had a positive impact, resulting in the recovery of approximately 86 kt N as organic fertilizers. However, concerns exist regarding the efficient utilization of these organic fertilizers by crops, similar to agricultural waste. Future options include promoting the recovery of reactive N as NH_3 or liquid fertilizers.

In Spain, landfills and incineration are widely used waste management options. However, in terms of N flows, they do not contribute significantly, except for the emissions to the atmosphere resulting from waste incineration, which amount to 11 kt N.

In summary, WWTPs have emerged as crucial players in the treatment of urban and industrial wastewater, providing opportunities for material recovery strategies, especially for nutrient cycles such as N and P. Efforts to reduce N concentrations in WWTP effluents can be costly, and biosolids, which contain a higher N content, are being largely valorized in agriculture. However, further exploration of efficient utilization methods and alternative N recovery options, such as NH_3 or liquid fertilizers, can enhance the sustainability of these practices. While landfills and incineration are common waste management approaches in Spain, their N related contributions are relatively minor, with waste incineration being associated with atmospheric N emissions.

6.2 N recovery and valorization as fertilizers

The N recovery was assessed by means of ion exchange with zeolites coupled with LLMCs. There was an initial optimization of the zeolites at lab scale, then the technology was scaled at pilot scale to be tested along with the LLMCs.

The key findings at lab scale are the following:

The efficiency of N recovery showed no significant differences across various operating conditions, except for the adsorption flowrate of 10 BV/h and a regeneration flowrate of 2 BV/h, which resulted in approximately 6% higher recovery. However, the flowrate directly affects the capacity of zeolites. Selecting a feed flowrate of 10 BV/h enabled achieving exchange capacities for ammonium of 9.8-9.9 mg N-NH_4/mg of zeolites, which directly impacts operating costs. Therefore, for regeneration, a flowrate five times lower than the feed is preferred to maximize recovery.

The hydraulic retention time (HRT) also plays a crucial role in the operating capacity for ammonium exchange when filtering wastewater through a zeolite packed column. In this study, HRTs ranging from 7 to 13 min were tested, and it was observed that there were no significant differences within this range. From 5 minutes onward, approximately 80% of the N was extracted. Based on the experiments conducted, the optimal mean HRT value is around 10 min.

The optimization of regeneration processes showed that successful ammonium recovery can be achieved by introducing sodium ions through NaOH, NaCl, or a combination of both, as revealed by batch desorption tests. Concentrations of NaOH at 0.5 M, NaOH at 0.1 M, and NaCl at 20 g/L resulted in 90% N recovery. While NaOH at 0.5 M displayed more consistent results, potentially due to the pH increase, the optimal regenerant solution was found to be a mixture of NaOH at 0.1 M and NaCl at 20 g/L, primarily due to its lower cost. The cost of NaOH at 0.5 M was 3 €/kg N recovered, whereas the cost reduced to 1.5 €/kg N recovered with the combination of NaOH at 0.1 M and 20 g/L of NaCl.

The performance of zeolites in ammonium recovery was evaluated through a pilot plant operating in both mainstream and sidestream processes of WWTPs. A comparison was made based on the adsorption efficiency and capacity of zeolites under different operating conditions.

It was observed that the adsorption efficiency of zeolites in mainstream processes was generally lower compared to sidestream processes. This can be attributed to the lower ammonium concentrations typically found in mainstream wastewater. In contrast, sidestream processes exhibited higher ammonium concentrations, leading to increased cation exchange capacity (CEC) of the zeolites.

The CEC was significantly influenced by the treatment of sidestream compared to mainstream. CEC values of around 20 mg N-NH_4/g was achieved in sidestream treatment, which is a crucial factor to consider when scaling up the technology. In mainstream treatment, the highest CEC value reached was 5.3 mg N/g.

The lifespan of the zeolites regenerated with NaOH in this study was found to be four cycles. Maintaining the zeolite's exchange capacity during the regeneration process is essential for sustainable operation. However, a concrete number of cycles for the lifespan of zeolites regenerated with NaOH was not determined.

In mainstream treatment, effluents with ammonium concentrations below 1 mg N-NH_4/L can be achieved, which is important for meeting stricter discharge limits in sensitive areas. Zeolites in sidestream treatment can produce effluents with concentrations lower than 150 mg N-NH_4/L, leading to a direct reduction in energy consumption for biological removal processes.

Regarding regeneration, the concentration factor was higher in mainstream treatment compared to sidestream treatment. However, due to the higher feed concentration in sidestream, the final concentration of the regenerant solution was also higher, which favors subsequent valorization processes. Generally, with a feed concentration of 50 mg N-NH_4/L, a concentration of 1 g N-NH_4/L can be achieved, while a concentration of up to 4000 mg N-NH_4/L is possible with a feed concentration of 800 mg N-NH_4/L.

The efficiency of N recovery ranged between 75% and 90% of the fed N. However, to understand the excess N found in the regenerations in the sidestream, further analysis of the accumulated N throughout the different cycles is necessary to obtain the overall recovery value of 80-84%.

In terms of quality, heavy metals were not concentrated by the zeolites, and their levels remained below detection limits, except for aluminum. The presence of aluminum at 0.28 mg/L and 12.75 mg/L in the regenerant stream from mainstream and sidestream, respectively, can be attributed to the partial dissolution of zeolites caused by the high pH of the regenerant stream. All parameters comply with current legislation considering thresholds established for sewage sludge and fertilizers.

For organic micropollutants, most of them were detected below quantification levels in the regenerant for both mainstream and sidestream processes. However, the ion exchange process seemed to concentrate certain micropollutants, such as Celestolide and Ibuprofen due to the sorption properties of the zeolite microstructure. On the other hand, other micropollutants like Sulfamethoxazole, Trimethoprim, and Citalopram were reduced to minimal levels or even below the quantification threshold.

Regarding the operation of the LLMCs, all the experiments were conducted using regenerant solution from zeolites at 4-5 g/L N-NH_4 (sidestream). However, the first experiment had an initial concentration of only 1.3 g/L N-NH_4, as the solution was stored at pH 12 for an extended period, resulting in N losses due to ammonia gas release. Despite this ammonia loss, the first experiment achieved a removal rate of 91.6%. In the second experiment, with an initial N-NH_4 concentration of 5.4 g/L, the removal rate reached 75.6%. Higher initial concentrations generally result in lower removal rates.

In summary, the pilot plant studies demonstrated the effectiveness of membrane contactor technology for removing ammoniacal N from wastewater treatment plant effluent and other water sources. However, it is important to raise the feed solution pH to at least 9, preferably 10, to convert ammonium species to ammonia gas. The addition of a CO_2 stripper section can help reduce costs associated with using sodium hydroxide to elevate solution pH, but it may also lead to precipitate formation, potentially causing equipment fouling and clogging.

The results showed the potential to achieve high removal rates in the membranes, with values reaching up to 96%. It was evident that dosing acid to maximize mass transfer resulted in a final product with a high N content. This product can be directly used as a fertilizer or serve as a raw material for fertilizer production.

By examining the variation of the water composition of the LLMC streams over the operation time, the impact of water transport became apparent. Each experiment started with 10 L of 0.4 M HNO_3 on the acid side to initiate operation, and then HNO_3 (58%) was added through the control loop to maintain a pH of 3.4. The amount of acid dosed ranged from 12 to 15 L. Considering that each experiment produced 50 L of fertilizer, it can be concluded that water transport of 20-25 L was experienced in each experiment.

Controlling the quality and concentration of the fertilizer produced is a critical aspect, as highlighted in the existing literature. It is essential to ensure that the overall composition of organic micropollutants (OMPs) in the fertilizer remains undetectable, even considering water transport, thereby guaranteeing its quality. This is supported by the absence of Ciprofloxacin and Oxytetracycline in the fertilizer while being present in the zeolites concentrate. The presence of heavy metals is negligible, with concentrations near the detection limit, whereas nutrient ions such as K, Mg, SO_4, and Ca are present in specific concentrations. Na stands out as the most significant ion, with concentrations of 3-4 g/L, which can be attributed to the influence of water transport and the high concentration of NaOH in the feed side. In Spain, the regulation of fertilizers is governed by Real Decreto 506/2013, which sets maximum allowable limits for metals and other elements. Comparing the metal levels presented in the provided table, it is evident that aluminum, arsenic, cadmium, cobalt, chromium, copper, nickel, lead, and zinc in all fertilizers are below the maximum allowable limits.

Integration of zeolite regeneration with the LLMC system for fertilizer production appears to be a promising approach for wastewater treatment. The zeolite regeneration process effectively captures ammonia, producing a regenerant solution that can then be used as feed for the LLMC system to produce fertilizers.

6.3 Life Cycle analysis of the whole value chain

To close the entire value chain, a comprehensive study was conducted to explore the economic and environmental implications of recovering N (in the form of ammonium nitrate) and P (in the form of struvite) from a WWTP for subsequent use as fertilizers in agriculture. The study employed a LCA to compare two scenarios: the Baseline Scenario, where conventional commercial fertilizers were used, and Scenario 1, which involved implementing the LIFE ENRICH configuration to recover N and P fertilizers.

The findings indicate that Scenario 1, which involves the use of recovered fertilizers (struvite and ammonium nitrate) for crop field application, resulted in a lower environmental impact compared to the Baseline Scenario in various categories. Notably, there were significant reductions in stratospheric ozone depletion (39%), freshwater eutrophication (12%), global warming (24%), land use (41%), water consumption (14%), and other impact categories. The lower environmental impact can be attributed to the decreased reliance on chemical reagents, such as nitric acid, which are extensively used in the Baseline Scenario for fertilizer production. Therefore, it can be concluded that the adoption of recovered fertilizers for crop field application offers an improved environmental outlook compared to the utilization of commercial nutrient solutions.

In contrast, Scenario 1 demonstrated a higher environmental impact in certain categories, including mineral resource scarcity (-34%), human carcinogenic toxicity (-17%), and freshwater ecotoxicity (-4%). The increased impact related to mineral resource scarcity can be attributed to the substantial consumption of chemicals in the ion exchange and LLMC systems used to recover N in the sludge line of the WWTP. Similarly, the higher impacts of freshwater ecotoxicity and human carcinogenic toxicity in Scenario 1 compared to the Baseline Scenario are a result of the elevated consumption of nitric acid for N recovery and the environmental impact associated with the disposal of zeolite slurry.

The use of commercial N and P based fertilizers has a significant impact on the environment due to the extensive consumption of chemical reagents and energy required for their production. It is noteworthy that nitric acid, a key component in the production of these fertilizers, accounted for 97% of the stratospheric ozone depletion and 65% of the global warming impact categories. This is primarily attributed to the potential emissions of nitrous oxide (N_2O) during the production of nitric acid, as N_2O is a potent greenhouse gas and ozone-depleting substance. In the case of Scenario 1, which involves N recovery through ammonium nitrate production, this process emerged as the most significant environmental contributor across nine of the evaluated impact categories.

The successful implementation of these innovative nutrient recovery technologies, leading to the production of value-added fertilizers such as ammonium nitrate and struvite, has significant implications for promoting resource recovery and circular economy in future WWTPs. However, despite the revenue generated from these fertilizers, the costs associated with their implementation, including both capital expenditure (CAPEX) and operational expenditure (OPEX), outweigh the financial benefits, resulting in a negative net present value (NPV). This highlights the need for further advancements and improvements in the efficiency of these technologies to achieve a positive economic balance.

It is important to note that this study was conducted at a pilot scale within the scope of a European project. If these technologies were to be scaled up to an industrial level, it is expected that the economic balance and environmental impacts would be more favorable compared to the results obtained in this study. For instance, the energy efficiency of the system would likely improve on an industrial scale, reducing the contribution of electricity costs, which accounted for 12.9% of the total system cost in this pilot-scale demonstration. Furthermore, the application of these nutrient recovery technologies has the potential to reduce the consumption of energy and chemicals in the water line of the WWTP, which could improve the economic balance of implementing these technologies. Finally, results also showed that using a fertilizer solution containing struvite and ammonium nitrate is less costly than using a typical commercial solution.

Based on these findings, it is reasonable to suggest that the WWTP has the potential to increase the selling price of struvite and ammonium nitrate in order to enhance its economic. In addition to the economic benefits, the recovery of P from wastewater plays a vital role in reducing the reliance on non-renewable phosphate rock. It is worth noting that phosphate rock is classified as a Critical Raw Material by the European Commission, underscoring the importance of P recovery as a sustainable solution for resource management.

The conducted sensitivity analysis examined the impact of a ±30% variation in the most significant input parameters on the economic analysis. The results highlighted that the cost of chemicals had the highest sensitivity among the economic parameters related to nutrient recovery in the WWTP. This emphasizes the critical importance of optimizing the chemical consumption to enhance the economic feasibility of implementing ion exchange + LLMC and struvite crystallization for nutrient recovery.

Furthermore, the revenue generated from the commercialization of ammonium nitrate was identified as the second most sensitive economic parameter. This finding carries significant implications, as it indicates that potential increases in the cost of fertilizers could contribute to the economic viability of nutrient recovery technologies. To further explore this aspect, an additional sensitivity analysis was conducted to assess how potential cost increments in the recovered fertilizers could affect the economic outlook for both the WWTP and crop field application. This analysis provides valuable insights into the potential economic benefits of implementing nutrient recovery technologies and helps inform decision-making processes in both the wastewater treatment and agricultural sectors.

The sensitivity analysis examined the economic prospect of implementing elutriation, struvite recovery, and ammonium nitrate recovery in a WWTP while varying the cost of fertilizers. The results indicate that the implementation would be economically feasible, with a positive NPV, if the cost of fertilizers increases by 66%. Specifically, the cost of ammonium nitrate should increase to approximately 0.68 €/kg, while the cost of struvite should increase to around 0.58 €/kg.

To illustrate this, a cost increment of up to 5,000,000 € was considered, representing a range of 0% to 100% cost increase for fertilizers (ammonium nitrate and struvite). The results, depicted by the light blue line, demonstrate that the economic feasibility (positive NPV) is achieved when the cost of fertilizers rises by 66%.

It is important to note that the cost of fertilizers may increase in the future due to factors such as the progressive rise in electricity prices. Considering this potential scenario, the findings suggest that the implementation of nutrient recovery technologies in the WWTP would still remain economically attractive and viable.

Overall, these results provide valuable insights into the economic implications of implementing nutrient recovery technologies, highlighting the potential for economic feasibility even with increased fertilizer costs. This information can support decision-making processes and encourage further exploration of sustainable solutions in wastewater treatment and agriculture.

Chapter 7

7 Chapter 7: Conclusions and outlook

7.1 Conclusions

According to United Nations projections, the global population is expected to reach 8.6 billion by 2030 and 9.8 billion by 2050. This increase in population, coupled with rising consumption levels, exerts significant pressure on the food industry to enhance its production capabilities. Meeting this growing demand necessitates intensified agricultural practices, which in turn leads to heightened usage of land, water, energy, and fertilizers. Consequently, there is a projected surge in the demand for plant nutrients. The current agricultural system heavily relies on non-renewable mineral fertilizers, comprising N, P, K, and Mg. These fertilizers serve as the foundation of modern agricultural practices.

As it has been pointed out in Chapter 1 there is an increasing need to recover nutrients and further valorize them through different routes in order to increase the circularity of the territory in order to reduce the external dependence as well as reduce the overall carbon footprint. This can be achieved through the production of fertilizers produced from the nutrients recovered. For this reason, the results of this thesis are structured in 3 different papers (Chapter 3,4, and 5). The first one focuses on mapping the flows of N along the whole country to assess potential improvements and identify the best recovery spots. The results of the first publication revealed that WWTP are really good spots with lots of potential for nutrients recovery, that is way a N recovery technology has been tested at pilot scale in VNG WWTP and Murcia ESTE WWTP (Spain). Finally, to assess the overall impact an LCC/LCA of the whole value chain was developed. Technologies such as struvite crystallization and ion exchange coupled with LLMC proved to be technically viable to recover and valorize N and P as fertilizers. Using a fertilizer solution containing the nutrients recovered in the WWTP was environmentally better than using a synthetic fertilizer solution in most of the evaluated impact categories. This fact highlights that using recovered fertilizers features a lower environmental impact than conventional N and P based fertilizers. From the economic point of view the revenues achieved from the commercialization of the recovered fertilizers did not offset the extra costs for their implementation in the current market and legal framework. However, changes in the current legal framework or possible shifts in the market derived from socio-political events can lead to a 66% increase in the selling price of ammonium nitrate and struvite. This increase would make the implementation of the nutrient recovery scheme economically feasible in WWTPs. Overall, the future full-scale application of struvite crystallization, ion exchange and LLMC has the potential to be an economically and environmentally attractive option for nutrient recovery.

Regarding the N management in Spain prioritizing biological treatment as the primary end-of-life scenario for compostable goods would be the most effective strategy to minimize N wastage into the environment, specifically in the atmosphere, water bodies, or soil. By avoiding incineration as an end-of-life scenario, it is estimated that approximately 11 kt of N per year could be prevented from reaching the atmosphere.

It is highly recommended to increase the adoption of circular strategies within the territory. One significant aspect of this strategy involves recovering nutrients present in wastewater and transforming them into fertilizers. Considering that Spain reports a N stock between 40% and 60%, actions should primarily focus on reducing N losses in water bodies in the agricultural sector, which currently account for 724 kt N/year.

In conclusion, implementing circular strategies in waste management, enhancing nutrient recovery from wastewater, and adopting sustainable agricultural practices are crucial steps to minimize N losses, protect water bodies, improve soil health, and address the environmental impacts associated with N use in Spain.

One way to achieve this circularity increase is by providing a legal framework that favors the implementation of new technologies capable of recycling these nutrients back into the country boundaries. In this thesis it has been proven that the N recovery from urban WWTP and its further valorization as fertilizer not only can be technical and economically feasible but also has a huge benefit at an environmental level.

7.2 Outlook and future prospects

Recycled nutrients are on the verge of being included in the EU Regulation, marking a significant step towards promoting their use as direct fertilizers or raw materials for fertilizing products in EU Member States. In 2019, struvite and similar phosphate salts were incorporated into the new EU Fertilizer

Products Regulation 2019/1009, set to take effect in July 2022. This regulatory inclusion not only encourages wastewater treatment plants (WWTPs) to implement nutrient recovery processes but also motivates the fertilizer industry and farmers to adopt these products, as harmonized regulation ensures both commercial benefits and product safety at the European level.

The STRUBIAS report, developed by the Joint Research Centre (JRC) of the European Commission, has played a crucial role in shaping the EU Fertilizer Products Regulation for struvite. It proposed specific criteria for phosphate salts, struvite, biochars from pyrolysis and gasification, and thermal oxidation materials (ashes). These criteria are now incorporated into the EU FPR, driving the adoption of struvite at the European level. The report engaged the entire stakeholder community from 2017 onwards, facilitating the discussion and implementation of P recovery as struvite in European practices. Additionally, it facilitated the establishment of quality standards and analytical parameters for struvite production, as seen in the ENRICH project, which anticipated the product's inclusion in the EU FPR ahead of regulatory changes.

While ammonium salts produced from nutrient recovery are not yet included in regulations, it is expected that they will follow a similar path to that of struvite in a short period. The successful adaptation of policies for struvite is a pivotal step for all recovered nutrients, setting a precedent for their acceptance and utilization. The STRUBIAS report remains a dynamic resource, continuing to lead the way in regulating recovered nutrients and other valuable products that can be obtained from WWTPs and alternative sources, offering more sustainable options than conventional ones.

End-of-Waste (EoW) status for recovered nutrients is currently granted at the national level in Belgium, Netherlands, and Germany, specifically for struvite. However, the new EU FPR presents an opportunity to change this situation in the short-term and expand EoW status to other countries.

In terms of trademarked products, those registered under the REACH regulation can be sold as fertilizers at the national level. Notable examples include Phosphocare™ (from the Phosphogreen process in Denmark), Crystal Green® (from the Pearl process in the United States/United Kingdom), and BIOSTRU© STRU-VITE (from the NuReSys process in Belgium).

The feasibility of using the recovered products for fertigation of tomato, lettuce, cauliflower, and broccoli was assessed in the ENRICH project in collaboration with the European Sustainable Phosphorus Platform (ESPP), providing a solid foundation for the success of this model. Moreover, a business plan for Spain has been defined based on the project's results, and the business models have been adapted for other European countries, considering the synergies and context of key players and the current and expected regulations in each nation.

To ensure the viability of these results and contribute to the updating of the legal framework, the project involved the administration, with the Ministry of Agriculture of Spain being one of the stakeholders. The ENRICH team recognizes the vital role of involving the administration in such projects to have a meaningful impact on policies.