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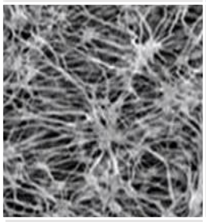

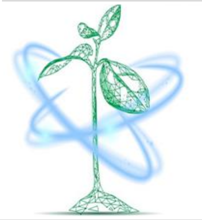

VALORISATION OF AGROINDUSTRIAL BY-PRODUCTS THROUGH THE APPLICATION OF MEMBRANE TECHNOLOGY

PhD THESIS - TESIS DOCTORAL

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PROGRAMA DE DOCTORADO EN CIENCIA E INGENIERÍA AGROALIMENTARIA Y DE BIOSISTEMAS

TESIS DOCTORAL:

VALORIZACIÓN DE SUBPRODUCTOS AGROINDUSTRIALES MEDIANTE LA APLICACIÓN DE TECNOLOGÍA DE MEMBRANA / VALORIZATION OF AGROINDUSTRIAL BY-PRODUCTS THROUGH THE APPLICATION OF MEMBRANE TECHNOLOGY

Presentada por ISABEL GONZÁLEZ GARCÍA
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A mis padres

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To all the colleagues with whom I have work during this thesis, especially Beatriz Molinuevo Salces, whose help in the laboratory, contributions throughout the work and comments for the articles were essential. Also, to Verónica Oliveira, for her invaluable help and sympathy throughout my stay at CERNAS in Coimbra (Portugal) and to Celia Días-Ferreira, for her kind welcome in Coimbra and her important comments. To Matias Vanotti, for his generosity in sharing experience and knowledge; to Rosa Cuéllar-Franca, for her great help regarding LCA and to Mari Carmen García-Gutiérrez, Araceli Ramos and the other colleagues in the laboratory for their great help.

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List of abbreviations

AD	Anaerobic digestion
AP	Apple pomace
CBE	Circular Bioeconomy
CE	Circular Economy
ED	Electrodyalitic
EU	European Union
F2F	Farm to Fork
FU	Functional unit
GHG	Greenhouse gases
GPM	Gas-permeable membrane
H_2SO_4	Sulfuric acid
HRT	Hydraulic retention time
IEM	Ion Exchange membrane
LCA	Life cycle assessment
N	Nitrogen
NH_3	Ammonia
NH_4^+	Ammonium
OLR	Organic loading rate
P	Phosphorus
PA	Partial alkalinity
SDG	Sustainable Development Goals
SETAC	Society of Environmental Toxicology and Chemistry
SM	Swine manure
TA	Total alkalinity
TAN	Total ammoniacal nitrogen
TCOD	Total chemical oxygen demand
TKN	Total Kjeldahl nitrogen
TS	Total solids
UNEP	United Nations Environmental Program
VFA	Volatile fatty acids
VS	Volatile solids

I. ABSTRACT

Waste does not exist in nature: the waste of some life forms is the raw material of others. Working in waste management makes it possible to see the great potential contained within residues that still can be extracted. In this line, this thesis is part of a new approach to explore innovative strategies and technologies that allow impacts produced by waste to be minimized, while at the same time recovering its remaining value. This thesis is focused on organic waste from the agro-industry, such as manure and food residues. These wastes have been traditionally managed by using them as organic fertilizers, but it has been stated that this practice can be ineffective, due to nutrient imbalance in the soil and also to potential polluting emissions to the atmosphere, water and soil as result of nutrient losses. Among these emissions, ammonia (NH_3) emissions stand out. These emissions are very harmful to the health of people and animals and to ecosystems. Fortunately, there are some technologies, such as the gas-permeable membrane (GPM) technology, that are capable of converting these NH_3 emissions into a valuable nitrogen-based fertilizer that can be used directly on crops. **The objective of this thesis** is to study several applications of these GPM on different wastewaters of the agro-industry sector, in order to minimize NH_3 emissions and nutrient losses, to valorize these waste streams while obtaining valuable bio-based fertilizers, and to reduce the potential environmental impacts.

The GPM technology has the capacity to be applied on NH_3-rich wastewaters to recover nitrogen as a nutrient. This work studies whether the GPM technology can be applied on existing waste treatment processes, such as biogas plants, where they can not only improve the amount of biogas produced, but also its quality. In addition, it is possible to apply them in the digestate produced by biogas plants, and to obtain high nitrogen recovery efficiencies. We have also tested its capability to be combined with other existing techniques for the recovery of other nutrients, such as phosphorus, which is another essential nutrient for plants. The results obtained have shown the great potential of these membranes and the importance of the application of novel nutrient recovery technologies. It is time to apply the best-known technologies for waste valorization, changing the waste management approach and to start considering waste as resources.

RESUMEN

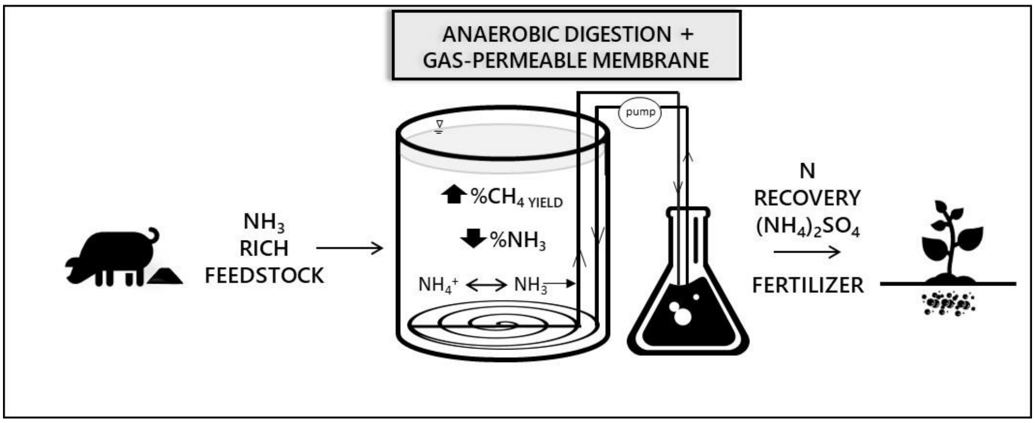
Los residuos no existen en la naturaleza: los desperdicios de una especie son la materia prima de otra. Trabajando en la gestión de residuos es posible ver el gran potencial que aún contienen los residuos y que puede ser recuperado. En este sentido, esta tesis forma parte de un nuevo abordaje de la investigación para explorar estrategias innovadoras y tecnologías que permiten minimizar los impactos producidos por los residuos, al mismo tiempo que recuperar el valor que contienen. Esta tesis está enfocada en los residuos orgánicos de la industria agro-alimentaria. Estos residuos han sido manejados tradicionalmente como fertilizantes orgánicos, pero recientemente se ha visto que esta práctica puede ser poco efectiva dado que el aporte al suelo de los nutrientes no está bien equilibrado. Asimismo, tienen un gran potencial para generar emisiones a la atmósfera y contaminación de los suelos y del agua debido al exceso de nutrientes que se pueden perder por lixiviación. Entre esas emisiones, el amoniaco (NH_3) destaca como un gas particularmente nocivo. Afortunadamente, hay nuevas tecnologías, como la de las membranas permeables a los gases (MPG), que son capaces de convertir esas emisiones de amoniaco en un valioso fertilizante nitrogenado que puede ser aplicado directamente sobre los cultivos. **El objetivo de esta tesis** es estudiar varias aplicaciones de estas MPG en diferentes aguas residuales del sector agroindustrial, con el fin de minimizar las emisiones de NH_3 y las pérdidas de nutrientes, valorizar estos flujos de residuos y obtener valiosos fertilizantes y reducir impactos ambientales potenciales.

La tecnología de las MPG es capaz de recuperar N como nutriente si se aplica en aguas residuales ricas en amoniaco. En este trabajo se ha estudiado la combinación de la tecnología de MPG con procesos de tratamiento de aguas residuales agro-industriales que ya existen, como las plantas de biogás, donde han mostrado que mejoran la producción de biogás y además aumentan su calidad. También es posible aplicarlas en el digestato resultante de estas plantas de biogás, obteniendo altos porcentajes de recuperación de nitrógeno. Se ha estudiado también su capacidad para ser combinadas con otras tecnologías para la recuperación de fósforo, otro nutriente esencial para las plantas. Los resultados obtenidos muestran el gran potencial de estas membranas, y la importancia de la aplicación de tecnologías novedosas para la recuperación de nutrientes. Es el momento de usar la mejor tecnología conocida para la valorización de residuos, cambiando la percepción del manejo de residuos para considerarlos recursos.

II. LIST OF SCIENTIFIC CONTRIBUTIONS

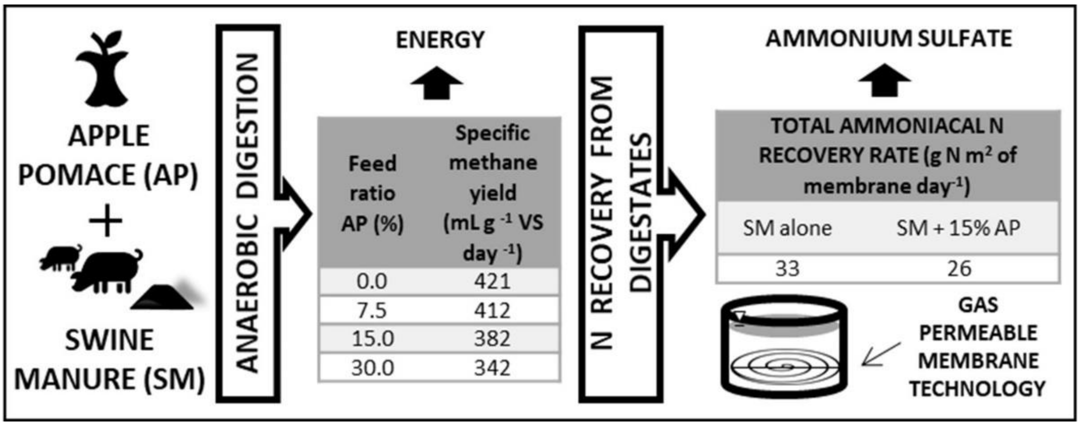
1) "Improved anaerobic digestion of swine manure by simultaneous ammonia recovery using gas-permeable membranes"

González-García, I., Riaño, B., Molinuevo-Salces, B., Vanotti, M. B., García-González, M. C. 2021. Improved anaerobic digestion of swine manure by simultaneous ammonia recovery using gas-permeable membranes. Water Res. 190, 116789. https://doi.org/10.1016/j.watres.2020.116789. Cited by 15. Journal: Water Research; JCR Journal Impact Factor: 13.4; Q1 for Environmental sciences; Water resources; Engineering, Environmental - SCIE



2) "Energy and Nutrients from Apple Waste Using Anaerobic Digestion and Membrane Technology"

González-García, I., Riaño B., Molinuevo-Salces B., García-González M. C. 2022. Energy and nutrients from apple waste using anaerobic digestion and membrane technology. Membranes 12, 9: 897. https://doi.org/10.3390/membranes12090897. Cited by 1. Journal: Membranes; JCR Journal Impact factor: 4.5; Q1 for Polymer science – SCIE.

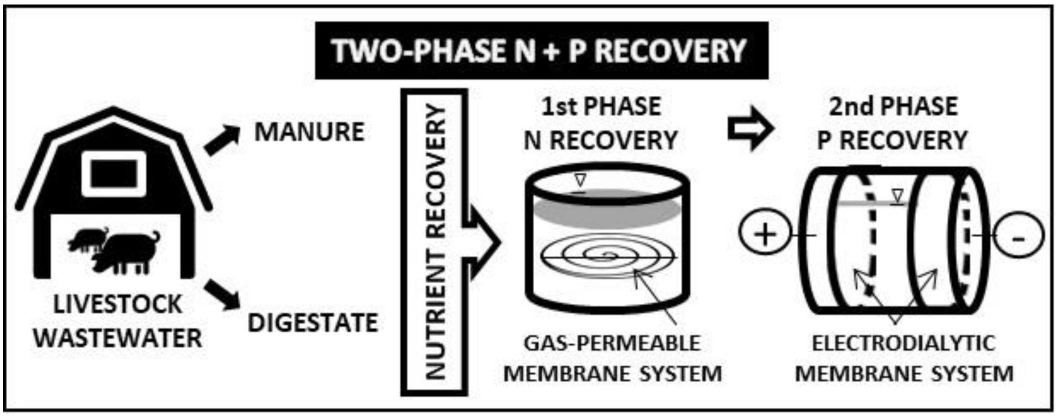


Feed ratio AP (%)	Specific methane yield (mL g $^{-1}$ VS day $^{-1}$)
0.0	421
7.5	412
15.0	382
30.0	342

TOTAL AMMONIACAL N RECOVERY RATE (g N m^2 of membrane day^{-1})	
SM alone	SM + 15% AP
33	26

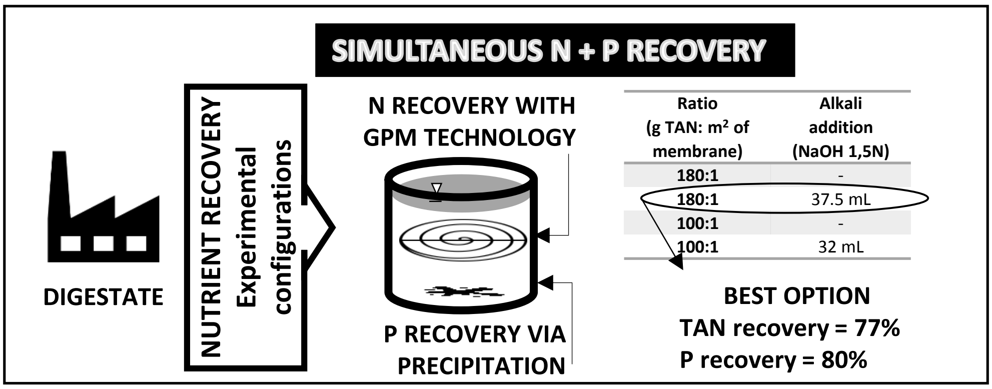
3) “Two-phase nutrient recovery from livestock wastewaters combining novel membrane technologies”

González-García, I., Oliveira, V., Molinuevo-Salces, B., García-González, M. C., Días-Ferreira, C., Riaño, B. 2022. Two-phase nutrient recovery from livestock wastewaters combining novel membrane technologies. Biomass Conv. Bioref. 12, 4563–4574. https://doi.org/10.1007/s13399-022-02546-6. Cited by 1; Journal: Biomass Conversion and Biorefinery; JCR impact factor: 4; Q2 for Engineering, chemical - SCIE.



4) “Effect of alkali and membrane area on the simultaneous recovery of nitrogen and phosphorous from digestate by membrane technology and chemical precipitation”

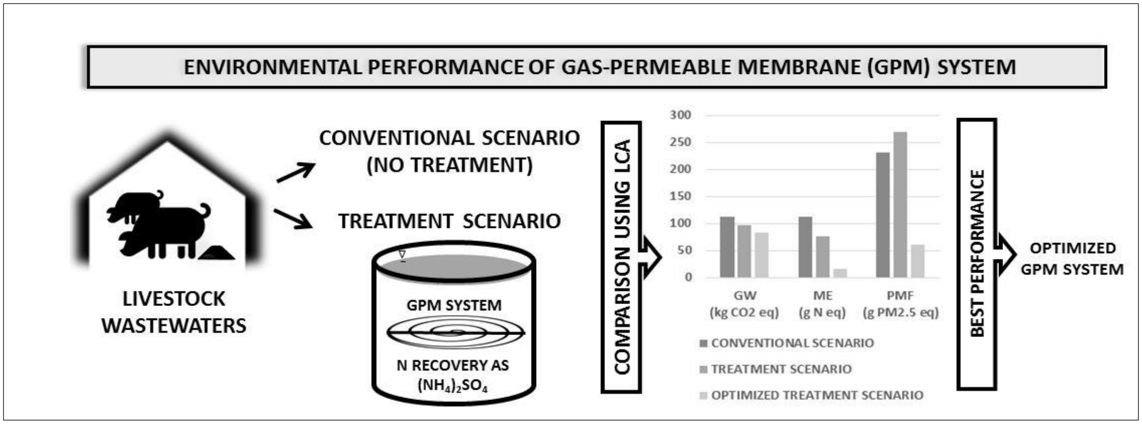
González-García, I., Riaño, B., Molinuevo-Salces, B., García-González, M.C. 2022. Effect of alkali and membrane area on the simultaneous recovery of nitrogen and phosphorous from digestate by membrane technology and chemical precipitation. Sustainability, 15, 3909. https://doi.org/10.3390/su15053909. Journal: Sustainability; JCR impact factor: 3.8; Q2 for Environmental Studies and Environmental Science.



Ratio (g TAN: m^2 of membrane)	Alkali addition (NaOH 1,5N)
180:1	-
180:1	37.5 mL
100:1	-
100:1	32 mL

5) **“Environmental sustainability performance of a membrane-based technology for livestock wastewater treatment with nutrient recovery”**

González-García, I., Riaño, B., Cuéllar-Franca, R. M., Molinuevo-Salces, B., García-González, M. C. 2022. Environmental sustainability performance of a membrane-based technology for livestock wastewater treatment with nutrient recovery. J. Environ. Chem. Eng. 10 (2), 107246 https://doi.org/10.1016/j.jece.2022.107246. Cited by 5. Journal: Environmental Chemical Engineering; JCR impact factor: 7.9; Q1 for Engineering, chemical – SCIE; Engineering, environmental – SCIE.



III. INTRODUCTION

1. FRAMEWORK OF NUTRIENT LOSSES IN THE AGRO-INDUSTRIAL SECTOR

The current global scenario, marked by changes resulting from a global pandemic, economic instability and climate change, presents major challenges that directly affect **energy and food security** (UN, 2022). To address these challenges, global strategies, such as the UN's Sustainable Developing Goals (SDG) or the recent European policies, propose the diversification of energy sources and the optimization of resources and processes in the food-industry within the framework of the Paris Agreements (EC, 2020; UN, 2022; UNEP, 2022).

The European Green Deal (EC, 2019a) was developed in relation to the security of these particular aspects (energy and food), specifically at a European level, in order to ensure a prosperous and competitive society, with zero net emissions by 2050 and a resource-efficient economy. Among its many objectives, supplying clean, affordable and secure energy and the design of a healthy and environmentally-friendly food system stand out. In the first case, the Green Deal proposes the use of renewable gases, such as biogas or hydrogen, and prioritizes energy efficiency (EC, 2019a). As for the second aspect, the Farm to Fork (F2F) strategy (EC, 2020) was developed to ensure sustainable food systems, while reducing the environmental footprint of the EU food system. For instance, it was agreed to reduce the use of antimicrobials on farm animals by 50% by 2030, as well as to reduce the use of pesticides by 50% and the use of **fertilizers** by at least 20%, while reaching the target of 25% of agricultural land under organic farming, among other measures.

The fertilization optimization strategies include knowledge of when, where and how to apply **nutrients**, such as N and P, to achieve the best fertilizer usage and uptake by crops. In this regard, the F2F strategy points out the importance of the application of a circular bioeconomy model as a powerful transition mechanism to achieve the aforementioned objectives (EC, 2020).

The **circular bioeconomy** (CBE) could be considered as a concept that unifies the bioeconomy and circular economy (CE) ideas. Bioeconomy can be defined as an economic system that is predominantly based on biomass as the raw material for the production of food, chemicals or energy (EC, 2019b; Kaltschmitt, 2019). Regarding the CE, although there is still no globally accepted definition (Kirchherr et al., 2017), we can take the concept proposed by the European Commission, where CE can be defined as a model where the value of products, materials and resources is maintained for as long as possible, and the generation of waste is minimized, using renewable energy sources (EC, 2015). Therefore, citing Stegmann et al. (2020), CBE could be considered as the model that "*focuses on the sustainable, resource-efficient valorization of biomass in integrated, multi-output production chains (e.g. biorefineries) while also making use of residues and waste and optimizing the value of biomass over time via cascading steps.*".

Figure 1 represents the two-sided material flows in a circular economy (Ellen McArthur Foundation, 2012). On the right is the technological cycle, where non-renewable materials circulate. On the left is the biological cycle, where organic matter and nutrients circulate (only biodegradable materials), and which the CBE flow can be resembled to. The **scope of this thesis** is framed in this biological cycle, and is represented by the **discontinuous orange line.**

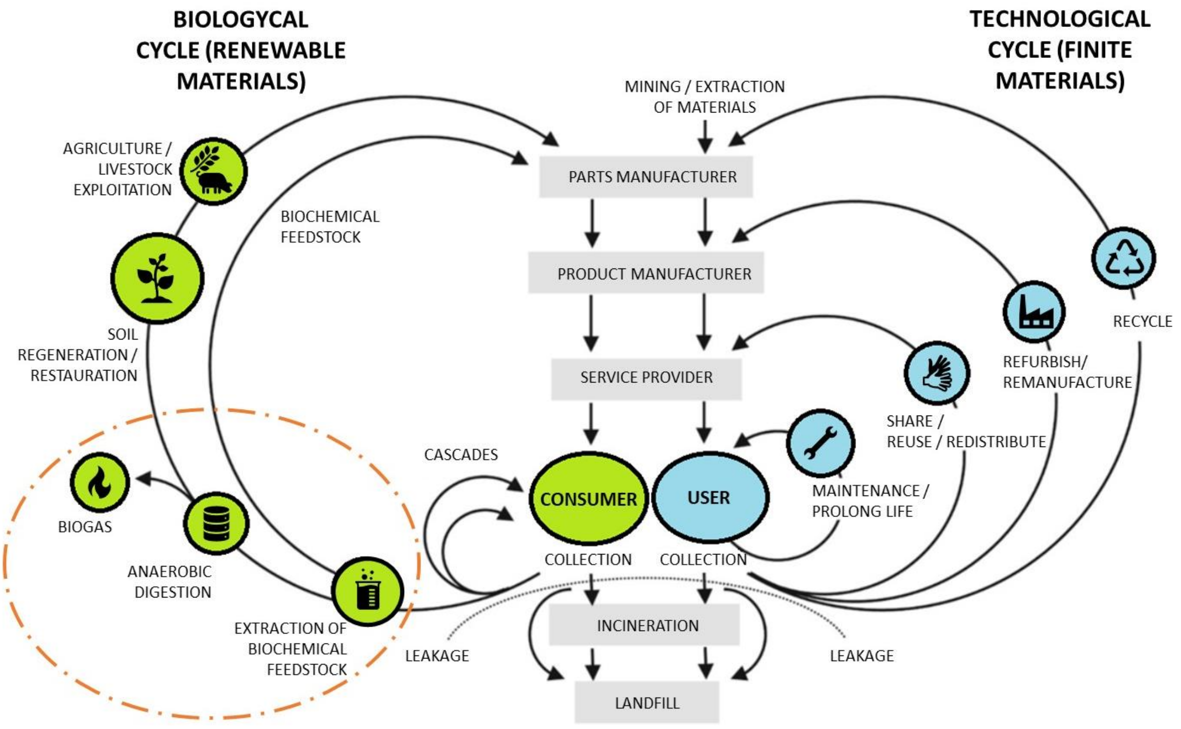


Figure 1. Flow diagram for the biological cycle and the technological cycle or "butterfly diagram of circular economy". Source: adapted from Ellen MacArthur Foundation (2012).

Both the definitions and the graphic representation show that waste management is at the core of CE, and waste management is precisely one of the largest areas of CE research (Merli et al., 2017). In this regard, European bioeconomy clusters are moving towards CBE, **taking residues and waste more into account as resources**, developing integrated biorefineries and focusing on materials and high-value applications of biomass (Stegmann et al., 2020).

In order to understand at which point in the biological cycle nutrient losses occur, it is important to know the nutrient cycles and locate the hot-spots. Within the biological cycle and the agroindustry sector, the possibilities of nutrient recovery correspond to essential nutrients and organic matter. **This thesis focuses on N and P recovery for residue valorization**.

1.1. Nitrogen in the agro-industrial sector

Nitrogen is the most common element in the atmosphere (78%) and it is essential for life, as it is the central component of DNA and RNA molecules. The generation of complex proteins by plants is the first step in the global food chain, and therefore, is essential for human food security. Figure 2 shows a simplified N cycle of the agro-industrial sector. Initially, N can enter the soil either as organic N by decomposition of organic matter or fixed by specialized bacteria. This N is mineralized to NH_4^+, which can be used by plants (Aczel, 2019). The NH_4^+ in the soil solution can be considered as a weak acid in equilibrium with its dissociation products NH_3 and H^+, depending on the pH and the temperature: high pH values and high temperature may enhance NH_3 losses (volatilization) from NH_4^+ - N (Cabrera et el., 2005).

$$NH_3 + H^+ \text{ - in soil} \longleftrightarrow NH_4^+ \text{ - in soil}$$

The NH_4^+ goes under a nitrification process to produce NO_3^-, which can also be used by plants. Finally, the NO_3^- goes under a denitrification process back into the atmosphere, in such a way that it is transformed into N_2O and NO, and subsequently into N. Also, NO_3^- can remain immobilized on the ground, or be carried by runoff to water bodies (Aczel, 2019).

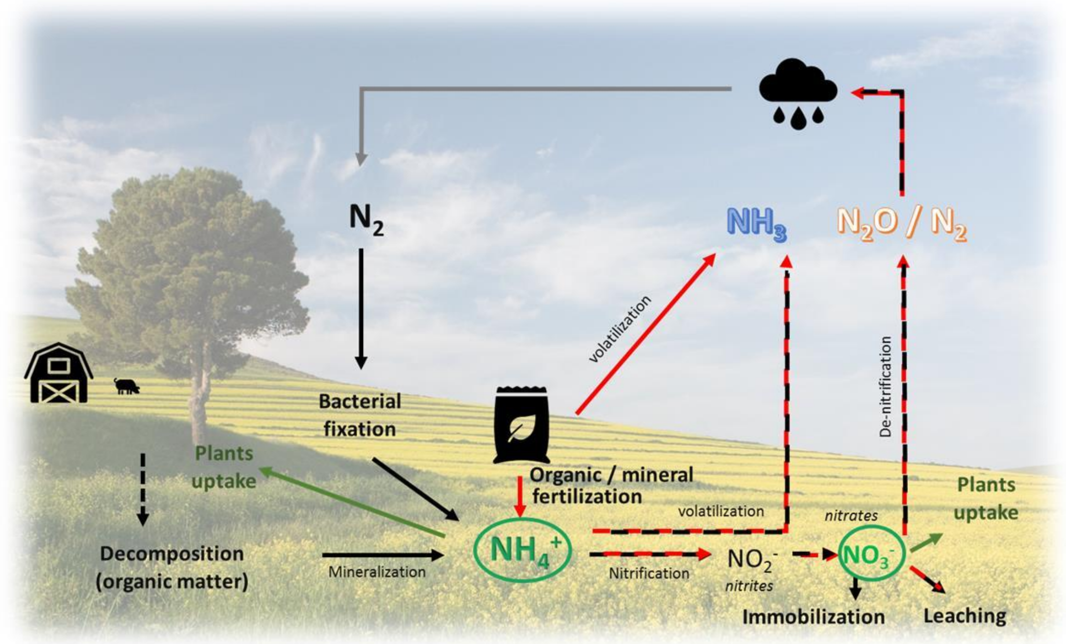


Figure 2. Simplified N cycle in the agro-industrial sector. The natural phases are represented in black, and the human contributions are represented in red. The N available as nutrient is represented in green circles. Source: modified from Aczel (2019).

In agricultural soils in Europe, it has been reported that the main losses on average of N are denitrification (44 kg N ha^{-1}), followed by NH_3 volatilization (17 kg N ha^{-1}), leaching (16 kg N ha^{-1}) and N_2O emissions (2 kg N ha^{-1}) and NO_x (2 kg N ha^{-1}), (Cameron et al., 2013; Velthof et al., 2009). These losses can be caused by type of soil and poor application methods, which can imply N losses up to 70% of the total available N (Anas et al., 2020). While the N losses due to leaching can be improved up to 30% with better agronomic practices and fertilization methods (Anas et al., 2020), the **NH_3 emissions to air remain one of the most prominent causes of N losses and environmental problems**. In this regard, the estimation of **global NH_3 emissions** is associated with large uncertainties due to the lack of knowledge about the sources among the different global geographical areas. Luo et al. (2022) used satellite observations from the Infrared Atmospheric Sounding Interferometer and reported an average of 780 million tons per year between 2008 and 2018, which is 30% higher than the emissions calculated using emission activity and emission factor methodologies. Therefore, we may be facing a bigger global problem than previously thought. It has been reported that at least 80% of NH_3 emissions correspond to human activities, particularly to agriculture, especially livestock production and fertilization applications, (Behera et al., 2013). The NH_3 emissions have been increasing over the past decades on a global scale, due to the increase of the use of fertilizers and the increment in livestock production, thus representing a major environmental issue (Behera et al., 2013; Luo et al., 2022). The NH_3 emitted to the air is a threat to human health, since it reacts with the acidic compounds of the atmosphere, contributing to the formation of fine particles (PM2.5) and the well-known acid rain (Apsimon et al., 1987). The NH_3 deposited on land or water can exceed critical N loads of ecosystems causing eutrophication and damage to forests, crops and other vegetation (Sutton et al., 2013). Eutrophication leads to severe reductions in water quality with the subsequent impacts, including biodiversity loss and toxicity effects (EEA, 2019). Ammonia volatilization is also a cause of indirect N_2O emissions, one of the most harmful greenhouse gases (Cai et al., 2021; Luo et al., 2022).

1.2. Phosphorus in the agro-industrial sector

Phosphorus is also a basic and limiting nutrient for plant growth. Phosphorus is involved in the photosynthesis process and it is an essential component of adenosine triphosphate (a vital nucleotide), which is present in all biochemical processes in plants. It also enables the nutrient extract processes from the soil. Moreover, P plays a critical role in cell development and DNA formation, plant development and formation, as well as in flowering and fruiting (Buckwell and Nadeu, 2016; Hyland, 2005). Figure 3 represents a simplified P cycle in the agro-industrial sector, where the forms in which P is found in the soil can be seen: inorganic P, plant available P, organic P, adsorbed P, and primary mineral P. Soils naturally present P-containing minerals that are weathered over time and become available for plants. Phosphorus can become unavailable if it precipitates with dissolved iron, aluminum, manganese or calcium (in alkaline soils), as it forms phosphate minerals. The process of mineralization is the microbial conversion of the organic P to $H_2PO_4^-$ and/or HPO_4^{2-}, forms of plant available P, usually known as orthophosphates. Immobilization occurs when the plant available P forms are consumed by microbes. This P becomes available again when the microbes die. The adsorption process is the chemical binding of orthophosphates to soil particles, which makes it unavailable for plants. Desorption is the release of adsorbed P from its bound state into the soil solution.

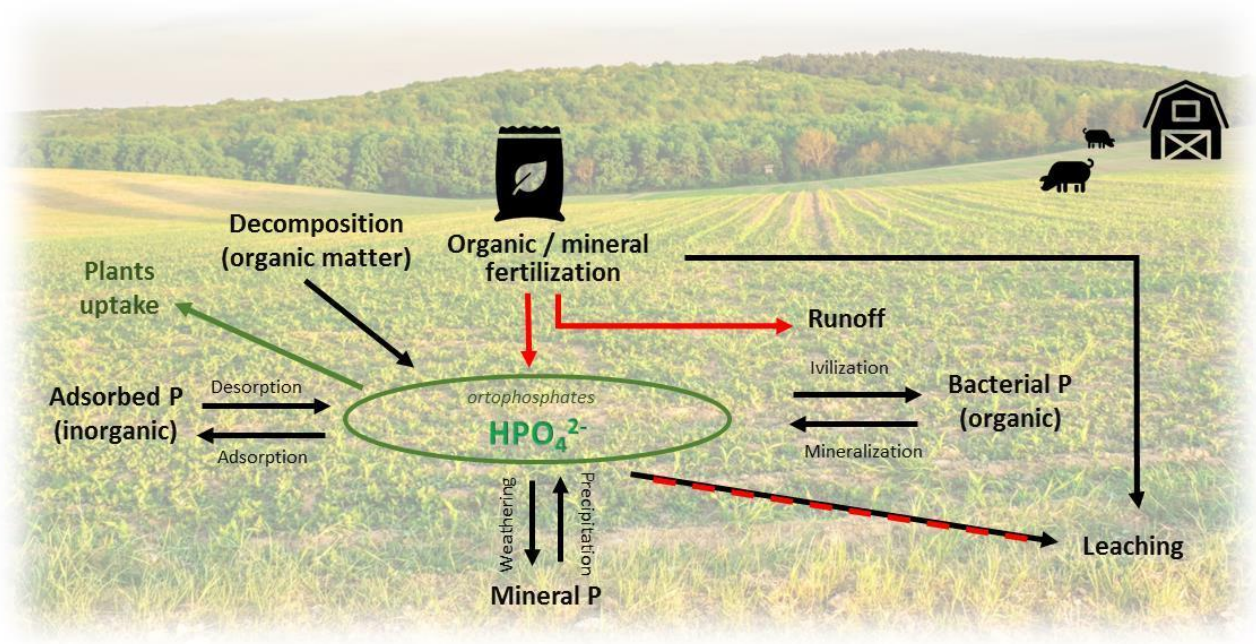


Figure 3. Simplified P cycle in the agro-industrial sector. The natural phases are represented in black, and the human contributions are represented in red. The P available as nutrient is represented in a green circle. Source: modified from Hyland (2005).

The P losses within the circle represented in Figure 3 vary greatly depending on the particular conditions of each soil: the combined action of low sorption capacity, high erosion risk and risk of drainage (Eurostat, 2012). Firstly runoff (drain away from the surface of an area of land) and secondly leaching (drain away from soil by the action of percolating rainwater), are considered the two main causes of nutrient loss and environmental problems caused by P. In these two processes, water carries particulate and dissolved P which will eventually affect freshwaters and coastal ecosystems, causing habitat degradation, algal blooms, eutrophication, hypoxia, groundwater pollution and biodiversity loss (Hyland, 2005). In addition, it has been reported that up to 33% of the P inputs in agricultural soils may be lost (Cordell et al., 2009).

The amount of N and P mineral fertilizers consumed in the agricultural sector for crop production in the EU was 11.2 million tons in 2020. This represents an increase of 3% compared with 2019 and of 8% compared to 2010. Phosphates are mined outside of the EU, which results in high production and transportation costs, linked to oil prices. The high demand of P in agriculture has been increasing over the past few decades, leading to the acceleration of the P cycle. Since there are no substitutes of P for plant production, the P supply is vital for food security. The military aggression in Ukraine by

Russia has led to sharply higher fertilizer prices, and it is expected that it will impact on the use of fertilizers in agriculture in the EU, and therefore in their production (Eurostat, 2022).

This thesis also focuses on the recovery of P, to avoid nutrient losses that may affect the environment, by using membrane technology and precipitation. According to Bouwman et al. (2013), at the beginning of the 20th century, nutrient budgets (i.e., the difference between nutrient inputs from organic or mineral fertilizers and the nutrients absorbed by plants) in the agricultural sector (crop and livestock production) were balanced and the surpluses were small. Nonetheless, these authors reported an increase of global total P inputs (mineral and organic fertilizers) between 1950 and 2000, from 11 million tons per year to 31, and they estimated a total P input of 49 million tons for year 2050. However, in the case of Europe, since the late 1980s the P application rates have been reduced due to different regulations to optimize fertilizers applications and to minimize environmental issues (Eurostat, 2012). Panagos et al. (2022) estimated, for EU with UK, a currently total P inputs to agricultural soils of approximately 2.74 million tons per year, where manure inputs as organic fertilizer represents the 48 % of the total P inputs in agricultural soils. These authors also reported an average surplus of 0.8 kg P per ha and year. Although there is no specific legislation in the EU that is directly related with the use of P in agriculture, the P problems are integrated in several regulations and directives, such as the Water Framework Directive (Directive 0060/2000) and the Integrated Nutrient Management Action Plan, as part of the European Green Deal for 2030. In any case, P issues are addressed by each country according to the existing agricultural and environmental legislation.

It can be concluded that within a CBE paradigm, it is necessary to close the nutrient cycles by optimizing their recycling, increasing the efficiency in the use of these nutrients and avoiding their losses. As has been mentioned above, **this implies considering residues and agro-industrial residues as resources**. In the particular case of N and P, this means helping to close the N and P cycles, lowering the emissions, and improving the use of N and P forms in the soil. In this sense, **this thesis focuses on reducing the NH_3 emissions from swine manure and digestate**, **using gas-permeable membrane (GPM) technology to recover N, and also to recover P**

through ion exchange membrane technology and precipitation in an available form for plants.

2. MAIN WASTE STREAMS IN THE AGRO-INDUSTRIAL SECTOR

To optimize the means of waste valorization, it is first necessary to know what the main waste streams are within a CBE scenario and to know what the possible improvements would be that can be carried out in each of them, within the nutrient recovery framework.

According to Buckwell and Nadeu (2016), organic waste presents three **main waste streams, depending on the source; these are: a) manure, from the agricultural sector, b) sewage sludge, and c) food waste from the food** processing and consuming chain. The same authors reported a total N loss of 73% in the agriculture category, 15% in sewage, and 13% in food waste. Furthermore, a total P loss of 63% in the agriculture category, 24% in food waste, and 13% in sewage were reported. Some of these streams are being collected and treated, but a limited percentage of nutrients are being recycled.

In the case of the agriculture category, the recovery and reuse (or recycling) of organic matter and nutrients from waste is not a new concept. For centuries, such practices as crop rotation, the incorporation of crop residues, or the application of manure to crop fields for fertilization and soil amendments have been carried out. These practices are still used today; however, only a limited part of what is returned to the field can be used by plants or can create a balanced soil (EC, 2020). Inefficient waste management causes harmful emissions and nutrient losses that lead to significant negative environmental impacts and can also disrupt natural cycle losses (Buckwell and Nadeu, 2016; EC, 2020). Therefore, **what the new paradigm of CBE aims to do is:** a) optimize the recycling of nutrients by applying innovative technologies to achieve high rates of nutrient recovery and organic matter (also from the other two categories of sewage and food waste), b) to use renewable energy sources in the process whenever possible, and c) to increase the efficiency in which those nutrients and organic matter are returned to the soil, to avoid nutrient losses (Buckwell and Nadeu, 2016; EC, 2020). In agriculture, CBE aims to go from a system in which waste can be occasionally reused, to a new system in which waste go through **valorization** processes to become a source of bio-based by-products (bio-based fertilizers; biochemicals and bioenergy (biogas)), **and this is the framework of this thesis**.

The **three waste streams previously described present the most promising possibilities for improvement**, given the amount of nutrient losses and the technological and economic feasibility of the recovery treatments that can be applied to them. The purpose and scope of this thesis is focused on the categories of food chain waste and manure. They are described in more detail in the following sections.

2.1. Food waste stream

The biodegradable waste produced by the food industry in the EU is made up of a wide variety of materials, such as fruit stones and peel, cereal waste, or dairy residues. The high potential for recovering nutrients from these waste streams lies in the large amounts of waste produced annually throughout the world, including the EU. According to the UN (2022), approximately 14% of the world's produced food is lost or discarded after harvest, and a further 17% of food is wasted in the supply chain by retailers and consumers. Food loss and waste implies land and water resources wasted, and the generation of large amounts of unnecessary GHG emissions during the production and disposal process, especially if the food waste ends up in landfills or open dumps. Therefore, it is essential to recycle these wastes, transforming them into valuable resources and to recover lost nutrients.

Due to its varied nature, it is difficult to estimate where the nutrient losses are produced within the entire food supply chain, and which residues have a higher content of N and P. Although the agro-industrial sector is facing many challenges, they are inclined to invest in recycling (Kretschmer et al., 2013). For example, it has been reported that 30% of the residues from the sugarcane industry (rich in both N and P) are recycled as fertilizer in agriculture (Buckwell and Nadeu, 2016). To make use of these residues, the common forms of treatment are: composting, incineration (P recovery from ashes) and more recently anaerobic digestion (AD) (Figure 4; Buckwell and Nadeu, 2016).

For this last option, several studies have addressed the use of food waste as substrate in the AD process. Some authors such as Paritosh et al. (2017), Morales-Polo et al. (2018), and Yang et al. (2022a), among others, determined that methane production through the AD process is an appropriate solution for food waste management, especially if mixed with manure. This mixture increases the amount of biogas and, therefore, the economic viability of the process. This aspect has been addressed in **section VI.2.**

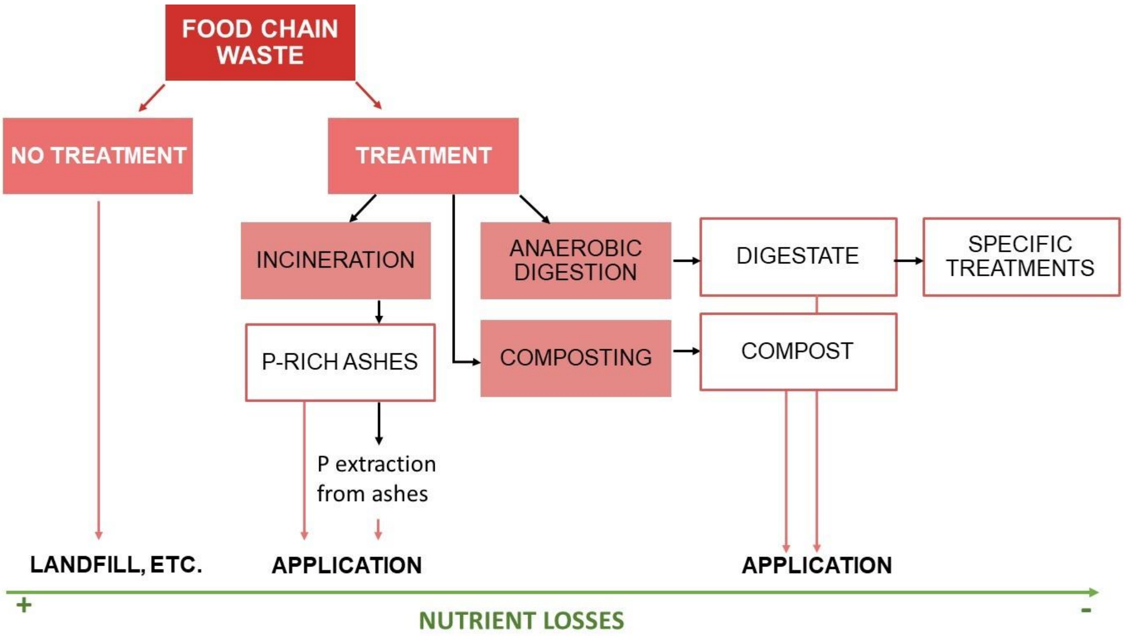


Figure 4. Routes for food chain waste use and nutrient recovery. *Specific treatments* are listed in Figure 5. Source: modified from Buckwell and Nadeu (2016).

2.2. Manure

Manure can be defined as the farm animals' excreta (urine and feces) without bedding materials (He, 2012). Manure use on land as organic fertilizer is regulated by the Nitrates Directive (91/676/EEC), which limits its application to 170 kg N/ha in Nitrate Vulnerable Zones.

2.2.1. Manure emissions and emission ceilings

It has been reported that the amount of N and P contained in European manure is of the same order of magnitude as that provided by mineral fertilizers (with some differences between member states) (Buckwell and Nadeu, 2016). The total annual production of liquid and solid manure in the EU was 1400 million tons, considering the total population of farm animals (pigs, cattle, poultry, sheep and goats); of these, 600 million tons per year come from swine and cattle farms (Buckwell and Nadeu, 2016). Considering the total annual amount (1400 million tons), between 7 to 9 million tons correspond to N, and almost 2 million tons correspond to P, from which 33% of N and 53% of P are applied to agriculture as organic fertilizer. In particular, liquid swine manure can contain approximately up to 8 kg of N per ton of manure, and up to 2 kg of P per ton of manure (Buckwell and Nadeu, 2016). Based on these data, it can be stated that the volume of waste produced is enormous, so it is necessary to implement management formulas for its use, but also that the amount of nutrients lost through conventional management is very high.

Emissions of NH_3: Global NH_3 emissions have been described in section 1.1 above. In this section, the NH_3 emissions of the agri-food sector and particularly in Europe are addressed. The EU reported approximately 3.755 million tons of NH_3 produced in 2010 and 3.892 in 2017, (EEA, 2019), which agrees with the estimations made by Luo et al. (2022) for Europe. From these 3.892 million tons of NH_3, the agriculture sector was responsible for 94% (EEA, 2019).

The NH_3 emissions in the agri-food sector mainly occur as a result of volatilization from manure inside the animal houses, manure storage, and manure land application. A small fraction results from the volatilization from mineral N-fertilizers and fertilized crops. The NH_3 emissions are closely related to the livestock production population, manure characteristics (animal diet, specie, etc.), farm housing systems, manure storage systems and manure management (FAO, 2011; Sutton et al., 2022).

Calculations for NH_3 emissions in the EU are made based on the estimations of activity data and applying emission factors for each country, taking into consideration specific environmental and manure management factors (EEA, 2019). With this regard, it was estimated that the EU was able to reduce emissions from 1990 to 2015 in approximately 24%, from 4.9 million tons in 1990 to 3.7 million tons in 2015. A small decrease was also reported in 2019, with 3.4 million tons of NH_3 produced. A great effort has been made by all the member states, (reduction of 28% compared to 1990), as this reduction is part of the goal of climate neutrality policy for 2050 (EC, 2020); however, there is still room for improvement. Looking at each member state individually, they present widely varying trends: while Greece was able to reduce the NH_3 agricultural emissions in approximately 25% in that period (from 85 kilotons in 1990 to 63 kilotons in 2015), Spain presented an increment of almost 12% in 2015 (410 kilotons more than in 1990), due to the increment in livestock production and the increase in the use of mineral fertilizers. Along the same lines, Spain, together with Austria, Denmark, Finland, Germany and Sweden, did not meet the NH_3 emission ceilings in 2019 set by the 2010 NEC Directive 2001/81/EC for NH_3 emissions ceilings (EEA, 2019; Eurostat, 2017). The type of agricultural practices and the livestock population density are key factors that determine NH_3 emissions. During the land application for organic fertilization, NH_3 emissions depend on the type of manure (N concentration), the weather conditions, and soil properties (ion exchange capacity, pH, etc.). When these factors prevent the ammonium (NH_4^+) adsorption by the soil, then the NH_3 emissions increase, as has been described in Figure 2 (EEA, 2019; Eurostat, 2017).

To address the environmental problems related to the NH_3 emissions at EU level, several regulatory instruments target NH_3 emissions, including the agricultural sector. The Protocol to Abate Acidification, (Gothenburg Protocol) worldwide (Sutton et al., 2022; UN, 2022), specified an NH_3 emissions reduction of 365 Gg for 2020 (or beyond), with respect to the NH_3 emissions of 2005. Furthermore, NH_3 emissions reduction is included under the European Commission Clean Air Europe Program (CAFE). This program led to the development of the Thematic Strategy on Air Pollution, with the objective of developing long-term strategies and policies to fight the negative effects of air pollution on human health and ecosystems. The new National Emissions Ceiling Directive (National Emissions reduction Commitments (NEC) Directive (2016/2284/EU); EU, 2016), requires the EU members to report their emissions and the limits and set emission reduction commitments for 2030 on the basis of 2005 levels, not only for NH_3, but also for NOx, and Not Methanogenic Volatile Organic Compounds (NMVOC). **Currently, for the EU, an NH_3 emission reduction of between 10% and 30% of the current levels for 2030 is needed** (minimum target of 3.044 Gg for 2030) (EEA, 2022a; Eurostat, 2017). Although the reduction of NOx have been relatively successful, NH_3 emissions have unfortunately not been significantly reduced to date, which implies the need for a greater commitment and a greater effort to limiting these emissions and their potential harms.

Emissions of greenhouse gases (GHG), methane (CH_4) and nitrous oxide (N_2O): Manure management in the EU produced a total of 63416 kt of GHG as CO_2 equivalents (CO_2 eq.) in 2020, where methane accounted for 41292 kt of CO_2 eq. and N_2O accounted for 22124 kt of CO_2 eq. (EEA, 2022b). The main factors that affect methane production from manure are the quantity of manure produced, its characteristics, the manure management system, and the climate (IPCC; 2019). Nitrous oxide is produced from the combined nitrification-denitrification process that occurs to the N in manure. Although the majority of N in manure is in the NH_3 form, nitrification occurs in aerobic conditions in the soil, where nitrifying bacteria converts the NH_3 into nitrate. Denitrification occurs in anaerobic conditions, and in this case, soil denitrifying bacteria convert the nitrate to nitrous oxide. Both methane and nitrous oxide are extremely potent GHGs, with respective global warming potentials of 21 and 310 times that of CO_2 (i.e., CO_2 eq.), respectively (IPCC, 2019). Regarding GHG emissions, the EU agreed on the net zero emissions target for 2050 in the European Climate Law of June 2021. This implies an immediate goal of reducing GHG by at least 55% by 2030 compared to 1990 levels (i.e., 5653.7 million tons of CO_2 eq.).

Phosphorus losses: The consumption of P in the EU for agriculture was 1.2 million tons, which implies an increase of almost 22% with respect to 2010. Mineral fertilizers of P accounted for approximately 51%, while manure contributed 53%. It has been estimated that approximately 25% of P applied per year is taken up by the crops, and that the remaining 75% becomes bond in the soil profile or is lost by runoff and leaching (Eurostat, 2014; Eurostat, 2022). Nowadays, the agro-industrial sector depends on mined P to keep the food production levels, and it has been estimated that 1000 million tons of mined P has been added to date to the environment, as P surplus, (soil and waterbodies) (Buckwell and Nadeu, 2016). Manure generally has a N/P ratio of between 2 and 8, in contrast to the N/P ratio of 7 –11 required by crops. Therefore, when the N requirements are met using manure alone as organic fertilizer, this results in an excess of P (Amery and Schoumans, 2014). This results in large accumulation of P in soils and waterbodies. Soluble forms of P in the soil are easily immobilized, and it has been estimated that less than 20% of added P remains available for plant uptake (Brady and Weil, 2010). Continuous application of P fertilizers has led to an accumulation of 1 million tons of P immobilized in European agricultural soils in 2005 (Van Dijk et al., 2016). The total P consumption in 2020 was particularly high in Spain, France, Poland, Germany and Italy, since these countries consumed between 100000 and 215000 tons of P for crop production. Constant P addition to soils may not be toxic by definition, but it represents very inefficient management, and huge nutrient losses. The P surplus in soil involves losses through runoff and leaching, causing the previously mentioned environmental problems. The risk and environmental implications of these P losses will depend not only on the amount, but also on the type of inputs, the characteristics of the manure application, soil type, precipitation and temperature, with important consequences in a climate change scenario (Buckwell and Nadeu, 2016). Maximum total P application standards depend on each EU country. Austria has no maximum phosphorus application rates or other P restrictions, and only the N regulations affect the applications and losses of P (e.g., Nitrates Directive, Good Agricultural Practices and erosion (Amery and Schoumans, 2014)). Spain does not consider general application limits either, and relies on the Nitrates Directive, except for the Extremadura region, where the P fertilization of olive, rice, tobacco and fruit trees is limited to 80 kg P_2O_5 per ha and per year, due to the soil characteristics. On the other hand, P application standards in the Netherlands are regulated depending on the agricultural land use: for grassland, it is 85-120 kg P_2O_5 per ha and per year; while for arable land, it is 55-120 kg P_2O_5 per ha and per year (Amery and Schoumans, 2014).

The **estimated annual costs to society in Europe of the pollution and leakages associated with nutrients** (N and P mostly) was 75 to 485 billion Euros (Van Grinsven et al., 2013). This is almost the same as the Gross Domestic Product of Belgium. The majority of these costs are related to damaged ecosystems and public health (Buckwell and Nadeu, 2016). Therefore, the use of the **best technology available to improve nutrient recovery and reuse and to reduce these emissions is crucial**.

In the case of nutrient recovery and reuse from manure, most of the research to date **on manure processing has been conducted on swine manure** (Buckwell and Nadeu, 2016). This is because swine exploitations often do not have enough land to dispose of all the manure they produce, and swine manure is expensive to store and transport due to its high-water content (Schoumans et al., 2010). The aim of the treatments described in Figures 4 and 5 is to reduce the volume of the manure and concentrate the nutrient content for its reuse, minimizing emissions, especially NH_3.

In the case of the AD process, it can break down organic materials while producing energy, and it can be easily combined with further specific treatments for nutrient recovery (Buckwell and Nadeu, 2016). Due to these particularities, **this thesis has focused on swine manure,** so the conclusions can serve to contribute to the goals of minimizing emissions and nutrient recovery from this waste.

2.2.2. Manure treatment technologies

Traditional manure management consisted of storage for further application on the fields. More recently, the manure treatment methodologies are: acidification, solid/liquid separation, AD process, composting, aerobic biological treatment, evaporation, stripping or drying (LifeManev project, 2016).

Figure 5 presents a summary of the main different treatments that can be applied to manage manure. These treatments could be organized depending on when they take place. In this sense, the green arrow shows that, from left to right, the nutrient loss decreases with the application of novel treatments.

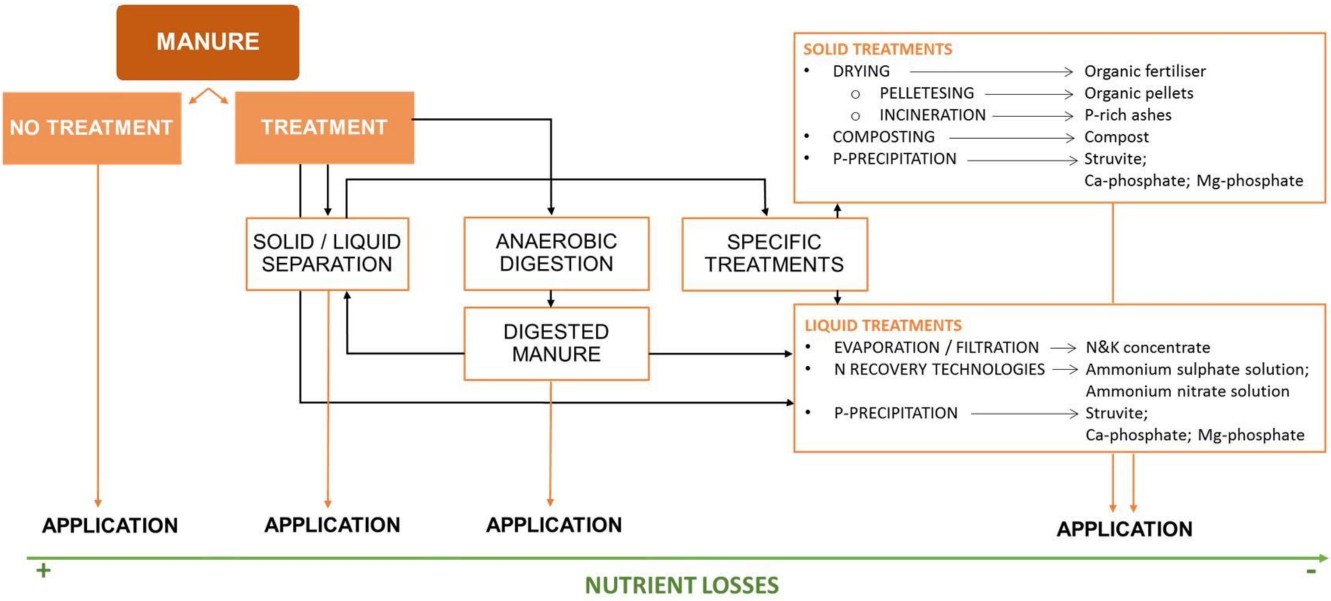


Figure 5. Manure treatment strategies for nutrient recovery. Source: own elaboration based on Buckwell and Nadeu (2016) and LifeManev project (2016).

The study of the application of novel technologies for nutrient recovery and reuse is the current trend in research, where new and better forms of valorization are investigated to increase sustainability, from an economic and environmental point of view. This would imply the need for a holistic approach, focusing on nutrient recovery across the entire food chain to reduce nutrient losses, but also to ensure that the treatment process does not contribute to NH_3, N_2O or CH_4 emissions (Hou et al., 2017; Sutton et al., 2013).

In this thesis, raw swine manure, anaerobically digested swine manure (digestate), and *centrate* (manure liquid fraction after solid/liquid separation) were used. In some works, a pre-treatment or treatment of swine manure has been done prior to the recovery of nutrients. The processes used are briefly described below.

i. Solid/Liquid separation

One of the most common treatments for the manure that is not directly applied to land is the solid/liquid separation. It is commonly done by screw press or centrifugation, with or without the addition of coagulants/flocculants (Buckwell and Nadeu, 2016; LifeManev project, 2016). The solid/liquid separation results in two fractions: a solid fraction, that can be used as organic fertilizer since it is rich in organic matter, N and P; and a liquid fraction (*centrate*), rich in elements such as N, P and K, which can be used for fertigation. The interest in solid/liquid separation has increased over the last few years, since it is an advantageous pre-treatment for nutrient recovery technologies, and it can be implemented in rural areas, where the resultant liquid and solid fractions can be stored, transported or applied, depending on the nearby crop necessities. In particular, the solid fraction contains a higher concentration of P than the liquid fraction; hence, with the application of the liquid fraction in the fields, P losses are minimized, as is the associated environmental damage (Fangueiro et al., 2017).

Solid/liquid separation is expected to improve in the future, reducing costs and increasing the concentration of nutrients in the separated solid fraction. The costs may vary depending on the technology used and the volume treated, but Møller et al. (2000) reported treatment costs (including fixed and operational) of 0.72 € and 3.6 € per ton of swine manure with simple mechanical separators and centrifugation, respectively. The solid/liquid separation can be combined with the AD process and also with further specific treatments to recover N and P or other valorization processes (Figure 5). A work with the liquid fraction of the swine manure has been done in **section VI.2.**

ii. Anaerobic digestion

The AD process is widely implemented nowadays, and the latest European strategies point to it as an important waste processing and bioenergy production system for the transition to net zero emissions (EC, 2020). For this reason, **AD has been the object of special attention in this thesis.**

The AD process can be defined as a complex biological process of transformation, in which the organic matter from organic waste (animal or vegetable) is converted into simpler and more stable compounds (the anaerobically digested product known as **digestate**) and into **biogas**, by a consortium of anaerobic bacteria (i.e., bacteria that thrive in anaerobic conditions) (Prasad et al., 2020). Biogas is considered the main product and it is described as a renewable energy source. It is composed of a mixture of methane (up to 70%), carbon dioxide (CO_2) (30 to 40%), and traces of other gases (N_2, H_2 and O_2) (EC, 2020; FAO, 2011). The physical-chemical characteristics of digestate can be very different, depending on the nature and composition of the substrates and also on the AD operational parameters. Nonetheless, it has been reported that in general, compared with manure, digestate presents lower total solids (TS) and total organic carbon (C) content, also lower carbon-nitrogen ratio (C: N) and a lower viscosity (Drosg et al., 2015). This may result in a relatively high biological stability of the residual organic matter content that may lead to good amendment properties for soils (Drosg et al., 2015; Schievano, 2009). In addition, the high mineralization of N and P make the digestate a good option as organic fertilizer to substitute mineral fertilizers (Buckwell and Nadeu, 2016; Schievano et al., 2009).

The AD process can be carried out at different temperatures: psychrophilic (15ºC to 25ºC), mesophilic (25ºC to 45ºC) and thermophilic (45ºC to 65ºC). Usually, higher temperatures favor the organic matter conversion into much simpler compounds (FAO, 2011). The AD phases are: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The first phase is the hydrolysis of complex particles and molecules (proteins, carbohydrates, and lipids) that are hydrolyzed by extracellular enzymes produced by acidogenic or fermentative microorganisms. As a result, simpler soluble compounds are produced (amino acids, sugars and long chain fatty acids) that will be metabolized by acidogenic bacteria, giving short chain fatty acid alcohols, hydrogen, carbon dioxide and other intermediate products. In the next phase, acetogenic microorganisms transform the short chain fatty acids into acetic acid, hydrogen and carbon dioxide. Finally, methanogenic microorganisms produce methane from acetic acid, H_2, and CO_2 (FAO, 2011; Prasad et al., 2020).

According to Sravan et al. (2021), the limiting factors for the AD process are mainly the hydrolysis phase, the pH, the temperature, and the type of substrate, along with the hydraulic retention time (HRT). Hydrolysis is the process that provides organic substrates for AD, and is usually the phase that limits the global process, especially when the residues have high solids content. The bacteria use part of the amino acids and peptides produced in this phase to survive and multiply, but the part they do not metabolize is degraded to volatile fatty acids (VFA), CO_2, H_2, and later to NH_4^+ and sulfur. Lignocellulosic materials (lignin, cellulose and hemicellulose) present slow degradation rates and tend to limit the hydrolysis process (FAO, 2011; Sravan et al., 2021). A pH of between 6.5 and 8 is considered ideal for the methanogenic bacteria, and therefore for methane production. Regarding temperature, mesophilic conditions provide comparatively better stability and microbial abundance, with a higher capacity for biogas production (Sravan et al., 2021). It is, therefore, the option selected for the present thesis. Optimal substrates can be obtained through the combination of two or more different residues (**co-digestion**), to obtain a balanced mixture as **feed or influent**, which presents complementary characteristics that can result in better AD performances. For example, the co-digestion of manure, which presents a low methanogenic capacity but a high buffer capacity, can be mixed with other residues with higher methanogenic potential but less buffer capacity (FAO, 2011; LifeManev project, 2016). This kind of synergies can result in high methane productions. The influent should also present balanced levels of nutrients, such as C or N. For example, a C/N ratio from 20:1 to 35:1 can be considered as optimal. Organic N is hydrolyzed during the AD process, giving rise to ammoniacal forms. Although NH_3 is vital for bacterial growth, a high N content in the substrate has toxic effects, limiting their growth, while low quantities of N cause nutrient limitation (FAO, 2011; Sravan et al., 2021). Residues that contain higher proportions of proteins or other N compounds are those that present problems of **inhibition by NH_3**., Therefore, NH_3 is considered one of the most common and important inhibitors during the AD process, especially if manure is used as a substrate (Yenigün and Demirel, 2013). Digesters operating at higher temperatures have been reported to be more sensitive to NH_3 toxicity than those operating in the mesophilic range. In the case of manure, it presents high NH_3 content, so the AD process may present inhibition problems (FAO, 2011). The way to transform this problem into an opportunity using GPM technology is examined **in section VI.1.** The GPM technology can capture NH_3, and may therefore improve the AD process if it is incorporated. The said section studies how membranes can work during AD, improving the quantity and quality of the biogas produced.

For optimal feed mixtures, it would also be necessary to consider the organic loading rate (OLR) for the AD reactor and the HRT (FAO, 2011; Prasad et al., 2020; Sravan et al., 2021). The ORL is the amount of organic matter loaded into the anaerobic reactor per unit of volume and time, and the HRT is the average time interval over which the substrate is kept inside the digester (Sravan et al., 2021). The HRT, along with the OLR, determined by the type of substrate, are the main design parameters that define the volume of the digester (FAO, 2011). The OLR has an inverse relationship with the retention time: as the OLR increases, the HRT decreases. It is important to obtain the adequate OLR and HRT balance for the AD process. For example, a higher OLR may lead to AD inhibition due to a decrease in the bacteria activity, or short HRT leads to VFA accumulation, which affects bacteria and inhibits the biogas production. Furthermore, with a longer HRT, the substrate components may not be used effectively, so the biogas production may decrease (Sravan et al., 2021). Therefore, it has been stated that the basic AD process for agro-industrial waste is performed in a completely mixed anaerobic digester, with an HRT in the range of 15-70 days in order to provide sufficient retention time for both operation and process stability (Ersahin et al., 2011; LifeManev project, 2016) (Figure 6). The importance and effects of a correct OLR and HRT for a proper AD process and biogas production can be seen in the studies in **sections VI.1 and VI.2.**

There are different reactors for the AD process that vary widely according to their mode of operation in relation to their power capacity (FAO; 2011; Prasad et al., 2020). There are three basic types: continuous, semi-continuous and discontinuous. **The discontinuous process is the most common process in medium scale plants and rural areas. The AD process of sections VI.1 and VI.2** was carried out on a laboratory scale with reactors operating in semi-continuous regime. In the semi-continuous process, the first load of the digester consists of a large amount of inoculum, and then the reactor is subsequently fed periodically with the substrate, calculated on the basis of the HRT and the total volume of the digester. The effluent is regularly discharged in the same quantity as the influent that was incorporated.

In the continuous process, the influent enters the digester in a non-stop process and the discharged effluent is equal to the feed that enters the digester. Since this type presents uniform biogas production over time, it is commonly used by large-capacity plants such as sewage plants. The digestate used in the studies of **sections VI.3 and VI.4** proceed from a full operational biogas plant with continuous reactors.

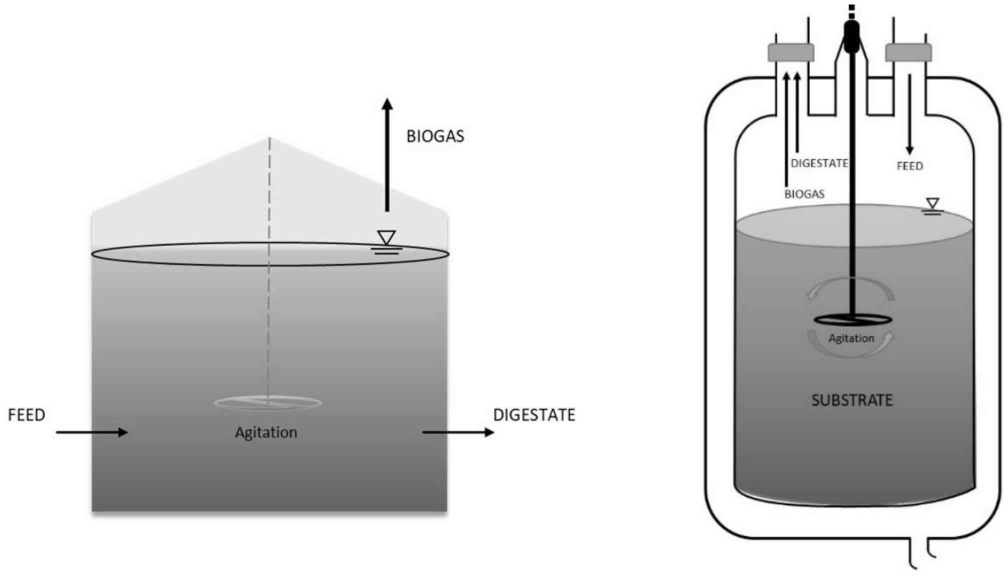


Figure 6. Schematic example of the AD operation of a biogas plant completely mixed anaerobic reactor, and the schematic example of a semi-continuous AD reactor used at laboratory scale. Source: modified from Ersahin et al. (2011).

From an environmental point of view, the AD process represents a potential effective treatment in reducing GHG emissions since, during the AD, the majority of fermentable organic matter is degraded to CH_4 and CO_2, resulting in lower potential emissions than no treatment of the influents (Fangueiro et al., 2017). The AD process is also capable of mitigating GHG emissions due to the replacement of fossil fuel consumption by biogas, and to the reduction of mineral fertilizer use (Bakkaloglu et al., 2022; Harrison and Ndewa, 2019). It has been reported that the reduction in fossil fuel emissions when substituted by biogas is estimated to be approximately 90% (LifeManev project, 2016). Different authors have reported that, with the AD of swine manure, it can be possible to mitigate between 15 and 20 kg CO_2eq per ton of swine manure, considering efficient biogas utilization and closed manure storage (De Vries et al., 2013; Prapaspongsa et al., 2010; Xie, 2011). Since different manure treatments and storage methods determine how much of these GHG are produced, it is recommended to design covered storage tanks for both the manure and the digestate (Bakkaloglu et al., 2022; Møller et al., 2022). From an economic perspective, the costs of an AD plant depend on the scale and the geographical area, the amount of feed to be treated, the type of reactors, the manure transportation and also on the application of government subsidies, if any. Carlini et al. (2017) presented a study for an economic evaluation of AD plants fed with agro-industrial waste, with an initial capital investment for an AD plant of 3 million euro. They considered a feed of olive mill residues (1800 tons) and manure (5940 tons), co-digested in batch-stirred tank reactors in mesophilic conditions (38ºC) with an HRT of 55 days, and with an installed electrical performance of 1000 kW. Their calculations showed that, with a break point of 20 years and a sale price of electricity of approximately 40 € per MWh, the AD plant would present paybacks in only 4 years. The future trend for the use of AD for manure management is focused on the increment of biogas production and the integration of AD in combined processes for nutrient recovery, to obtain more sustainable strategies for manure processing (LifeManev project, 2016), as studied in **sections VI.1 and VI.2.**

The **digestate is the larger output in volume from the AD treatment of manure**, where 56 million tons of digestate are produced annually in Europe, 80% of which is used in agriculture (Buckwell and Nadeu, 2016). It can be applied directly to soils by injection or band spreading, as organic fertilizer. Jurgutis et al. (2021) studied the potential of digestate as a source of income in AD plants. They considered the digestate produced in eight AD plants, using different agricultural residues and manure as substrates, co-digested under mesophilic conditions (36 – 42 ºC) with an HRT up to 44 days. They finally estimated a value for the digestate in the range of 2.88–7.89 € per ton for liquid digestate and 7.62–13.61 € per ton for solid digestate, based on the commercial market price of NPK, organic carbon, Cu, Zn and Mg fertilizers. They concluded that the digestate produced in a 1000 kW AD plant could be worth from 941 to 2095 € per day, besides the energy sales income. Therefore, as mentioned previously, the digestate has an interesting potential as an organic fertilizer, as it has different physical and chemical characteristics to manure. It contains higher mineralized fractions of N and P, and particularly, the digestate presents a higher NH_4^+ concentration than manure (Buckwell and Nadeu 2016; Prasad et al., 2020; Risberg et al., 2017; Schievano et al., 2009). These particular characteristics make it a **good candidate for nutrient recovery through specific treatments**, as can be seen in **sections VI.2, VI.3 and VI.4.**

3. Specific treatments for nutrient recovery and reuse

Manure is not a balanced organic fertilizer, and its application in crops to meet the requirements of one nutrient, for example N, can lead to an excess of another, such as P, with very negative environmental implications (Buckwell and Nadeu, 2016; LifeManev project, 2016). In addition, the digestate with high concentrations of NH_4^+ used as organic fertilizer may present N leaks to soil and water, leading to environmental issues. To avoid these problems, **nutrient removal technologies** (such as nitrification/denitrification) were proposed in the past, **but more recently, nutrient recovery technologies** are being considered as the most interesting option. **Nutrient recovery is preferred over nutrient removal, due to its strategic interest for agriculture**, so nutrient recovery technologies are receiving more attention and technological development. In this regard, a brief description of the best-known nutrient recovery technologies for N and P is presented in Tables 1 and 2**.**

A detailed comparison, **including an economic evaluation**, of nutrient recovery technologies is presented in **sections VI.3 and VI.4.**

3.1. Main nutrient recovery technologies, advantages and drawbacks

In this section, the characteristics and the performance of the GPM technology and the most common P recovery technologies are compared with other N and P recovery technologies. They are presented in such a way that the advantages and disadvantages can be easily seen (Table 1 and Table 2).

The GPM technology presents high recovery rates with low operational costs, requires low energy, and the use of alkalis for pH control can be substituted by aeration. In addition, there is no need for a pre-treatment of the wastewaters or post-treatment of the final product obtained. Also, it can be integrated with anaerobic digestion to enhance biogas production, while recovering N in the process, and also with other nutrient recovery technologies (Table 1). Due to these outstanding qualities, the GPM technology presents an enormous application potential. **Its economic feasibility and potential benefits have been compared with the other technologies, and are described in detail in section VI.3.**

For P recovery, it is worth mentioning the options of chemical precipitation, due to its versatility, and the electrodialytic method due to the purity of the P recovered. As in the case of the GPM technology**, its economic feasibility and possible benefits are detailed in section VI.3.**

Table 1. Description, advantages and challenges of the most common nitrogen recovery technologies.

N recovery technology	Operation	Advantages	Drawbacks
Air stripping	NH_3 air stripping is a physical-chemical process whose objective is to transfer volatile NH_3 contained in an NH_3 rich flow (usually manure or digestate), from its liquid phase to its gas phase, through liquid-gas contact and its subsequent recovery in an acidic solution, as ammonium salt or by condensation. It is carried out in a column, where the manure or the digestate enters through the upper part while a gas phase enters through the lower part, counter currently. This gas phase can be air below 100ºC, although for greater efficiency it is usually steam. Alkalis, such as lime or NaOH, are previously added to the manure or digestate to increase the pH and enhance the formation of the NH_3. The released NH_3 is usually recovered by absorption in a second column or by steam condensation (LifeManev project, 2016).	High N recovery in form of ammonium (Zarebska et al., 2015). It can be used in conjunction with anaerobic digestion (before or after, depending on the VS content) (Serna-Maza et al., 2017). There are several full-scale conventional air stripping installations implemented to recover N as ammonium from municipal wastewaters, digested sludge, pig slurries, cattle manure, and fermented chicken manure (Beckinghausen et al., 2016).	The NH_3 removal and recovery efficiency could be heterogeneous, and highly dependent on the wastewater type (Pandey and Chen, 2021). The alkalis required to elevate the pH, the air stripping column functioning and the energy required for elevating air, manure or digestate temperatures can significantly increase the operational cost (Pandey and Chen, 2021). The tower systems present clogging problems (Ma et al., 2013).
Ion exchange (zeolites)	Zeolites are inorganic porous materials, with a well-known adsorption capacity for small molecules. The ammonium contained in an ammonium rich waste stream, such as manure or digestate, can be absorbed by a zeolite crystal, to produce an ammonium rich solid compound that has a consistency similar to mold. Waste streams with acidic pH (<8.0) enhance nutrient solubility and maximize adsorption on the sorbent. Once the ammonium is captured by the zeolites, this solid compound can be separated from the liquid phase of the manure or the digestate by a decanter centrifuge. This solid compound can be used as fertilizer by applying it directly on the soil (Zarebska et al., 2015).	Zeolites are available at low cost (Kocatürk-Schumacher et al., 2013). It can be used in conjunction with anaerobic digestion, therefore used for manure or digestate (Milan et al., 2001). Ammonium-zeolite complex can be used as a slow-release fertilizer (Zarebska et al., 2015). It can be used to recover both N and P (Williams et al., 2015).	Due to the limited number of studies, the removal effectiveness of the ion-exchange method is unclear (Pandey and Chen, 2021). Ions present in animal manures, such as K^+, can interfere with the exchange/capture of ammonium during the ion exchange process (Pandey and Chen, 2021). To achieve high recovery efficiencies, the manure or digestate needs to be pre-treated which increases the operational costs (Pandey and Chen, 2021). Natural zeolites need to be treated with other ions to improve efficiency (Pandey and Chen, 2021). The method is affected by high concentrations of suspended solids present in livestock manure (Milan et al., 1997). Once the adsorbents are saturated, they need to be replaced regularly (Pandey and Chen, 2021).

Table 1 (continuation). Description, advantages and challenges of the most common nitrogen recovery technologies.

N recovery technology	Operation	Advantages	Drawbacks
Chemical precipitation (struvite)	Struvite precipitation is a well-known process to recover dissolved components in a waste stream into an inorganic compound. The supersaturated conditions may modify the pH, temperature and/or addition of metal ions (e. g., Mg^{2+}, Ca^{2+}, etc.) to facilitate the struvite precipitation. Struvite forms from 1:1:1 ratio of magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphate (PO_4^{3-}). $MgCl_2$ and NaOH are added to balance the Mg^{2+} to PO_4^{3-} ratio, increase the pH (>8), and improve the efficiency of the process. Struvite usually contains approximately12% P and 5% N, with minimal heavy metal or biological contamination (Mehta et al., 2015; Vanotti et al, 2017).	Struvite precipitation can be applied to simultaneously recover N and P from nutrient rich streams such as manure and digestate (Mehta et al., 2015). Medium ammonium removal efficiency (20–30% of soluble NH_3 from the waste streams) (Mehta et al., 2015). Physical structures, such as membranes or towers, are not required, only the chemicals for precipitation (Mehta et al., 2015).	The addition of PO_4^{3-}, and Mg^{2+} for pH adjustment, can increase the operation costs (Pandey and Chen, 2021). The influence in the precipitation of other ions (such as Ca^{2+}, and Fe^{2+}), and the organic impurities present in the manure can reduce the efficiency of the process (Rahman et al., 2014).
Gas-permeable membrane (GPM) technology	The GPM technology consists of a tubular and hollow hydrophobic gas-permeable membrane, made of expanded polytetrafluoroethylene, which is submerged in the N rich waste stream (manure or digestate). A trapping solution, which is usually diluted H_2SO_4, circulates inside the membrane. The NH_3 passes through the micropores of the hydrophobic membrane by diffusion, and is captured in the trapping solution to form an ammonium sulfate salt, which is a valuable fertilizer. The process requires a pH of approximately 8.5, which can be obtained by aeration or the addition of alkali (García-González et al., 2015; Vanotti and Szogi, 2015). **This technology will be explained in detail in section V.**	High NH_4^+-N removal efficiency. No clarification pre-treatment of the manure is needed (García-González and Vanotti, 2015). The use of alkali can be avoided and be substituted by aeration to increase the pH, reducing the operational costs (Dube et al., 2016; García-González et al., 2015; Riaño et al., 2019). It can be integrated with the AD process (González-García et al., 2020; Lauterböck et al., 2012; Molinuevo et al., 2018). It does not allow carbonaceous compounds to permeate through them (García-González and Vanotti, 2015; Vanotti and Szogi, 2011). It presents a high recovery rate of NH_3 disregarding the manure type used (Pandey and Chen, 2021). Low energy requirements (Munasinghe-Arachchige and Nirmalakhandant, 2020).	The high dependence of the process on pH and temperature (Pandey and Chen, 2021). The high costs of the materials (Pandey and Chen, 2021).

Table 2. Description, advantages and challenges of the most common phosphorus recovery technologies.

P recovery technology	Operation	Advantages	Drawbacks
Chemical precipitation (struvite)	(see Table 1)	High purity and efficiency of P removal; crystalline form (80–90% of soluble phosphates) (Mehta et al., 2015; Perera et al., 2019). It can be combined with other technologies for nutrient recovery, such as anaerobic sludge digester supernatant in enhanced biological phosphorus removal (Perera et al., 2019). Considered a good slow-release fertilizer that contains Mg as an additional nutrient (Perera et al., 2019).	Requires chemical addition for pH adjustment (Mg^{2+}), (Mehta et al., 2015; Zarebska et al., 2015). The chemical requirements for P removal from dilute solutions increase the operational costs (Perera et al., 2019).
Ion exchange (several sorbents)	The chemical principle has been presented in Table 1. In this case, PO_4^{3-} is adsorbed on to a P-selective media. The type of ion-exchange sorbent selected depends on the type of nutrient desired, and on the nutrient concentration in the waste stream. For P recovery from nutrient concentrated waste streams, such as manure or digestate, red mud, metal oxide/hydroxide, and zirconium sorbents are used instead of zeolites that are used for N recovery (Mehta et al., 2015; Perera et al., 2019).	High quality and high concentration of P recovery (Mehta et al., 2015; Perera et al., 2019). No pH adjustment is needed (Perera et al., 2019).	Chemicals are required for the regeneration of the sorbent (Mehta et al., 2015). The selectivity is limited. The reaction and competition of other ions (such as SO_4^{2-}, Al^{3+}, Ca^{2+}) may affect the process and therefore the concentrations and the quality (Perera et al., 2019). There is a need for a low concentration of suspended solids to avoid clogging (Perera et al., 2019).
Electrodialysis	In this process, anions such as PO_4^{3-} and cations such as NH_4^+or Ca^{2+}, Mg^{2+} are separated using ion-exchange membranes in the presence of an electric field. This process is commonly used to concentrate P so it can be subsequently precipitated and recovered as struvite (Zarebska et al., 2015).	High efficiency of recovery. It can also be used for NH_3 recovery (Zarebska et al., 2015).	The catholyte can accumulate heavy metals (Perera et al., 2019). For P recovery, there is a need for chemical addition and energy consumption, which can increase the operational cost (Zarebska et al., 2015; Perera et al., 2019).

Table 2 (continuation). Description, advantages and challenges of the most common phosphorus recovery technologies.

P recovery technology	Operation	Advantages	Drawbacks
Electrodialytic process (ED)	This method applies a low direct current and it was used initially to remove contaminants, as remediation of fine-grained materials in suspension. The process uses a cell divided into three compartments: a central compartment with the P- rich wastewater (such as sewage sludge, manure or digestate), and two others, one on each side, containing an electrolyte solution that recirculates, and where the electrodes are placed. The central compartment is separated from the other two by ion exchange membranes (an anion and a cation exchange membrane). The PO_4^{3-} will migrate towards the cathode once the current is applied, and it will be concentrated in the end of the process in the electrolytic solution, turning it into a P-rich solution. Difference with electrodialysis: The principle of ED is similar to electrodialysis, but the former is an historic evolution of waste treatment, while the latter evolves from water treatment processes. The electrodialysis setup, in stacks of alternating membranes, is not suited for water or wastewater with a high content of solids, because the suspended material blocks the membranes and the fluid circulation channels. So, its application to wastewater is limited to very few situations, where the content of suspended solids is very low (Jensen et al., 2010).	High P recovery efficiency (Oliveira et al., 2020; Oliveira et al., 2021). Low energy requirements and short time to achieve good performance (Oliveira et al., 2019). It can be applied directly to nutrient-rich wastewater, without the need for prior treatments, such as dilution, or suspended solids removal (Oliveira et al., 2019). This process can also be used as a first step to concentrate P and precipitate it as struvite in a second step (Oliveira et al., 2019; Oliveira et al., 2020).	Possible interference of unwanted ions (Oliveira et al., 2019). High cost of the ion-exchange membranes and the NaOH (Oliveira et al., 2021).

3.2. Gas-permeable membrane technology

Nitrogen in manure and digestate is mainly present as NH_4^+ (a dissolved form of N), and NH_3 (a volatile form of N). The equilibrium between both species is strongly dependent on pH and temperature. The form NH_4^+ is more abundant when the pH is below 7, regardless of the temperature. The equilibrium shifts towards the NH_3 form when the pH rises (García-González and Vanotti, 2015).

$$NH_3 + H^+ \longleftrightarrow NH_4^+$$

$$NH_4^+ + OH^- \longleftrightarrow NH_3 + H_2O$$

In the same way, the amount of NH_4^+ decreases when the temperature increases, favoring the formation of NH_3. Based on this knowledge, Vanotti and Szogi (2015) patented a system for a passive capture of NH_3, to drive the passage of NH_3 through a **tubular microporous hydrophobic gas-permeable membrane**, where the NH_3 is captured in an acidic solution that circulates inside the membrane.

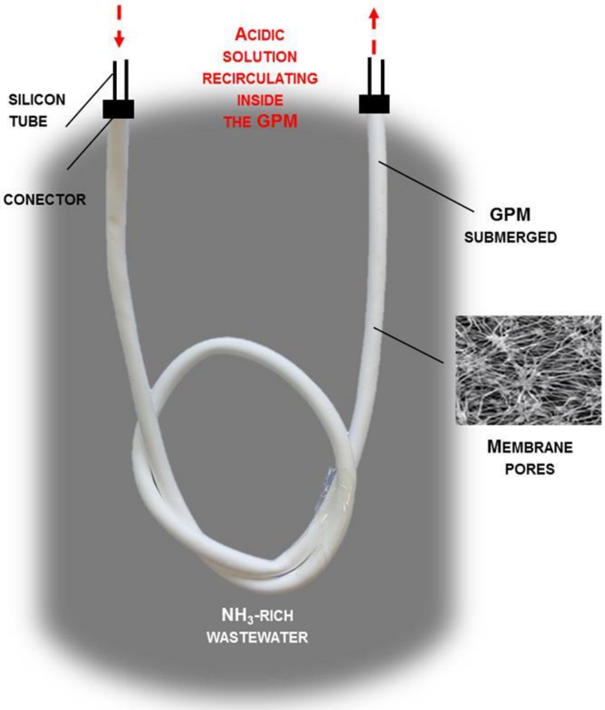


Figure 7. Schematic system view of the GPM technology operation. Source: modified based on García-González and Vanotti (2015). Membrane pores image source: Vanotti and Szogi (2015).

Inside the membrane, the NH_3 chemically reacts with an acidic solution that captures the NH_3, becoming a concentrated and non-volatile ammonium salt (Figure 7). **A more detailed scheme of the membrane characteristics and operation is presented in section V.** Since the GPM system is a technology capable of capturing NH_3 gas present in high concentrations in a fluid, it can also be applied to NH_3 capture from the air. Therefore, it could be an interesting solution for NH_3 removal, for example from the air of enclosed spaces, such as intensive farms (Soto-Herranz et al., 2019). This technology can also be applied in NH_3-rich wastewaters, such as municipal or industrial wastewaters, where the NH_3 volatilizes, causing harmful emissions.

Figure 8 represents a transversal cut of the membrane, where it is possible to see the chemical process. Based on Vanotti and Szogi (2015), the acidic solution consists of sulfuric acid 1N, used as the trapping solution to capture the NH_3, resulting in ammonium sulfate, which is a valuable fertilizer.

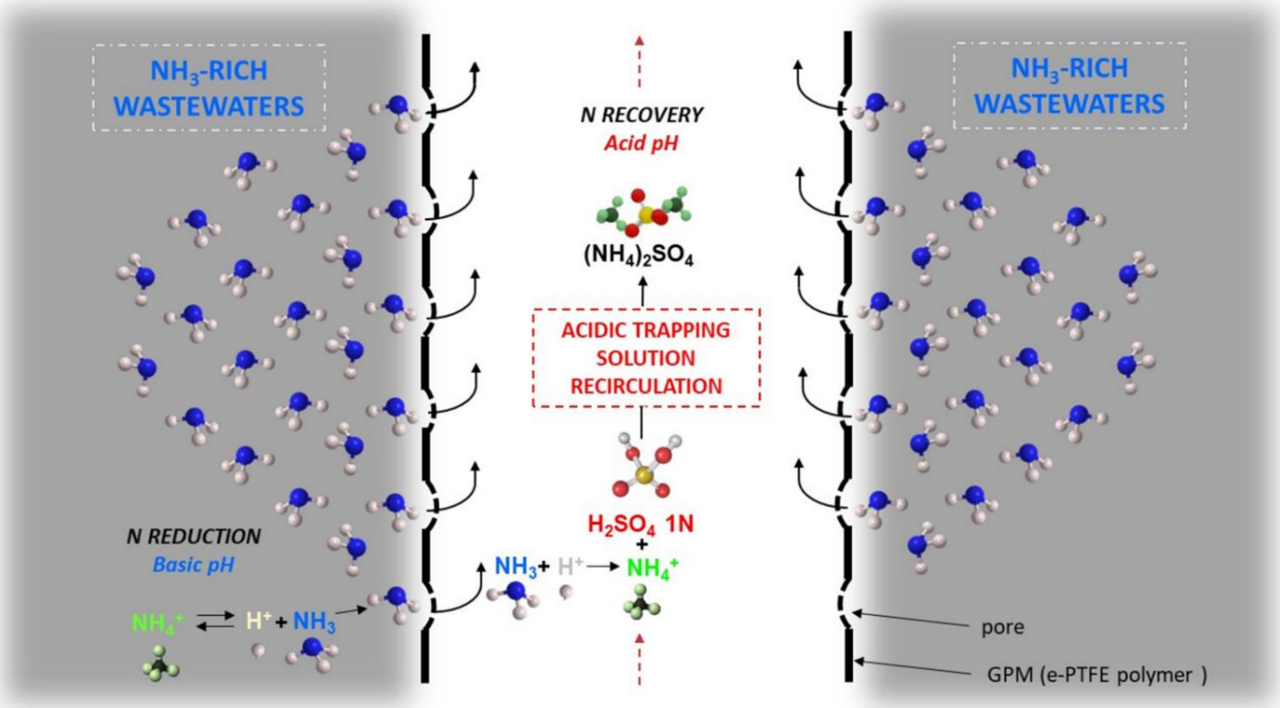


Figure 8. Transversal cut of the membrane showing the operating principle. Source: own elaboration based on García-González and Vanotti (2015).

The GPM technology has been successfully applied to recover N from livestock waste and anaerobic digestate at laboratory scale (García-González et al., 2015; García-González and Vanotti, 2015; Riaño et al., 2019). More recently, Molinuevo-Salces et al., (2020a) and Riaño et al. (2021) reported the application of the GPM technology on a pilot-scale plant to recover N from swine manure and digestate, achieving a good technical performance. How the optimization of the membrane area in contact with the wastewaters can improve the N recovery has also been studied (Riaño et al., 2022). In the past years, GPM technology has been regarded as one of the best technologies reported in the literature for recovering N from agro-industrial residues (Beckinghausen et al., 2020; Munasinghe-Arachchige and Nirmalakhandan, 2020; Pandey and Chen, 2021). More recently Al-Juboori et al. (2023) made a thorough analysis of the membrane technologies for N recovery, considering energy requirements, recovery efficiency, and process scale, and determined that the GPM technology, applied alone or in combination with other technologies for nutrient recovery, **is the most promising nutrient recovery technique**, and it deserves greater attentions and investments from the agri-food sector. **This involves the special relevancy of works like this thesis.**

IV. JUSTIFICATION, OBJECTIVES AND COHERENCE OF THE THESIS

1. Justification

The efficient treatment of waste from a circular perspective implies its transformation into by-products and, therefore, into secondary raw materials that can be used, thus closing cycles. Moreover, it may also imply the extraction, whenever possible, of high-value added products through innovative and efficient technologies.

Within the agro-industrial sector, the GPM technology can be applied to manure and digestate from biogas plants. These two substances, with high NH_3 content, can be used as organic fertilizers, but with the treatment of the GPM technology, the emissions of this polluting gas would be reduced and, at the same time, a high-value by-product is produced (ammonium sulfate), thus achieving the objectives of the circular economy. Therefore, the application of this membrane technology would be in line with the requirements of environmental strategies for minimizing environmental impacts and closing loops through waste valorization.

2. Objective

The **main objective** of this thesis is to study the application of the novel GPM technology, and its potential combinations with other waste treatment techniques, on raw livestock wastewaters and anaerobically digested wastewaters, in order to minimize NH_3 emissions and nutrient losses, through nutrient recovery (N and P) as valuable bio-based fertilizers (ammonium sulfate solution, a P-rich solution and a P-precipitate), to valorize these waste streams and to reduce potential associated environmental impacts. To achieve this goal, different sub-objectives have been proposed in each different study, which would allow **a comprehensive coherence to be maintained in the thesis (Figure 9).**

Sub-objective 1: Firstly, it was proposed to study the potential of GPM technology in combination with well-known and already implemented waste treatment technologies from the agro-food industry, such as AD. In the case of AD in particular, NH_3 is a well-known inhibitor of the process, therefore: could GPM technology improve the AD operating inside the anaerobic reactor throughout the process, capturing NH_3 and preventing inhibition? In that case, what would the methane yields and the N recovery efficiency be? **The specific objective in this case** was to address these issues by studying the performance of AD and N recovery efficiency with the GPM technology operating inside the AD reactor (**section VI.1**).

Sub-objective 2: since the co-digestion of food waste with manure has proved to be an interesting solution for the valorization of both types of waste, it was proposed in the study presented in **section VI.2** to conduct an AD experiment with food waste and manure as feed, and later to apply the GPM technology on AD resultant digestates. **The specific objective of this study** was to find an optimal proportion of food waste and swine manure for an AD with a good performance, and later, to apply the GPM technology to the resultant digestates to determine what the N recovery efficiency would be, and if the ratio of food waste added to the co-digestion with manure would affect the N recovery efficiency.

Sub-objective 3: in addition to evaluating the potential of combining GPM technology with the AD process for waste management, it was considered whether it would be possible to combine GPM technology with other innovative techniques to also recover other nutrients. How do the different techniques interact? What would the nutrient recovery yields then be? With the **specific objective of addressing these questions,** a study was carried out in **section VI.3,** in which the GPM technology is combined with electrodialytic membranes, in a two-phase N and P recovery system, (and later in section VI.4), with different configurations of gas-permeable membranes and the simultaneous chemical precipitation of P.

Sub-objective 4: Along the same lines as those of the sub-objective 3, the combination the GPM technology with chemical precipitation for P recovery was proposed. This is based on the premise that the N removal from the digestate and its recovery in the trapping solution creates advantageous conditions for obtaining high recovery rates of precipitated P**.** Would the increment in the membrane area affect the NH_3 recovery, and therefore the P recovery? Would the alkali addition favor the nutrient recoveries? What would the nutrient recovery rates then be**? Therefore, the specific objective was to answer these questions, proposing two sets of experiments,** where the effect of the membrane area and the addition of alkali on N and P recovery efficiencies were studied (**section VI.4)**.

Sub-objective 5: the proposal was to study the GPM technology performance from an environmental point of view. The application of GPM technology not only implies the recovery of N, but also the reduction of NH_3 emissions; however, what if we are generating other environmental impacts applying this technology? At this point, the **specific objective proposed was to verify the potential environmental impact of the application of the membranes.** In **section VI.5** the life cycle analysis (LCA) of a scenario was carried out where the GPM technology was applied to recover N from swine manure, and then it was compared with a scenario where the manure receives no treatment whatsoever.

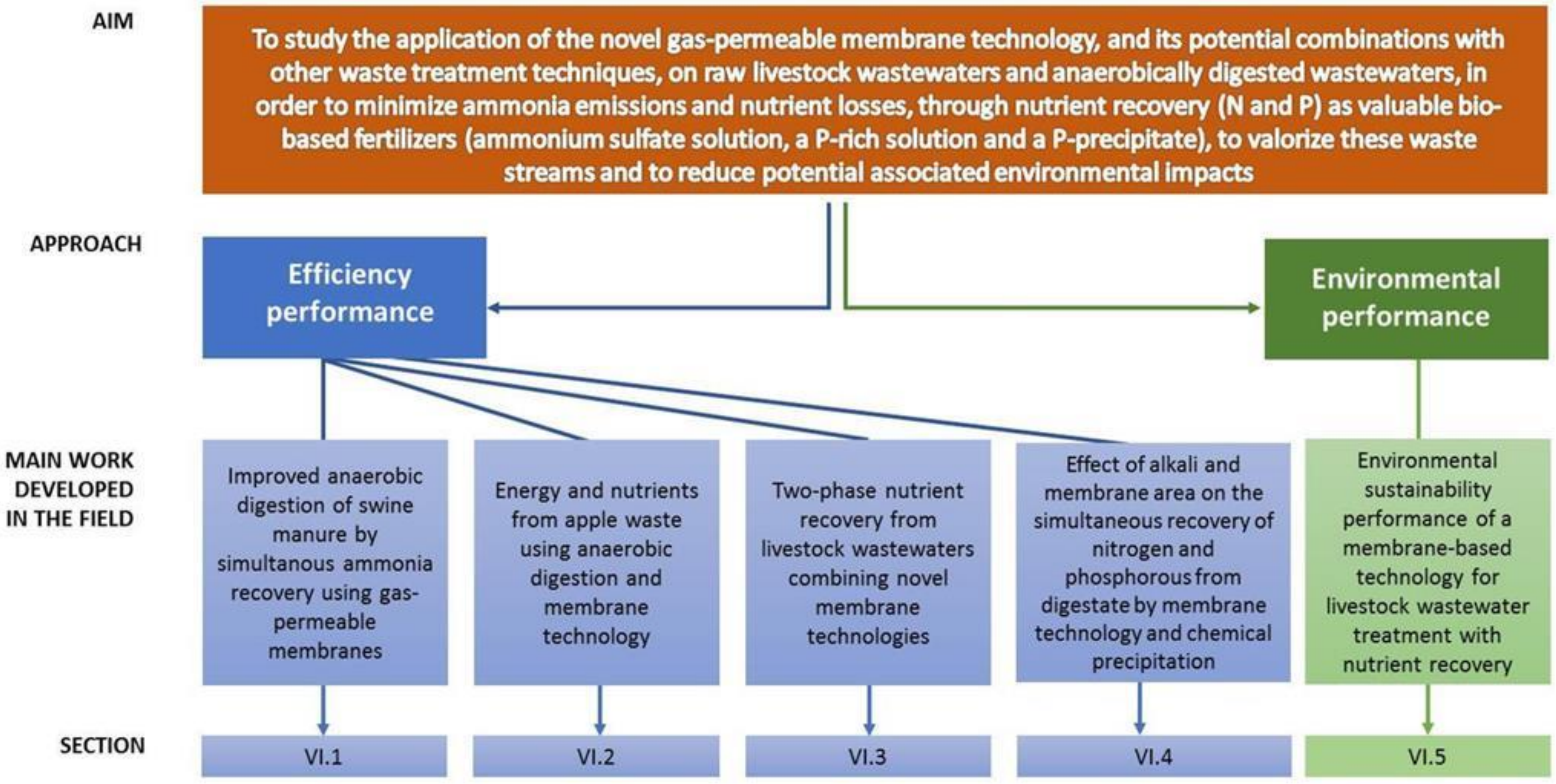


Figure 9. Organization of the work developed in the thesis.

V. MATERIAL AND METHODOLOGY

1. Material

This Material and Methodology section **focuses on the GPM as the main common material** to all studies **and its method of operation, which** allows the capture of NH_3. This section provides precise information on the physical characteristics of the membrane and its operation. The analytical methods may vary depending on each study; so, for the sake of clarity and consistency, they have not been included in this section, but they can be seen in each respective publication.

Figure 10. Detailed view of the GPM. Source: Zeus Company Inc.

The GPM used in this thesis was an *Aeos*™ ePTFE Porous Tubing biomaterial, manufactured by ZEUS Industrial Products Company Inc., Orangeburg, South Carolina 29118, United States (Figure 10). The expanded polytetrafluoroethylene (e-PTFE) membrane density was 0.95 g cm^{-3}, with a wall thickness of 0.56 mm and a pore of 0.2 µm – 1.0 µm (Zeus, 2019).

2. Methodology

The GPM technology is based on the mass transfer driven by the difference in NH_3 gas concentration between both sides of the GPM: on one side the digestate or the manure, and on the other the acidic trapping solution. Figure 11 shows the complete GPM experimental set-up that consists of a) the membrane submerged in the manure or the digestate (N rich wastewaters), b) a peristaltic pump that keeps the acidic trapping solution continuously recirculating, c) an aeration device (optional), and d) a N recovery tank.

The operating process works at atmospheric pressure and as follows: the gaseous NH_3 passes through the pores of the membrane by diffusion. Inside the membrane a strong acid, H_2SO_4 1N (solution from 96–98%, Panreac), recirculates at a flow rate of 12 L d^{-1} by means of the peristaltic pump (Pumpdrive 5001, Heidolph, Schwabach, Germany) in a closed-loop. The NH_3 then chemically combines with the acid to give an ammonium sulfate solution ($(NH_4)_2SO_4$. The manure or digestate volume, the acidic solution volume, and the membrane area used vary depending on the experiment, and can be found specified in section VI, in each publication.

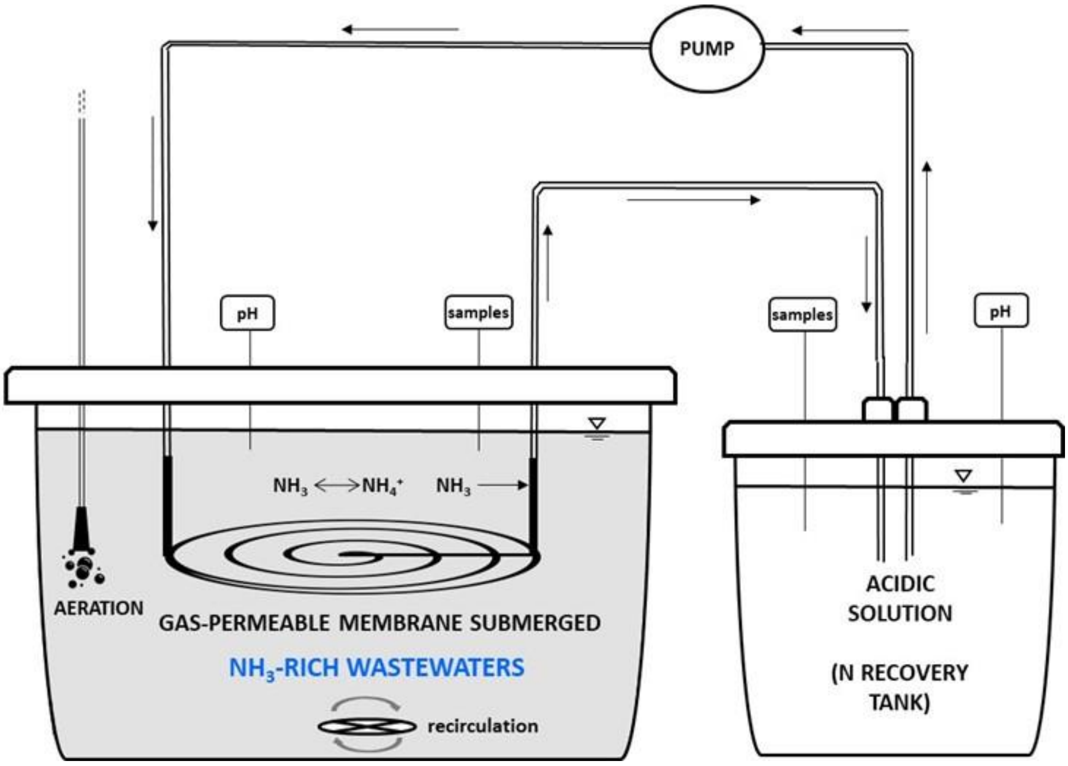


Figure 11. GPM technology experimental set-up.

Both the concentration of N recovered in the acidic solution and the concentration of N that decreases in the wastewater are given as **total ammoniacal nitrogen**, NH_3-N (TAN). In the first case it would be TAN recovery and in the second TAN removal. The TAN concentration was calculated using the APHA methodology (2005). The volume of the acidic solution was measured daily in order to calculate the mass of TAN recovered by the GPM system.

The amount removed and recovered with regard to the initial amount in the manure or digestate is presented as a percentage (Equations 1 and 2). The average TAN recovery rates are also often reported as mg N m^{-2} d^{-1} (Equation 3).

$$TAN\ removal\ (\%) = \frac{(Initial\ mass\ of\ TAN - Final\ mass\ of\ TAN)}{(Initial\ mass\ of\ TAN)} \times 100 \qquad \text{(Eq. 1)}$$

$$TAN\ recovery\ (\%) = \frac{Final\ mass\ of\ TAN\ in\ the\ trapping\ solution}{mass\ of\ TAN\ removed\ from\ the\ wastewater} \times 100 \qquad \text{(Eq. 2)}$$

$$Average\ TAN\ recovery\ (mg\ N\ m^{-2}\ day^{-1}) = \frac{\begin{matrix} mass\ of\ TAN\ recovered \\ in\ the\ acidic\ solution \end{matrix}}{\begin{matrix} m^2 of\ membrane\ and \\ days\ of\ experiment \end{matrix}} \times 100 \qquad \text{(Eq. 3)}$$

The **free ammonia (FA)** is the NH_3 gas that is available to pass through the membrane pores. The FA content has been stated as one of the main variables affecting TAN recovery using the GPM technology, along with pH and temperature. Other factors that may influence capture are the amount of the membrane surface in contact with the wastewater, agitation, and the particular characteristics of the membrane type (Soto-Herranz et al., 2021).

The FA is calculated using the equation of Hansen et al. (1998), as un-ionized NH_3 (Eq. 4):

$$NH_3/tNH_3 = (1 + (10^{-pH}/10^{-(0.09018 + 2729.92/T)}))^{-1} \qquad \text{(Eq. 4)}$$

where, the pH is the pH measured in the wastewaters, NH_3 is the FA content, tNH_3 is the total NH_3 concentration and T is temperature in Kelvin.

The FA also influences the GPM transfer coefficient Km ($m\ d^{-1}$), (Samani-Majd and Mukhtar, 2013), which is calculated as follows:

$$J = K_m\,(C1 - C2) \qquad \text{(Eq. 5)}$$

where J is the TAN mass flux per area ($g\ m^{-2}\ d^{-1}$), and C1 and C2 correspond to the concentrations of FA in the wastewaters and in the trapping solution, respectively. The GPM transfer coefficient varies in each particular application and can also be affected by other factors, such as the flow rate of the trapping solution and the membrane characteristics (e.g., morphology, density, pore size or thickness). The GPM transfer coefficient was **calculated in sections VI.1 and VI.3.**

It can be added alkali to optimize the NH_3 availability in the manure or in the digestate, (Vanotti and Szogi, 2015), but the NH_3 availability can be improved also by applying a **low aeration** (González-García et al., 2015). In this case, the low aeration allows the use of chemicals that would increase operating costs to be avoided. The low aeration in the correspondent experiments was applied using an air pump (Hailea, Aco-2201, Guangdong, China), and it was used a rotameter to keep a rate flow of 0.24 L air L^{-1} min^{-1} (Aalborg, Orangeburg, NY, USA), in order to keep the equilibrium NH_4^+/NH_3 towards NH_3 and thus capture more NH_3.

The pH of the acidic solution was monitored daily and whenever the pH reached 2, concentrated H_2SO_4 (96–98%, Panreac) was added to the N concentration tank to an endpoint of pH<2. The pH 2 was selected as the upper set point based on Vanotti and Szogi (2015), which indicated that NH_3 recovery in the closed-loop GPM system, is optimized when the pH of the stripping tank solution is kept below 2.

VI. RESULTS AND DISCUSSION by SCIENTIFIC CONTRIBUTIONS

1. “Improved anaerobic digestion of swine manure by simultaneous ammonia recovery using gas-permeable membranes”. Article published (© Elsevier Ltd.). Photographic annex pictures 3 – 5.

This study focuses on the recovery of NH_3 with GPM for the improvement of the anaerobic digestion (AD) of swine manure. For the evaluation of the effect of the removal of NH_3 by GPM, the performance of the AD process was evaluated, as well as the production of biogas and its quality, using swine manure as raw material.

The AD experiments were carried out in batches and in a semi-continuous regime under mesophilic conditions. Two reactors were used: reactor R1, with GPM to extract NH_3 and recover it as nitrogen (N), and reactor R2 without GPM as a control. The volume of biogas produced was measured daily by volume displacement, and the biogas composition was measured weekly by chromatography. Samples of influent and effluent were taken twice a week and analyzed for total alkalinity (TA), partial alkalinity (PA), total solids (TS), volatile solids (VS), volatile fatty acids (VFA), total chemical oxygen demand (TCOD), TAN, and total Kjeldahl nitrogen (TKN). The experimental set up was configured as shown in the previous section, without aeration. The ratio of the membrane area exposed to swine manure from the anaerobic reactor per reactor volume was 0.004 m^2 per liter. The flow rate of the acidic solution was 12 L d^{-1}. The N concentration tank consisted of a sealed 570 mL glass container containing an acidic solution (150 mL of 1N H_2SO_4). The pH of the acidic solution was monitored daily and every time the pH reached 2, concentrated sulfuric acid was added to reach a pH below 2.

The batch experiment was carried out for 10 days. After these 10 days of operation, the membrane reactor presented a lower concentration of TAN compared to the reference (749 ± 16 mg N L^{-1} versus 1033 ± 27 mg N L^{-1}), which implied a reduction of 28%. The free ammonia (FA) also presented a reduction of 23%. The membrane reactor presented a methane yield of 70 N mL CH_4 g VS^{-1} compared to a yield of 64 N mL CH_4 g VS^{-1} of the reference reactor. Moreover, the biogas obtained in the membrane reactor had a higher percentage of CH_4 (78%) compared to the reference reactor (63%).

In the semi-continuous experiment, in the reactor with N recovery by the membranes, the TAN concentration was reduced by 23% on average compared to the reactor without NH_3 recovery. The FA concentrations were also reduced by 4% on average. These reductions in TAN and FA by the GPM system positively impacted both the quality and quantity of biogas produced by AD from swine manure. In particular, the specific yield of methane increased by up to 27.6% (on average 16.7%) in the semi-continuous experiment. In addition, higher percentages of methane in the biogas were obtained, 11% on average (range 8.3-13.6%). Simultaneously, a uniform TAN recovery rate of 6.7 g N TAN per m^2 of membrane per day was obtained during the 205 days of semi-continuous operation. Ammoniacal N was recovered as ammonium sulfate solution.

Therefore, the AD-GPM configuration produces beneficial results in biogas quantity and quality, while recovering ammoniacal nitrogen in the form of ammonium sulfate.

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Improved anaerobic digestion of swine manure by simultaneous ammonia recovery using gas-permeable membranes (©ELSEVIER)

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ABSTRACT

In feedstocks containing high ammonia (NH_3) concentration, removal of the NH_3 during the anaerobic digestion (AD) process can improve AD process performance. In the present study, the effect of NH_3 removal using gas-permeable membrane (GPM) technology on AD process performance and biogas production was investigated using swine manure feedstock. Batch and semi-continuous AD experiments were carried out under mesophilic conditions. In the reactor with NH_3 recovery, total ammonia nitrogen (TAN) concentration was reduced 28% in batch experiments and 23% on average in the semicontinuous experiment compared with the reactor without NH_3 recovery. Free ammonia (FA) concentrations were also decreased by 23% and 4% on average in batch and semicontinuous experiments, respectively. These reductions in TAN and FA by GPM system positively impacted both the quality and quantity of the biogas produced by AD of swine manure. Specifically, the specific methane yield increased 10% in the batch experiment and 17% on average in the semicontinuous experiment. Furthermore, higher percentages of methane in biogas were obtained during AD retrofitted with GPM system, 24% increase in the batch experiment and 11% on average in the semicontinuous experiment (range 8.3-13.6%). Simultaneously, a uniform TAN recovery rate of 6.7 g TAN per m^2 of membrane and per day was obtained for the 205 days of semicontinuous operation. Therefore, the AD-GPM configuration produces beneficial results on biogas quantity and quality while recovering ammonia nitrogen in form of ammonium salt.

2. **“Energy and nutrients from apple waste using anaerobic digestion and membrane technology”.** Article published (open access on MDPI). Photographic annex pictures 6 – 8.

This study proposed the evaluation of biogas production from fruit residues and N recovery from the digestate obtained. To do so, a co-digestion of apple pomace (AP), apple remains from the cider industry) with swine manure (SM) was studied and the effect of different proportions of AP (0, 7.5, 15 and 30%, based on VS) on methane production and process stability was evaluated. Subsequently, the GPM technology was applied to two of the digestates resulting from AD (7.5% of AP and SM; and SM only) to recover N in the form of ammonium sulfate. Anaerobic digestion was carried out under a semi-continuous regime and mesophilic conditions. The volume of biogas produced during the AD phase was measured daily by volume displacement, and the biogas composition was measured weekly by chromatography. Samples of the swine manure and the SM mixed with AP that was added to the reactors, as well as the effluent, were taken twice a week and analyzed to determine the TA, TS, VS, VFA, TCOD, TAN and TKN.

The N recovery was performed after the AD. In this phase, two sets of experiments were carried out, one for the digestate with 7.5% of AP and SM, and another for SM only. The experimental set up was configured as shown in the previous section with aeration. The GPM was immersed in the tank, in 1.5 L of digestate, with a length of 120 cm. The relationship between the surface area of the membrane and the volume of the digestate was 0.013 m^2 per liter. The reactors were continuously agitated using a magnetic stirrer at 250 rpm. The acid bottles used to recover TAN consisted of 0.5 L unsealed glass jars, initially containing 0.3 L of acidic solution (1N H_2SO_4). The TAN analysis of the acidic solution was carried out to determine the concentration of N they contained and thus evaluate the recovery efficiency.

The results showed that the co-digestion of 7.5% and 15% of AP with SM presented a methane production similar to the AD from SM alone. The subsequent application of the GPM technology on the resulting digestates, with SM alone and 7.5% AP and SM mixed, showed TAN recovery rates of 32.9 and 25.8 g N per m^2 of membrane and per day.

These results indicate that the valorization of AP through the AD process followed by the recovery of N from the digestate could be a good agro-industrial residue management strategy.

membranes

Article

Energy and Nutrients from Apple Waste Using Anaerobic Digestion and Membrane Technology

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Abstract: The worldwide increment of food waste requires innovative management solutions, aligned with sustainability, energy, and food security. Anaerobic digestion (AD), followed by nutrient recovery, may be considered an interesting approach. This study proposed a co-digestion of apple pomace (AP) with swine manure (SM) to study the effect of different proportions of AP (0, 7.5, 15, and 30%, on a volatile solids (VS) basis) on the methane production and the stability of the process. Subsequently, the gas-permeable membrane (GPM) technology was applied to recover nitrogen (N) as ammonium sulfate (bio-based fertilizer) from the digestates produced after the AD of 7.5% of AP and SM, and SM alone. The results showed that the co-digestion of 7.5% and 15% of AP with SM presented a methane production similar to the AD of SM alone (with 412.3 ± 62.6, 381.8 ± 134.1, and 421.7 ± 153.6 mL g VS^{-1} day^{-1}, respectively). The later application of the GPM technology on the resulting digestates, with SM alone and with 7.5% of AP with SM, showed total ammoniacal N recovery rates of 33 and 25.8 g N m^{-2} d^{-1}, respectively. Therefore, the AP valorization through the AD process, followed by N recovery from the digestate, could be a good management strategy.

Keywords: nutrient recovery; bioeconomy; waste valorization

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1. Introduction

The apple production in the world in 2020 was 86.44 million tons, of which 11.48 million tons came from the European Union [1]. Around 20% of this production is used by the food industry to produce cider, jelly, and juice as the main products [2]. After this processing, 25% of the fresh apple becomes waste, in the form of skin, seeds, and pulp, known as apple pomace (AP), which is usually destined for landfills, incineration, or composting [2]. These forms of disposal generate environmental and human health issues related to greenhouse gas emissions [2,3].

In recent years, the valorization of agro-industrial and food waste through its transformation into by-products with added value has gained importance as one of the main solutions for waste management, following the principle of the end-of-waste and nutrient recovery criteria within the circular economy model [4]. One of the main technologies for waste management is anaerobic digestion (AD), a consolidated process widely used for livestock waste treatment [5,6]. AD allows for the production of biogas from agriculture waste and residues, such as manure, contributing to the production of renewable energy, while the resulting effluent of the process (digestate) can be used as a valuable organic fertilizer, reducing the dependency on expensive mineral fertilizers [7]. Several works have studied the co-digestion of different food wastes and manure over the last few years. For example, Labatut et al. [8] co-digested different co-substrates (cheese whey, plain pasta, used vegetable oil, cabbage, and raw potatoes, among others) with dairy manure. Bres et al. [9] studied the performance of semi-continuous AD by co-digesting poultry manure with fruit and vegetable waste, while Riaño et al. [10] studied the co-digestion of pepper waste and swine manure (SM).

However, only a few works have studied the use of apple residues as co-substrates for the AD process, and most of these studied the process under batch conditions.

Riggio et al. [11] studied apple waste valorization using different mixtures of apple pulp, cow manure, and olive pomace and compared the methane production under batch conditions, obtaining the highest methane production (216.3 L CH_4 kg volatile solids $(VS)^{-1}$) with a mixture of 85% cattle slurry, 10% olive pomace, and 5% apple pulp (w/w). Molinuevo-Salces et al. [12] studied the effect of AP in the mixture during the co-digestion with SM in the range of 0–100% (on a VS basis) following a central composite design, obtaining the highest methane yield (596 mL CH_4 gVS^{-1}) with 14.6% of AP in the mix. They also found differences between the methane potential of apple residues from the cider industry and the juice industry. Kafle and Kim [13] studied the co-digestion of fresh crushed apples as apple waste (AW) and SM, using different proportions of AW in the mixture under semi-continuous conditions (AW:SM ratios of 25:75; 33:67, and 50:50 on a VS basis). They observed positive synergetic effects on biogas production when the AW content in the feed increased from 25% to 33% (on a VS basis), but a further increase in the AW content from 33% to 50% had a negative synergetic effect due to the rapid accumulation of total volatile fatty acids (TVFA). Nevertheless, as the substrate used by these authors was fresh apples instead of real waste, it may not perform similarly to industrial apple waste. Therefore, a deeper knowledge of the use of real apple waste as a substrate in anaerobic co-digestion with SM under semi-continuous regimen is required. Furthermore, the study of the potential relationship between AD and nutrient recovery has arisen as an important new trend [5].

The use of the digestate as organic fertilizer may involve storage and transportation problems, as well as land application limitations related to the addition of nitrogen (N) rich substances in agricultural fields, leading to nitrate emissions and nutrient losses [14,15]. The application of nutrient recovery technologies can address these issues and prevent nutrient losses; thus, the interest and incentives for nutrient recovery and reuse of AD effluents have been increasing over the last few years, [4,16]. For N recovery from a digestate, the most commonly used technologies are air stripping, ion exchange, ultrafiltration, reverse osmosis, or gas-permeable membrane technology (GPM) [17]. Specifically, the GPM technology is considered as one of the most valuable novel technologies to recover N, attending to both economic and energetic aspects [17–19]. This technology is based on the mass transfer driven by the difference in ammonia (NH_3) gas concentration between both sides of a gas-permeable hydrophobic membrane. The membrane is submerged in the wastewater, and the NH_3 passes through the pores. Then it is trapped by the acidic solution that circulates inside the membrane, being recovered as an ammonium salt solution (bio-based fertilizer) [20,21]. In this way, the treated digestate can be applied in the field to provide the advantages of a fertilizer rich in organic matter, but without N excess. The GPM technology has been successfully used in several studies for N recovery from such organic wastes as SM, obtaining N recovery percentages up to 98% [22–24], and from different digestates generated in anaerobic co-digesting systems, with N recovery percentages up to 99% [6,25,26]. Some of these studies used SM co-digested with organic co-substrates, such as fruit and vegetable sludge from peppers and artichokes, as well as by-products of the tomato processing industry [26], or tobacco powder and cereal powder [6]. However, so far, the N recovery from digestates of AP residues has not been addressed.

To the best of our knowledge, a study of the efficiency of the AD process with different proportions of AP as the co-substrate, with the subsequent recovery of N from the resulting digestate, has never before been conducted. The aim of the present work was to assess the effect of the addition of different ratios of AP from the cider industry with SM in the AD process, under semi-continuous operation and mesophilic conditions, followed by the application of the GPM technology for the N recovery from the digestate in the form of a valuable ammonium salt solution, and to determine if the use of AP as a co-substrate could affect the N recovery process. This approach can provide valuable information to stakeholders in the agri-food sector, offering a point of view not only focused on energy, but also on the potential production of a bio-based fertilizer.

2. Materials and Methods

2.1. Origin and Characterization of Apple Pomace, Manure, and Inoculum

AP was provided by the Regional Research and Development Service of Asturias (SERIDA) (Asturias, Spain). The AP was a solid fresh waste obtained after apple pressing for cider production. It was transported to the ITACyL in plastic containers and kept frozen for further use. The AP presented a content of total solids (TS) of 268.7 ± 14.5 g kg^{-1} and a content of VS of 265.4 ± 14.4 g kg^{-1}.

The SM used was centrate collected after on-farm centrifugation from a pig farm located in Narros de Cuéllar (Segovia, Spain). The collected manure was put in plastic containers, transported to the ITACyL laboratory in Valladolid (Spain), and stored in the laboratory at 4 °C for further use. The mean characteristics of the SM were pH of 7.2 ± 0.1, 41.8 ±7.1 g TS L^{-1}, 30.6 ± 4.5 g VS L^{-1}, 139.1 ± 94.9 g total chemical oxygen demand (TCOD) L^{-1}, 36.2 ± 2.2 g soluble chemical oxygen demand (SCOD) L^{-1}, 4762 ± 62 mg total Kjeldahl nitrogen (TKN) L^{-1}, and 3607 ± 308 mg total ammoniacal nitrogen (TAN) L^{-1}.

The inoculum used was obtained from an anaerobic digester of the municipal wastewater treatment plant in Valladolid (Spain). The inoculum had a concentration of 10.9 ± 0.1 g VS L^{-1}.

2.2. Experimental Set-Up

2.2.1. Semi-Continuous Co-Digestion of Different Mixtures

Semi-continuous co-digestion was carried out using two identical continuously stirred tank reactors (CSTRs) with a total volume of 7 L and a working volume of 5 L, namely R1 and R2. A water bath was used to maintain the temperature of the reactors at 38 °C (mesophilic conditions). The reactors were mounted separately, and the mixture was homogenized by continuous stirring (37 rpm). The outlets provided on the top of each reactor were used for feeding the influent, withdrawing the effluent, and for collecting the biogas. The volume of biogas produced was measured daily by water displacement (Figure 1).

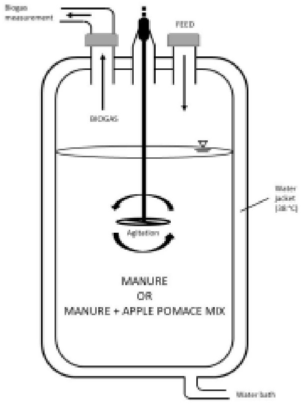


Figure 1. Experimental set-up of an anerobic reactor for the AD experiments. The arrows indicate the direction of the flows.

The semi-continuous co-digestion was performed for 240 days. The reactors were initially filled with 5 L of inoculum. After that, manual feeding of the reactors was performed once per day, every weekday. Prior to each feeding, a volume equal to the feeding volume was removed to maintain a constant reactor volume. Initially, an organic loading rate (OLR) of 1.04 g VS L^{-1} d^{-1} and a hydraulic retention time (HRT) of 25 days were applied in both reactors (initial period). In this initial period (0–26 days), R1 was fed with

SM alone; whereas R2 was fed with a mixture of SM and AP in a feed VS ratio of 85.0% SM and 15.0% AP. This percentage was used based on a previous work that investigated the influence of the percentage of AP on anaerobic co-digestion of AP and SM, following a central composite design, and obtaining the highest methane yield with a percentage of AP in the mixture of 15% [12]. Since a progressive destabilization of both reactors occurred during the initial period (Figure 2), the applied OLR was decreased to 0.78 g VS L^{-1} d^{-1}, and the HRT was increased to 33 days, maintaining these conditions during the rest of the experiment.

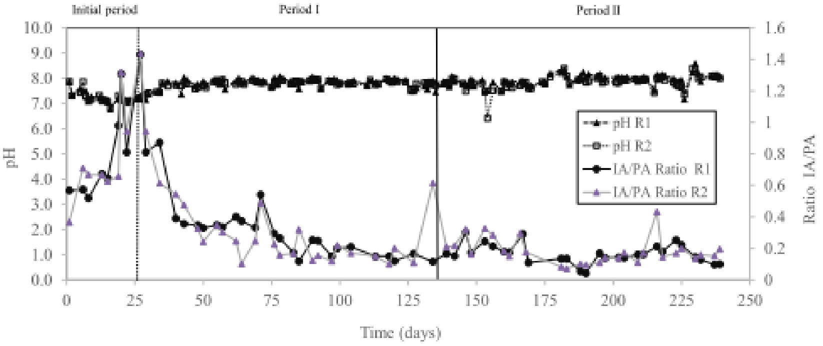


Figure 2. The pH and IA/PA ratio evolution for both reactors during the semi-continuous AD operation.

In period I (27–138 days), R1 was used to digest SM alone; whereas R2 was used to co-digest SM with AP in a feed VS ratio of 85.0% SM and 15.0% AP. In period II (139–240 days), R1 was fed with a mixture of SM and AP in a feed VS ratio of 92.5% SM and 7.5% AP, and R2 was fed with a mixture composed of 70.0% SM and 30.0% AP on a VS basis. Table 1 shows the chemical composition of the influents for R1 and R2 for both periods.

Table 1. Composition of feedstocks at different mixture ratios. Standard deviations are shown in parenthesis. No significant differences were found among the analytical values ($p > 0.05$).

	R1			R2		
Parameters	**Initial Period**	**Period I**	**Period II**	**Initial Period**	**Period I**	**Period II**
Apple pomace (%)	0	0	7.5	15	15	30
pH	7.19 (0.14)	7.40 (0.36)	6.98 (0.24)	7.19 (0.14)	7.40 (0.36)	6.98 (0.24)
TA (mg $CaCO_3$ L^{-1})	11882 (1565)	13626 (3268)	8453 (2007)	11882 (1565)	13626 (3268)	8453 (2007)
TCOD(g L^{-1})	107.11 (60.54)	92.00 (23.43)	99.90 (25.23)	89.58 (60.18)	81.06 (17.32)	90.09 (16.60)
SCOD (g L^{-1})	32.51 (5.27)	36.39 (4.81)	37.81 (1.79)	31.77 (3.42)	32.26 (6.91)	35.92 (6.77)
TS (g L^{-1})	40.51 (0.41)	42.79 (10.98)	50.99 (12.69)	43.68 (2.03)	38.43 (11.34)	44.95 (9.57)
VS (g L^{-1})	28.95 (4.11)	24.83 (6.53)	36.74 (12.86)	29.15 (1.92)	21.91 (5.49)	32.68 (9.75)
TVFA(mg TCOD L^{-1})	n.d.	26243 (5839)	31883 (1421)	n.d.	19219 (394)	26735 (6218)
TKN (mg N L^{-1})	5121 (391)	5085 (823)	5048 (670)	4665 (289)	4519 (465)	4235 (628)
TAN (mg N L^{-1})	3806 (179)	3793 (193)	3874 (424)	3286 (118)	3325 (221)	3182 (480)

n.d.: not determined. TA stands for total alkalinity; TCOD stands for total chemical oxygen demand; SCOD stands for soluble chemical oxygen demand; TS stands for total solids; VS stands for volatile solids; TVFA stands for total volatile fat acids; TKN stands for total Kjeldahl nitrogen; TAN stands for total ammoniacal nitrogen.

Influent and effluent samples were taken twice a week and analyzed for total alkalinity (TA), partial alkalinity (PA), TS, VS, TCOD, SCOD, TKN, and TAN. The pH was monitored daily in both the influents and effluents. Total TVFA were obtained from samples every two weeks. The composition of the biogas was analyzed once a week. The methane volumes were converted to standard temperature and pressure (0 °C and 101.325 kPa); therefore, the specific methane yield was calculated as normalized mL of CH_4 produced per g VS added to the digester per day (N mLCH_4 VS^{-1}). The results were used to evaluate the effect of co-digestion on the biogas production, the process stability, and the biodegradability.

2.2.2. Nitrogen Recovery from Digestate Using Gas-Permeable Membranes

The performance of GPM technology for TAN recovery from the digestates obtained in the experiments described in Section 2.2.1 was evaluated. Therefore, two experiments were carried out using the digestate generated in period I in R1 and R2, namely D-R1 (anaerobically digested SM alone) and D-R2 (anaerobically digested SM and AP, with a ratio of 85% and 15% on a VS basis, respectively). D-R1 was selected as the reference (SM) for the N capture, and D-R2 was selected as the digestate with the highest AP ratio in the feed mix with SM, presenting the best performance in the co-digestion in terms of stability and methane production. This allowed for the discovery of whether the addition of the AP in the co-digestion of SM could influence the further N recovery process.

Each experiment was performed in duplicate using 2 identical PVC reactors, with a total effective volume of 1.5 L (diameter 16.5 cm, height 17.5 cm), Figure 3.

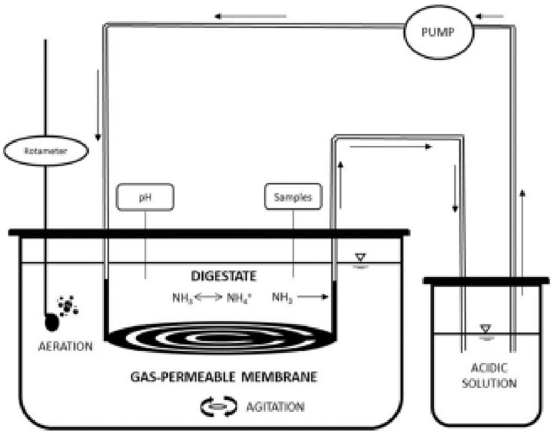


Figure 3. Experimental set-up of the N recovery experiments using the gas-permeable membrane technology. The arrows indicate the direction of the flows. The pH measurement and sampling were carried out through the reactor lid.

The acid tanks used to recover TAN consisted of 0.5 L flasks, initially containing 0.3 L of acidic solution (0.5 mol L^{-1} H_2SO_4). This acidic solution was continuously recirculated using a peristaltic pump (Pumpdrive 5001, Heildolph, Schwabach, Germany) through a gas-permeable tubular membrane. The recirculation flow rate of the acidic solution through the tubular membrane was 9 L d^{-1}. The tubular membrane was made of expanded polytetrafluoroethylene (e-PTFE) (Zeus Industrial Products Inc., Orangeburg, SC, USA), with a length of 120 cm, an external diameter of 5.2 mm, a wall thickness of 0.56 mm, and a density of 0.95 g cm^{-3}. The ratio of the membrane surface area to the volume of the digestate was 0.013 m^2 L^{-1}. The tubular membrane was placed in a horizontal configuration and held by plastic connectors to ensure that the membrane was completely submerged throughout the experiments. To keep the pH of the digestate high and thus ensure the formation of NH_3 [22], air was supplied using an aquarium pump (Hailea, Aco-2201, Guangdong, China) from the base of the reactor through a porous stone. The air flow rate was controlled by a rotameter (Aalborg, Orangeburg, NY, USA) and was kept constant at 0.24 L air L^{-1} min^{-1}. The reactors were not hermetically sealed. The pH of the acidic solution was kept under 2 to optimize the TAN recovery process. Thus, the pH of the acidic solution was monitored daily, and whenever the pH reached 2, concentrated H_2SO_4 (96–98%, Panreac) was added to an endpoint of pH <2. All experiments were carried out at room temperature (25 ± 1 °C). The duration of the experiments was 7 days. Daily samples of the digestate and acidic solution were taken for pH and TAN determination. Analyses of the TS, VS, TA, and TKN of the digestates were also performed at the beginning and end of the experiments.

The TAN removal, TAN recovery efficiencies, and average TAN recovery rate by the GPM system in the digestate were calculated according to Equations (1)–(3), respectively:

$$TAN\ removal\ (\%) = \frac{(Initial\ mass\ of\ TAN - Final\ mass\ of\ TAN)}{Initial\ mass\ of\ TAN} * 100 \tag{1}$$

$$TAN\ recovery\ (\%) = \frac{Final\ mass\ of\ TAN\ in\ the\ acidic\ solution}{mass\ of\ TAN\ removed\ from\ the\ digestate} * 100 \tag{2}$$

$$Average\ TAN\ recovery\ \left(mg\ N\ m^{-2}\ day^{-1}\right) = \frac{\begin{array}{c} mass\ of\ TAN\ recovered \\ in\ the\ acidic\ solution \end{array}}{\begin{array}{c} m^2\ of\ membrane\ and \\ days\ of\ experiment \end{array}} * 100 \tag{3}$$

Free ammonia (FA) was calculated using the equation of Hansen et al. [27], as un-ionized ammonia (Equation (4)):

$$\frac{NH_3}{tNH_3} = (1 + \left(10^{-pH}/10^{-(0.09018+2729.92/T)}\right)^{-1} \tag{4}$$

where NH_3 was the FA content, tNH_3 was the total NH_3 concentration, and the pH and T (in Kelvin) were measured in the digestate inside the reactors.

2.3. Analytical Methods and Statistical Analysis

Analyses of TCOD, SCOD, TS, VS, TKN, and TAN were performed in duplicate in accordance with APHA [28]. For the analysis of TCOD and SCOD, a closed reflux colorimetric method was used. TS content was calculated by drying the sample to a constant weight at 103–105 °C. The TS residue was ignited at 550 °C to constant weight, and therefore, the weight lost on ignition corresponded to the VS content. The TKN was measured using the Kjeldahl digestion, distillation, and titration method. TAN was measured using the distillation and titration method. The pH was measured using a Crison Basic 20 pH-meter (Crison Instruments S.A., Barcelona, Spain). Total and partial alkalinity (TA, PA) were calculated by measuring the amount of 0.1 N H_2SO_4 needed to bring the sample to a pH of 4.3 and 5.75, respectively, and expressed as mg $CaCO_3$ L^{-1}. Intermediate alkalinity (IA) was calculated by subtracting the PA from TA.

The TVFA concentrations (acetic, propionic, hexanoic, hepta, isobutyric, butyric, isovaleric, valeric, hexanoic, and heptanoic) were determined using a gas chromatograph (Agilent 7890A, Santa Clara, CA, USA) with a Teknokroma TRB-FFAP column of 30 m length and 0.25 mm diameter, immediately followed by a flame ionization detector (FID), where the carrier gas was helium (1 mL min^{-1}) and the temperature of the detector and the injector was 280 °C. TVFA were calculated as the sum of those acid concentrations after applying the corresponding TCOD conversion factor.

Biogas composition was determined using a gas chromatograph (Agilent 7890A, Santa Clara, CA, USA) with a thermal conductivity detector, provided by an HP-Plot column (30 m 0.53 mm 40 µm), followed by an HP-Molesieve column (30 m 0.53 mm 50 µm). The carrier gas was helium (7 mL min^{-1}). The injection port temperature was set at 250 °C, and the detector temperature was 200 °C. The temperature of the oven was set at 40 °C for 4 min and was thereafter increased to 115 °C.

The results obtained were analyzed using one-way ANOVA, with significance at $p < 0.05$.

3. Results and Discussion

3.1. Semi-Continuous Co-Digestion of Different Mixtures

During the initial period, an OLR of 1.04 g VS L^{-1} d $^{-1}$ and an HRT of 25 days were applied. As can be seen from Figure 4, a decrease in the specific methane yields in both reactors was observed from day 6.

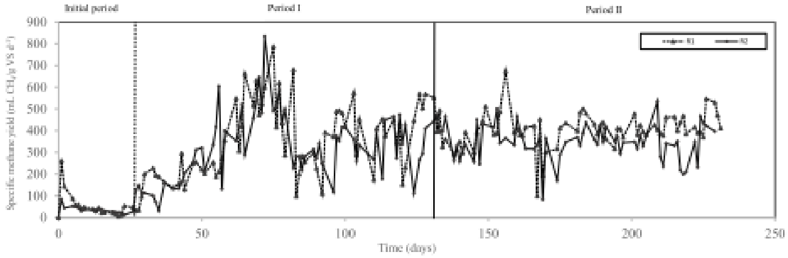


Figure 4. Methane yields during semi-continuous operation of R1 and R2.

In addition, an increase in the IA/PA ratios was also detected from day 6 (Figure 2). The ratio IA/PA plays a functional role in providing a rapid response to unstable states of the anaerobic digestion process. Thus, an IA/PA ratio of below 0.3 indicates a good performance of the anaerobic process [29]. In this study, the high IA/PA ratios (from 0.36 up to 1.4) during the initial period, along with the low methane yields, indicated an unstable operation of the anaerobic process under the two studied conditions (i.e., SM alone in R1, and co-digestion of SM and AP in a feed ratio of 15% on a VS basis in R2). The instability could be caused by a short HRT, since feeds containing fiber or celluloses (as is the case with the AP) may require relatively longer HRT [30]. For this reason, the OLR applied in both reactors was decreased to 0.78 g VS L^{-1} d^{-1}, and the HRT was increased to 33 days in periods I and II.

The values of the monitored parameters in both reactors during periods I and II are summarized in Table 2.

Table 2. Performance of AD treatment of four mixtures of SM and AP. Standard deviations are shown in parenthesis, followed by the descriptive coefficients indicating the statistically significant differences. The means within each parameter (horizontal) followed by different letters represent significant differences ($p < 0.05$).

	R1		R2	
Parameters	**Period I**	**Period II**	**Period I**	**Period II**
Apple pomace (%)	0.0	7.5	15.0	30.0
Biogas (mL day^{-1})	3057 (1255) ^{a}	3529 (542) ^{b}	2828 (1135) ^{a}	3030 (1130) ^{a}
Methane (CH_4) (%)	61.57 (4.28) ^{a}	61.96 (1.23) ^{a}	59.28 (2.04) ^{ab}	57.96 (3.02) ^{b}
Specific methane yield (mL g VS^{-1} day $^{-1}$)	421.7 (153.6) ^{a}	412.3 (62.6) ^{a}	381.8 (134.1) ^{ab}	341.9 (78.1) ^{b}
TCOD reduction (%)	52.78 (13.43) ^{a}	51.27 (11.50) ^{a}	57.01 (12.07) ^{a}	54.85 (15.10) ^{a}
SCOD reduction (%)	48.57 (14.42) ^{a}	58.94 (11.53) ^{b}	67.13 (7.13) ^{cd}	70.58 (7.79) ^{d}
VS reduction (%)	32.29 (15.01) ^{a}	44.27 (15.98) ^{b}	31.05 (10.48) ^{ab}	39.71 (14.51) ^{ab}
TVFA (mg TCOD L^{-1})	5755 (18) ^{a}	1767 (586) ^{b}	1661 (119) ^{b}	144 (9) ^{c}
IA/PA ratio	0.23 (0.11) ^{a}	0.15 (0.05) ^{b}	0.22 (0.14) ^{b}	0.25 (0.07) ^{b}

TCOD stands for total chemical oxygen demand; SCOD stands for soluble chemical oxygen demand; VS stands for volatile solids; TVFA stands for total volatile fat acids; IA/PA ratio stands for intermediate alkalinity/partial alkalinity ratio.

Similar specific methane yields ($p > 0.05$) were obtained when digesting SM alone and with up to 15% of AP in the feed mixture, with average values varying between 421.7 N mL CH_4 g VS^{-1} d^{-1} and 381.8 N mL CH_4 g VS^{-1} d^{-1} (Table 2; Figure 4). However, a significant decrease in the specific methane yield (i.e., 341.9 N mL CH_4 g VS^{-1} d^{-1}) was detected when digesting a feed mixture with 30% of AP in R2 in period II (Table 2). Similarly, the methane content significantly decreased from 61.6% to 58.0% when increasing the AP in the feed to 30% (Table 2). In the present study, the pH in both reactors was constant during the whole experimental period, approximately in the range of 6.8 and 8.6 (Figure 2). Additionally, the IA/PA ratios were lower than 0.3 (Table 2; Figure 2), which indicated that the reactors were stable during both experimental periods. The TVFA concentration in R1 in period I was 5755 ± 18 mg COD L^{-1}, and it decreased to 1767 ± 586 mg COD L^{-1} in period II (Table 2). In the same line, the TVFA concentration in R2 in period I was 1661 ± 119 mg COD L^{-1}, and it decreased to 144 ± 9 mg TCOD L^{-1} in period II (Table 2). Therefore, a VFA accumulation did not occur.

In the case of Kafle and Kim [13], the destabilization and the decrease in the methane production of the AD process occurred due to the accumulation of VFA when the AW of the mix was increased to 50% (on VS basis). In this study, the decrease in the specific methane yield with the increment of AP in the feed mix up to 30% (on VS basis) might be caused by the lower biodegradability of the AP in comparison with the SM. Labatut et al. [8] stated that co-digestion with lignocellulosic substrates could imply lower biodegradability, therefore leading to lower methane yields. AP presents a high fiber (or lignocellulose) content, which is composed of cellulose, hemicellulose, and lignin, all of which are poorly biodegradable compounds. The fiber content of AP could be between 51–58% (on a dry weight basis), with 15–24% lignin, 12% hemicellulose, and 7–31% cellulose [31,32]. The AP used in this study contained 16.1% hemicellulose and 21.5% lignin (on TS) [12]. Hence, the increase in the AP percentage in the feed mix up to 30% would imply a significant increase in the lignocellulose in the substrate, hindering the biodegradability and leading to a significantly lower methane production.

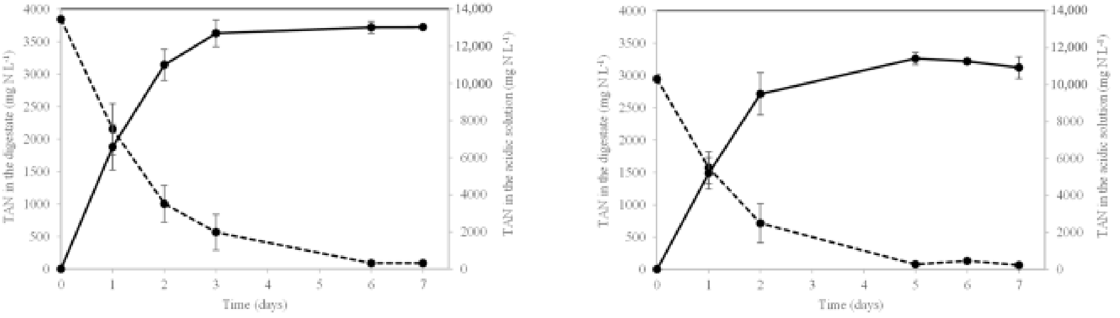
There were no significative differences in the TCOD removal efficiencies, regardless of the percentage of AP in the mix (Table 2). The TCOD is a measurement of the chemically oxidizable material, so it indicates the maximum chemical energy present in the material [33]. Thus, similar TCOD removal efficiencies in both reactors in all periods showed that the chemically oxidizable components did not change significantly during the experiment. Similarly, the VS removal efficiency ranged between 31.1% and 44.3%, with no significant differences when comparing the digestion of SM alone and the co-digestion of SM and 30% AP (Table 2). However, the SCOD removal efficiency increased with the increment in the proportion of AP in the fed mix (Table 2). Although the SCOD concentrations of the influent were similar in all periods in both reactors, with values varying between 32.3 and 37.8 g L^{-1} (Table 1), the different nature of the organic compounds and their biodegradability could lead to different methane productions.

The results showed that the methanogenic potential of fresh solid AP residues from the cider industry can be improved by the co-digestion of the AP with SM. The AD process in the reactors, where AP was used as the feed, had a similar AD performance to the one with SM alone, and a decrease in the specific methane yield was only observed when the AP content was increased to 30% in the feed mix (on a VS basis). Thus, despite the fact that no improvement in the methane production was detected with the addition of AP, the AP can be used as an AD substrate, thus relieving the industries in the area of the burden of this residue. With an adequate proportion, the reactor can operate with high biogas yields, without collapsing due to the accumulation of volatile fatty acids associated with the organic fraction of the substrate.

3.2. Nitrogen Recovery with GPM Technology

For the N recovery experiments, two different digestates were used: D-R1 (anaerobically digested SM with no addition of AP), and D-R2 (anaerobically digested SM with 15% of AP in the feed mixture). DR-1 and D-R2 presented different initial concentrations of TKN (4650 and 3300 mg N L^{-1}, respectively), TAN (3845 and 2944 mg N L^{-1}, respectively), VS (20.43 and 12.89 g L^{-1}, respectively), alkalinity (20115 and 15,668 mg $CaCO_3$ L^{-1}, respectively) and pH (8.57 and 8.20, respectively).

For DR-1, the TAN concentration in the digestate decreased to 89.4 mg N L^{-1} on day 7 (Figure 5a), leading to a TAN removal efficiency of 97.6% (Table 3).



(**a**) (**b**)

Figure 5. Evolution of TAN concentration in the digestates in D-R1 (**a**), and D-R2 (**b**) (discontinuous line), and TAN concentration in the acidic solutions for D-R1 (**a**) and D-R2 (**b**) (continuous line).

Table 3. Mass balances of the recovery of TAN from the digestates D-R1 and D-R2.

		TAN in Manure (mg N)	**TAN in the Acidic Solution (mg N)**	**TAN Removal Efficiency (%)**	**TAN Recovery Efficiency (%)**	**Average TAN Recovery Rate (g N m^{-2} day^{-1})**
D-R1	Initial	5768 (0)	0 (0)	97.6	77.2	32.9
	Final	133 (44)	4383 (42)			
D-R2	Initial	4416 (73)	0 (0)	97.8	75.8	25.8
	Final	98 (17)	3434 (136)			

TAN stands for total ammoniacal nitrogen.

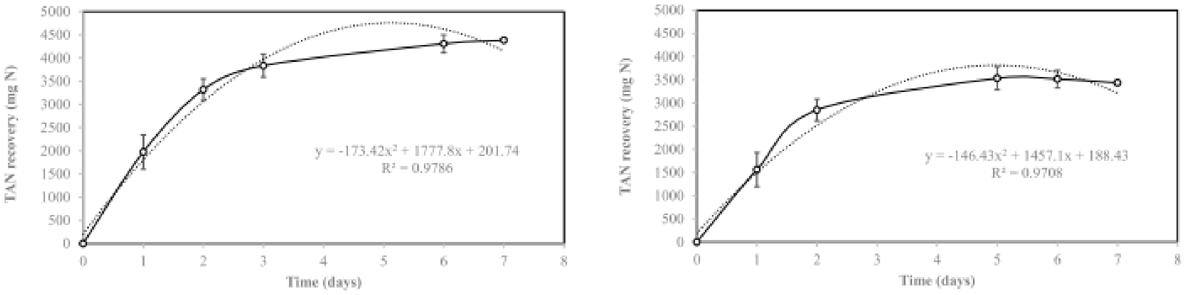
For DR-2, the TAN concentration decreased to 65 mg N L^{-1} on day 7 (Figure 5b), with a TAN removal efficiency of 97.8% (Table 3).

The percentage of removed TAN that was recovered by the GPM in the form of ammonium salt was 77.2% for D-R1 and 75.8% for D-R2 (Table 3). The TAN concentration in the acidic solutions on day 7 reached values of 13,029 ± 106 mg N L^{-1} for DR-1 and 10,924 ± 596 mg N L^{-1} for D-R2 (Figure 5a,b).

For both D-R1 and D-R2, most of the TAN recovery occurred in the first 4 days of the experiment. In both cases, the TAN recovery was much faster in the early days, as it followed a second order equation (Figure 6).

The decrease in the TAN recovery rate can be attributed to the reduction in the FA content in the digestate over time. In this context, the FA content in wastewater has been stated as one of the main variables affecting TAN recovery using the GPM technology, along with pH and temperature. The pH affects the acid-based chemical balance of ammonium/ammonia (NH_4^+/NH_3) in the wastewater, where values near 9 cause the release of ammonia, passing thorough the membrane pores to be captured by the acid [23] (Figure 6).

In the present study, a clear reduction in the TAN recovery was found from day 2 for both digestates, in which the FA content was 305 mg N L^{-1} for D-R1 and 278 mg N L^{-1} for DR-2 (Figure 7).



(**a**) (**b**)

Figure 6. TAN recovery in the acidic solutions of DR1 (**a**) and D-R2 (**b**). Continuous lines correspond to TAN recovery, and dotted lines correspond to second order polynomial curves.

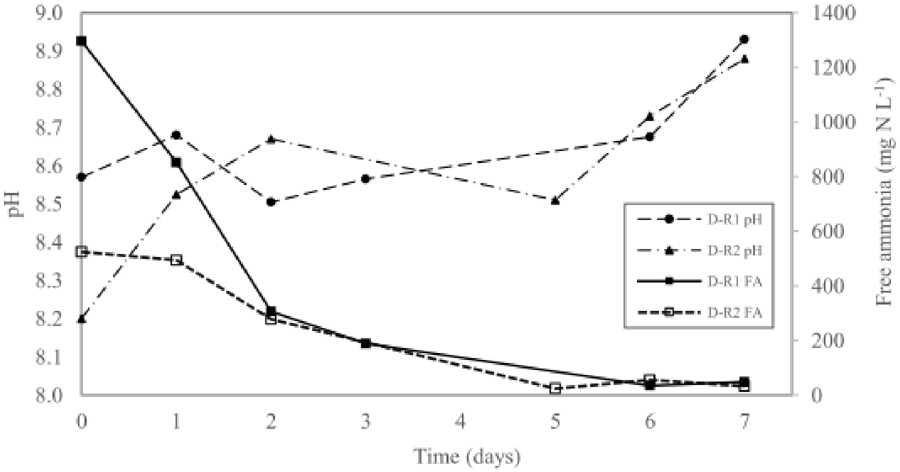


Figure 7. The evolution of the pH and the free ammonia (FA) for D-R1 and D-R2 during the N recovery experiments.

These values were higher than the thresholds reported in the literature. For example, Riaño et al. [10] observed that the TAN recovery rate decreased when the FA content in the digestate was lower than 95 mg N L^{-1}. The average TAN recovery rate was 22% lower for D-R2 (25.8 g N m^{-2} day^{-1}) than for D-R1 (32.9 g N m^{-2} day^{-1}) (Table 3). This could be attributed to the higher FA content availability in D-R1 as compared to D-R2, as a consequence of its higher initial TAN concentrations and similar values of pH throughout the experimental period (Figure 7). In this vein, García-González and Vanotti [22] studied TAN recovery from swine manure with different TAN concentrations and concluded that, as available FA content increased in the manure, the TAN recovery rate also increased. Therefore, although the co-digestion of AP and SM did not affect the subsequent N recovery using GPM technology, it did affect the TAN recovery rates, which should be considered in larger scale nutrient recovery processes.

The application of this type of innovative solution favors energy and agronomic autonomy, while representing a solution for the treatment of waste from the agri-food industry, according to the principles of the circular bio-economy.

4. Conclusions

The results showed that fresh AP from the cider industry can be successfully valorized through anaerobic digestion. With up to 15% of AP in the feed mix with SM (on a VS basis), a methane yield of 381.8 ± 134.1 mL CH_4 g^{-1} VS day^{-1} was achieved, while higher percentages may decrease the methane yields. The sequential treatment of the AD digestate using the novel GPM technology enables an up to 76% recovery of the N present in the form of an ammonium sulfate solution, with a concentration of $10{,}924 \pm 596$ mg N L^{-1}. This solution is a bio-based fertilizer which can be easily stored, transported, and directly applied to crops, without any necessary post-treatment, avoiding the use of mineral fertilizers. Therefore, this organic waste treatment combination of anaerobic digestion and membrane technology can be considered as an efficient form of waste valorization for energy and nutrient generation.

Author Contributions: Conceptualization, B.R., B.M.-S. and M.C.G.-G.; formal analysis, I.G.-G.; funding acquisition, M.C.G.-G.; investigation, I.G.-G.; methodology, I.G.-G., B.R. and B.M.-S.; project administration, M.C.G.-G.; supervision, B.R., B.M.-S. and M.C.G.-G.; writing—original draft, I.G.-G.; writing—review and editing, B.R., B.M.-S. and M.C.G.-G. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author (ITACyL, Agricultural Technological Institute of Castilla y León. Ctra. Burgos, km. 119, 47071 Valladolid, Spain) upon request.

Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationship that could be construed as a potential conflict of interest.

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3. **"Two-phase nutrient recovery from livestock wastewaters combining novel membrane technologies".** Article published (© Springer Ltd.). Photographic annex pictures 10 – 13.

This study evaluated the combination of two nutrient recovery technologies in two different livestock agro-industrial wastewaters: swine manure (SM) and anaerobically digested SM (digestate). In a first step, GPM technology recovered N from wastewater as an ammonium sulfate solution. In a second step, the electrodialytic (ED) process recovered P, as an electrolytic solution, from which the P could then be precipitated as struvite (a slow-release fertilizer). This task was developed during a stay at the Research Centre for Natural Resources, Environment and Society, in Coimbra (Portugal), as a scientific collaboration.

For the recovery of N, the experiments were carried out by sets: the first set for SM and the second for digestate. The containers consisted of non-hermetically sealed plastic vessels with a volume of 700 mL. The experimental set was configured as shown in the previous section with aeration. The membrane had a length of 50 cm and the ratio of the membrane surface per volume of wastewater was 0.004 m^2 per liter. The content of the vessels was continuously stirred using a magnetic stirrer. The acidic solution was 1N H_2SO_4, with an initial volume of 50 mL. Daily samples of the acidic solution and SM and digestate were taken to monitor the pH and TAN content. Experiments were performed at 22°C and in duplicate. In a second step, the effluents treated to recover N with GPM were subjected to a new treatment for the recovery of P through an ED process. These effluents were placed in a Plexiglas® cylindrical laboratory cell and assembled with 3 compartments. The central compartment (II) contained a specified volume of effluent and was constantly agitated using an overhead agitator. The side compartments (I and III), contained 500 mL of 0.01 M $NaNO_3$ each, as an electrolytic solution, to recover anions and cations respectively. The electrodes were placed in the lateral compartments. Each compartment was separated by an ion exchange membrane (IEM). A cation exchange membrane was used between the right and central compartments and an anion exchange membrane between the left and central compartments. Each membrane placed in the cell had an effective surface area of 0.005 m^2. Since the phosphorus was in anionic form (as HPO_3^-), it passed through the cationic membrane, where it was trapped by the electrolytic solution so that it could be recovered. The electrolyte solution was recirculated by means of a peristaltic pump between the compartment and an external tank. A power supply was used to maintain a constant current of 50 mA. Daily samples of the effluent and electrolyte solution were taken to monitor pH, conductivity, and Pt. Both voltage and electrical current were also monitored daily.

The results showed great potential for this combination of membrane technologies. The GPM technology applied in the first step achieved TAN recovery rates of 8.0 g N per m^2 of membrane and per day for SM, and 25.7 g N per m^2 of membrane and per day for digestate, corresponding to TAN recovery efficiencies of 53% and 94% for manure and digestate, respectively. The ED process, applied in a second step, achieved rates of 12.5 g P per m^2 and per day for the manure and 4.4 g P per m^2 of membrane and per day for the digestate; meaning a recovery of P_t from the manure of 100% and 74% for manure and digestate, respectively. The processes also generated two different valuable marketable bio-based fertilizers: an ammonium sulfate solution and a phosphorus-rich solution.

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Two-phase nutrient recovery from livestock wastewaters combining novel membrane technologies (©SPRINGER)

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ABSTRACT

The application of new technologies in the agro-industrial sector is needed to close the loop of the nutrient cycle in the food chain. The aim of this work is to study the feasibility of the combination of two nutrient recovery technologies. In a first step, the novel gas-permeable membrane technology recovers N from the wastewater as an ammonium sulfate solution (a bio-based fertilizer). Secondly, the electrodialytic process recovers P, as an electrolyte solution, from which P can then be precipitated as struvite (a slow-release fertilizer). The process was tested in two different livestock wastewaters: swine manure (SM) and anaerobically digested SM (digestate). Recovery efficiencies for N were 53% for SM and 94% for digestate; for P, the efficiencies were 100% and 74% for SM and digestate, respectively. The results showed a great potential of combining these novel membrane technologies in livestock wastewaters, promoting the sustainability of the sector in the realm of the bioeconomy.

4. **“Effect of alkali and membrane area on the simultaneous recovery of nitrogen and phosphorous from digestate by membrane technology and chemical precipitation”.** Article published (open access on MDPI). Photographic annex pictures 14 – 16.

This study focused on the simultaneous recovery of N and P from digestate, where the recovery of N was carried out using GPM technology, and the recovery of P was done through precipitation.

Two different sets of experiments were carried out: set 1 and set 2. In both sets, two non-hermetically closed plastic container reactors with an effective volume of 1.5 L of digestate were used, with the membrane immersed in the digestate. The experimental set up was configured as shown in the previous section with aeration. For the recovery of P, the same precipitating agent was added in both sets of experiments: magnesium chloride $MgCl_2$ (as $MgCl_2.6H_2O$), with 0.551 g of $MgCl_2$ being added at the beginning of the experiments. The amount was calculated according to the initial concentration of total P in the digestate (0.473 g P per L), to obtain a Mg:P molar ratio of 1.2:1. The P precipitated at the same time as the recovery of N was carried out using the GPM technology.

In set 1, the nutrient recovery efficiency was studied with a ratio of 180 g of TAN in the digestate per m^2 of membrane, first without the addition of alkali and later with the addition of alkali (1.5 N NaOH). In set 2, the efficiency of the nutrient recovery was evaluated with a ratio of 100 g of TAN in the digestate per m^2 of membrane, first without alkali, and later with the addition of alkali. The experiments were carried out in duplicate and at a temperature of 20°C. In set 1, the length of the membrane was 1.6 m and the surface area of the membrane per volume of digestate was 0.0175 m^2 per liter of digestate. In set 2, the length of the membrane was 3 m and the surface area of the membrane in relation to the volume of digestate was 0.0314 m^2 per L of digestate. The N recovery tank consisted of a glass bottle containing 250 mL of acidic solution (1 N H_2SO_4). The pH of the acidic solution was monitored daily and each time the pH reached 2, concentrated H_2SO_4 (98%) was added to an end point of pH <2 to ensure efficient N capture. At the beginning of the experiments, samples were taken to analyze the concentration of total P (P), TA, TS, VS, TAN, TKN, Ca^{2+}, Mg^{2+} and K^{+}. Daily samples of the digestate of the acidic solution were taken to monitor the pH and TAN concentrations during the experiments. Likewise, at the end of the experiments were taken samples to determine TA, TS, VS, TAN and TKN, and also the cations Ca^{2+}, Mg^{2+} and K^{+} to find possible interference from the formation of other unwanted precipitates, as well as the P contained in the solid phase of the digestate, in order to estimate the recovery of P in the form of a precipitate.

The results showed high nutrient recovery efficiencies, of 77% for N and 80% for P, after 10 days of experiments, with a ratio of 180 g N per m^2 of GPM and the addition of NaOH (1.5 N), along with the precipitant agent ($MgCl_2$) for P precipitation. Hence, a combined configuration was proposed to perform an effective simultaneous recovery of N and P with the minimum amount of membrane needed in a short time.

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Article

Effect of Alkali and Membrane Area on the Simultaneous Recovery of Nitrogen and Phosphorous from Digestate by Membrane Technology and Chemical Precipitation

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Abstract: Nutrient recovery from the agri-food sector waste is an increasingly recognized option within the framework of the bioeconomy. Membrane technologies and chemical precipitation are among the best valued options for their economic and practical feasibility. In this study, the combination of gas-permeable membrane (GPM) technology for the recovery of nitrogen (N) and the chemical precipitation for phosphorous (P) recovery from anaerobically digested swine manure is evaluated. This work studies the effect of the membrane area and the addition of alkali on N and P recovery efficiencies. Specifically, two different membrane area ratios (180 and 100 g of N per m^2 of membrane) with and without the addition of alkali were studied. High nutrient recovery efficiencies, of 77% for N and 80% for P, were obtained after 10 days of experiment with a ratio of 180 g N per m^2 of GPM and the addition of NaOH (1.5 N), along with the precipitant agent ($MgCl_2$) for P precipitation. Hence, a combined configuration was proposed to perform an effective simultaneous recovery of N and P with the minimum amount of membrane needed in a short time.

Keywords: waste valorization; ammonia; phosphate; gas-permeable membrane; circular economy

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1. Introduction

Nutrient recovery and reuse from the main waste streams are at the core of the international sustainability strategies [1]. The objectives are to reduce the dependence on fossil-based fertilizers and the environmental and economic problems derived from waste mismanagement, while also closing the nutrient cycles [2–4]. Livestock waste provides over 70% of the total N and P when used as organic fertilizer (manure) [3]. However, manure must be managed properly to avoid environmental impacts, such as particulate matter formation, acidic rain, and eutrophication, due to emissions into the air, soil, and water bodies of ammonia (NH_3), methane (CH_4), nitrous oxide (N_2O) nitrates, and nitrites (NO_3^- NO_2^-) [4]. The stabilization of manure is also an important factor when using it as an organic fertilizer. The anaerobic digestion (AD) is a well-known process and widely used manure management system, which has proved useful to reduce greenhouse emissions [5]. Manure treatment with the AD process results in biogas (renewable energy) and digestate production, which is a more stable substance than manure, which can be used as organic fertilizer and contains the same amount of original nutrients as the manure, since anaerobic digestion does not remove them [3,6]. Thus, the application of digestate may also cause environmental issues due to nutrient losses when it is not properly managed, such as an excess of N and P in soils and water bodies, resulting in eutrophication, decreased biodiversity, and toxicity [3]. Therefore, it is important to consider the application of innovative treatment technologies for the recovery of nutrients from the digestate. This would allow the environmental impacts to be minimized and the recovered nutrients to be stored, transported, and applied more easily where needed.

According to Buckwell and Nadeu [3], the average production of digestate in the EU 27 is 56 million tons annually, 80% of which is used for agriculture as organic fertilizer. Therefore, the digestate is a nutrient-rich by-product and is also currently the largest output product obtained from manure treatment. Interest in the application of innovative technologies to reduce the environmental impacts of poor manure management is increasing, alongside economic investments to optimize nutrient recovery.

Among the most known technologies for N recovery from digestate, such as air stripping, ion exchange or chemical precipitation, the novel gas-permeable membrane (GPM) technology has recently been recognized as one of the most effective technologies from an energetic, economic, and environmental perspective [7–9]. On the basis of literature reviews that considered such relevant factors as recovery performance, operating conditions, and energy and chemical demand, the GPM technology stood out due to its high capacity for N recovery, its low energy requirement, and no need of post-treatment. In this sense, it has been reported that the GPM technology presented a recovery efficiency of over 98%, and an energy cost within a range of 0.17 to 1.2 kWh per kg of N recovered and a chemical cost of 1.41$ per kg of N recovered [7–9]. In addition, Beckinghausen [7] compared the operations costs of N recovery (energy and chemicals) using different N recovery technologies, with the potential sales revenue of the obtained product. They found that the GPM technology presented a total benefit of 284.45$ per ton of ammonium salt produced. The GPM technology consists of a hollow tubular microporous hydrophobic gas-permeable membrane submerged in ammonia (NH_3)-rich wastewaters, while an acidic trapping solution is recirculating inside the membrane. The NH_3 passes through the membrane by diffusion and is captured by the acidic trapping solution, which becomes an ammonium salt solution, a valuable bio-based organic fertilizer [10].

The digestate has a higher concentration of ammonium than swine manure [6,11], since organic nitrogen is transformed into ammonium during the AD process. This makes it an interesting candidate as a substrate for applying the GPM technology, which has shown high N recovery efficiencies (over 98% of the N removed from the substrate) in raw and anaerobically digested swine manure [12–14]. An important aspect of the GPM technology is that it can be combined with other nutrient recovery technologies, especially P recovery technologies. In this context, although the combination of nutrient recovery technologies could lead to a greater competitiveness of the systems [15], only a few studies have considered this aspect. Oliveira et al. [16] combined the GPM technology with ion-exchange membranes for the simultaneous recovery of N and P (as total P) from anaerobically digested swine manure, obtaining recovery rates of 19 g N m^{-2} of GPM day^{-1} and 6.3 g P m^{-2} of anion exchange membrane day^{-1}. González-García et al. [17] evaluated the combination of GPM with ion-exchange membranes to recover N and P in a two-step system, obtaining recovery efficiencies of 25.7 g N m^{-2} GPM day^{-1} and 4.4 g P m^{-2} of ion exchange membrane day^{-1} from anaerobically digested swine manure. Vanotti et al. [18] also applied the GPM technology to recover N and P from anaerobically digested swine manure. These authors reported recovery rates of up to 16.7 g N m^{-2} of GPM day^{-1} with a nitrification inhibitor, but without the addition of alkali, and up to 18.1 g N m^{-2} of GPM day^{-1} and 0.5 g precipitated P day^{-1}, with the addition of a nitrification inhibitor and alkali (NaOH). This work showed that, after the N recovery, the resultant substrate presented a high pH, a low concentration of NH_4^+ and a low alkalinity, which are favorable conditions for P precipitation by applying a metal salt [18–20]. In the case of Vanotti et al. [18], they focused on how the application of the GPM technology can influence the type of magnesium phosphate obtained via precipitation. This study considered that premise, of using GPM technology to recover N and chemical precipitation to recover P as magnesium phosphates using $MgCl_2$; however, it also considered other factors affecting nutrient recovery. In particular, the N removal from the digestate and its recovery in the trapping solution creates advantageous conditions for obtaining high recovery rates of precipitated P as magnesium phosphates [18]. Following this postulation, the aim of the present work was to study the simultaneous recovery of N and P from anaerobically digested swine manure, using the GPM technology for N recovery and the application of a precipitating agent for the recovery of P. To do so, two factors were evaluated: the influence of the membrane area in contact with the digestate for nutrient recovery, and the addition of NaOH as the alkali to act as the pH control agent together with the precipitating agent. The results offer an insight into what could be the best configuration for the combination of these two nutrient recovery techniques.

2. Materials and Methods

2.1. Experimental Set-Up and Operations

Two different sets of experiments were carried out: Set 1 and Set 2 (Table 1).

Table 1. Experimental configurations for N and P recovery.

Experimental Sets		Ratio (g TAN: m^2 of Membrane)	Alkali Addition (NaOH 1.5N)	Nutrient Recovery Configuration Name
Set 1	Experiment 1	180:1	-	N1
				P1
	Experiment 2	180:1	37.5 mL	N2
				P2
Set 2	Experiment 3	100:1	-	N3
				P3
	Experiment 4	100:1	32 mL	N4
				P4

Two plastic vessels' reactors, not hermetically sealed, were used in both sets, with an effective volume of 1.5 L of digestate.

The same precipitating agent was added to both sets of experiments: $MgCl_2$ (as $MgCl_2 \cdot 6H_2O$, Panreac). To calculate the necessary amount of $MgCl_2$, the initial concentration of the total P in the digestate (0.473 g P L^{-1}) was considered in order to obtain a molar ratio of Mg:P of 1.2:1. As a result, 0.551 g of $MgCl_2 \cdot 6H_2O$ was added at the beginning of the experiments. Therefore, the P precipitated at the same time as the N recovery was carried out by the GPM technology.

In Set 1, the nutrient recovery efficiency, with a membrane ratio of 180 g total ammonia nitrogen (TAN) per m^2 of membrane, both without the addition of alkali (Exp. 1) and with the addition of alkali (NaOH 1.5N) at the beginning of the experiment (Exp. 2), was studied.

In Set 2, the nutrient recovery efficiency with a membrane ratio of 100 g of TAN per m^2 of membrane, both without the addition of alkali (Exp. 3) and with the addition of alkali at the beginning of the experiment (Exp. 4), was evaluated (Table 1). The 180 g TAN:m^2 membrane ratio was selected based on the previous work of Vanotti et al. [18] as reference. The 100 g TAN:m^2 membrane ratio was selected as a new configuration, with a higher membrane area, in order to study the effect of this factor on the N capture. The optimal pH value considered for the N recovery was 9.2 [18]. To reach this pH value, 37.5 mL of NaOH 1.5 N were added to the digestate in Exp. 2 and 31.0 mL of NaOH 1.5 N in Exp. 4.

2.2. Origin of the Digestate

The digestate was obtained from a biogas plant located in Juzbado (Salamanca, Spain). This biogas plant was designed to treat mainly raw livestock waste from nearby farms, as well as agricultural waste from the area, such as cereal dust, harvest remains, etc. These residues are transported to the plant, stored, and then enclosed in an airtight concrete tank—or digester—which, in the absence of oxygen and through a process of anaerobic digestion, transforms these wastes into biogas and digestate. The plant works in the mesophilic range (35 °C) and with an average hydraulic retention time of 75 ± 5 days, producing approximately 6000 m^3 of digestate per year [14]. The digestate from the plant was collected and stored in a plastic container in the ITACyL laboratory at 4 °C for later use. The chemical characterization of the digestate is presented in Table 2.

2.3. Nutrient Recovery Process

The recovery process of N and P occurred simultaneously inside the reactors that contained the digestate. The chemical reagents were added at the beginning of the experiment, for P precipitation and pH control (when applicable). Each nutrient recovery process is described in detail in the following sections.

2.3.1. Nitrogen Recovery Process

The GPM was completely submerged in the digestate (Figure 1).

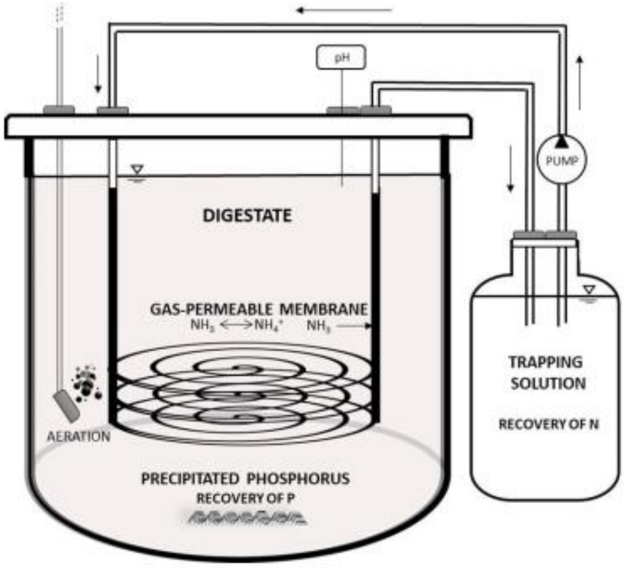


Figure 1. Experimental set up for simultaneous recovery of N and P. Design based on Vanotti and Szogi [10].

The experimental design was intended for optimal membrane performance. The membrane used was *Aeos™ ePTFE porous tubing*. This tubular membrane was made of expanded polytetrafluoroethylene (e-PTFE), (Zeus Industrial Products Inc., Orangeburg, SC, USA), with a diameter of 5.2 mm, a wall thickness of 0.56 mm and a density of 0.95 g cm^{-3}. In the first set of experiments (Set 1), the length of the membrane was 1.6 m and the membrane surface area to the volume of the digestate was 0.0175 m^2 L^{-1}. In the second set of experiments (Set 2), the length of the membrane was 3 m and the membrane surface area to the volume of the digestate was 0.0314 m^2 L^{-1}. A peristaltic pump (Pumpdrive 5001, Heidolph, Schwabach, Germany) was used to continuously recirculate the trapping solution through the membrane at a flow rate of 12 L d^{-1}. A magnetic stirrer was placed at the bottom of the vessel to ensure the homogenization of the digestate. The N recovery tank consisted of a glass bottle containing 250 mL of trapping solution (H_2SO_4 1 N). The pH of the trapping solution was monitored on a daily basis and, whenever the pH reached 2, concentrated H_2SO_4 (96–98%, Panreac) was added to an endpoint of pH < 2 to ensure an efficient N capture. As pH is the determining factor for free ammonia (FA) availability, it is therefore crucial for the N recovery. To ensure FA availability in the digestate, a low aeration was applied to maintain high pH values [13]. Aeration was applied in both sets of experiments using an air pump with a porous stone placed in the bottom of the reactor (Hailea Aco-2201), and an aeration rate of 0.36 L air L^{-1} min^{-1} controlled with a rotameter (Aalborg, Orangeburg, NY, USA). To ensure the previously mentioned optimal pH value (9.2), the alkali was added at the beginning of the experiments. All the experiments were carried out at room temperature (20 °C). Daily samples of the digestate and the trapping solution were taken to monitor pH and TAN content. Furthermore, samples were taken at the beginning and end of the experiments to analyze the content of P, TA, TS, VS, TKN, Mg, Ca, and K.

In each set of experiments, the TAN removal, the TAN recovery efficiency, and the average TAN recovery rate by the GPM system in the digestate were calculated according to Equations (1)–(3) as follows:

$$\text{TAN removal }(\%) = \frac{(\text{Initial mass of TAN} - \text{Final mass of TAN})}{(\text{Initial mass of TAN})} \times 100 \quad (1)$$

$$\text{TAN recovery efficiency }(\%) = \frac{\text{Final mass of TAN in the trapping solution}}{\text{mass of TAN removed from the digestate}} \times 100 \quad (2)$$

$$\text{Average TAN recovery }\left(\text{g N m}^{-2}\text{ day}^{-1}\right) = \frac{\begin{array}{c}\text{mass of TAN recovered}\\ \text{in the trapping solution}\end{array}}{\begin{array}{c}\text{m}^2\text{ of membrane and}\\ \text{days of experiment}\end{array}} \times 100 \quad (3)$$

Free ammonia (FA) was calculated using the equation of Hansen et al. [21], as un-ionized ammonia Equation (4):

$$\frac{NH_3}{tNH_3} = (1 + (10^{-pH}/10^{-(0.09018+2729.92/T)})\ ^{-1} \quad (4)$$

where, NH_3 was the FA content, tNH_3 is the total considered NH_3 concentration, and both pH and T (in Kelvin) of the digestate were measured daily. The N recovery experiments were stopped once a minimum TAN removal of 90% was reached.

2.3.2. Phosphorus Recovery Process

The recovery of P (as total phosphorus) through precipitation was studied for each set of experiments, under the different favorable conditions created by the N recovery treatment.

Initial and final samples of the digestate were taken to determine the total P recovered. The concentration of the Mg^+, Ca^+ and K^+ ions was also analyzed at the end of the experiments, to verify whether there was any interference in the formation of the magnesium phosphates. In addition, the P recovery efficiency was also calculated, as follows Equation (5):

$$\text{P recovery efficicency }(\%) = \frac{\text{mass of P recovered in the solid fraction}}{\text{initial mass of P in the digestate}} \times 100 \quad (5)$$

Table 2. Chemical characterization of the digestate at the beginning and end of the experiments. Standard deviations are shown in brackets.

Experiments		**Parameters**											
		pH	**TA (mg $CaCO_3$ L^{-1})**	**TAN (mg N L^{-1})**	**TKN (mg N L^{-1})**	**TCOD (mg O_2 L^{-1})**	**SCOD (mg O_2 L^{-1})**	**TS (g L^{-1})**	**VS (g L^{-1})**	**Mg^+ (mg L^{-1})**	**Ca^+ (g L^{-1})**	**K^+ (g L^{-1})**	**P (mg P L^{-r1})**
Exp. 1	Initial	8.25 (-)	27,439 (-)	3318 (29)	5271 (7)	74,537 (681)	30,889 (1467)	82.1 (2.3)	45.3 (1.3)	932.8 (15)	8.1 (0.4)	3.1 (0.2)	473 (2)
	Final	8.53 (0.04)	25,585 (513)	243 (16)	2489 (167)	73,493 (248)	16,857 (891)	65.2 (17.1)	44.2 (4.9)	-	-		266 (5)
Exp. 2	Initial	8.21 (-)	40,664 (-)	3419 (9)	5553 (55)	77,857 (240)	35,894 (469)	88.9 (1.2)	51.9 (3.2)	940.2 (4.6)	8.5 (0.1)	2.9 (0.1)	426 (2)
	Final	9.16 (0.08)	22,138 (8844)	270 (129)	2419 (139)	55,495 (3568)	19,423 (1674)	74.2 (0.5)	19.7 (7.9)	-	-	-	139 (8)
Exp. 3	Initial	8.31 (-)	49,796 (-)	3365 (25)	5446 (121)	69,376 (3694)	32,394 (1358)	80.0 (6.5)	40.1 (5.5)	992.9 (1.1)	10.9 (1.1)	3.7 (0.6)	467 (1)
	Final	8.47 (0.06)	45,560 (197)	227 (5)	2489 (197)	70,600 (1766)	17,037 (1146)	79.6 (0.7)	24.5 (4.8)	-	-	-	243 (4)
Exp. 4	Initial	8.85 (-)	41,683 (-)	3511 (20)	5784 (10)	70,395 (449)	32,564 (228)	84.1 (0.8)	47.7 (0.3)	979.1 (9.9)	9.2 (0.2)	2.2 (0.1)	410 (33)
	Final	9.35 (0.01)	22,857 (8591)	291 (1)	2577 (163)	68,989 (66)	15,572 (777)	78.1 (0.7)	21.8 (3.2)	-	-	-	13 (16)

Considering TA as total alkalinity; TKN as total Kjeldahl nitrogen; TCOD as total chemical oxygen demand; SCOD as soluble chemical oxygen demand; TS as total solids; VS as volatile solids; Mg as Magnesium; Ca as calcium; K as potassium; and P as total phosphorus.

2.4. Analytical and Statistical Methods

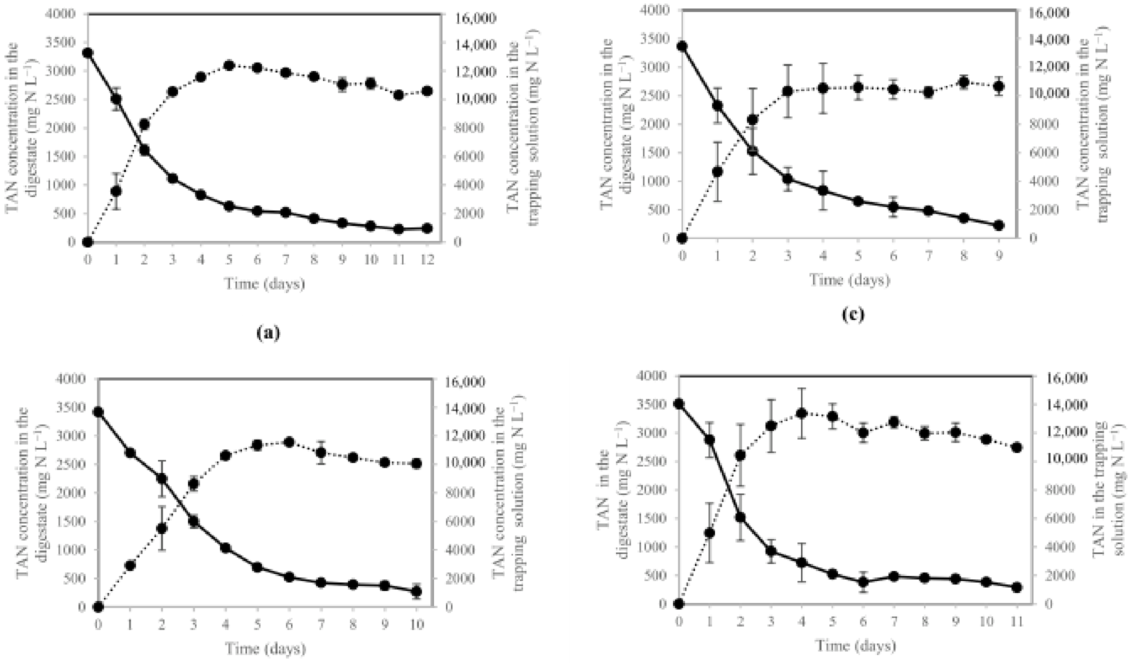
Analyses of the TAN, TS, VS, TCOD, SCOD, TKN, and P were performed in duplicate, in accordance with APHA Standard Methods [22]. For the TS content, a sample was dried to a constant weight at 105 °C. The TS residue was ignited at 550 °C to a constant weight, and therefore the weight lost on ignition was the VS content. The TAN was measured according to the distillation and titration method. The TKN was measured according to the Kjeldahl digestion, distillation, and titration method. The TA was calculated by measuring the amount of 0.1 N H_2SO_4 needed to get the pH of a sample of digestate to 4.5, expressed as mg $CaCO_3$ L^{-1}. The chemical determination of the P concentration was carried out according to the vanadate-molybdate acid colorimetric method, at a wavelength of 470 nm (spectrophotometer Thermo Scientific, model Helλos γ), after the pre-digestion of the samples according to the Method 4500 PC [22]. The concentration of Ca^+, Mg^+ and K^+ in the digestate was determined using microwave acid digestion (model CEM MARSX), with HNO_3 at 65%, followed by the inductively coupled plasma (ICP) analysis (Method 3125, [22]).

The results obtained for TAN recovery and for P recovery were analyzed using one-way analysis of variance (ANOVA), with significance at $p < 0.05$, to determine the significant differences in the experimental configurations.

3. Results

3.1. Nitrogen Recovery and Phosphorus Precipitation in Experiments 1 and 2 (Set 1)

The performance of the experiments can be seen in Figure 2.



(a)

(c)

(b)

(d)

Figure 2. TAN removal in the digestate (continuous line, primary axis) and recovery in the trapping solution (discontinuous line, secondary axis) for the four different configurations, where (**a**,**b**) correspond to a ratio 180 g TAN:1 m^2 of membrane, and (**c**,**d**) correspond to a ratio 100 g TAN:1 m^2 of membrane. Also, (**b**,**d**) correspond to the configurations with the addition of alkali.

The N recovery (N1) efficiency of the 180 g TAN:m^2 membrane ratio, without the addition of alkali, was assessed in Exp. 1. The results show that the initial TAN concentration in the digestate of 3318 ± 29 mg N L^{-1} decreased to 243 ± 16 mg N L^{-1} in 12 days. This means a removal of 3075 ± 13 mg N L^{-1}. The mass of TAN removed was 4611 ± 22 mg N and the TAN removal accounted for 93%. The TAN concentration in the trapping solution achieved a value of 10,581 ± 0 mg N L^{-1} on day 12 (Figure 2a).

During Exp. 1, the volume of the trapping solution increased from an initial value of 250 mL to a final value of 354.8 ± 0.6 mL due to the diffusion of water vapor through the membrane (i.e., osmotic distillation). The total mass of TAN recovered in the trapping solution was 3636 ± 32 mg N, which implied a TAN recovery efficiency of 79% (Table 3). The TAN recovery rate was 11.5 g N m^{-2} d^{-1}.

Table 3. Changes in chemical characteristics of the digestate during the different experiments. Standard deviations are shown in brackets.

	Parameters							
Experiments	**Initial TAN in the Digestate (mg N)**	**Removed TAN from the Digestate (mg N)**	**Recovered TAN in the Trapping Solution (mg N)**	**TAN Recovery Efficency (%)**	**Initial P in the Digestate (mg P)**	**Recovered P in the Solid Precipitate (mg P)**	**Recovered P in the Solid Precipitate per Day (mg P day^{-1})**	**P recovered in the Solid Precipitate (%)**
Exp. 1	4976 (44)	4611 (22)	3636 (32)	79 (1)	709 (3)	451 (30)	37.5 (2.4)	64 (5)
Exp. 2	5127 (14)	4734 (198)	3652 (60)	77 (2)	639 (3)	512 (3)	51.2 (0.3)	80 (1)
Exp. 3	5049 (38)	4711 (37)	3986 (213)	85 (4)	700 (1)	523 (77)	58.2 (8.5)	75 (11)
Exp. 4	5268 (30)	4848 (66)	4376 (52)	90 (1)	614 (33)	537 (4)	48.7 (0.4)	88 (5)

The N recovery with a 180 g TAN:m^2 membrane and the addition of 37.5 mL of NaOH 1.5 N at the beginning of the experiment to increase the initial pH to 9.2 was evaluated in Exp. 2. The N recovery in this case was designated as N2. In this experiment, the initial concentration of TAN in the digestate was 3419 ± 9 mg N L^{-1} and it decreased to a concentration of 270 ± 129 mg N L^{-1} after 10 days (Figure 2b). This implies a removal of 3149 ± 138 mg N L^{-1} (92%) and the mass of TAN removed was 4734 ± 198 mg N. In the case of the TAN concentration in the trapping solution, it rose to a value of 10,060 ± 292 mg N L^{-1} on day 10 (Figure 2b). As in the previous experiment, the volume of the trapping solution increased due to osmotic distillation, from an initial volume of 250 mL to a final value of 363.8 ± 5.7 mL. The total mass of TAN recovered in the trapping solution was 3652 ± 60 mg N, which implied a TAN recovery efficiency of 77% (Table 3). The TAN recovery rate was 13.9 g N m^{-2} d^{-1}.

In Exp. 1, the P recovery was designated as P1, and the initial concentration of P in the digestate was 473 ± 2 mg L^{-1}, which corresponds to a mass of P of 709 ± 3 mg. The mass balances are presented in Table 3, from which the average amount of P present in the liquid fraction at the end of the experiment was 266 ± 6 mg P, and in the solid fraction or precipitate was 451 ± 30 mg P. The P recovered is considered to be the total P precipitated in the solid fraction; therefore, the recovery efficiency in this experiment was 64% (Table 3).

Regarding the P recovery in Exp. 2 (P2), the initial concentration and mass of P were 426 ± 2 mg P L^{-1} and 639 ± 3 mg P, respectively. The mass of P in the liquid fraction at the end of the experiment was 139 ± 8 mg P and in the solid fraction was 512 ± 3 mg P. Therefore, the average P recovery in this experiment was 80% (Table 3).

3.2. Nitrogen Recovery and P Precipitation in Experiments 3 and 4 (Set 2)

In Exp. 3, the N recovery was designated as N3 and a 100 g TAN:m^2 membrane ratio was applied. In this experimental configuration, the initial TAN concentration in digestate was 3365 ± 25 mg N L^{-1} and it decreased to a value of 227 ± 0 mg N L^{-1} on day 9 (Figure 2c), which means a removal of 3076 ± 115 mg N L^{-1}. Taking this into account, the mass of TAN removed was 4711 ± 37 mg N, which means a removal of 93%. The TAN concentration in the trapping solution increased from 0 to 10,654 ± 643 mg N L^{-1}, which implies an amount of TAN recovered from the digestate of 3986 ± 213 mg N, and thus a TAN recovery efficiency of 85% (Table 3). The TAN recovery rate was 9.7 g N m^{-2} d^{-1}. In this case, the trapping solution increased its volume from 250 mL to a final value of 380.7 ± 5.9 mL due to the water vapor that passed through the membrane (i.e., osmotic distillation).

In Exp. 4, the N recovery (N4) was performed with a 100 g TAN:m^2 membrane ratio, and the addition of 31 mL NaOH to obtain a pH of 9.2 at the beginning of the experiment. The digestate initial TAN concentration was 3511 ± 20.5 mg N L^{-1} and it decreased to a value of 291.5 ± 0 mg N L^{-1} on day 9 (Figure 2d), which means a removal of 3220 ± 48 mg N L^{-1}. Therefore, the TAN removed was 4848 ± 66 mg N, which means a removal of 92%. The TAN concentration in the trapping solution increased from 0 to 10,970 ± 151 mg N L^{-1}, which implies an amount of TAN of 4376 ± 52 mg N recovered from the digestate, and therefore a TAN recovery efficiency of 90% (Table 3). The initial volume of the trapping solution (250 mL) increased to a total of 399 mL at the end of the experiment. The TAN recovery rate was 8.4 g N m^{-2} d^{-1}.

For Exp. 3, the P recovery was designated as P3. In this case, the initial concentration of Pt was 466 ± 1 mg L^{-1}, which represented an amount of Pt of 700 ± 1 mg P. The mass of Pt in the liquid fraction accounted for 243 ± 4 mg P and, in the solid fraction, this was 523 ± 77 mg P. Therefore, the P recovery efficiency in this experiment was 75% (Table 3).

In Exp. 4, the initial concentration and mass of P were 409 ± 22 mg P L^{-1} and 614 ± 33 mg P (Table 2), respectively. In this configuration, the P in the solid fraction accounted for 537 ± 4 mg P, so the average P recovery efficiency was 88% (Table 3).

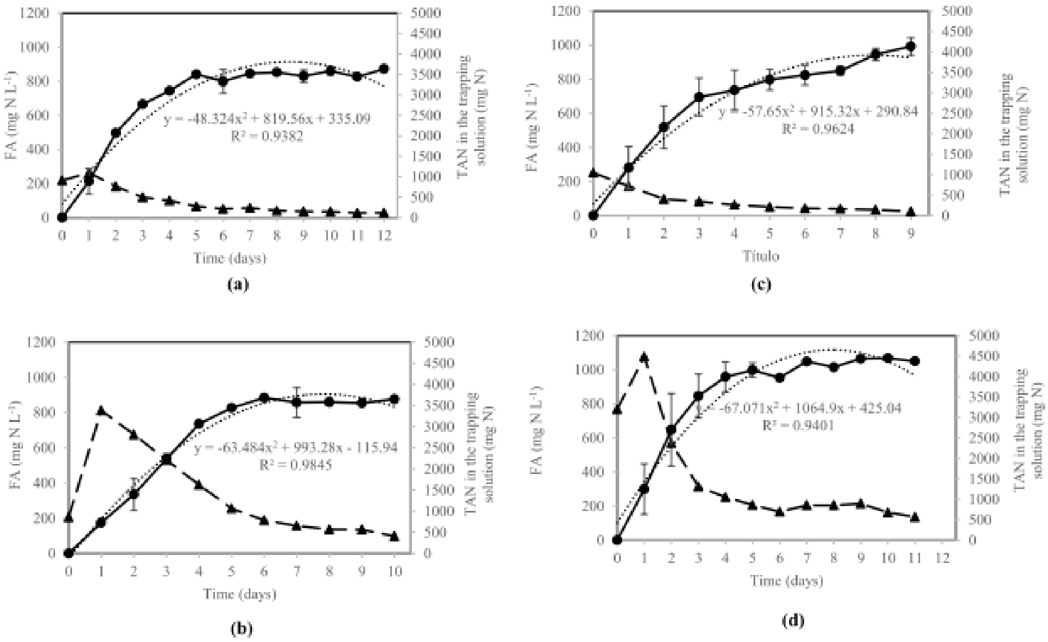
4. Discussion

4.1. N Recovery

The main differences found between configurations N1 and N2 were related to the duration of the experiments and the TAN recovery rates. This can be attributed to the differences in the FA content. The FA content in the digestate is one of the main factors affecting TAN recovery when using the GPM technology and is determined by pH and temperature Equation (4). The pH affects the acid-based chemical balance between the ammonia and the ammonium (NH_4^+/NH_3), and it has been stated that a pH value close to 9 shifts the chemical equilibrium favoring the release of NH_3. An increase in the FA concentration on the first day with respect to the initial value of FA of the digestate was observed in both experiments. This is due to an increase in the pH (Figure 3a,b; Figure 4) caused by the aeration alone for N1 (up to 262 mg L^{-1}), and the aeration plus the addition of alkali for N2 (up to 811 mg L^{-1}).

The average FA for N1 configuration was 94 mg L^{-1}, while for the N2 configuration it was 325 mg L^{-1}. This difference is due to a higher pH in the N2 configuration (up to 9.28) (Figure 4). Most of the TAN recovered for the N1 configuration occurred in the first five days, then remained almost constant until the end of the experiment (Figure 3). This agrees with Riaño et al. [14], who determined that the TAN recovery rate decreases when the FA content available in the digestate is lower than 95 mg N L^{-1}. As for the N2 configuration, most of the TAN recovery occurred in the first six days (Figure 3) and, in this case, a higher availability of FA favored the TAN recovery, the TAN recovery rate being approximately 21% higher than for the N1 configuration.

The percentages of N recovery in N1 and N2 were similar (79 and 77%, respectively, Table 3); nevertheless, the N2 configuration achieved this percentage in less time. It can be stated that the N2 configuration, with the addition of alkali, reduces the time of operation by two days to achieve an N recovery of 77% over an N removal of 90%.



(a) **(c)**

(b) **(d)**

Figure 3. TAN recovery in the trapping solution (continuous line; mg N; secondary axis) with the polynomic equation and the R2 coefficient (dotted line) and free ammonia (FA) available in the digestate (discontinuous line; mg N L^{-1}; primary axis) for the four different configurations, where (**a**,**b**) correspond to a ratio 180 g TAN:1 m^2 of membrane, and (**c**,**d**) correspond to a ratio 100 g TAN:1 m^2 of membrane. Also, (**b**,**d**) correspond to the configurations with the addition of alkali.

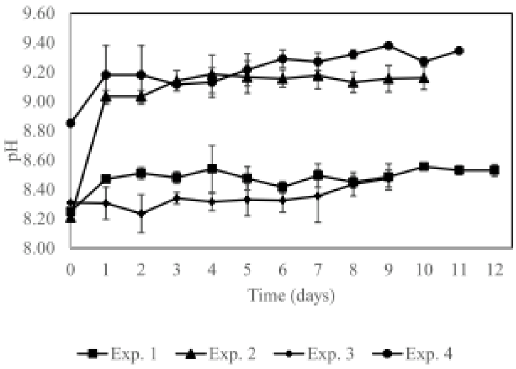


Figure 4. pH values for the four different experiments.

In the case of the N3 and N4 experimental configuration, with the 100 g TAN:m^2 membrane ratio, the main differences were due to the duration of the experiments and the FA content. Unlike the other configurations, N3 did not present an increase in the FA on day 1 (Figure 3c). This was due to the pH of the digestate, which remained close to 8 throughout the experiment. Despite this, the N3 configuration presented a TAN recovery rate of 9.7 g N m^{-2} d^{-1}, and a percentage of N recovery of 85% in nine days. The majority of the TAN recovery for N3 occurred in the first three days, and decreased on day four, when the FA presented values below 95 mg N L^{-1} (Figure 3c). In the case of configuration N4, the average FA concentration was 356.4 mg N L^{-1}, and the majority of the

N recovery occurred in the first four days of the experiment. Although there was a higher availability of N in the digestate, the TAN recovery rate was lower than in the previous configurations: 8.42 g N m^{-2} d^{-1}. Nevertheless, N4 presented the highest N recovery percentage (90%) in only two days more of experiment as compared to N3 (Figure 3d). The TAN recovery rate results agree with the results of García-González et al. [13], who obtained an average TAN recovery rate of 9.5 g m^{-2} d^{-1} when treating raw swine manure with GPM technology. Nevertheless, they were lower than those reported by Vanotti et al. [18] (up to 18.4 g m^{-2} d^{-1}). This could be explained by the difference in the membrane model.

It can be stated that, between the configurations of Exp. 1 and Exp. 2, both with a 180 g TAN:m^2 membrane ratio, the second option (N2) with the addition of alkali presented a better performance, with a higher TAN recovery rate, a shorter time and a high percentage of recovery of N (77%). However, the N3 and N4 configurations (Set 2, with 100 g TAN:m^2 membrane ratio) presented 9% and 19% higher N recovery efficiency as compared to N2, although the TAN recovery rates for N3 and N4 as compared to N2 were approximately 30% and 40% lower (Figure 5). This is an important result because a high N recovery efficiency (average of 83% ± 3) and high N recovery rate using less membrane can be obtained with the N2 configuration.

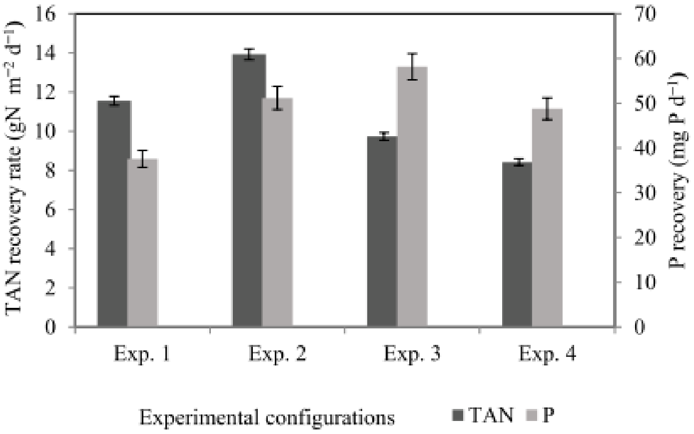


Figure 5. Comparison of the different experimental scenarios.

This implies a significant cost reduction when applying this technology for waste treatment and nutrient recovery.

4.2. P Recovery

The P recovery efficiencies were between 64% for P1 and 88% for P4 (Table 3). These results for P recovery are consistent with those reported by Brown et al. [23], who obtained 80% total P recovery from anaerobically digested manure, using stirred reactors for struvite precipitation, also with $MgCl_2{\cdot}6H_2O$ and at pH 8.7, and using NaOH to control the pH. The results obtained are also in agreement with those reported by Taddeo et al. [24], who obtained a P recovery efficiency of approximately 80% from co-digested and raw swine slurry, also using NaOH to obtain pH values of 10, but MgO as the Mg source. Vanotti et al. [18] reported recoveries of nearly 100% of the removed P from the liquid manure as solid precipitate, also using $MgCl_2$, $6H_2O$ and NaOH for pH control. This may be due to the influence of a higher pH (up to 9.7) for a quick elimination of the NH_4^+ ion, which may result in a more efficient P precipitation.

It was observed that configuration P2, with a ratio of 180 g TAN: m^2 membrane plus the addition of alkali, as compared to P1 with the same ratio but without alkali, showed an increase in P recovery of 16%. In the same way, P4, with a 100 g TAN: m^2 membrane and the addition of alkali, as compared to P3 with the same membrane ratio but without

NaOH addition, presented a P recovery 13% higher (Table 3). Nevertheless, the statistical analysis shows that no significant differences ($p > 0.05$) were found in the P recovery efficiencies between the different configurations, except between P2 and P4 ($p < 0.05$), where P4 presented 4% more recovery of P. This suggests that, with an increase in the membrane and the addition of alkali, a higher P recovery can be obtained via precipitation, as indicated by the initial premise. However, P4 had a duration of one more day compared to P2, which implies that the P recovery in mg per day for P4 is 5% less than P2 (Figure 5).

In this sense, by taking into account the duration of the experiments to be compared, the TAN recovery rate together with the P recovery per day for each configuration can be observed in Figure 5. The configuration for Exp. 3 presented the highest P recovery (58.2 mg P d^{-1}); however, it has a low N recovery rate (9.7 g N m^{-2} d^{-1}).

Therefore, it can be stated that the configuration that presents the best performance is Exp. 2, with the highest N recovery rate (13.9 g N $m^{-2}d^{-1}$), and an N recovery efficiency of 77% and a P recovery of 51.2 mg P d^{-1}, which is only 7% lower than P3, and a P recovery efficiency of 80% (Table 3, Figure 5).

Regarding the foreign ions, their content was measured in the solid fraction of the digestate at the end of the four experiments as percentage of dry matter. The content of Ca^+ was in a range between 2.05% and 4.10%, and the content of K^+ was in a range from 0.31% to 0.38%. This indicates that any phosphates that may have been formed from these elements were not important contributors to the resultant precipitate. These results agree with those obtained by Vanotti et al. [18].

4.3. Future Perspectives of These Nutrient Recovery Technologies

In the case of N and P, it has been stated in the literature that membrane-based technologies and chemical precipitation are the two options for nutrient recovery with the highest technical and economic feasibility [8,25]. What is more, it has been reported that the combination of different recovery technologies could increase the quality and quantity of the recovered nutrients and that it would make them more viable in the future [26,26]. This makes this study especially relevant.

Specific technologies that recover such nutrients as N and P from wastes have experienced a great development in recent years due to the environmental limitations on organic fertilization, particularly with the continued increase in the prices of mineral fertilizers (30% more from early 2022) [27,28]. However, the question of whether these technologies could be economically viable is always related to this development.

The GPM technology and P recovery via precipitation present very high nutrient recovery rates (>90%), and the bio-based fertilizers obtained could be applied directly without further treatment in the soil. Furthermore, in the case of P recovery by precipitation, phosphate precipitates present good solubility in soils and have a high plant nutrient uptake (>76%), [29]. These characteristics make them economically attractive [25].

The GPM technology is one of those with the most efficient performance from an economic, energetic, and environmental point of view [8,17,30], and it is capable of a total benefit profit for products up to 0.32$ per kg [19]. P recovery via precipitation is an easy-to-operate process and can be used to meet low P discharge limits in the environment [31]. A market value has been calculated for P recovered as struvite of 2.9$ per kg of P produced, although the potential profits may vary depending on the conditions and the cost of chemicals in each case [32]. Even though there is not yet a precise market value for the recovery nutrients, these estimations can be very useful for future investments. It has been reported that mineral fertilizers are now more affordable for farmers [32], but their prices do not consider externalities, such as the environmental costs associated with their extraction. The negative environmental impacts related to the intense exploitation of mines and the greenhouse gas emissions associated with the mineral fertilizers' production must be added to the rapid consumption of phosphate-based rocks and costly ammonium production; therefore, investing in additional technologies may be necessary [3,25].

In addition to better environmental performances, nutrient recovery technologies can have other advantages, such as state incentives, as well as their capability to eliminate unwanted precipitates in waste streams, thereby facilitating management and reducing wastewater treatment costs [25,33].

In this context, this study showed the possibility of effectively combining GPM technology with P precipitation and obtaining high recovery rates, corresponding to the Exp. 2 configuration.

5. Conclusions

The combination of nutrient recovery technologies from agro-industrial residues is a field with great application potential. The combination of GPM technology to recover N together with chemical precipitation to recover P resulted in high recoveries of both nutrients. It has been seen that the ratio of 180 g of N per m^2 of membrane with the addition of alkali can achieve TAN recovery efficiencies of up to 77%, similar to those that can be obtained with a membrane ratio of 100 g of N per m^2. Also, the 180 g of N per m^2 of membrane presented the highest TAN recovery rate compared to the other scenarios with a larger membrane surface. This means lower capital costs. This configuration is also capable of obtaining recovery efficiencies of P of 80% and a P recovery of 51.2 mg per day. The comparisons performed and the proposed configuration could be particularly useful for agribusiness stakeholders when exploring the application of nutrient recovery techniques, especially when it comes to essential nutrients such as N and P.

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Conflicts of Interest: The authors declare no conflict of interest.

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5. “Environmental sustainability performance of a membrane-based technology for livestock wastewater treatment with nutrient recovery”.

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In this study, the potential environmental impacts of the GPM technology were evaluated for the first time, using the Life Cycle Assessment (LCA) tool. The study is based in a real scenario where the GPM were applied on a pilot plant on a farm (treatment scenario), in order to compare the environmental advantages and disadvantages of traditional swine manure management without any type of treatment (conventional scenario).

The evaluation of the environmental sustainability of the application of the GPM technology in the pilot plant for the manure (ammonia extraction and N recovery in the form of ammonia sulfate), compared to conventional management practice, was carried out using the methodology LCA ISO 14040 and 14044 (ISO 14040, 2006; ISO 14044, 2006), in combination with the UNEP/SETAC recommendations. The study followed the attributional approach for LCA, which provides information on the impacts of processes related to the production, consumption and disposal of the systems under study. The functional unit (FU) considered was 1 m^3 of swine manure produced, and the Open LCA V 1.10 software (GreenDelta version of 2016) was used to perform the LCA modeling. The environmental impacts were assessed with the updated version of the ReCiPe 2016 method, V1.1 for midpoints. The following seven impact categories related to the system under study were estimated: global warming, fine particle formation, freshwater eutrophication, marine eutrophication, ozone formation (human health and terrestrial ecosystems), and terrestrial acidification. The data for the primary life cycle inventory for the treatment scenario were obtained from the pilot plant in operation located on a pig farm in Guardo, in the north of Spain. For the conventional scenario, the data were obtained from calculations based on the annual manure production volumes of the farm and nearby fields. Additional inventory data were obtained from the relevant literature and databases: Ecoinvent 1.10, Agribalyse V3, ELCD 3.2, and Environmental Footprint 2.0. The farm considered in this study generates around 17136 m^3 of manure per year, which was taken as the basis for this study. The calculations and the evaluation were considered for a complete year of treatment operation.

The principle of operation of the GPM technology is the same as described in the previous section with aeration. The complete pilot plant configuration can be seen in Molinuevo-Salces et al. (2020a). The GPM system worked in batch mode where the swine manure had a residence time of seven days in the tank. For every m^3 of slurry treated, around 0.05 m^2 of membrane surface was needed. In addition, it was assumed that, during one year of operation, it was necessary to replace 10% of the membrane for maintenance. This is equivalent to using 2.82 g of e-PTFE membrane, with a density of 2.16 g per cm^3. The amount of sulfuric acid (98% concentrated) required to capture TAN was estimated at 4.39 kg per m^3 of manure. The power requirements of the GPM system were monitored using a power grid analyzer and the resulting power consumption was estimated at 28 kWh per day or 39.2 kWh per m^3 of manure. Electricity was used for the aeration, recirculation, and heating of a blanket that warmed the acidic solution for a better performance.

The conventional scenario consisted of three main stages: storage in uncovered lagoons for a period of six months, transportation to the application area, and finally application of the organic fertilizer in the field, thus replacing mineral fertilizer. The treatment scenario consisted of five stages: first, the slurry was stored on the farm in a closed storage tank, and then it was treated with the GPM system to extract the NH_3 and recover the N in the form of ammonium sulfate solution. Subsequently, the manure with a lower TAN concentration and the ammonium sulfate solution obtained were stored and finally used as fertilizers when necessary. The treated manure was transported and applied as organic fertilizer, while the ammonium sulfate solution was transported separately for application when necessary. The potential environmental impacts were calculated for each phase within each scenario, taking into account the characteristics of each one of them (energy expenditure, emissions, etc.).

The results of the environmental impacts per FU indicated that the GPM treatment reduced the impacts in the global warming and marine eutrophication categories by 14% and 32% respectively, compared to the conventional scenario. These impacts are directly related to climate change and pollution problems in freshwater ecosystems, and ultimately marine ones, due to dissolved inorganic N emissions. Therefore, the significant reduction achieved is considered to be very important. In addition, when using membrane technology, a reduction in impacts was observed in the category of ozone formation, this being a harmful gas for both human health and ecosystems when it appears in the lower layers of the atmosphere. Specifically, for the impacts on human health, a decrease of 48% was obtained and for ecosystems a decrease of 50%, compared to the scenario without slurry treatment. For freshwater eutrophication the net value was similar for both scenarios. In contrast, the impacts for the particle formation and ground acidification categories were increased by the membrane treatment by 16% and 17%, respectively, due to some NH_3 volatilization.

In addition, a sensitivity analysis was carried out to model an optimized treatment system, which resulted in even greater reductions of between 26% and 86% for global warming, marine eutrophication, particulate formation and terrestrial acidification compared to the conventional scenario. In addition, it was observed that a greater capture of NH_3 implied that a greater amount of slurry could be applied to the crops to cover the N requirements, leading to a P surplus and therefore to freshwater eutrophication potential impacts. To avoid this type of contamination, it was concluded that it would be necessary to capture ammoniacal N until equilibrium was reached with P, in order to balance the cultivation needs of both elements. Therefore, it can be concluded that the GPM technology treatment of swine manure is more environmentally sustainable compared to the no-treatment scenario, making it an attractive option for environmental management systems.

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Environmental sustainability performance of a membrane-based technology for livestock wastewater treatment with nutrient recovery (©ELSEVIER)

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ABSTRACT

The gas-permeable membrane (GPM) technology is one of the most novel techniques capable of minimizing ammonia (NH_3) emissions associated to wastewaters, while recovering nitrogen as nutrient. This study conducted for the first time a life cycle assessment of this technology (treatment scenario), to compare the environmental trade-offs with the conventional manure management (conventional scenario), and determine which strategy performs better. The environmental impact results per m^3 of manure, estimated using the ReCiPe method V 1.1, indicated that the treatment scenario reduces global warming (GW) by 14% and marine eutrophication (ME) by 32% with respect to the conventional scenario, whilst it increases particulate matter formation (PMF) and terrestrial acidification (TA) by 16% and 17%, respectively, due to some NH_3 volatilization. Other impact categories considered were ozone formation (affecting human health (HOF) and ecosystems (EOF)), where the treatment scenario was able to reduce this impact by 48% and 50%, respectively. For freshwater eutrophication (FE), the net value was similar for both scenarios. A sensitivity analysis looking at optimum membrane design parameters (optimized treatment scenario) resulted in further reductions between 26% and 86% for GW, ME, PMF and TA with respect to the conventional scenario, although one potential drawback is the application of higher amount of phosphorous with the organic fertilizer, which resulted in higher FE impacts. Overall, the GPM system-based treatment is more environmentally sustainable compared to the conventional scenario thus making this an attractive option for environmental management systems, especially in areas with low water quality or high nutrient imbalance.

6. Joint discussion

Continuing with the work presented in previous publications, this section proposes a joint discussion to bring together the most relevant aspects of each work, integrating the main findings to demonstrate the coherence among the developed articles of the thesis, and their relevance in the scientific field.

The AD process and the GPM technology tandem

The AD-GPM technology was studied in the initial phase of the thesis, sections VI.1 and VI.2. The work stated from the premise that the TAN reduction from the N-rich livestock wastewaters, before or during the AD, may prevent NH_3 inhibition problems in the AD process. However, most of the studies found in the literature applied the techniques for N extraction related to AD either before the process or afterwards on the digestates produced (Ma et al., 2021; Romero-Güiza et al., 2016); while techniques applied simultaneously with AD are less common and are usually focused on NH_3 removal instead of on N recovery (Krakat et al., 2017; Lauterböck et al., 2012). Hence, the works developed in this thesis and its good results constitute a great novelty.

Krakat et al. (2017) described different treatments for N removal coupled with AD, such as anaerobic ammonia oxidation, ultrasonication or microwave. Dai et al. (2015) studied the treatment of municipal wastewater combining the AD process with the nitrification–anammox process under ambient temperatures, with an N removal efficiency of 81%. Staunton et al. (2015) coupled AD with the nitrification-denitrification process on swine wastewater for energy production and N removal, obtaining an N removal efficiency of 83%. However, although N removal may be an interesting approach to avoid inhibition by ammonia, the N removed is lost and not recovered, and the process has a high energy cost, despite using part of the biogas generated. Thus, Dai et al. (2015) estimated a net energy consumption for the combined process of 0.09 kWh per m^3 of treated wastewater. It is worth mentioning the work developed by Lauterböck et al. (2012) that used hollow fiber hydrophobic membrane contactors, made of polypropylene, and NH_3-rich slaughterhouse waste as substrate on direct continuous NH_3 recovery directly during the AD process. These authors compared the performance of a reference reactor (without the membrane) and a reactor coupled with the membrane for N recovery. The results showed a significant improvement in the amount of biogas produced in the membrane reactor.

However, this combination of AD and GPM technology had not been applied to swine manure, a high-ammonia, strategically important waste that requires immediate solutions. **Therefore, the novelty of the work developed in section VI.1 lies in the application of the GPM technology in the AD process with raw swine manure, for N recovery and biogas production,** presenting excellent results: there was obtained a remarkable improvement of the quality and quantity of the methane produced in the membrane reactor (an average of 17% more of biogas and with a 15% more of CH_4, compared to the reference reactor), and N was also, recovered in the form of ammonium sulfate at a rate of 6.7 g N per m^2 of membrane and per day during the 205 days of the experiment. Since it has been reported that ammonium salt obtained from GPM technology may present an approximate total benefit of 262.8 € per ton of ammonium salt produced (Beckinghausen et al. 2020), this could represent an important incentive for the implementation of this technology in anaerobic reactors.

Continuing with the AD-GPM technology tandem, an AD experiment was performed to study the co-digestion of food waste and swine manure (section VI.2), followed by N recovery from the obtained digestates. The work stated from the premise that the use of co-digestion has been increasing in AD plants near farms, to valorize the livestock waste and other agricultural waste such as crops waste.

The current trend is to make the most of the potential of the AD process, using optimized co-digestion and digesters in multi-purpose bio refineries, for the production of energy, nutrients, proteins, bio-chemicals such as bio-based fertilizers, or bio alcohols.

Along the same line, the work of Molinuevo-Salces et al. (2020b) should be highlighted. This work proposed the valorization of apple pomaces for biofuel production within a biorefinery approach. The author of this thesis had the opportunity to participate as a co-author of the said research. In line with this, in section VI.2, the work focuses on the potential of the use of apple pomace from the cider industry combined in different proportions with swine manure for methane production. The promising results in biogas production **imply that this type of waste can be valorized, thus avoiding the environmental damage** related to their disposal in landfills or their incineration (Buckwell and Nadeu, 2016). In a later phase, the N was recovered by using GPM technology, specifically from anaerobically digested swine manure with no addition of AP (D-R1), and from the anaerobically digested swine manure with 15% of apple pomace in the feed mixture (D-R2). The results showed a TAN recovery efficiency of 77.2% and 75.8% for D-R1 and DR-2, respectively. Also, TAN recovery rates of 32.9 g N m^2 day^{-1} and 25.8 g N m^2 day^{-1} were obtained, respectively. These recovery efficiencies are in agreement with those reported by Oliveira-Filho et al. (2018), which also used GPM technology for N recovery applied on anaerobically digested effluents from agro-industrial waste. Oliveira-Filho et al. (2018) applied the GPM technology on co-digested organic substrates (fruit and vegetable sludge from peppers and artichokes, and tomato processing industry residues) mixed with swine manure. They reported a TAN removal efficiency of approximately 78% and a TAN recovery of 96% of the TAN removed. The authors reported higher TAN recovery rates, with an average of 55.4 g N m^{-2} d^{-1}, which can be due to a higher NH_4^+ initial concentration in the digestates combined with a high total alkalinity, as well as to a different type of ePTFE membrane. On the other hand, Riaño et al. (2021), applied GPM technology on the digestate of a biogas plant composed of swine manure, tobacco powder and cereal powder; while Ukwuani and Tao (2016), used vacuum thermal stripping for N recovery from high ammonia food waste digestate. Both studies reported lower TAN recovery efficiencies of the removed TAN (55.3% and 54.45%, respectively). Therefore, it can be stated that more studies on nutrient recovery in digestates are necessary, since results may vary due to different feedstock characterizations for co-digestion (Bolzonella et al., 2023; Xie et al., 2018). In particular, it would be particularly relevant for agro-industrial waste that, due to their seasonality or their composition, there is no easy way to recycle them alone, such as **apple pomace**.

These promising results for N recovery using the GPM technology agree with the statements of the foremost reviewed literature, where the nutrient recovery from anaerobically digested agro-industry waste presents important environmental and economic advantages, in a circular economy and a mineral fertilizers scarcity framework (Buckell and Nadeu, 2016; Romero-Güiza et al., 2016; Martín-Hernández et. al., 2022). Therefore, the results obtained are **especially relevant in the current global context.**

The GPM technology for N recovery combined with P recovery technologies

The works developed in this knowledge area focused on N and P recovery from waste streams, combining novel technologies to close nutrient cycles as well as a strategic approach to help economic stability in the CBE context. The combination of GPM technology with P recovery techniques in this phase of the work has shown promising results. In section VI.3, **the GPM technology was combined with the ED method (that uses ion exchange membranes), in a two-phase process, to recover N and later P, producing an ammonium sulfate solution and a P-rich solution, respectively.** The combination of these technologies was initially applied on swine manure and later on digestate, to compare the performance of the processes in these two different wastewaters. In terms of N recovery rates, 8.0 g N m^{-2} day^{-1} were obtained with the swine manure and 25.7 g N m^{-2} day^{-1} for the digestate. These results for swine manure are in agreement with previous research (García-González et al., 2015) and also, with the TAN recovery rate obtained in the work of the previous section VI.1. The results obtained for digestate are also in agreement with previous research (Dube et al., 2016), as well as with the TAN recovery rates obtained in previous section VI.2. In terms of P recovery, recovery rates of 12.5 g P m^{-2} day^{-1} were obtained for the swine manure and 4.4 g P m^{-2} day^{-1} for the digestate, being both in agreement with previous research (Oliveira et al., 2021). With the application of the GPM technology in a first step, the ammonia ions were significantly reduced; therefore, with the application of the ED on the effluent in a second step, the process of P recovery **was more efficient,** since all the energy in the system was used for the transport of PO_4^{3-} ions. Therefore, the ED process becomes more effective, and so, there were obtained P recovery efficiencies of 100% in 4 days for the swine manure and of 74% in 7 days for digestate. **The experimental work carried out in this section VI.3 was completed with an extensive comparative analysis of the GPM technology and the ED process with the rest of the most innovative nutrient recovery technologies, in terms of type of waste (manure,**

digestate, sewage sludge, etc.), scale (laboratory or pilot plant), nutrient removal and recovery efficiency, and operational costs (€ per kg of N or P). From the results obtained in the experimental part and from the comparison with other nutrient recovery technologies, it can be stated that the application of the GPM technology on wastewaters, particularly on the digestates obtained from agro-industrial waste, can be of great economic interest. Since the membranes can be easily integrated into the waste treatment process, in a complementary way, they can provide great added value in the form of bio-based fertilizer. Furthermore, GPM technology can be easily combined with other nutrient recovery technologies, such as the ED process, which is an even greater advantage and brings even more relevance to the waste valorization process.

Continuing along with the same line of research, in section VI.4 an experimental work was carried out to evaluate the performance of **the simultaneous N and P recovery, combining GPM technology with P chemical precipitation** from digestate, produced in a fully operational biogas plant. Specifically, the effects of the addition or not of alkali (NaOH), and the application of two different membrane areas (a ratio of 180 g of N per m^2 of membrane, and a ratio of 100 g of N per m^2 of membrane) in the nutrient recovery process were studied. Of the four possible combinations studied, the one that offered the best results was the one that combined the addition of alkali with a ratio of 180 g of N per m^2 of membrane (Exp. 2). With this combination, a TAN recovery rate of 13.9 g N m^{-2} d^{-1} and a P recovery rate of approximately 51.2 mg P d^{-1} were obtained. Comparatively, the results showed similar nutrient recovery efficiencies with 1.6 m of membrane (ratio of 180 g of N per m^2 of membrane) than with 3 m of membrane (ratio of 100 g of N per m^2 of membrane). Hence, since one of the biggest drawbacks for GPM technology application may be the capital costs, the fact that it can be obtained similar TAN recovery efficiencies with less membrane could be an interesting result for potential applications.

Currently, the best known methodology to recover N and P together from wastewaters is the struvite precipitation. This technique consists in obtaining a precipitate magnesium ammonium phosphate hexahydrates ($MgNH_4PO_4$ $6H_2O$) as a fertilizer that has the same quality as the mineral (Desmidt et al., 2015; Karunanithi et al., 2015; Nelson et al., 2003). Nevertheless, this method presents important drawbacks, especially when applied to agro-industrial wastewaters, such as livestock wastewaters, due to their high heterogeneity. The struvite formation requires ratios of magnesium (Mg^{2+}), NH_4^+ and phosphate (PO_4^{3-}) in a 1:1:1 proportion. It also depends on a combination of thermodynamic and mass transfer properties, different physico-chemical factors (pH, supersaturation, mixing, crystal sizes), and it can be adversely affected by the presence of foreign impurities (other ions such as Ca^{2+} or K^+). Although the struvite methodology was considered a viable technique for N recovery, in livestock wastewaters only about <15% of the N contained in the influent could potentially be recovered through struvite because of the very high NH_4^+ to PO_4^{3-} ratio in these effluents (Ariyanto et. al, 2014; Vanotti et al., 2017). Complementary treatments have been recently proposed to improve the precipitation of struvite; however, at the moment, all the treatments are focused on municipal wastewater. For instance, Thant-Zin et al. (2021) used a pretreatment of integrated hydrolysis and incineration of sewage sludge, and recovered N and P as struvite, with a NH_4^+ recovery efficiency of 88% and a PO_4^{3-} recovery efficiency of 94.1%. Along the same lines, Thant-Zin et al. (2021) investigated the N and P recovery from sewage sludge ash and food wastewater as struvite, using biochar, reporting a PO_4^{3-} recovery efficiency of 92.2% and a NH_4^+ recovery efficiency of 54.8%. In addition, the work of Oliveira et al. (2021) should be highlighted, as it combined GPM technology and the ED process to recover N and P simultaneously from municipal waste, and the author of this thesis had the opportunity to participate as a co-author. In that work, two purified nutrient solutions were obtained, which were synthesized as bio-fertilizer through precipitation (secondary struvite), through a highly efficient precipitation process (99.5%), with a recovery efficiency of 81% for P and 74% of NH_4^+.

In any case, it is believed that more studies are needed to take advantage of the maximum potential of the agro-industrial residues, and therefore, **the techniques proposed in this thesis represent a novel advance. One of the most outstanding advantages of the recovery of N and P in two phases is that two different bio-based fertilizer solutions would be obtained** that could be stored, transported and applied on fields depending on the needs of each agronomic area, facilitating planning and avoiding excess application of nutrients, while also, avoiding potential environmental damage. **In the same line, with the simultaneous recovery of N and P through the application of GPM technology and precipitation,** N and P were recovered at the same time, but each one in a different way: N in the form of an ammonium sulfate solution and P precipitated in the solid phase of the digestate. In this case, the combination of technologies allows nutrient extraction to be carried out simultaneously but retains the advantages of separating each one for its independent application.

Life cycle approach to study GPM technology sustainability

As presented in section VI.5, the developed work was the LCA of the application of the GPM technology, installed in a fully functional pilot plant on a pig farm, to recover N and minimize NH_3 emissions. This treatment scenario consisted of the storage, treatment, by-products storage, and the application of both the organic fertilizer (treated manure) and the ammonium sulfate solution obtained. The results were compared with the scenario in which the swine manure remained untreated and was stored, transported and applied directly on the crop fields. The **analysis of the potential environmental impacts of the application of the GPM technology was carried out for the first time.** The LCA was carried out with primary data, which implies a high-quality LCA, and the databases were only used if there were no other sources of data. For instance, the database provided the information necessary for the use of the permeable membrane for N recovery, which would otherwise remain uncounted, since the details of the membrane production are the property of the manufacturing company (Zeus Inc.), to which there is no access.

It has been stated in recent literature that most nutrient recovery related LCA studies considered a "process perspective", where a single process configuration with nutrient recovery was assessed, or where the nutrient recovery of different process configurations were compared. The "process perspective" was mostly chosen since the goal of these studies was waste treatment, while nutrient recovery is a plus. In these studies, the common FU is 1 m^3 or 1 ton of wastewater treated. Only a few studies have used "product perspective", but it is becoming more common, since the interest in nutrient recovery is gaining attention. In these studies, the FU chosen is kg of N (or P) applied to agricultural land (Lam et al., 2020). **In the work carried out in section VI.5, both perspectives were considered.** This is because, in the treatment scenario, the manure was treated with GPM technology (process), from which a bio-based fertilizer and an organic fertilizer are obtained (products). Furthermore, in the conventional scenario, the manure was used as an organic fertilizer (product). Therefore, the FU used allowed the LCA to be applied with both perspectives: 1 m^3 of raw manure, to be treated and used as a product. Also, the benefit of avoiding mineral or fertilizers was taken into account, specifying the types (diammonium phosphate (as P_2O_5), urea ammonium nitrate (as N), and ammonium sulfate (as N)), as well as the type of crop and its N needs. This implies that, unlike many other studies, the mineral fertilizers were not chosen arbitrarily or according to those available in the database (Lam et al., 2020), but the choice of the types of fertilizers and the calculations were made according to the needs of previously studied crops.

Another point that should be highlighted is that the work presented a sensitivity analysis to optimize the treatment scenario. Sensitivity analysis often involves changing selected input parameters one at a time to examine how sensitive the LCA results are to each change. In the case of the work carried out, the sensitivity analysis showed how, with the optimization of the membrane surface, the impacts of global warming and marine eutrophication, among others, decreased significantly. It has been stated that combining sensitivity analysis with uncertainty analysis will help to understand the impact of any uncertainty on the results, and to identify weak points in the inventory data (Hauschild et al., 2017). The major uncertainties reported are related to missing inventory data for non-full-scale technology, the variability of water and sludge quality parameters, the variability of spatial characteristics for decentralized recovery, non-localized inventory for background data, temporal representativeness of background data, and the emissions from field application of recycled nutrient materials (Lam, et al., 2020). In the case of the present work, no uncertainties related with the categories mentioned above were found, since the primary data obtained from the farm and from the **pilot plant for the treatment with GPM technology eliminated any gap.** Only the heterogeneity of the raw manure composition may represent some uncertainty. However, the high ammonia concentration in raw swine manure makes GPM technology an interesting option.

Finally, it should be noted that the results of the work developed in section VI.5 showed that the application of the GPM technology significantly reduces potential environmental impacts for raw swine manure treatment, and this agrees with the conclusions of the study carried out by Lam et al. (2020). In their work, 65 publications that applied LCA for environmental assessment of the treatment and recovery of nutrients in wastewaters were reviewed, and the majority suggested positive environmental outcomes from wastewater-based nutrient recycling, especially when chemical inputs are minimized.

Challenges, strengths and future perspectives

In the field of nutrient recovery from waste streams, several fundamental challenges have been described: a greater need for the characterization of waste streams, a greater commitment to political actions to stimulate the sector, concerns of culture and safety in the population, and the absence of a market and business (Buckwell and Nadeu, 2016). In the case of agro-industrial wastewaters, it has been stated that the scientific community has already done invaluable work in quantifying the flows of nutrients through the food chain and demonstrating the enormous wastage and damaging leakage into the environment, while also proposing many different alternatives to recover the nutrients that otherwise may be lost (Buckwell and Nadeu, 2016; Yang et al., 2022b). In addition, to counteract the aforementioned problems, the initiatives of different associations in the EU have opened their way, (such as the European Sustainable Phosphorus Platform, or the Dutch Nutrient Platform), requesting the consideration of externalities in conventional fertilizers, and specific political actions to open up the market to bio-based fertilizers. However, the biggest problem continues to be the economic feasibility of applying new technologies. In this regard, different review works have been carried out that support the economic viability of new technologies (Bekinghausen et al., 2020; Pandey and Chen, 2021); nonetheless, it has been stated that most of the works are based on laboratory experiences (Yang et al., 2022b). As previously seen, the GPM technology is one of the technologies that presents the most advantages, and that has already been studied at pilot scale on farm, so its N recovery and economic performance have been observed on-site (Molinuevo-Salces et al., 2020b); and their environmental advantages have been analyzed in section VI.5. In any case, during the development of this thesis, some aspects have been observed that must be taken into account when continuing with the application of GPM technology:

In section VI.3 a difference between recovery rates of swine manure and digestate was found. This could be attributed to different parameters, such as microbial activity, which oxidize NH_4^+ to nitrites and nitrates, as well as an imbalance between inorganic carbon and NH_3 content (Daguerre-Martini et al., 2018; Oliveira-Filho et. al., 2018). In addition, in section VI.3, a difference regarding the performance between the swine manure and the digestate it was found, that can be attributed to the different chemical forms of P. This represents an important factor that should be considered in the case of further application on larger scales.

In section VI.5, it was found that, despite the better global environmental performance of the GPM technology treatment of swine manure, the further application of the manure after treatment, as organic fertilizer, may lead to potential higher freshwater eutrophication impacts. The GPM system reduces N levels, whilst maintaining the same P levels in the treated manure. This implies that the greater the quantity of organic fertilizer applied to meet the N requirements of the crops, the greater the quantity of P is applied, and this could reach groundwater reservoirs or water bodies. This specific aspect can be a great opportunity to apply P recovery technologies in combination with the GPM technology.

In general terms, the results of this thesis concerning the application of the GPM technology in agro-industrial waste streams are in line with those reported in literature, where the N recovery leads to lower levels of marine eutrophication, saves energy consumption, reduces GHG emission and promotes the N cycle. Therefore, it can be stated that considering these advantages, the GPM technology may be the most viable from a commercial point of view, due to its high recovery efficiencies and its environmental and operational benefits. Also, it is expected that the first engineering applications (as marketable prototypes) can be applied soon with the corresponding economic evaluation, as for example in the Green Ammonia project (2023).

VII. CONCLUSIONS

The development of this thesis has been based on the main objective of studying several relevant aspects when applying the novel GPM technology, and its potential to valorize agro-industrial waste through the recovery of valuable nutrients (specifically N and P). Those relevant aspects were described previously as sub-objectives.

According to the results obtained with the experimental work proposed in all the studies, **it is considered that the main objective, and each one of the sub-objectives previously described, have been satisfactorily achieved.**

The conclusions have been placed following the order proposed in section IV, that refers to the coherence of the thesis:

First: The GPM technology can improve the AD process operating inside the anaerobic reactor, capturing NH_3 and preventing inhibition, producing more biogas and with better quality. In the semi-continuous experiment carried out for 205 days in the AD reactor with the GPM technology, the total ammonia nitrogen was reduced by 23% and the free ammonia by 14%. Furthermore, the specific methane yield in the membrane reactor increased by 27.6% and the methane content in the biogas was higher (up to 13.6%).

Second: The co-digestion of 7.5% and 15% of apple pomace with swine manure presented a methane production similar to the AD from swine manure; so the AD can be a good alternative for the valorization of apple pomace waste. The GPM technology applied to the resultant digestates with swine manure alone and swine manure and 7.5% of apple pomace showed total ammonia recovery efficiencies of 77% and 76%, respectively.

Third: The two-step combination of the GPM technology for N recovery with the electrodialytic method for P recovery in manure and digestate showed a great potential. The GPM achieved TAN recovery efficiencies of 53% and 92% for manure and digestate, respectively, and the electrodialytic method achieved P recovery efficiencies of 100% and 74% for swine manure and digestate, respectively. These high nutrient recovery efficiencies were obtained in short periods of time, with an average of 10.5 ± 2.5 days for N recovery and 5.5 ± 1.5 days for P recovery.

Fourth: The simultaneous recovery of N and P using GPM technology and chemical precipitation showed promising results in short periods of time. Different GPM technology configurations were studied for the recovery of the two nutrients proposed, using two different membrane ratios, with and without the addition of alkali. The results showed that the best recovery rate and highest nutrient recovery efficiencies, of 77% for N and 80% for P, were obtained for the configuration that used 180 g N per m^2 of GPM and the addition of NaOH (1.5 N), along with the precipitant agent ($MgCl_2$) for P precipitation. With this configuration, less membrane is used, which can mean a lower initial cost, in a full scale application of these membranes.

Fifth: The application of the GPM technology on raw swine manure presented a better environmental performance than the traditional manure management. The environmental assessment of the application of the GPM technology was done using Life Cycle Assessment with primary data of a real pilot plant on a farm. The GPM treatment reduced the impacts of global warming and marine eutrophication categories by 14% and 32%, respectively. Greater reductions can be achieved by optimizing the membrane treatment. It would be necessary to capture ammoniacal N until equilibrium is reached with P to avoid P losses and therefore potential freshwater eutrophication impacts.

Sixth: The application of the GPM technology reduced the N levels in manure and digestate producing marketable ammonium sulfate, it was lead to lower levels of marine eutrophication and reduced GHG emissions and help to close the N cycle. This implies that this technology can significantly contribute to fight the current situation of excess ammonia emissions and nutrient losses in the agro-industrial sector, minimizing the associated environmental impacts. Additionally, it can be combined with other exiting techniques for P recovery; therefore, it is considered that the proposed main objective has been successfully achieved.

Seventh: The comparison of the GPM technology with the other existing N recovery technologies, from the efficiency, economic and environmental perspectives, based on the results obtained and on the extensive review of existing literature carried out in this work (section VI.3), points the GPM technology as one of the most interesting nutrient recovery technologies for its application on a real scale. It is expected that the first marketable prototypes will be developed soon to be applied directly in the field.

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IX. OTHER PUBLICATIONS AND MERITS

PUBLICATIONS AS CO-AUTHOR

B. Molinuevo-Salces, B. Riaño, M. Hijosa-Valsero, I. González-García, A.I. Paniagua-García, D. Hernández, J. Garita-Cambronero, R. Díez-Antolínez, M.C. García-González. 2020. Valorization of apple pomaces for biofuel production: a biorefinery approach. Biomass & Bioenergy, 142, 105785, https://doi.org/10.1016/j.biombioe.2020.105785 Impact factor 5.7; JCR Q1

V. Oliveira, C. Dias-Ferreira, I. González-García, J. Labrincha, C. Horta, M.C. García-González A novel approach for nutrients recovery from municipal waste as biofertilizers by combining electrodialytic and gas permeable membrane technologies. Waste Manag., 125, 293-302, https://doi.org/10.1016/j.wasman.2021.02.055 Impact factor 8.8; JCR Q1

TRAINING ACTIVITIES

These are the training activities carried out within the Doctorate in Agri-Food Science and Engineering and Biosystems program (University of Valladolid):

- "Information resources for PhD students";

- "Information Management: Bibliographic Managers and Bibliography";

These training activities included valuable information for database management and efficient forms of bibliographic search, writing and information management. Both were focused on the use of the resources made available to students by the Library of the University of Valladolid, with the aim of facilitating the doctoral students the task of finding and storing resources that will be used as references throughout the thesis. , and quoted at the time of final writing.

- "Guidance for the continuation of the research activity after the thesis." The main purpose of this training activity is to give doctoral students a perception of the options after finishing their doctorate; For those who are starting their doctorate, this activity can be very helpful to have a global vision of the options to be able to guide their research and training activities from the beginning of the thesis. This activity was recommended by the University of Valladolid. The activity ended with a colloquium in which the last-year doctoral students expressed their concerns and gave advice, something that can be very interesting for those who are starting their research.

COURSES

OpenLCA Life Cycle Assessment Course "Basic & Intermediate training" by GreenDelta, October 6-9, 2020

The training included the following modules:

•Module A1: Introduction to open LCA

•Module A2: Analysis and interpretation of results

•Module B1: Modeling with parameters and sensitivity analysis

•Module B2: End of life modeling

•Module B3: Assignment and expansion of the System

PRESENTATIONS AT INTERNATIONAL AND NATIONAL CONFERENCES, SYMPOSIUMS OR SEMINARS

International conference 9th International Conference on Sustainable Solid Waste Management

As first author: Poster "Apple pomace anaerobically co-digested with swine manure for organic waste valorization", June 15 - 18, 2022, Corfu, Greece. Authors: I. González-García, B. Riaño, B. Molinuevo-Salces, M.C. García-González. http://corfu2022.uest.gr/posters.html number 077

As co-author: Poster "Volatile fatty acid production from apple pomace via anaerobic digestion" June 15 - 18, 2022, Corfu, Greece. Authors: B. Riaño, B. Molinuevo-Salces, I. González-García, M.C. García-González. http://corfu2022.uest.gr/posters.html number 004

International online conference WORKSHOP Interreg Symbiosis II Project (POCTEP 0745_Symbiosis_II_3_E) – Oral presentation by doctoral student Isabel González García "Nutrient recovery in two phases from pig effluents using membrane technologies." Author: Isabel González García, December 21, 2021. 10:00-11:30h

International Congress online 8th International Conference on Sustainable Solid Waste Management, in Thessaloniki, June 25-25, 2021.

As first author, oral presentation by doctoral student Isabel González García of the communication "Two-phase nutrient recovery from swine manure using membrane technology". Authors of the communication: I. González-García, V. Oliveira, B. Molinuevo-Salces, B. Riaño, M.C. García-González, C. Dias-Ferreira. https://thessaloniki2021.uest.gr/proceedings.html hours: 15.15h-15.30h

As co-author Poster sessions “NH_3 recovery from digestate using gas-permeable membranes: Effect of wastewater pH”. Authors of the communication: B. Molinuevo-Salces, B. Riaño, D. Hernández, I. González-García, M. B. Vanotti, M. C. García-González. http://thessaloniki2021.uest.gr/posters.html number 100.

Red Remedia Workshop National Congress,

Poster-type communication by doctoral student Isabel González García, "Minimization of ammonia emissions by applying membrane technology with different acids", September 22 and 23, 2020 in Elche (Alicante, Spain). https://redremedia.org/project/workshop-2020/#resumenes “Libro de Actas”, section S2-22-P

Red Española de Compostaje. Webinars 2020. “Revalorización de subproductos de la industriade la sidra: efecto de la extracción de compuestos antioxidantes en la producción de biogás”: Authors: B. Riaño, B. Molinuevo Salces, S.Simal, C. Reche, I. González-García, M. C. García-González. http://www.compostandociencia.com/wp-content/uploads/2021/01/REC-CompostajeWebinars-2020.pdf page 47.

International Congress IWA RR 2019: Presentation of a poster “Ammonia Recovery By Gas-permeable Membranes Enhances Anaerobic Digestion Of Swine Manure”, Venice, Italy, September 8 – 12, 2019. Authors of the communication: Isabel González-García, Berta Riaño, Beatriz Molinuevo-Salces, M. C: Vanotti, María Cruz García-González.

https://water2return.eu/wp-content/uploads/2019/10/IWARR2019_Book-of-Abstracts-2.pdf page 528

X. PHOTOGRAPHIC ANNEX

Picture 1. Technological Agricultural Institute of Castilla y León (ITACyL; Valladolid, Spain).

Picture 2. ITACyL Residues Unit Laboratory.

Picture 3. Anaerobic digestion with nitrogen recovery set up for the first experiments (section VI.1).

Picture 4. Anaerobic reactors R1 and R2, this functioning with the membrane inside (section VI.1).

Picture 5. Anaerobic reactors R1 and R2 at the end of the experiments (membrane has been tainted due to organic materials) (section VI.1).

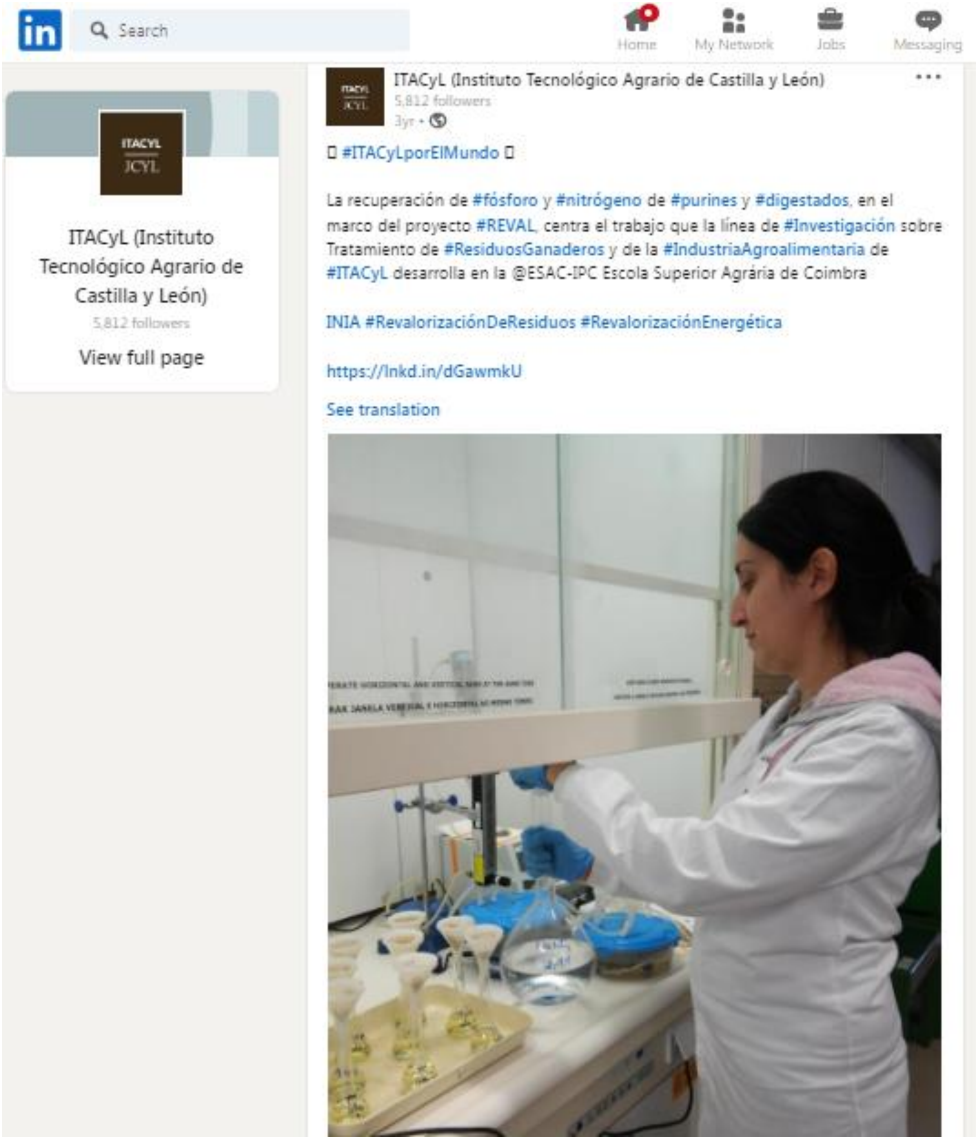
Picture 6. Anaerobic digestion process reactors (R1 and R2), fed with t
pomace and swine manure mix (section VI.2).

Picture 7. Apple pomace residues from the cider industry (section VI.2).

Picture 8. Nitrogen recovery phase from the obtained digestates (section VI.2).

Picture 9. Research Centre for Natural Resources, Environment and Society (CERNAS), at the Agrarian School of Coimbra (ESAC), Portugal.

Picture 10. CERNAS laboratory (section VI.3).



ITACyL (Instituto Tecnológico Agrario de Castilla y León)

▯ #ITACyLporElMundo ▯

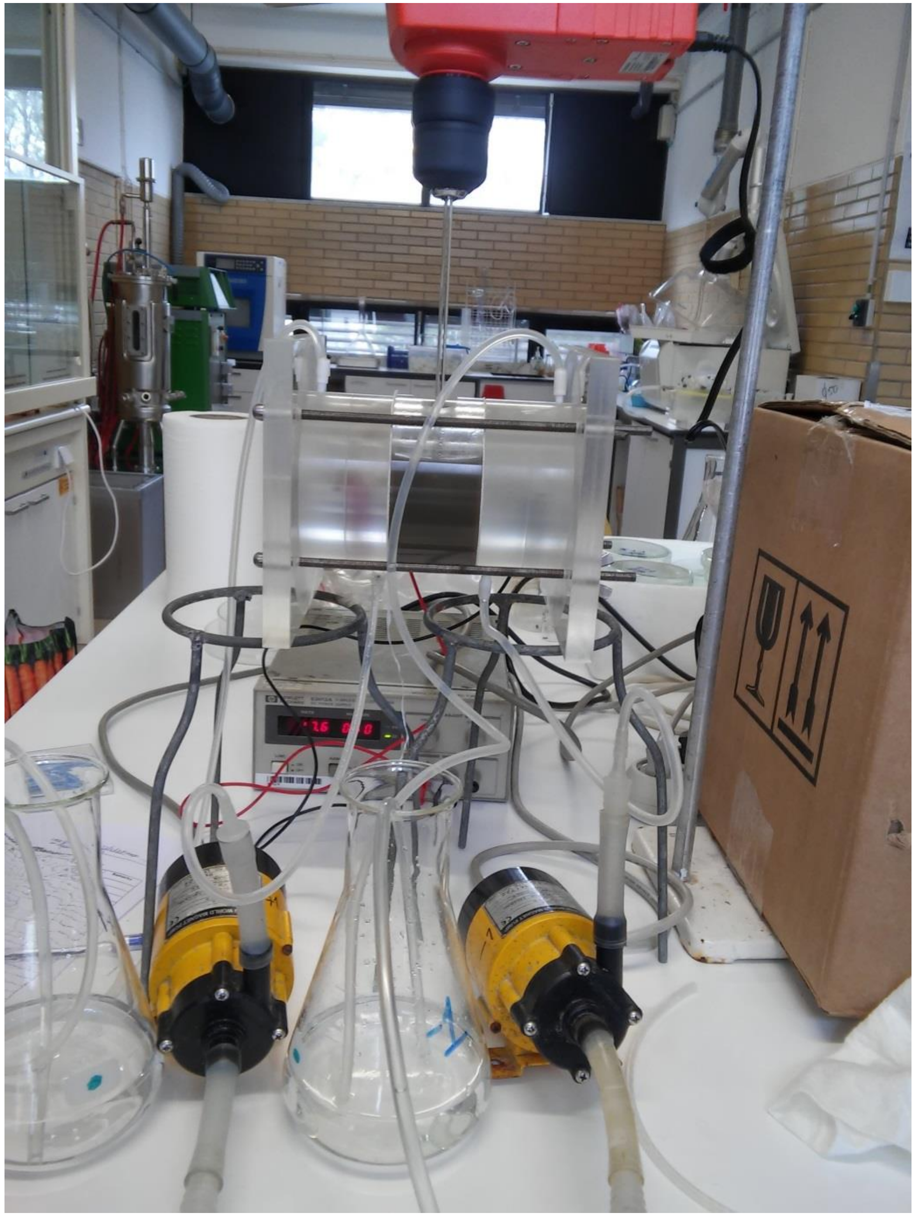
La recuperación de #fósforo y #nitrógeno de #purines y #digestados, en el marco del proyecto #REVAL, centra el trabajo que la línea de #Investigación sobre Tratamiento de #ResiduosGanaderos y de la #IndustriaAgroalimentaria de #ITACyL desarrolla en la @ESAC-IPC Escola Superior Agrária de Coimbra

INIA #RevalorizaciónDeResiduos #RevalorizaciónEnergética

https://lnkd.in/dGawmkU

See translation

Picture 11. N and P recovery experiments. ITACyL social media plan for international doctoral stay (section VI.3).



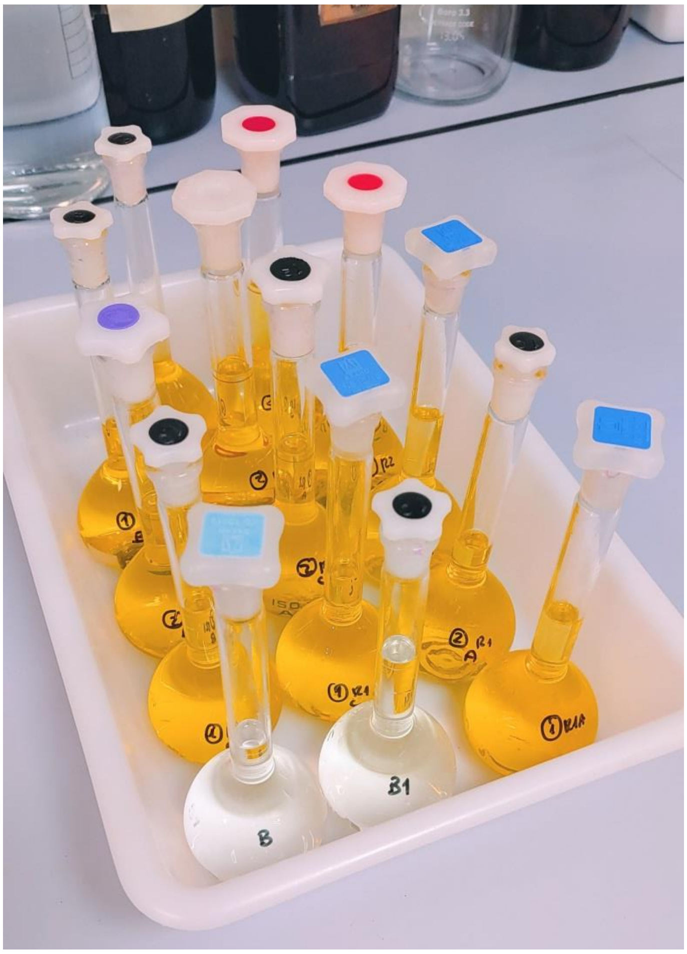
Picture 12. Nitrogen recovery phase with the GPM technology (section VI.3) (up).

Picture 13. P recovery with the ED process (right).

Picture 12. At the 9th International Conference on Sustainable Solid Waste Management, Corfú, Greece.

Picture 13. At the IWA 2019 Congress, Venice (Italy).

Picture 14. Simultaneous N and P recovery. Final experiments at ITACyL (section VI.4).



Picture 15. Analysis of phosphorus. Final P recovery experiments at ITACyL (section VI.4).

Picture 16. Final P recovery experiments at ITACyL (section VI.4).

Picture 17. Participating in the “3 Minutes Thesis” (3MT) contest.