PROGRAMA DE DOCTORADO EN INGENIERÍA QUÍMICA Y AMBIENTAL

TESIS DOCTORAL:

Optimization of Membrane Processes for the Recovery of NH$_3$ and Improvement in the Treatment of Agro-industrial Wastewater

Presentada por **Fanny Maritza Rivera Mejía**
para optar al grado de Doctora
por la Universidad de Valladolid

Dirigida por:
Dr. Antonio Hernández Giménez
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Memoria para optar al grado de Doctora,

con **Mención Doctorado Internacional**,

presentada por:

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Resumen

El cambio climático, impulsado principalmente por actividades humanas como la combustión de combustibles fósiles y la deforestación, presenta diversos desafíos para el medio ambiente, los ecosistemas naturales y la sociedad. Los aumentos previstos en la temperatura global, atribuidos principalmente a las emisiones antropogénicas de gases de efecto invernadero (GEI), representan amenazas como el aumento del nivel del mar, la intensificación de eventos climáticos extremos y el daño a la biodiversidad. Además, los impactos en la seguridad alimentaria y del agua, así como en la salud humana, empiezan a ser evidentes al día de hoy. Acciones urgentes en varios niveles de gobernanza son cruciales para abordar efectivamente estos impactos y alcanzar los objetivos climáticos. En este contexto, la substitución de combustibles fósiles por fuentes de energía renovable como el biogás, representa una ruta efectiva para la mitigación del cambio climático.

Aunque el amoniaco no es directamente un GEI, este compuesto desempeña un papel crucial en el ciclo del nitrógeno y a su vez representa un precursor de la formación de GEIs. Al descomponerse en la atmósfera, puede contribuir a la formación de partículas de aerosol que pueden afectar a la radiación solar y los patrones climáticos. El uso excesivo de fertilizantes que contienen amoniaco conlleva en último término la formación de N_2O, que es un GEI con un potencial de calentamiento global ~ 300 superior al del CO_2. El amoniaco emitido por la agricultura puede depositarse en los ecosistemas terrestres y acuáticos, alterando los ciclos bioquímicos y afectando la biodiversidad y la capacidad del suelo para almacenar carbono. Puede provocar eutrofización y acidificación del agua, exacerbando la contaminación del aire y los peligros para la salud. Por consiguiente, una gestión adecuada de las emisiones de amoníaco es importante para mitigar su impacto en el cambio climático y en el medio ambiente en general. En la actualidad, se están llevando a cabo esfuerzos para mitigar las emisiones de amoniaco, con acuerdos internacionales y directivas dirigidas a reducir su impacto ambiental y salvaguardar el bienestar humano.

El amoniaco también está presente en las aguas residuales provenientes de diversas actividades humanas. Estas aguas residuales conllevan riesgos ambientales y de salud pública si no se gestionan adecuadamente. Debido a la presencia de múltiples contaminantes a altas concentraciones, incluidos nutrientes y patógenos, el adecuado tratamiento de aguas residuales es esencial para proteger los cuerpos de agua. Las aguas

residuales municipales, industriales, agrícolas y ganaderas difieren en composición y flujos. Por su parte, las aguas residuales ganaderas, constituidas mayoritariamente por purines de cerdo, vaca y gallinaza, contienen altas concentraciones de materia orgánica y nutrientes. En la actualidad, existen varios procesos biológicos para el tratamiento de aguas residuales con alto contenido de materia orgánica y nutrientes a escala comercial, como los lodos activados, filtros percoladores, digestores anaerobios, etc. El proceso biológico más eficiente para la gestión adecuada de las aguas residuales ganaderas es la digestión anaerobia (DA) por su capacidad de biotransformar materia orgánica en biogás, aunque su capacidad para eliminar nutrientes es muy limitada. El biogás producido de la digestión anaerobia de aguas ganaderas es crucial para la sostenibilidad ambiental y la viabilidad económica de las granjas de animales, y para ayudar a mitigar el cambio climático. La DA es un proceso natural en el que los microorganismos descomponen la materia orgánica en ausencia de oxígeno, produciendo metano y dióxido de carbono, junto con un efluente rico en nutrientes llamado digestato. Sin embargo, las altas concentraciones de ciertos compuestos como el NH_3, que se encuentra presente en residuos orgánicos ricos en nitrógeno como los purines, pueden inhibir el proceso de DA. Esta inhibición afecta principalmente la actividad de los metanógenos, los microorganismos responsables de la producción de metano en la DA, lo que lleva a una disminución en la generación de biogás y de la eficiencia del proceso. Concentraciones elevadas de nitrógeno amoniacal total pueden exacerbar la inhibición, con niveles por encima de 400 mg NH_3-N L^{-1} causando problemas significativos. Las estrategias para mitigar la inhibición de NH_3 incluyen la extracción de nitrógeno amoniacal total de los digestores, con el objetivo de mejorar la productividad del biogás y la estabilidad general del proceso.

En las últimas décadas, la eliminación de NH_3 del agua potable y las aguas residuales se ha convertido en un punto focal en el sector del agua. Se han empleado diversas tecnologías para la eliminación de NH_3 durante el tratamiento de aguas residuales municipales, agrícolas, ganaderas e industriales, que abarcan procesos físicos, químicos y microbianos. Cada método tiene sus ventajas y desventajas, dependiendo de las condiciones específicas de tratamiento. Los enfoques biológicos, como la nitrificación-desnitrificación y la oxidación anaerobia de amonio (anammox), han sido investigados ampliamente y son tecnologías establecidas para la eliminación de nitrógeno. Mientras tanto, se proyecta que los métodos de tratamientos químicos y físicos alcanzarán una escala comercial para 2025 y 2031, respectivamente. Los métodos físicos permiten tanto la

eliminación como la recuperación de NH₃ de las aguas residuales. En este contexto, la implementación exitosa de métodos de separación es crucial para eliminar eficazmente el amoníaco de los efluentes generados por actividades domésticas, industriales, ganaderas y agrícolas, promoviendo así la utilización eficiente de recursos y avanzando en el marco de la economía circular.

La presente tesis evaluó el desempeño de la DA combinada con la tecnología de membranas permeables al gas amoniaco, con el objetivo de disponer de una plataforma tecnológica sostenible para extraer nitrógeno del purín de cerdo y gallinaza, reduciendo así las emisiones de NH₃ y proporcionando productos valiosos como fertilizantes y mayores productividades de biogás (como consecuencia de la disminución en la inhibición del proceso de DA por NH₃). La tecnología de membranas, conocida por su diseño compacto y bajo consumo de energía, está siendo cada vez más considerada para la recuperación de NH₃ de aguas residuales de alta carga debido a sus ventajas económicas, facilidad de operación y mayor sostenibilidad. Los contactores de membranas separan eficientemente el NH₃ del agua residual, requiriendo menos energía en comparación con los métodos tradicionales de eliminación de NH₃ como los procesos microbiológicos de nitrificación-desnitrificación, y permitiendo una extracción in-situ. Las membranas hidrofóbicas facilitan la transferencia de NH₃ hacia la fase líquida receptora, donde puede convertirse en fertilizantes comerciales como el sulfato de amonio. El uso de ácido sulfúrico en el proceso resulta en una captura eficiente de NH₃, produciendo fertilizantes de alta calidad. En general, la recuperación de NH₃ basada en membranas presenta un enfoque prometedor para el tratamiento sostenible de residuos y la recuperación de recursos.

Con esta finalidad, el primer objetivo de esta tesis se centró en recuperar NH₃ de digestatos anaerobios sintéticos y reales utilizando membranas planas hidrofóbicas con soluciones de H₂SO₄. Se investigó el impacto del material de la membrana, el caudal y el pH del digestato en la recuperación de NH₃. El proceso se operó a 35°C con una solución de H₂SO₄ de 1 M o 0.005 M en un lado de la membrana, y membranas de politetrafluoroetileno con un radio nominal de poro de 0.22 µm. Las recuperaciones de NH₃ de los digestatos sintéticos y reales fueron del 85% y del 72%, respectivamente, durante 3.5 horas con una solución de H₂SO₄ de 1 M y un flujo de recirculación de 0.030 m³ h⁻¹. La recuperación de NH₃ siguió una cinética de primer orden, siendo más rápida a pH y caudales más altos. El ensuciamiento provocó cambios en la morfología de la

membrana y en el tamaño de poro, confirmados por microscopía de fuerza atómica y porometría de desplazamiento de aire.

Posteriormente, se evaluó la influencia de los sólidos suspendidos y el pH en el purín de cerdo digerido anaeróbicamente en la extracción de NH_3 con membranas en ensayos en lote. El aumento del pH en el caldo de cultivo de 8 a 9 resultó en un aumento en las eficiencias de eliminación de NH_3 del 16% al 21%, independientemente de los sólidos suspendidos. También se evaluó la influencia de la extracción de NH_3 basada en membranas en el tratamiento anaerobio de aguas residuales porcinas en un reactor continuo de mezcla perfecta interconectado con un módulo de membrana de politetrafluoroetileno. La disminución de las concentraciones de nitrógeno total kjeldahl (NKT) inducida por la operación de la membrana provocó un aumento en el rendimiento de producción de CH_4 de 380 a 566 NmLCH$_4$ g VS alimentado^{-1}. Asimismo, las eficiencias de eliminación de demanda química de oxígeno (DQO) y sólidos volátiles (SV) aumentaron significativamente del 33 % y 26 % al 62 % y 38 %, respectivamente. Asimismo, la disminución en la concentración de NH_3 implicó una asimilación completa de ácidos grasos volátiles (AGV). A continuación, se investigó la mejora en el rendimiento de la extracción de amoníaco basada en membranas en el tratamiento de aguas residuales de purines. La extracción de amoníaco resultó en una disminución del nitrógeno amoniacal total en un 65% y del nitrógeno total en un 53%, lo que conllevó un aumento en los rendimientos de metano de 360 a 574 NmL CH$_4$ g VS alimentado $^{-1}$. Además, las eficiencias de eliminación de DQO y SV aumentaron del 59% y 57% al 79% y 66%, respectivamente. También se evaluaron los costes totales de recuperación de nitrógeno total amoniacal en una planta de digestión anaerobia de gallinaza acoplada con un sistema de extracción de amoníaco basado en membranas, basándose en datos de los experimentos a escala de laboratorio. Para una granja de 1.200 m^2 (13.400 cabezas de pollo) y un digestor de 150 m^3 de capacidad se recuperarían 5.475 kg año^{-1} de nitrógeno total amoniacal, obteniendo ganancias anuales de 54.000 € por la venta de biogás y 12.800 € por la de sulfato de amonio.

Finalmente, la investigación se centró en el estudio del impacto del pH del purín de cerdo (modificado mediante la adición de NaOH) en la recuperación de NH_3 y en el rendimiento de la digestión anaerobia utilizando un reactor continuo de mezcla perfecta acoplado con un módulo de extracción de membranas. Durante 360 días, el módulo de membranas redujo gradualmente la concentración de amoníaco total de 1.27 a 0.62 g L^{-1}.

Esta extracción provocó un aumento en el rendimiento de CH_4 de 1.3 veces, mientras que las eficiencias de eliminación de DQO y SV aumentaron hasta 1.2 y 1.5 veces, respectivamente, con el aumento del pH del purín de entrada de 7.5 a 12. Es importante destacar que las eficiencias de eliminación de AGV fueron mayores a un pH del purín de 9.

En general, la eficiencia de las plantas de DA a gran escala podría mejorarse mediante la reducción in-situ de las concentraciones de NH_3 con el uso de una unidad de extracción de membranas acoplada a los digestores, que también permitiría la recuperación de amoníaco. Esta tecnología innovadora tiene el potencial de contribuir a la producción de productos valiosos como el biometano como fuente de energía sostenible y el sulfato de amonio como fertilizante. El desarrollo de nuevos conceptos de biorrefinería para la gestión de residuos orgánicos, como los validados en esta tesis doctoral, son cruciales para garantizar un suministro efectivo de recursos y avanzar en el marco de la economía circular.

Abstract

Climate change, primarily driven by anthropogenic activities such as the combustion of fossil fuels and deforestation, presents various challenges for the environment, natural ecosystems, and society. Increases in global temperature, attributed mainly to anthropogenic emissions of greenhouse gases (GHGs), entail severe threats such as sea level rise, intensification of extreme weather events, and biodiversity loss. Additionally, impacts on food and water security, as well as human health, start to be evident nowadays. Hence, urgent actions at various governance levels are crucial to effectively address these impacts and achieve climate goals. In this context, the substitution of fossil fuels with renewable energy sources such as biogas represents an effective pathway for climate change mitigation.

Although ammonia is not directly a GHG, this compound plays a crucial role in the nitrogen cycle and also acts as a precursor of GHG formation. When NH_3 decomposes in the atmosphere, it can contribute to the formation of aerosol particles that can affect solar radiation and climate patterns. The excessive use of fertilizers containing ammonia ultimately leads to the formation of N_2O, which is a GHG with a global warming potential ~ 300 times higher than that of CO_2. Ammonia emitted by agriculture can deposit in terrestrial and aquatic ecosystems, altering biochemical cycles and affecting biodiversity and soil's ability to store carbon. Uncontrolled NH_3 emissions can also lead to eutrophication and acidification of water, exacerbating air pollution and health hazards. Therefore, proper management of ammonia emissions is important to mitigate its impact on climate change and the environment. Currently, efforts are underway to mitigate ammonia emissions, with international agreements and directives aimed at reducing their environmental impact and safeguarding human well-being.

Ammonia is also present in wastewater from various human activities. These wastewater streams cause environmental and public health risks if not managed properly. Due to the presence of multiple contaminants at high concentrations, including nutrients and pathogens, a proper wastewater treatment is essential to protect water bodies. Municipal, industrial, agricultural, and livestock wastewater differ in composition and flowrates. Livestock wastewater, primarily composed of pig, cow, and poultry manure, contains high concentrations of organic matter and nutrients. Currently, there are several

biological processes for treating wastewater with a high organic matter and nutrient content on a commercial scale, such as activated sludge, trickling filters, anaerobic digesters, etc. The most efficient biological process for a proper management of livestock wastewater is anaerobic digestion (AD) due to its ability to biotransform organic matter into biogas, although its capacity to remove nutrients is very limited. The biogas produced from anaerobic digestion of livestock wastewater is crucial for environmental sustainability and economic viability of animal farms, and for helping to mitigate climate change. AD is a natural process in which microorganisms break down organic matter in the absence of oxygen, producing methane and carbon dioxide, along with a nutrient-rich effluent called digestate. However, high concentrations of certain compounds such as NH_3, which is present in nitrogen-rich organic wastes like manures, can inhibit the AD process. This inhibition primarily affects the activity of methanogens, the microorganisms responsible for methane production in AD, leading to a decrease in biogas generation and process efficiency. High concentrations of total ammonia nitrogen can trigger inhibition, with levels above 400 mg NH_3-N L^{-1} causing significant problems. Strategies to mitigate NH_3 inhibition include the extraction of total ammonia nitrogen from digesters, aiming to improve biogas productivity and the overall process stability.

In recent decades, the removal of NH_3 from drinking water and wastewater has become a focal point in the water sector. Various technologies have been employed for NH_3 removal during the treatment of municipal, agricultural, livestock, and industrial wastewater, encompassing physical, chemical, and microbial processes. Each method has its advantages and disadvantages, depending on the specific treatment conditions. Biological approaches, such as nitrification-denitrification and anaerobic ammonium oxidation (anammox), have been widely investigated and are nowadays established technologies for nitrogen removal. On the other hand, it is projected that chemical and physical treatment methods will reach commercial scale by 2025 and 2031, respectively. Physical methods allow both NH_3 removal and recovery from wastewater. In this context, the successful implementation of separation methods is crucial for effectively removing ammonia from effluents generated by domestic, industrial, livestock, and agricultural activities, thereby promoting efficient resource utilization and advancing the framework of the circular economy.

This thesis evaluated the performance of AD combined with gas permeable membrane technology for ammonia extraction, aiming to provide a sustainable technological platform for nitrogen removal from swine and poultry manure. This approach reduces NH_3 emissions and provides valuable products such as fertilizers and higher biogas yields (as a result of the decreased inhibition of the AD process by NH_3). Gas-permeable membrane technology, known for its compact design and low energy consumption, is increasingly being considered for NH_3 recovery from high-strength wastewater due to its economic advantages, ease of operation, and greater sustainability. Membrane contactors efficiently separate NH_3 from wastewater, requiring less energy compared to traditional NH_3 removal methods like microbiological nitrification-denitrification processes, and allowing for in-situ extraction. Hydrophobic membranes facilitate the transfer of NH_3 to the receiving liquid phase, where it can be converted into commercial fertilizers such as ammonium sulfate. The use of sulfuric acid in the process results in an efficient NH_3 capture, producing high-quality fertilizers. Overall, membrane-based NH_3 recovery presents a promising approach for the sustainable treatment of waste and resource recovery.

With this purpose, the first objective of this thesis focused on recovering NH_3 from synthetic and real anaerobic digestates using hydrophobic flat membranes with H_2SO_4 solutions. The impact of membrane material, flow rate, and digestate pH on NH_3 recovery was investigated. The process was operated at 35°C with a 1 M or 0.005 M H_2SO_4 solution on one side of the membrane, and polytetrafluoroethylene membranes with a nominal pore radius of 0.22 μm. NH_3 recoveries from synthetic and real digestates accounted for 85% and 72%, respectively, over 3.5 hours with a 1 M H_2SO_4 solution and a recirculation flow rate of 0.030 m^3 h^{-1}. NH_3 recovery followed first-order kinetics, being faster at higher pH and flow rates. Fouling caused changes in membrane morphology and pore size, confirmed by atomic force microscopy and air displacement porometry.

Subsequently, the influence of suspended solids and pH in anaerobically digested swine manure (SM) on NH_3 extraction with membranes was evaluated in batch trials. Increasing the pH in the culture broth from 8 to 9 resulted in an increase in NH_3 removal efficiencies from 16% to 21%, regardless of suspended solids. The influence of membrane-based NH_3 extraction on anaerobic treatment of piggery wastewater was also evaluated in a continuously stirred tank reactor (CSTR) interconnected with a Polytetrafluoroethylene membrane module. The decrease in total Kjeldahl nitrogen (TKN) concentrations induced

by membrane operation led to an increase in methane production yield from 380 to 566 NmLCH4 g VS fed^{-1}. Additionally, chemical oxygen demand (COD) and volatile solids (VS) removal efficiencies increased significantly from 33% and 26% to 62% and 38%, respectively. In addition, the decrease in NH_3 concentration implied a complete assimilation of volatile fatty acids (VFAs). Next, the improvement in membrane-based ammonia extraction performance in manure wastewater treatment was investigated. Ammonia extraction resulted in a 65% decrease in total ammonia nitrogen and a 53% decrease in total nitrogen, leading to an increase in methane yields from 360 to 574 NmL CH_4 g VS fed^{-1}. Furthermore, COD and VS removal efficiencies increased from 59% and 57% to 79% and 66%, respectively. Total costs of total ammonia nitrogen recovery were also evaluated in a chicken manure anaerobic digestion plant coupled with a membrane-based ammonia extraction system, based on laboratory-scale experiment data. For a 1,200 m^2 plant (13,400 heads of chicken) and a 150 m^3 digester capacity, 5,475 kg year^{-1} of total ammonia nitrogen would be recovered, resulting in annual profits of €54,000 from biogas sales and €12,800 from ammonium sulfate sales.

Finally, the impact of pig slurry pH (modified by adding NaOH) on NH_3 recovery and anaerobic digestion performance using a CSTR coupled with a membrane extraction module was investigated in this thesis. Over 360 days, the membrane module gradually reduced the total ammonia concentration from 1.27 to 0.62 g L^{-1}. This extraction led to a 1.3-fold increase in CH_4 yield, while COD and VS removal efficiencies increased up to 1.2 and 1.5 times, respectively, with the increase in slurry pH from 7.5 to 12. It is important to stress that VFA removal efficiencies were higher at a slurry pH of 9.

Overall, the efficiency of large-scale AD plants could be improved by in-situ reduction of NH_3 concentrations using a membrane extraction unit coupled to digesters, which would also allow for ammonia recovery. This innovative technology has the potential to contribute to the production of valuable products such as biomethane as a sustainable energy source and ammonium sulfate as fertilizer. The development of new biorefinery concepts for organic waste management, as validated in this doctoral thesis, is crucial to ensuring effective resource supply and advancing the framework of the circular economy.

List of Publications

The following publications are presented as part of the current thesis. All papers were published in international journals indexed in ISI Web of Knowledge.

1. **F. Rivera**, R. Muñoz, P. Prádanos, A. Hernández, L. Palacio, A Systematic Study of Ammonia Recovery from Anaerobic Digestate Using Membrane-Based Separation, Membranes (Basel). 12 (2022) 19. https://doi.org/10.3390/membranes12010019

2. **F. Rivera**, L. Villareal, P. Prádanos, A. Hernández, L. Palacio, R. Muñoz, Enhancement of swine manure anaerobic digestion using membrane-based NH_3 extraction, Bioresour. Technol. 362 (2022) 127829. https://doi.org/10.1016/j.biortech.2022.127829

3. **F. Rivera**; Joseph Akpan; Pedro Prádanos; Antonio Hernández; Laura Palacio; Raúl Muñoz, Side-stream membrane-based NH_3 extraction to improve the anaerobic digestion of poultry manure, J. Water Process Eng. 54 (2023)103990. https://doi.org/10.1016/j.jwpe.2023.103990

4. **F. Rivera**, Cristian A. Sepúlveda-Muñoz, P. Prádanos, A. Hernández, L. Palacio, R. Muñoz, Influence of pH on the performance of anaerobic piggery wastewater treatment coupled with membrane-based NH_3 extraction, J. Water Process Eng. 55 (2023)104226. https://doi.org/10.1016/j.jwpe.2023.104226

Contribution to the papers included in the thesis

1. In this work, I was responsible for the design, start-up, operation of the experimental set-up, results evaluation and preparation of the manuscript under the supervision of Dr. Laura Palacio, Dr. Pedro Prádanos, Dr. Antonio Hernández and Dr. Raúl Muñoz.

2. In this research, I was responsible for the design, start-up and operation of the experimental set-up in collaboration with Luis Villarreal and under the supervision of Dr. Raúl Muñoz. I performed the results evaluation and the preparation of the manuscript in collaboration with Dr. Raúl Muñoz, Dr. Pedro Prádanos, Dr. Antonio Hernández and Dr. Laura Palacio.

3. In this work, I was responsible for the design, start-up and operation of the experimental set-up in collaboration with Joseph Akpan and under the supervision of Dr. Raúl Muñoz. I performed the results evaluation and the preparation of the manuscript in collaboration with Dr. Raúl Muñoz, Dr. Pedro Prádanos, Dr. Antonio Hernández and Dr. Laura Palacio.

4. In this research, I was responsible for the design, start-up and operation of the experimental set-up in collaboration with Cristian Sepúlveda and under the supervision of Dr. Raúl Muñoz. I performed the results evaluation and the preparation of the manuscript in collaboration with Dr. Raúl Muñoz, Dr. Pedro Prádanos, Dr. Antonio Hernández and Dr. Laura Palacio.

Chapter 1

Introduction

1.1.   The threat of climate change

One of the most important environmental issues that humanity is facing in this twenty-first century is climate change. The Earth's climate is changing rapidly mainly due to human activities such as the combustion of fossil fuels, deforestation, and industrial processes. Multiple challenges to the environment, ecosystems and human society will be caused by climate change in the next decades. As a result of the increasing greenhouse gas emissions (GHG) into the atmosphere, which prevent heat from escaping the Earth, global warming is predicted to cause a rise of 1.5 °C in the Earth temperature between 2030 and 2052. The latest report of the IPPC (Chevuturi et al., 2022) revealed that, on average, a 1.5 ℃ increase in global temperature is predicted during the next 20 years. This report also confirmed that anthropogenic GHG were the primary cause of the roughly 1.1 ℃ warming observed 2000 at a global scale (**Fig. 1**).
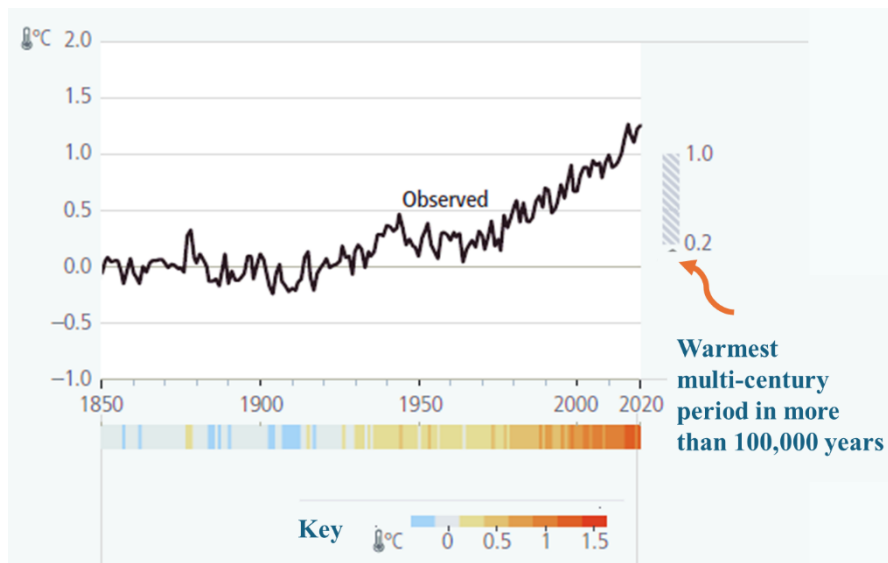
Fig. 1. Time course of the global surface temperature. Adapted from (Chevuturi et al., 2022).

The most important GHG is carbon dioxide (CO_2). CO_2 is emitted by burning fossil fuels and by deforestation, among other processes, and naturally by respiration and volcanic eruptions. CO_2 accounts for 76% of global GHG and is used as a proxy for global warming potential (GWP) (IPPC, 2015). Methane (CH_4) is the second most relevant GHG, with a GWP 23 times greater than that of CO_2. Anthropogenic processes including intensive farming, natural gas processing, ruminant farming, and waste treatment emit CH_4, a hydrocarbon that is also naturally produced from the fermentation of organic materials

Chapter 1

(Shine et al., 2005). The chemical industry and intensive agriculture emit nitrous oxide (N_2O), which has a GWP 296 times higher than carbon dioxide and accounts for 6% of all GHG emissions (Shine et al., 2005).

The rise in global sea levels is one of the most obvious and physically distressing effects of climate change. This phenomenon is caused by the melting of glaciers and polar ice caps as well as the thermal expansion of saltwater. Islands that are low lying and coastal are more susceptible to erosion and flooding. The homes and livelihoods of millions of people might be threatened by sea level rise by several feet by the end of the century if current trends continue, according to the IPCC (IPCC, 2021). Hurricanes, droughts, floods, and heatwaves are among the extreme weather events that are becoming more frequent and severe due to climate change. Rising GHG concentrations cause the Earth's atmosphere to become more energetic, which intensifies storms and modify conventional weather patterns. In addition, ecosystems and biodiversity are also seriously threatened by climate change. Natural environments can be disturbed by changes in temperature, precipitation patterns, and sea levels, which can exert a negative impact on the distribution and behavior of plant and animal species. Many species are finding it difficult to move or adapt, which might result in extinctions and a loss of ecological resilience. This is according to the Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services (IPBES), which issues warnings about the alarming rates of biodiversity loss (IPBES, 2019). Global food and water security are also significantly impacted by climate change. Variations in temperature and precipitation directly affect agricultural production, change the length of the growing season, and make pests and illnesses more common. The supply of water for millions of people who rely on glacial meltwater for agriculture and drinking water is impacted by rising temperatures, which also contribute to the melting of mountain glaciers. According to World Bank projections, if appropriate adaptation measures are not immediately taken, the effects of climate change on agriculture might result in a decrease in global food output, endangering the food security of vulnerable populations (Atwoli et al., 2021). Human health is also under risk, both directly and indirectly, from the changing climate. Increased temperatures during heatwaves can worsen heat-related ailments and even cause death. Climate change is also associated with shifts in the distribution of infectious diseases, including vector-borne illnesses like dengue fever and malaria. Furthermore, extreme weather might interfere with the infrastructure and services provided by the healthcare system, making it more difficult to handle medical crises. Particularly at

danger are vulnerable groups, such as the elderly and those with underlying medical concerns (Sanderson et al., 2017; Son et al., 2019).

Evaluating the impact of the policies and activities of regional, national and local authorities and municipalities is crucial because of their significant role as decision-makers and players in achieving global climate change mitigation objectives (Azevedo and Leal, 2017). Governments and communities have been progressively realizing the significance of local energy and climate policy over the last few years.

1.2.   Wastewaters as a promising resource for energy and water generation

The term wastewater typically refers to a water that has been utilized and polluted by a variety of human activities, such as household, industrial, and agricultural operations. Wastewaters entail a complex combination of several contaminants, including nutrients, pathogens, suspended particles, and organic and inorganic substances. To safeguard the environment, public health, and water supplies, wastewater must be managed and treated properly before discharge to natural water bodies (Tchobanoglous et al., 2014). In recent years, wastewater generation has grown alarmingly, raising serious concerns for the environment and human health at a global scale. Untreated wastewater discharge into groundwater or surface bodies of water is illegal and can also hasten the onset of waterborne illnesses (Philipp et al., 2021; Singh, 2021). Rising quality of life, industrialization, and fast population increase are some of the causes underlying this increase in the volume of wastewater (Feng et al., 2009). **Table 1** shows the most important contaminants in wastewater. Color, turbidity, temperature, and odor are also significant physical properties that originally helps characterizing the quality of a wastewater (Muralikrishna and Manickam, 2017).

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Table 1. Key contaminants in the treatment of wastewater. Adapted from (Muralikrishna and Manickam, 2017).

Contaminants	Reason for importance
Suspended Solids	Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged in the aquatic environment.
Nutrients	Both nitrogen and phosphate, along with carbon, are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatic life. When discharged in excessive amounts on land, they can also lead to the pollution of groundwater.
Priority pollutants	Organic and inorganic compounds selected based on their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. Many of these compounds are found in wastewater.
Refractory organics	These organics tend to resist conventional methods of wastewater treatment. Typical examples include surfactants, phenols, and agricultural pesticides.
Heavy Metals	Heavy metals are usually discharged to wastewater from commercial and industrial activities and must be removed if the wastewater is to be reused.
Dissolved organics	Inorganic constituents such as calcium, sodium, and sulfate are added to the original domestic water supply because of water use and may have to be removed if the wastewater is to be reused.

Wastewaters are typically characterized into three main categories as a function of their origin: municipal, industrial, and agricultural and farm wastewater. The most common contaminants found in municipal wastewater include suspended solids, a variety of heavy metals, salts, biochemical oxygen demand (BOD), various hydrocarbons (including those found in medications and personal hygiene products), and coliforms. Due to the dynamic nature of municipal wastewater generation, which often exceeds the capacity of typical treatment systems, these systems must be robust enough to handle extremely changing water budgets and quality requirements (Kataki et al., 2021). Municipal wastewater typically has the following composition: total phosphorous (TP): $6 - 20$ mg L^{-1}, BOD: $100 - 800$ mg L^{-1}, chemical oxygen demand (COD): $200\text{-}100$ mg L^{-1}, total suspended solids (TSS): $100 - 350$ mg L^{-1}, total dissolved solids (TDS): $350 - 1200$ mg L^{-1}, total nitrogen (TN): $20 - 85$ mg L^{-1}, and ammoniacal nitrogen (NH$_4^+$-N): $10 - 60$ mg L^{-1} (FAO, 2020).

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In contrast to the generally uniform content of municipal wastewaters, the composition of industrial effluents varies greatly, exhibiting various degrees of toxicity and biodegradability (Skrzypiecbcef and Gajewskaad, 2017). The primary characteristics of industrial wastewater are high organic loads, high acidity or alkalinity, color, turbidity, nutrient loads, TSS, salts, colloids, and particular hazardous pollutants (Wu et al., 2015). Examples of industrial wastewater are effluents from leather tanning (pH: 9, TN/NH_4 - N: 119 – 1076 mg L^{-1}, TP/PO_4 – P: 2.5 – 8), potato processing effluents (pH: 8.5 – 8.7, TN/NH_4 - N: 208 – 426 mg L^{-1}, TP/PO_4 – P: 43 - 127), yeast industry (pH: 9.5, TN/NH_4 - N: 161 mg L^{-1}, TP/PO_4 – P: 17.4), etc. (Saliu and Oladoja, 2021). Industrial wastewater, such as that from rice wine distillery, can reach COD values of up to 82,000 mg COD L^{-1} (Ling et al., 2016). On the other hand, agricultural wastewater contains pathogens, fats, oils, grease, total solids (TS), nitrogen, phosphorous, organic matter, pesticides and herbicides (Kataki et al., 2021). Agricultural wastewater is mainly composed of TN/NH_4 - N: 251.6 ± 30 mg L^{-1}, TP/PO_4 – P: 96.3 ± 30 and exhibit a neutral pH (Saliu and Oladoja, 2021).

Livestock wastewaters from pig, cow and chicken farming are considered agricultural wastewaters. Swine manure (SM) is composed of pig feces and urine, mixed with rainwater, farm cleaning water, water troughs, and leftover food. A SM composition of 50-55 g COD L^{-1}, 1.60 - 1.62 g NH_3 L^{-1}, 4.2 - 5.5 g TKN L^{-1}, 28 - 32 g TS L^{-1}, 20 – 23 g VS L^{-1} and pH 7.5 – 7.6 is typically reported after screening (Rivera et al., 2022b). CH_4 and N_2O, two potent GHGs are also abundantly found in slurry emissions (Kavanagh et al., 2019). On the other hand, Poultry manure (PM) is an organic waste product made up of the feces and urine of poultry species, such as chickens. With an average weight of 1,810 g per bird, 20,000 tons of PM are produced annually for every 100,000 birds worldwide (Ashworth et al., 2020). Rivera et al. (2023a), reported a PM composition of 30 - 34 g COD L^{-1}, 0.6 – 0.8 g TAN L^{-1}, 30 - 33 g TS L^{-1}, 20 - 23 g VS L^{-1}, with a pH of 7.3-7.5. PM is rich in nitrogen, phosphorus, potassium, and other essential nutrients. Poultry farming accounted for 8–9% of agricultural emissions, with agriculture representing 9.9% of EU GHG emissions (Leip et al., 2010). Nevertheless, in terms of both overall emissions and emissions per kilogram of manure, the GHG linked to the production of pigs and ruminants are higher than those of poultry agriculture (Leip et al., 2010).The disposal and storage of SM and PM are nowadays strictly regulated in most international regulations. To reduce

waste and recover bioenergy and nutrients, cost-effective treatment techniques for large volumes of livestock wastewaters should be developed (Zhou et al., 2016).

Preventing environmental contamination and managing agricultural wastewaters in a cost-effective manner without compromising the economic viability of the farm is a challenge. There is a need to find alternatives of treatment and recovery of the material and energy resources contained in these wastewaters (Sońta et al., 2020). In this context, the most common technological approach to sustainably treat agricultural wastewaters (eventually in combination with other organic wastes) is based on anaerobic digestion (AD), which produces biogas (mostly CH_4 and CO_2) and a liquid effluent namely digestate (Sońta et al., 2020). When oxygen and nitrate/nitrite are absent in the bioreactor, AD facilitates the biological conversion of residual organic waste into a methane-rich biogas and a nutrient-rich digestate (Reyes et al., 2015). Biogas is a sustainable gaseous energy vector with the potential to replace fossil fuels in transportation and natural gas in gas grids, which will help mitigating climate change and enhance the long term economic viability of the farm (after upgrading) (Andriani et al., 2014; Kang et al., 2020).

1.3.   Recovery of ammonia
1.3.1. Ammonia as a pollutant

Ammonia (NH_3) is a gas consisting of one nitrogen atom covalently bonded to three hydrogen atoms. It has no color and emits a distinct sharp smell, easily dissolving in water. With vital roles in biological functions, NH_3 is widely applied in industry, agriculture, and household items. Crucial in manufacturing fertilizers, explosives, and cleaning products, ammonia is also naturally generated through organic matter decay and nitrogen compound metabolism. NH_3 is a crucial gas for atmospheric chemistry, air-surface exchange mechanisms, and environmental impacts (Erisman et al., 2007). Its environmental presence holds significant implications for ecosystems and human well-being. Nitrogen is naturally produced via biofixation of atmospheric N_2 by cyanobacteria and *Rhizobium* bacteria living in symbiosis with plants. NH_3 emissions may increase crop productivity in regions with low nitrogen levels, but in locations with a high nitrogen availability, these emissions may have negative effects on the ecosystem. In this context, atmospheric depositions of NH_3, or the unproper management of animal manures and crop residues contribute to the

pernicious release of nitrogen to the environment. On the other hand, the Haber-Bosch process synthesizes NH_3 in industry via N_2 fixation (Vaclav, 1999). This industrial process is powered by coal or CH_4, using massive amounts of energy and producing over half of the world's total hydrogen (~ 3.6 million tons) (Ashik et al., 2015). When NH_3 is carried by rain, it can boost the eutrophication and acidification of water bodies, forming particles that pose risks to human health when mixed with other pollutants in the air (Erisman et al., 2007; Kavanagh et al., 2019). Indeed, NH_3 emissions play a key role in fine particulate matter ($PM_{2.5}$) pollution by chemically generating particulate ammonium sulfate and ammonium nitrate, leading to tens of thousands of annual deaths. Agricultural sources, including ammonia-based fertilizers and animal manure, contribute to nearly 90% of global NH_3 emissions (Ma et al., 2021). Hence, 54 Mt of N-ammonia are emitted globally, with anthropogenic sources responsible for about 60% of the world's NH_3 emissions (Asman et al., 1998). In addition, NH_3 emissions are atmospheric precursors of N_2O, a potent GHG that can cause lung disorders and cancer (Temkin et al., 2019).

NH_3 has a wide range of negative impacts on the environment. Indeed, uncontrolled ammonia release is becoming a global problem that requires international agreements for its mitigation. An integrated strategy that focuses on reducing reactive nitrogen production and/or concentrating nitrogen in intensive agricultural regions is required due to the cascade of reduced nitrogen (such as ammonia, ammonium and amines) through the agricultural system and the environment (Erisman et al., 2007). The United States, European Union, and China have set discharge standards for ammonia nitrogen into surface water of 17 mg L^{-1}, 1.5 –10 mg L^{-1}, and 1.5 – 5 mg L^{-1}, respectively (Chen et al., 2021). In fact, NH_3 emissions will be required to be reduced by up to 3% between 2020 and 2029, and by up to 16% from 2030 onwards under the European Directive 2016/2284 (European Parliament & Council, 2016).

1.3.2. Limitations of NH_3 in the anaerobic digestion process

AD is a natural process in which microorganisms decompose organic materials like animal manure, food scraps, or sewage in the absence of oxygen. This enzymatic breakdown results in the production of biogas, mainly composed of methane and carbon dioxide, as well as a nutrient-rich byproduct known as digestate. AD serves various purposes including waste management, renewable energy generation, and nutrient reuse

(Nkoa, 2014). The low biomass yields of the microbial communities involved in AD typically support a poor nutrient removal. An extensive list of chemicals has been documented to inhibit the microbiological processes involved in AD. An undesirable suppression of bacterial or archaeal growth, or negative modification of microbial metabolisms are two examples of scenarios when a substance is considered inhibitory. In this context, high levels of ammonia, often found in systems treating nitrogen-rich organic waste such as animal manure, can hinder anaerobic digestion. This inhibition affects the activity of methanogens, the microorganisms responsible for methane production in anaerobic digestion, leading to decreased biogas generation and a lower overall process efficiency (Hansen et al., 1998). Lower steady-state rates of CH_4 generation and the buildup of organic acids concentration typically occur during inhibition of the AD process (Kroeker et al., 1979). Methane-forming and acid-forming microbes in AD exhibit very different physiologies, dietary requirements, growth kinetics, and mechanisms of adaptation to the environment (Pohland and Ghosh, 1971), which hinders the achievement of robust balances between both groups of microorganisms and ultimately causes reactor instability (Demirel and Yenigün, 2002).

NH_3 mediated inhibition increases at high pH levels and total ammoniacal nitrogen (TAN) concentrations (Liu and Sung, 2002; Procházka et al., 2012). In this context, concentrations of TAN ranging from 1,700 to 14,000 mg N L^{-1} might result in a 50% decrease in CH_4 production during AD. Similarly, concentrations higher than 400 mg NH_3 - N L $^{-1}$ cause inhibition problems during AD (Chen et al., 2008; Hendriksen and Ahring, 1991; Liu and Sung, 2002; Procházka et al., 2012). The most vulnerable microbes to NH_3 toxicity are methanogens (Chen et al., 2008). Ammonia inhibition also leads to the accumulation of volatile fatty acids (VFA), especially propionate, which can trigger inhibition, create instability in the process, and decrease CH_4 productivities (Banks et al., 2012). This build-up of VFA can lead to the acidification of the process (Siegert and Banks, 2005), which ultimately results in process failure. Therefore, TAN extraction from anaerobic broths in digesters might help to partially reduce this inhibition, increase the biogas productivities, and boost the recovery of nitrogen.

1.3.3. Current technologies used for ammonia treatment in wastewater

In the last several decades, ammonia removal from water and wastewater has attracted significant attention in the water sector. Multiple methods have been used to remove ammonia during the treatment of municipal, agricultural, and industrial wastewaters, including physical processes (membrane separation, ion exchange, physical adsorption, air stripping, microwave radiation, and electrokinetics), chemical processes (chlorination, advanced oxidation, and chemical precipitation), and microbial processes (nitrification–denitrification, and anammox). All technologies exhibit advantages and disadvantages depending on the specific treatment conditions (Ronan et al., 2021). Huang et al. (2018) described the advantages and disadvantages of the main methods for ammonia recovery and removal (**Table 2**). Biological approaches have been extensively studied and are well-established technologies for nitrogen removal, whereas chemical and physical treatment methods are anticipated to reach full commercialization by 2025 and 2031, respectively. In this context, physical methods hold significant promise for both ammonia removal and recovery.

The successful removal of ammonia from waste effluents generated by domestic, industrial, and agricultural activities hinges on the implementation of source-separation methods. These methods are vital for ensuring efficient resource supply and advancing the future circular economy framework.

**Table 2.** Summary of most ammonium removal technologies in wastewaters. Adapted from (Huang et al., 2018).

Removal technologies	Removal efficiency	Advantages	Disadvantages	References
Biological method	70% – 95%	Most used method. Effectively remove ammonium.	High costs. Require specific temperature and climate conditions. High energy use. High risk during subsequent processes. High ammonium concentration after treatment.	(Bernet et al., 2000; Feng et al., 2012; Tahir and Everest, 2016; Thornton et al., 2007)
Air stripping	50% – 90%	Commonly used process for wastewater pre-treatment. Simple equipment. Not sensitive to toxic substances.	Require certain pH, temperature, and flow rate. Require large stripping towers. Time consuming process. High energy consuming. Scaling and fouling on packings.	(Guštin and Marinšek-Logar, 2011; Huang et al., 2015; P. H. Liao, 1995)
Ion Exchange and adsorption	80% – 95%	Easy operation. Effectively remove ammonium. Low cost Relatively low Total dissolved solids effluent.	Certain pH ranges. Different adsorbents have different removal efficiencies. Require waste brine disposal.	(Marañón et al., 2006; Mazloomi and Jalali, 2016; Uurlu and Karaolu, 2011; Widiastuti et al., 2011)
Microwave radiation	80% aprox.	Medium cost. Suitable for high ammonium concentrations.	Affect by pH and radiation time, initial ammonia concentration and aeration. Evaporation of NH_3. Difficult for full scale application.	(Lin et al., 2009; Quan et al., 2004)
Chemical precipitation	20% – 30%	A valuable slow-release fertilizer. Medium cost. Reduce the amount of sludge and maintenance costs.	Require certain pH and temperature. Affect by chemical position and other ions. Introduce new pollutants.	(Chen et al., 2016; Huang et al., 2015; Uludag-Demirer et al., 2005; T. Zhang et al., 2011)
Oxidation and breakpoint chlorination	80% – 95%	Rapid destruction of organic wastes. Produce water, carbon dioxide and molecular nitrogen.	High cost. Affect by temperature and excess oxygen. Salt precipitation. High chlorine consumption under high organic matter.	(Bermejo et al., 2008; Du et al., 2013; Pressley et al., 1972)

1.3.3.1. Physical Processes
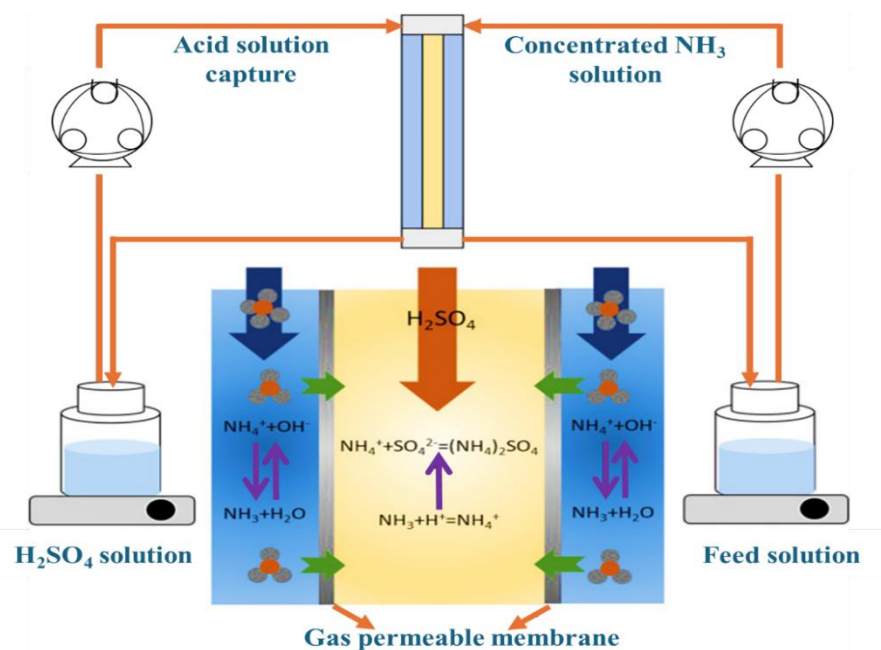
1.3.3.1.1. Membrane contactors

Membrane contactors are identified by their hollow fibers manufactured from hydrophobic and gas-permeable materials through which gas molecules can pass (Tan et al., 2006). Hollow fiber membrane contactors are characterized by their tiny pore size (<0.3 mm), thin walls (<1 mm), narrowed internal diameters (<1 mm), and large volumentric contact areas. They are frequently assembled with physically resistant tube shells that reduce space requirements and secure the membranes (Mandowara and Bhattacharya, 2011). The persistent fouling that typically tears membranes represents the main disadvantage of membrane technology. The partial pressure differential of ammonia gas on either side of the membranes, which supports the chemical potential promoting NH_3 separation, is the main mechanism of ammonia treatment applying membrane materials (Ulbricht et al., 2013). NH_3 extraction from wastewater can benefit from this mass transfer, which is generated by the difference in concentration and vapor pressure across the membrane (Klaassen and Jansen, 2001). Optimal membrane materials induce common acid ions, such SO_4^{-2}, to pass through to the lumen side, where they combine with ammonia gas to create ammonium sulfate as shown in **Fig. 2** (Darestani et al., 2017). Ammonia removal and recovery are conducted using hydrophobic polymer membranes made of polyethylene (PE) (Ashrafizadeh and Khorasani, 2010), polypropylene (PP) (Hasanoĝlu et al., 2010), polyvinylidene fluoride (PVDF) (Tan et al., 2006), or polytetrafluoroethylene (PTFE) (Ahn et al., 2011; Rivera et al., 2022a). In this process, the ammonium-ammonia equilibrium on the shell side is unbalanced, and ammonium ions in the wastewater side often dissociate into protons and ammonia gas, which moves through the hydrophobic membrane (Wäeger-Baumann and Fuchs, 2012).
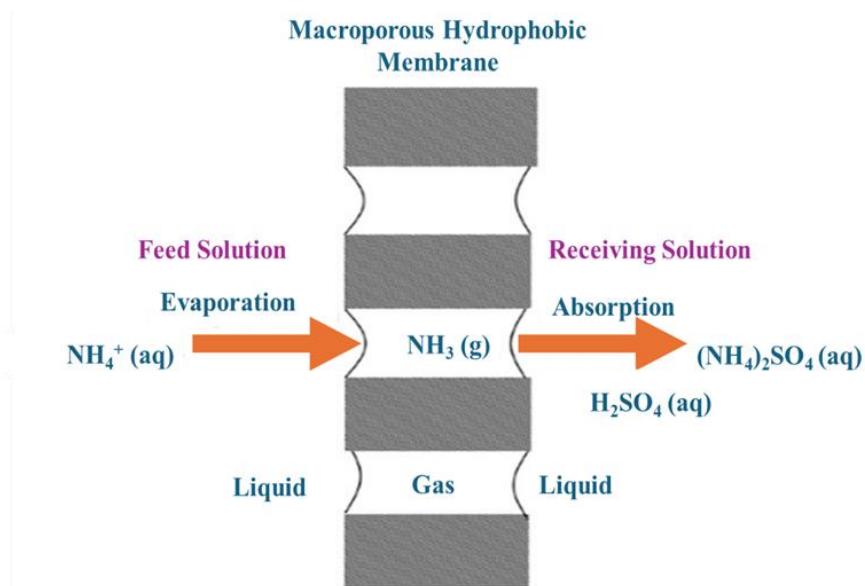
Fig. 2. Principle of ammonia separation with membrane contactors. Adapted from (Hasanoĝlu et al., 2010).

The setup of batch membrane contactors for ammonia recovery is shown in **Fig. 3**. The feed solution (a wastewater containing ammonia) and the acid solution (e.g. H_2SO_4) are recirculated through the membrane contactor. Sulfate ions react with ammonium ions that are passing through the membrane and $(NH_4)_2SO_4$ is produced. Membrane contactors are an excellent option with a low fouling and no post-effluent needs. Their application for ammonia removal is comparable to other stripping procedures in terms of gas-liquid interface, mass transfer, selective removal, and application flexibility. The larger contact surface area of membrane contactors at the gas-liquid interface compared to traditional air stripping entails a significantly higher mass transfer efficiency (Ahn et al., 2011). Alkali chemicals might be required for maintaining the driving force of separation and regulating the pH of the solution. Most wastewater exhibit a pH ranging from 6 to 8, which limits NH_3 recovery. Chemical addition for pH regulation in membrane contactors may be expensive, but need if high NH_3 extraction efficiencies are requested. In brief, membrane contactor technology is a valuable method for ammonia removal and recovery, and it may find commercial applications. The removal of dissolved CO_2 from digesters can be combined with membrane ammonia stripping to raise pH and, as a result, ammonia separation (Yang et al., 2017).

Fig. 3. Ammonia recovery from wastewater using a membrane contactor. Adapted from (Chen et al., 2021).
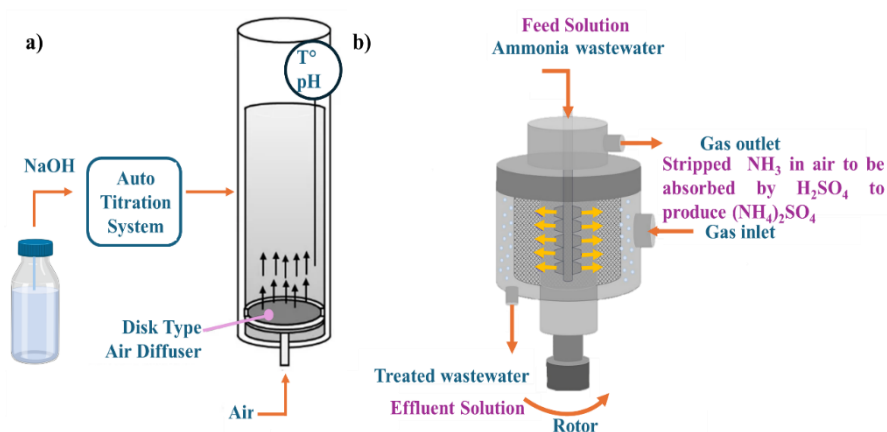
1.3.3.1.2. Air stripping

For the recovery of ammonia from wastewater containing high nitrogen concentrations, ammonia stripping is an exceptionally successful method (Bonmatí and Flotats, 2003; Vaddella et al., 2013). Ammoniacal nitrogen is extracted as a gas in an ammonia stripping system by feeding a gas, such as steam or air as shown in **Fig. 4** (Bonmatí and Flotats, 2003; Jia et al., 2017; Vaddella et al., 2013; Zeng et al., 2006). Typically, the reactor is a packed bed tower or fixed-bed column to boost the contact between the gas and liquid phases (**Fig. 5a,b**) (Bonmatí and Flotats, 2003; Jia et al., 2017; Vaddella et al., 2013; Zeng et al., 2006). Ammonia mass transfer in tower-type reactors is accomplished via gas-liquid interaction inside the packing material (Kinidi et al., 2018). In order to optimize the working conditions of packed towers, a systematic evaluation of the liquid-gas ratio is necessary (Kim et al., 2021). Conventional ammonia stripping procedures are normally carried out in the pH range of 10 –12 and at a temperature between room temperature and 50 °C (Guštin and Marinšek-Logar, 2011; Kim et al., 2021; Liu et al., 2015; Zhu et al., 2017). To adjust the pH in these processes, significant amounts of chemicals are needed (Guštin and Marinšek-Logar, 2011; Jiang et al., 2014). A basic reagent is used to raise the pH during ammonia stripping and for wastewater treatment and disposal, the pH needs to be brought to neutral once ammonia has been removed. High-temperature stripping is a technique that can help to cut down the dosage of chemicals required, since it can

accomplish the same removal effectiveness at a higher temperature using less reagents (Jiang et al., 2014). Despite the challenge of the availability of low-cost heat for high-temperature stripping, waste heat can help reducing the amount of heat energy required. For instance, the temperature of the hydrothermal carbonization (HTC) reaction ranges from 180 to 260 °C. By supplying HTC heat, the wastewater may be heated to a temperature of 70 to 80 °C (Escala et al., 2013; Wang et al., 2018). Furthermore, the high-temperature operation may be run at a lower cost by reducing the air supply (Jia et al., 2017).
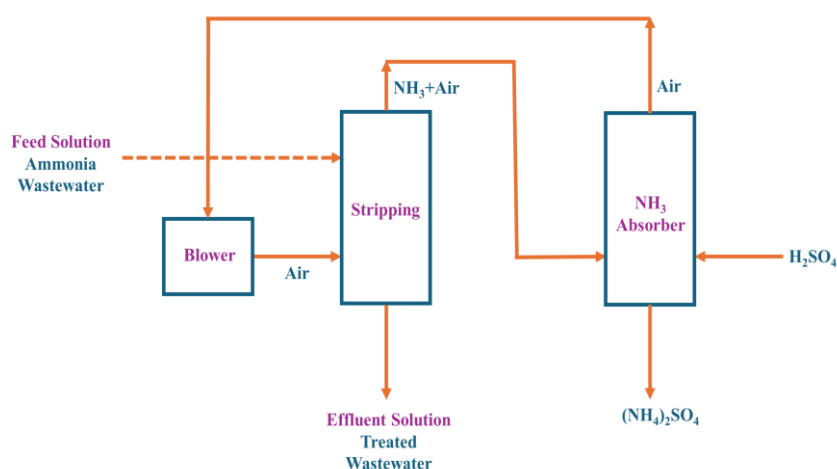
Fig. 4. Principle of ammonia separation by ammonia stripping. Adapted from (Lorick et al., 2020).


Fig. 5. A schematic representation of a rotating packed bed for ammonia removal by air stripping (a) and of an ammonia stripping column (b). Adapted from (Chen et al., 2021; Kim et al., 2021).

1.3.3.1.3. Adsorption

Natural zeolites are hydrated aluminosilicate minerals that are crystalline and have numerous pores that are filled with water, alkali, and alkaline earth cations. They are also known for their useful physicochemical characteristics, which include ion exchange, unique selective sorption, and thermal stability. Natural zeolites have been widely used for wastewater treatments and are widespread in the environment as shown in **Fig. 6** (Ates, 2018; Lin et al., 2014; Valdés et al., 2014). Previous research focused on the utilization of natural, modified, and synthetic zeolites to remove trace and low-concentrations of ammonium (less than 0.20 g N L^{-1}) from tap water, groundwater, and domestic wastewater (Guaya et al., 2015; Guo, 2016). Turkish sepiolite is the most effective adsorbent for removing ammonium from water and wastewater because it is accessible, simple to use, promptly eliminates ammonium, and is affordable. During physical and chemical treatments, the adsorption capacities of most zeolites and clays are enhanced although further optimization is required to lower the total operation costs. Compared to natural and manufactured zeolites, polymeric ion exchangers have a higher absorption capacity and higher chemical and mechanical stability. However, polymeric ion exchangers may not offer the same cost-effectiveness as natural zeolites. Ammonium removal using carbon-based adsorbents is also quite successful, nevertheless more research is needed for their regeneration. Hydrogels have good regeneration, fast kinetics, and a high adsorption capacity. Nevertheless, their preparation should be improved because it is still quite complex to be cost-effectively implemented at industrial scale (Huang et al., 2018). To lower the total operation costs, further optimization is required in all cases. Compared to natural and manufactured zeolites, polymeric ion exchangers have a higher absorption capacity and higher chemical and mechanical stability, however they may not offer the same cost-effectiveness as natural zeolites. Ammonium removal using carbon-based adsorbents is also quite successful, nevertheless more research is needed on their regeneration. It is suggested that Turkish sepiolite should be employed in large-scale commercial and wastewater treatment facilities as an effective, economical, and environmentally safe adsorbent as shown in **Fig. 7**. Furthermore, ferrosilicon alloy and KU-2-8 resin are excellent alternatives for ammonium removal (Huang et al., 2018).
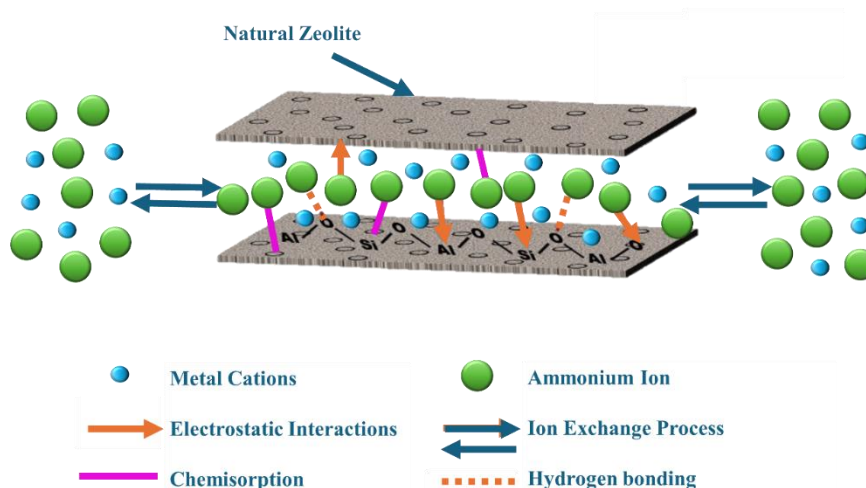
Fig. 6. Principle of separation in the adsorption mechanism of ammonium by the natural zeolite. Adapted from (Liu et al., 2021).
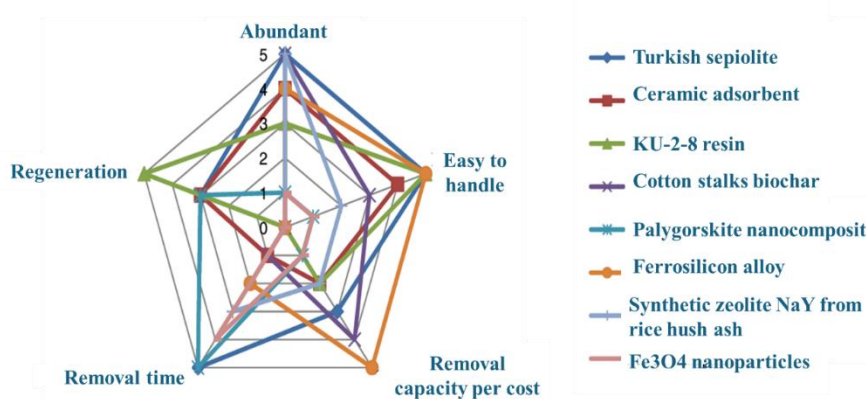
Fig. 7. Performance of several adsorbents. Adapted from (Huang et al., 2018).

In summary, adsorption exhibits several advantages, including a strong affinity for ammonium, affordability, ease of designing setups, and environmental friendliness (Huang et al., 2018). Due to these benefits, it is both ecologically and economically feasible to polish effluents from industry that contains high concentrations of ammonium (Liu et al., 2021). In the lab, many tests lead to good outcomes, but in the field, they may not provide efficient results.

1.3.3.1.4. Ion Exchange

Ion-exchange is based on the reversible exchange of ions between the liquid and solid phases. The mobile ions in the exchange material may be substituted for similarly charged ions from the media that surrounds them. Ion exchange has been used recently to remove ammonia from aqueous solutions due to its high removal efficiency and simple operation (Bashir et al., 2010).

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There are two types of solid ion exchangers: manufactured organic resins and inorganic particles found in nature. Natural zeolite was the first ion exchanger to be utilized in the market (Bashir et al., 2010). It has been observed that zeolites have a strong affinity for ammonium ions and resemble the conventional aluminosilicate cage as shown in **Fig. 8** (Karadag et al., 2008; Lin et al., 2014). One naturally occurring zeolite that has an exceptional attraction for ammonium ions is clinoptilolite (Semmens et al., 1981). Previous research has demonstrated the effectiveness of clinoptilolite and several other natural zeolites in eliminating ammonia from effluents (Nguyen and Tanner, 1998). With a silica-rich structure and a reduced cation exchange capacity, clinoptilolite is a naturally occurring zeolite that has a high affinity for ammonium, with values ranging from 0.94 to 21.52 g NH_4^+ - N kg^{-1} (Thornton et al., 2007). Nevertheless, compared to naturally generated materials utilized by earlier authors, MesoLite has an improved ammonium exchange capacity (45–55 g NH_4^+ - N kg^{-1}). Zeolite N, a synthetic zeolite, was created by the alteration of clay and other minerals containing aluminum to create MesoLite ion exchange media (Mackinnon et al., 2003). As an outcome, there are more exchange sites accessible, which increases the media's surface area and exchange capacity relative to the original material (Mackinnon et al., 2012).
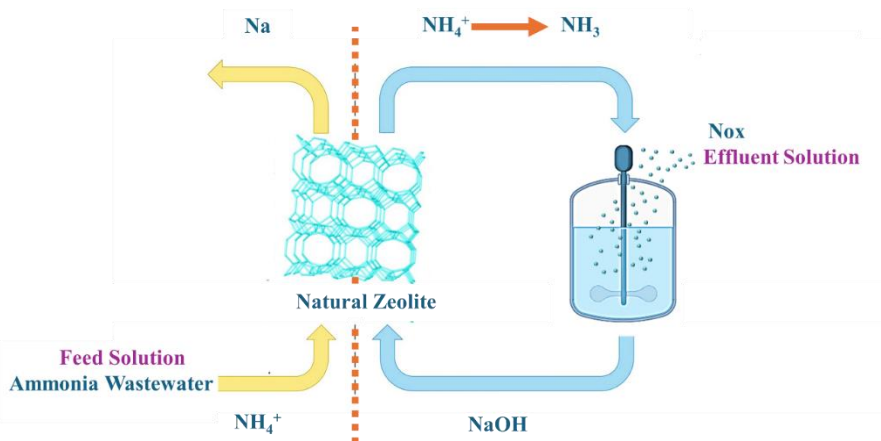
Fig. 8. Principle of ammonia separation by ion exchange with natural zeolites. Adapted from (Lubensky et al., 2019).

Nevertheless, since synthetic ions exchangers have a larger ion-exchange capacity, a more rapid exchange rate, and a longer lifespan than natural zeolites, they have replaced them in nearly all of the current applications (Reinke, 1951). High molecular weight polyelectrolytes are used to create synthetic organic resins, which are composed of a cross-linked polymer matrix to which charged functional groups are covalently bonded (Cheremisinoff, 2002). Resins may be created for a range of applications because of their

adjustable polymer matrices, functional groups, capacity, and porosity, throughout the process of manufacture (Reinke, 1951). Previous research has validated the efficacy of several ion-exchange resin types in eliminating ammonia from aqueous solutions. Na type Dowex HCR-S strong acid cationic resin was used to remove 100% of the synthetic ammonia solution (20 mg L^{-1} at pH=6) (Aral et al., 1999). Recently, ion exchange has found increased use due to the availability of polymeric macronet exchangers (Purolite), which may be used in settings that are not suited for conventional exchangers (Jorgensen and Weatherley, 2003). At an initial TAN concentration of 200 mg L^{-1}, ion exchange resins such as Dowex 50W-X8 and Purolite MN500 exhibit an ion exchange yield of ~39 and 29 mg/g, respectively (Jorgensen and Weatherley, 2003).

The short contact times, low energy consumption, and simple operation of the ion exchange make it a promising technology for ammonia removal. Furthermore, the regenerated resins can be used to recover ammonium to be utilized as fertilizers. Because natural zeolites are expensive to mine, transport, and process, they might not be suitable for large-scale ammonium recovery despite the intensive research carried out (Malovanyy et al., 2013).

1.3.3.1.5. Microwave radiation

An innovative approach for lowering ammonia nitrogen concentrations in wastewater is the combination of microwave radiation and ammonia stripping. When air stripping systems use microwave radiation for heating, it generates molecular upward momentum that causes dissolved ammonia to evaporate (Remya and Lin, 2011). A microwave-assisted air stripping system is schematically depicted in **Fig. 9**, combining ammonia stripping, acid absorption, and a batch module of microwave radiation. In this system, ammonia stripping is fostered by heat, which shifts the NH_4^+/NH_3 equilibrium composition of the gas-liquid phase toward ammonia. Thus, Lin et al. (2009) achieved 80% ammonia removal efficiency from coke-plant effluent using a pilot-scale system constructed with microwave radiation for ammonia stripping. Similarly, Ata et al. (2017) demonstrated a maximum ammonia removal ratio of 94.2% when the system was operated with an initial ammonia concentration of 1.800 g L^{-1}, 7.5 L min^{-1} of airflow rate, 60 °C of temperature, 500 rpm of stirring velocity and 200 W of microwave power. In a different scenario, ammonia stripping

of swine wastewater with microwave supported 83.1% of NH_3 removal within 30 min (La et al., 2014).

Another procedure based on microwave radiation is microwave ammonia synthesis. This technique has generated a lot of attention recently since it is extremely selective, has a rapid reaction time, and entails beneficial reaction conditions specifically when it comes to heterogeneous catalysis (Satoshi and Nick, 2015). These advantages are mostly acquired by the unique properties of microwaves in direct and controlled heating (Hunt et al., 2013). Catalysts serve as the microwave energy absorber in microwave-enhanced heterogenous catalysis. In this context, it is desirable to have catalysts with a high dielectric sensitivity (**Fig. 10**). The reactors are typically made from materials that are transparent to electromagnetic radiation, such as glass, quartz, and ceramics, in order to accomplish efficient catalyst heating and efficient microwave use (Barham et al., 2019). Utilizing a microwave reactor facilitates a reliable ammonia synthesis process to operate on sporadic renewable power sources (Wang et al., 2021).
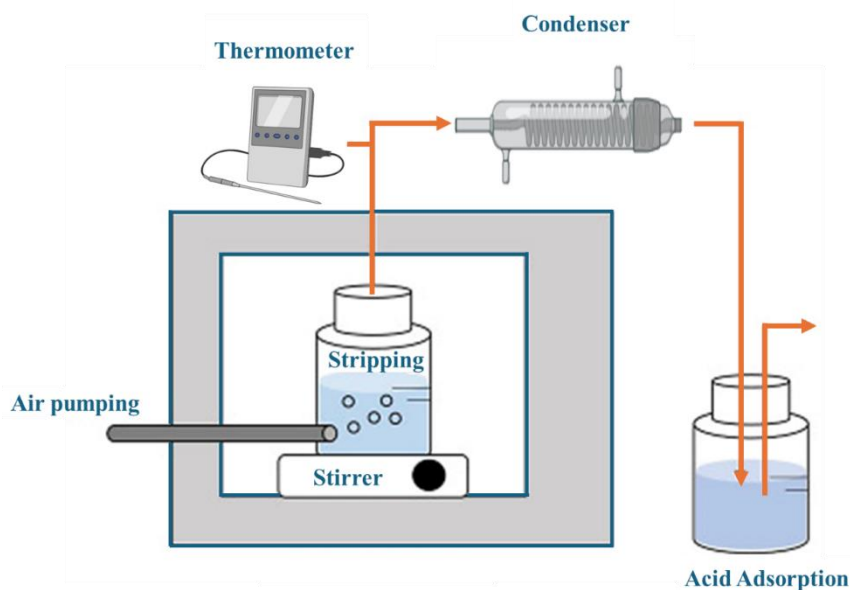
Fig. 9. Representation of a microwave assisted ammonia stripping system. Adapted from (Chen et al., 2021).
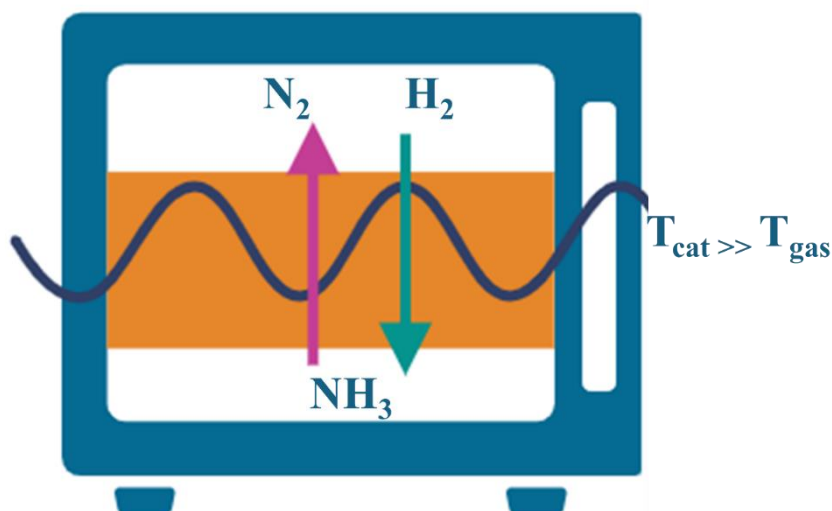
Fig. 10. Representation of microwave ammonia synthesis. Adapted from (Wang et al., 2021) .

1.3.3.2. Chemical Processes

1.3.3.2.1. Chemical precipitation

The ammonium and phosphorus present in the treated effluent following AD can be recovered and removed using a combined approach called chemical precipitation (**Fig. 11**). Struvite, or magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4·6H_2O$), is a precipitate marketed as a slow-release fertilizer. Struvite is a white, crystalline solid produced in accordance with the following reaction: $Mg^{2+} + NH_4^+ + PO_3^- + 6H_2O \rightarrow MgNH_4PO_4 · 6H_2O$ (Uludag-Demirer et al., 2005). Struvite has an unstable market and a low-price tag. To make the fertilizer commercially feasible, heavy metals and other contaminants co-precipitated must be eliminated (Bianchi et al., 2020). A number of variables, including the pH, the chemical composition of wastewater (degree of the solution's saturation with calcium, ammonium, and magnesium; concentration of other ions; solution's ionic strength), and temperature, influence the precipitation of struvite (Parsons and Doyle, 2002). Nucleation along with growth are the two steps of struvite precipitation. Nucleation is the process when ions unite to create crystal growth. Growing crystals persist until they achieve equilibrium (Song et al., 2021). Crystal development may never stop in systems that are continually supplied with struvite ingredients, such as wastewater treatment facilities.

Since the concentrations of the ions that produce struvite are all pH dependent, the precipitation of struvite in a solution is essentially regulated by pH. For example, as the pH rises from 7 to 9, the concentration of NH_4^+ reduces considerably from 99 to 64%, nevertheless the concentration of PO_4^{-3} increases 250-fold in the same pH change range (Werner et al., 1991). Multiple wastewater effluents have been treated with the struvite precipitation technique, such as animal manure, agro-industrial wastewater, landfill leachate, cattle manure, coke production, leather tanning, and side streams from anaerobic digesters (Uludag-Demirer et al., 2005). Since it could considerably reduce the expenses related to the treatment of NH_4^+ in wastewater, struvite production has received an increasing attention in the last 10 years. One of the most traditional methods for recycling struvite is sodium hydroxide pyrogenation (Huang et al., 2011) and direct pyrolysis (Sugiyama et al., 2005).
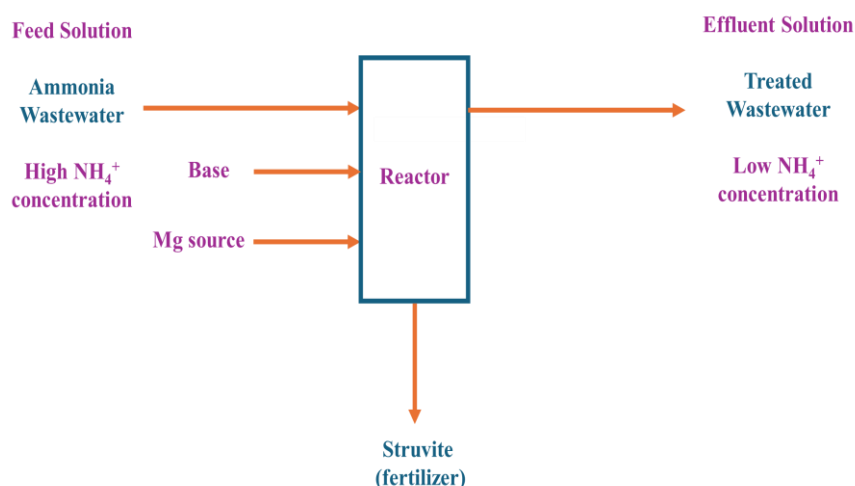
Fig. 11. Simplified chemical precipitation process. Adapted from (Lorick et al., 2020).

1.3.3.2.2. Oxidation

Heterogeneous photocatalytic and electrochemical oxidation of ammoniacal nitrogen in water and wastewater have been thoroughly investigated to reduce ammonia from aqueous streams. Potent oxidants generated in situ, such as hydroxyl radicals and holes, constitute the core basis of photocatalytic ammonia oxidation. Nevertheless, their reactivities with ammonia are comparatively slower at the pH values relevant to the environment (Zhang et al., 2021). Additionally, while using hydroxyl radicals as highly effective oxidants in the photocatalytic process, there has been a noteworthy an increase in

research recently on the breakdown of contaminants using other oxidative radical species like superoxide, oxysulfur, and chlorine-based radicals for specific water and wastewater treatments (Zhang et al., 2020; Zhou et al., 2019).

Breakpoint chlorination is the method in which ammonia is oxidized in the following reactions (Qi, 2018; Zhang et al., 2022):

$$Cl_2 + H_20 \rightarrow HOCl + H^+ + Cl^- \tag{1}$$

And further:
$$NH_4^{\ +} + 1.5\ HOCl \rightarrow 0.5\ N_2 + 1.5\ H_2O + 2.5\ H^+ + 1.5\ Cl^- \tag{2}$$
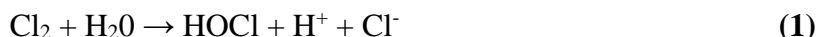
The breakpoint on the residual chlorine versus additional chlorine dose curve occurs when a specific dosage of chlorine is applied. At this stage, the content of NH_4^+ in the treated water drops to zero and the amount of chlorine in the effluent is reduced. The concentration of chlorine in the treated wastewater will rise as the dosage of additional chlorine increases, which is called breakpoint (Qi, 2018; Zhang et al., 2022).

This technique has the benefits of high efficacy and efficiency and low investment. The high cost of operation and the high degree of acidity produced by the process are its main drawbacks: four moles of acids are produced for every mole of ammonium oxidized, and these acids need to be neutralized by adding an alkaline reagent like calcium oxide. In addition, secondary production arises from the chloramine and the organics chlorinated throughout the procedure. This technique is appropriate for treating wastewater with low ammonium concentrations in order to comply with wastewater discharge regulations (Qi, 2018; Zhang et al., 2022).

Lab-scale experiments have consistently shown the effective photochemical generation of radical species and degradation of contaminants by using a variety of substrate pollutants, including organics (hydrocarbons, dyes, pesticides, aromatics, organic acids, personal care products, pharmaceuticals, antibiotics, etc.) and inorganics (ammonia, heavy metals, etc.), as well as algae and microbial bacteria (Ryu and Choi, 2008; G. Zhang et al., 2011; Zhao et al., 2020). Similarly to heterogeneous photocatalytic oxidation, electrochemical oxidation of wastewater can in-situ produce hydroxyl radicals and other

oxidative species, such as active chlorine species, for the treatment of various contaminants in water (Martínez-Huitle and Brillas, 2009). Electrochemical oxidation may be precisely regulated and adjusted to oxidize multiple contaminants in wastewater by adapting the electrode materials, voltage utilized, and current density, among other factors. The electrochemical oxidation treatment of wastewater shows comparatively more advanced improvement in terms of practical applications compared to photocatalytic oxidation particularly due to the its lower number of limitations (Zhang et al., 2021).

Extensive research has been done on ammonia treatment based on photocatalytic and electrochemical oxidation processes due to the importance and necessity of decentralized ammonia removal from water and wastewater (Bian et al., 2015; Liu et al., 2023). **Fig. 12** shows the separate impacts of noble metals on the selective production of oxidation products. For photocatalytic oxidation of ammonia on TiO_2-based photocatalyst, there are two primary reaction routes. Considering the different surface affinities of noble metals with atomic nitrogen, the main oxidation substances produced by ammonia in the presence of Pt or Pd co-catalyst are usually dinitrogen via Path I, which generates N_{ad}, NH_{ad}, and NH_{2ad} species. In contrast, nitrate and nitrite via Path II, which generates $\cdot NH_2$ and $\cdot NHOH$ intermediates, are the main oxidation products of ammonia in the presence of Ru, Rh, Ag, Au, or without co-catalyst (Lee et al., 2002).
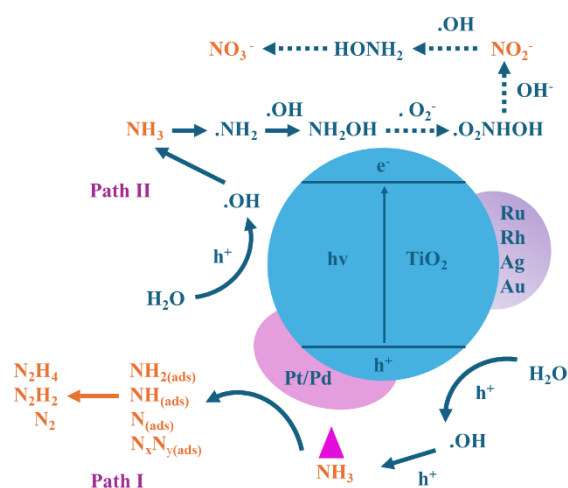
Fig. 12. Potential reaction pathways for the photocatalytic oxidation of ammonia using several co-catalysts. Adapted from (Lee et al., 2002).

In summary, the indirect electrochemical oxidation of ammonia based on active chlorine species is more efficient and has certain advantages over the chemical chlorination technique (Zhang et al., 2021).

1.3.3.2.3. Electro-kinetic

Several electro-kinetic separation techniques have been designed and tested for ammonia removal and recovery as co-products (Chen et al., 2021). Electrically powered ion-exchange membrane separation methods known as electrodialysis are mostly used in wine refineries and other specialized applications including the recovery of salty and wastewater. In a multi-compartmented cell, the electrodialysis layer is typically comprised of cation and anion exchange membranes that are alternately positioned between two electrodes and join the dilute and concentrate channels (Al-Amshawee et al., 2020). To accomplish separation and purify the wastewater, this system electrically transports the ions in the feed flow such as contaminated water or wastewater through the ion exchange membranes and into the concentrate chamber. These ionic fluxes are maintained once within the concentrate chambers by the ion-selective membranes that are positioned between them and reject ions that have the opposite charge. To transfer the electric current (and thus, the electric field) produced on the electrodes, electrolyte solutions (such as inorganic salt solution) are pumped via electrode rinse chambers (Van Oss, 1979).

Stripping and absorption of concentrated ammonia are simultaneously required in ammonia recovery electrodialysis (Desloover et al., 2012; Ippersiel et al., 2012). Desloover et al. (2012) achieved a 96% ammonia charge transfer efficiency using electrodialysis combined with stripping and absorption, and it was found that certain cations, including Na^+ and K^+, hinder the ammonia recovery results when using 120 g N $m^{-2} d^{-1}$ of NH_4^+ flux.

Electrodeionization is a hybrid method that combines ion exchange with electrodialysis. The effectiveness of deionization is increased in electrodeionization layers by combining concentration polarization (a phenomenon entailing a high cumulative resistance within the cell is built up) with chemical renewal (Alvarado and Chen, 2014).

The technique of capacitive deionization involves periodically charging and discharging the electrodes. Porous carbon electrodes are employed to eliminate ionic species from aqueous solutions by initially electrically adsorbing the ions within the electrode double-layer, followed by releasing the ions from the surface of the electrodes for regeneration (Dykstra et al., 2016). Activated carbon aerogel is a popular electrode for capacitive deionization because of its monolithic structure and large specific surface area (AlMarzooqi et al., 2014). Because there is a constant supply of uncharged carbon particle slurry, flow-electrode capacitive deionization has the benefit of offering limitless adsorption capacity. With this design, the target ions are concentrated in the carbon slurry, while the ions from the influent are transferred into the flowing electrode chambers (Zhang et al., 2019). Since its electrodes are constantly renewing, flow-electrode capacitive deionization has the potential of extracting and recovering high-value byproducts from wastewater, such as ammonia/ammonium ion (Fang et al., 2018). The capacity to stimulate ion transport by an electrical field and electron flow is crucial for the successful recovery of ammonia through bioelectrochemical systems. Ammonium ions are transferred from the feed solution to the capture (also known as the concentrate) solution by use of cation exchange membranes (**Fig. 13**). The oxidation of organic substrates at the anode and the reduction of oxygen at the cathode in bioelectrochemical systems generate the source and sink electrons, respectively (Kuntke et al., 2018).
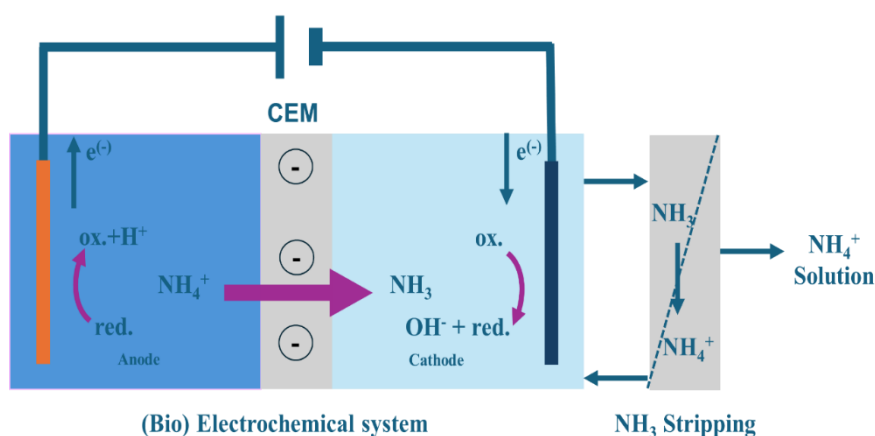

Fig. 13. Scheme of a bioelectrochemical system for TAN recovery. Adapted from (Kuntke et al., 2018).

1.3.3.3. Microbial Processes

1.3.3.3.1. Nitrification-denitrification

Biological nitrification–denitrification is the most popular nitrogen removal method from wastewaters. The aerobic oxidation of ammonia to nitrite and subsequently to nitrate is the first stage, known as nitrification. Nitrifying bacteria obtain their energy from the oxidation of these nitrogen molecules and carbon from CO_2 (Weissman, 2012). To guarantee total denitrification, there is a continuous recirculation of the mixed liquor between the anoxic tanks and the aeration tanks (**Fig. 14**). Aeration is the main operating cost associated to nitrification since a complete ammonia oxidation requires 224 g O_2/g NH_4^+ (Chang, 2017). Afterwards, nitrate (produced in the nitrification process) is anoxically bioconverted into nitrite, N_2O, nitric oxide, and eventually gaseous nitrogen, in a process called denitrification. Heterotrophic denitrifying bacteria use nitrate or nitrite as their ultimate electron acceptor in the absence of dissolved oxygen. Denitrification requires organic matter or H_2S as electron donor, which is oxidized during the reduction of nitrate or nitrite (Barnes, D., & Bliss, 1983). Ammonium-rich wastewater treatment plants have extensively used biological nitrification and denitrification processes, where ammonia is first oxidized to nitrate, which is subsequently converted to nitrogen gas via oxidation of organic carbon (Ali and Okabe, 2015; Lan et al., 2011; Yang et al., 2020b, 2020a). Nitrification can occur at temperatures between 5 and 45°C. Interestingly, methanotrophs may aerobically oxidize ammonium at 53 °C even in the absence of CH_4 (Pel et al., 1997).
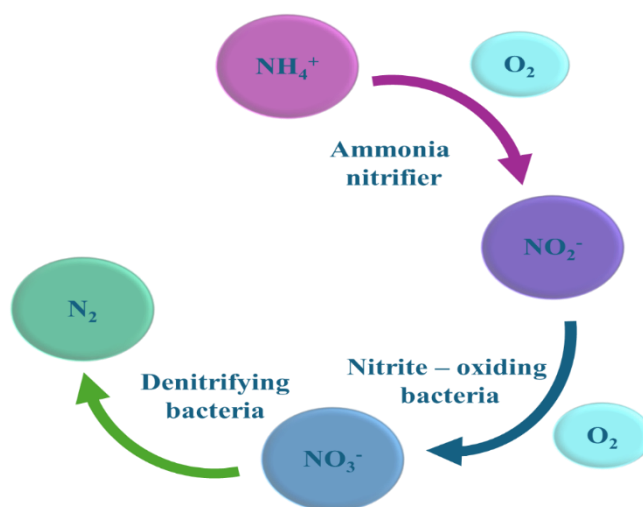
Fig. 14. Conventional nitrification-denitrification pathways. Adapted from (Martin and Clark II, 2017).

In the absence of inhibitory compounds of nitrifying organisms, trace levels of ammonia (<2 mgL^{-1}) are typically found in well-operated domestic wastewater treatment plants WWTPs (**Fig. 15**) (Burghate et al., 2013).
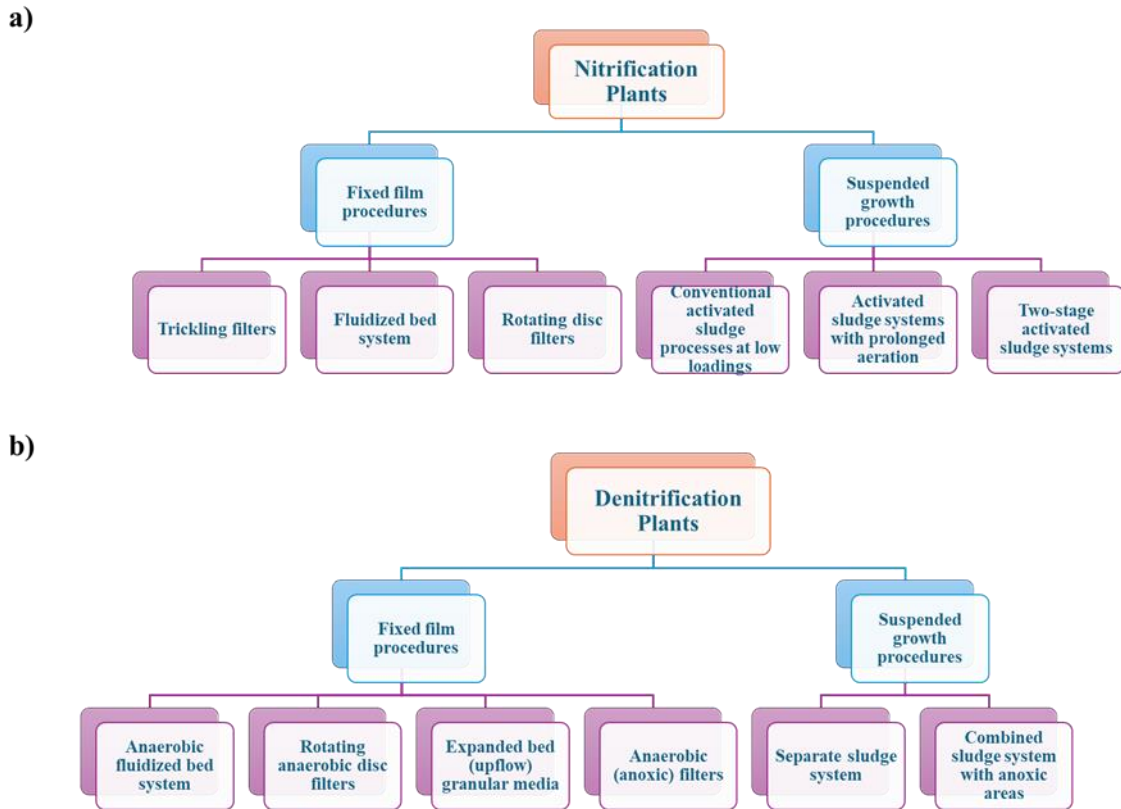
Fig. 15. Types of plants required for the nitrification and denitrification processes. Adapted from (Burghate et al., 2013).

However, due to the high oxygen requirements for complete nitrification and the production of high volumes of sludge and concentrations of N$_2$O during heterotrophic denitrification, biological nitrification and denitrification is not the most efficient method for removing nitrogen from the environment (S. Wang et al., 2018).

1.3.3.3.2. Anammox

The process known as anaerobic ammonium oxidation (anammox) is recognized as an effective nitrogen removal method (Lu et al., 2021). Nitrogen gas is directly produced from

ammonium and nitrite by the anammox process (**Fig. 16**). In this reaction, nitrite serves as the electron acceptor (Kartal et al., 2013). Anammox bacteria are found in a vast species (micro)diversity in almost any anoxic habitat with fixed nitrogen, despite their long-standing neglect. These "impossible" microorganisms are thought to be the source of almost 50% of all nitrogen gas discharged into the environment (Kartal et al., 2013).
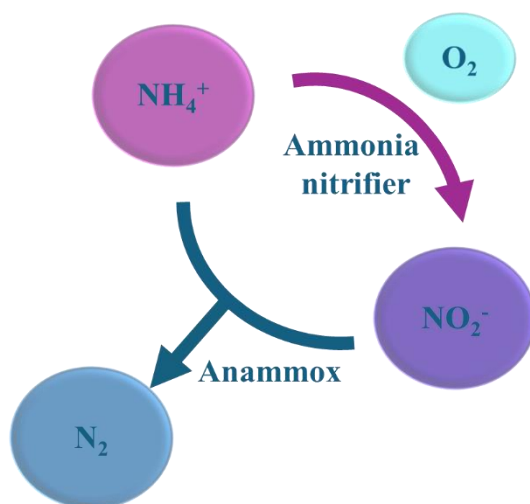
Fig. 16. Anammox nitrogen removal pathway. Adapted from (Martin and Clark II, 2017).

Nevertheless, compared to traditional WWTP developing anammox-inoculated WWTPs capable of efficient inorganic nitrogen removal takes longer because of the long doubling time and disadvantaged biological output of anammox bacteria in bioreactor systems (Ali et al., 2015). Visual anammox bacterial granules frequently develop six to nine months after the primary inoculation of WWTPs (Yang et al., 2018). In order to discover more on the structure of the primary microbial population in WWTPs, high-throughput sequencing was employed (Yang et al., 2020b, 2020a). Numerous microbial pathways are important for the nitrogen transformation process in anammox-inoculated WWTPs, with the anammox process holding a key position. The two stages in the anammox process are partial nitrification (in which about half of the NH_4^+ is oxidized to NO_2^-) and the anammox process (in which the NH_4^+ is oxidized with NO_2^- to N_2 gas) under anoxic conditions. This approach removes nitrogen from wastewaters without organic matter requirements. The term partial nitrification and anammox (PN&A) refers to this combination. Initially, the PN&A process was applied independently in two stages: the anammox process occurring after the partial nitrification process in the first stage. Later on, single stage reactors were used to simultaneously carry out partial nitrification and

anammox processes (Third et al., 2001). Wastewater streams containing high NH_4^+ concentrations such as digestates are often suitable for treatment using anammox processes. Typical full-scale anammox reactors have cope with influent ammonium concentrations ranging from 500 to 3000 mg-N L^{-1} and a volumetric nitrogen loading rate (NLR) varying from 0.1 to 7.0 kg-N m^3 d^{-1}. For single-stage systems, the typical range of NLR employed is 2 to 2.4 kg-N m^3 d^{-1}. The presence of free ammonia (NH_3), which is known to negatively impact on the metabolisms of aerobic ammonium-oxidizing bacteria (AOB) and anammox bacteria (Jaroszynski et al., 2012; Li et al., 2012). Single-stage systems typically operate under microaerophilic environments with dissolved oxygen levels in the range of 0.2–1.5 mg–O_2 L^{-1}. The COD/N ratio, which varied from 0.2 to 3.8, is another crucial factor to consider considering that wastewaters containing ammonia do not always contain biodegradable organic matter. When ammonia reduction dropped to 80%, a threshold COD/N ratio for anammox inhibition was observed at 3.1 (Ni et al., 2012). For each type of wastewater and reactor configuration, the operating conditions should be adjusted.

It has been demonstrated that the anammox process is more effective than the conventional nitrification–denitrification process, supporting a 90% decrease in sludge production, 100% reduction in the need for organic carbon sources, 60 % reduction in oxygen demand (such as aeration), and barely any N_2O emissions (Okabe et al., 2011; Wu et al., 2019; Yang et al., 2020b, 2020a). However, the full-scale practical implementation of anammox-based treatment processes still faces some obstacles, such as prolonged start-up period, limited applicability to conventional municipal wastewater, and low effluent water quality (Ali and Okabe, 2015).

1.4. Anaerobic digestion combined with membrane-based NH₃ extraction

Membrane gas extraction stands out as a promising option for extracting ammonia from waste streams due to its intrinsic qualities, bringing forth numerous benefits. This method has proven highly effective in removing oxygen, carbon dioxide, and other gas compounds from water. In this method, the feed water is directed to one side of a membrane designed to allow the passage of gas-phase molecules exclusively. The membranes commonly employed for this purpose typically feature sub-micron-sized pores filled with air and possess hydrophobic surfaces, which effectively resist pore wetting (Lee et al., 2021). On

the opposing side (known as the stripping side) of the membrane, either a vacuum pressure, a sweep gas flow, or a liquid flow (ideally one with significantly higher solubility for the targeted substance) is applied. This setup establishes a partial pressure gradient, thereby sustaining a flux of gas molecules from the feed side to the stripping side through the membrane pores (Naim et al., 2012). This method can be employed to extract ammonia from liquid waste streams by employing an aqueous solution as a stripping solution with a significantly lower pH value than that of the feed (Darestani et al., 2017). This configuration creates the driving force for ammonia mass transfer, primarily the partial pressure disparity between the feed solution and the acidic stripping solution. The benefits of ammonia harvesting through membrane gas extraction, also known as ammonia recovery via membrane contactor, are numerous. The exchange of substances between the feed and stripping sides takes place through the air-filled pores of the membrane, rendering it an effective barrier against any additional constituents present in the water feed, provided that fouling and wetting are effectively managed (Tan et al., 2006). This characteristic holds considerable benefits for resource recovery from waste streams. The primary barriers to utilizing recovered products are the associated risks and consumer reluctance stemming from potential impurities (Darestani et al., 2017). By adjusting the pH difference between the feed solution and the stripping solution, it is possible to reduce the ammonia partial pressure on the stripping side to insignificance compared to that on the feed side, across almost any practical range of TAN concentrations on both sides. Essentially, by controlling the pH of the stripping solution, the driving force for ammonia mass transfer can be solely determined by the characteristics of the feed solution (i.e., TAN concentration and pH), directing the transfer from the feed solution to the stripping solution. Consequently, a highly concentrated ammonia solution can be eventually obtained on the stripping side, which holds significant value as a resource (Lee et al., 2021).

Recent advancements in membrane technology have allowed achieving a high membrane packing density, resulting in a small footprint for nitrogen recovery units. The high modularity of membrane units facilitates the application of the nitrogen recovery process at any scale, ranging from highly decentralized setups, such as household-level applications, to highly centralized systems covering metropolitan areas (Lee et al., 2021).

AD and gas-permeable membrane technology may be used to extract nitrogen from SM, which can help reducing ammonia emissions and providing a sustainable method for

the treatment of animal waste. Furthermore, a range of products that are beneficial are produced using this innovative approach, including fertilizers (such as ammonium sulfate solution and anaerobic digestate) and sustainable energy in the form of CH_4. Membrane technology is considered a favorable wastewater treatment method because of its compact design and reduced energy demands. Hence, it has been recently suggested that the use of membranes to extract NH_3 from high strength wastewater is an economical and sustainable way to recover residual nitrogen. For instance, a thorough economic study by Brennan et al. (2020) showed that, at a pilot plant scale, NH_3 recovery using membranes is more feasible than using traditional techniques. Because membrane contactors have a large specific surface area and can separate NH_3 more quickly from the aqueous matrix, they require less energy. Indeed, membrane contactors have been successfully implemented to capture NH_3 from gaseous emissions (Mahmud et al., 2000; Malek et al., 1997; Yeon et al., 2003), and for the direct recovery of NH_3 from wastewater (Sheikh et al., 2022; Vecino et al., 2020, 2019). This method relies on hydrophobic membranes that consist of polymers highly permeable to ammonia, which is transferred into the receiving liquid phase and then circulated via the permeate side of the membrane pores (Carter et al., 2015; Hasanoĝlu et al., 2010; Tan et al., 2006). An acid present in the permeate side of the membrane interacts with this permeating ammonia. Ammoniacal nitrogen must be present in its volatile form (NH_3) for the process to be effective, and this may be done by increasing the pH and temperature of the wastewater (Norddahl et al., 2006). When applying H_2SO_4 to improve ammonia diffusion, membrane-based NH_3 recovery can produce ammonium sulphate, a commercial chemical fertilizer (Equation (3)) (Darestani et al., 2017). Chemical fertilizers like ammonium phosphate and ammonium nitrate are also produced when H_3PO_4 and HNO_3 are used on the permeate side (Sheikh et al., 2022; Vecino et al., 2020, 2019). However, H_2SO_4 mediates a more efficient ammonia capture than H_3PO_4 and HNO_3, according to (Damtie et al., 2021).

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \qquad\qquad \textbf{(3)}$$

Previous studies conducted a thorough evaluation of the efficacy of commercial flat sheet membranes to recover NH_3 from both synthetic and real digestates. The impact of digestate pH and recirculation flow rate was studied using various concentrations of sulfuric acid on the opposite side of the membrane in order to optimize the operating conditions (Rivera et al., 2022a). The study focused on testing commercial membranes that

were used for different applications in order to make this novel ammonia process accessible. Without utilizing non-commercial and the most advanced materials, the optimal operation was elucidated by examining the variables that are adjustable at the installation site. Overall, the objective was to propose an alternative that farmers might use at their premises. Ultimately, the surface morphology of the membranes was examined using Atomic Force Microscopy (AFM) to investigate membrane fouling, and the corresponding modifications in the membranes' pore diameters were ascertained using Air Displacement Porometry (ADP).

Fig. 17 depicts a typical schematic illustration of the experimental lab-scale setup utilized to extract ammonia from digestates. In a custom-built cell module, the target digestate (real or synthetic) was continuosly pumped across the membrane's active layer using a peristaltic pump. On the membrane's support layer, a similar peristaltic pump was used to circulate a sulfuric acid solution. **Table 3** lists the membranes that were employed along with their primary properties. The outstanding properties of PTFE and PVDF for the separation of light molecules from water in a gaseous phase resulted towards their selection as prototype commercial membranes (Rivera et al., 2022a).
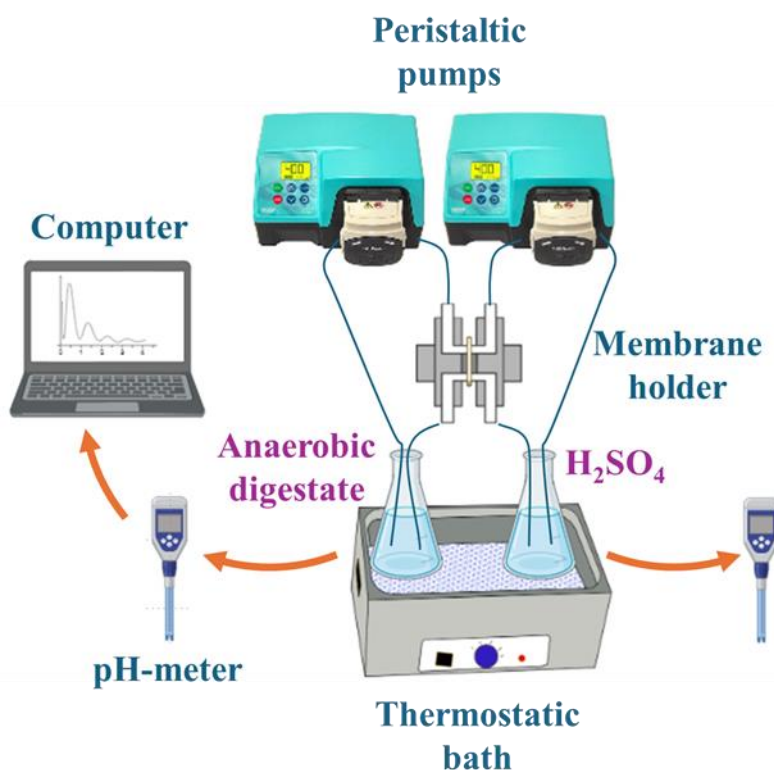
Fig. 17. Representation of an ammonia recovery system with membranes. Adapted from (Rivera et al., 2022a).

Table 3. Description of the commercial membranes studied (Rivera et al., 2022a).

| Membrane	Material	Pore Size	Nominal Thickness (μm)	Contact angle (θ)	Porosity (%)	Wettability	Manufacturer
PVDF-100	PVDF	100 kDa	160	130-135	*	hydrophilic	KOCH
PVDF-0.10	PVDF	0.10 μm	130	130-135	*	hydrophobic	Sterlitech
PTFE-0.20	PTFE	0.20 μm	139	142	*	hydrophobic	Pall Gelman
PTFE-0.22	PTFE	0.22 μm	175	150	70	hydrophobic	Millipore
PTFE-0.45	PTFE	0.45 μm	135	155	*	hydrophobic	Pall Gelman

* Information not supplied by manufacturers.

When 1 M sulfuric acid was added and the digestate's pH was raised to 10, the maximum ammonia recovery was achieved. NH_3 recovery also increased at greater digestate circulation flow rates, which prevented membrane fouling and therefore avoided pernicious increases in mass transfer resistance. It was demonstrated that NH_3 recovery on the digestate side of the membrane followed first order kinetics and occurred more rapidly at alkaline pH, and with high H_2SO_4 concentrations and high recirculation flow rates. Under ideal operating conditions, a PTFE-0.22 membrane supported NH_3 recoveries of 72% and 85% using real and synthetic digestates, respectively, within 3.5 hours. According to the kinetics observed in this thesis, 94% NH_3 recoveries could be achieved in synthetic digestate under comparable operating conditions after 6 hours of operation. When employing real digestate, membrane fouling was significant and resulted in a decrease in membrane pore diameter as well as increasing surface deposition (Rivera et al., 2022a).

Although this technology has been successfully tested to extract NH_3 from anaerobic digester effluents, only few studies have been carry out to enable *in-situ* ammonia recovery and improve a continuous AD process directly within an anaerobic digester (Rivera et al., 2023a, 2023b, 2022b). In this context, Rivera et al. (2022b) investigated the potential benefits of using hydrophobic flat sheet membranes to remove NH_3 both *in-situ* and *ex-situ* during the anaerobic digestion of SM. In order to assess the effects of pH and suspended particles on NH_3 extraction from anaerobically digested piggery effluents, batch tests were first carried out *ex-situ* utilizing both circular and rectangular PTFE hydrophobic membrane configurations. Using the membrane designs mentioned above, researchers additionally examined how the AD process was affected by the *in-situ* NH_3 extraction from the culture broth of a continuous anaerobic digester that treated piggery wastewater.

Rivera and co-workers also investigated the effects of pH and suspended solids on NH_3 removal from digested SM. This research involved continuously recirculating anaerobically digested SM over the active layer of a PTFE hydrophobic membrane in two custom membrane holders (**Fig. 18**). By using membrane-assisted NH_3 extraction to lower the NH_3 concentrations in the anaerobic broth, the anaerobic treatment of SM can be potentially improved. In this context, the digestate's ammonia recovery increases as the pH level increases. Under short-term operation, the concentration of suspended solids in the anaerobic broth exhibited no noticeable impact on NH_3 extraction. During continuous anaerobic SM treatment, NH_3 extraction from the anaerobic digester enabled improvements in COD and volatile solids (VS) removal efficiency by 87% and 48%, respectively, and allowed a full VFA assimilation. Furthermore, a 49% increase in CH_4 yields was observed despite the biogas composition was maintained constant (Rivera et al., 2022b).
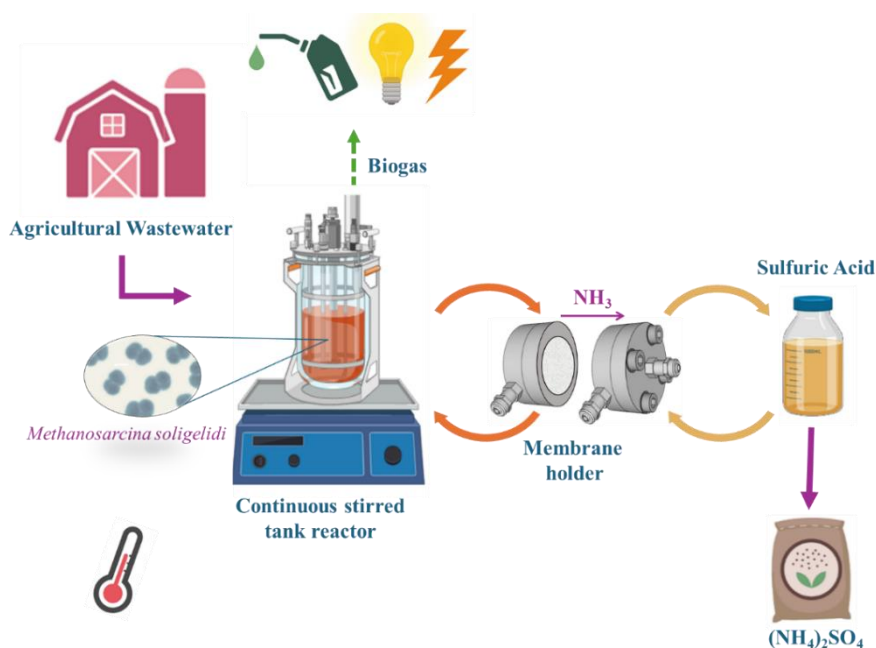
Fig. 18. Schematic representation of the lab-scale CSTR combined with an ammonia extraction system based on membranes for anaerobic SM treatment at different pHs (Rivera et al., 2023b).

The influence of pHs in a CSTR connected to a membrane-based extraction module to determine its impact on ammonia recovery and AD performance during SM treatment was also studied. The flat sheet PTFE membrane module was operated continuously at 250 mL min^{-1} liquid recirculation rate, while the anaerobic digester was run at 37 °C for 20 days at a hydraulic retention time. After 360 days of operation, the membrane module was able to

progressively lower the TAN concentration from 1.27 to 0.62 g L^{-1}. The NH_3 extraction process using membranes increased the CH_4 yield by a ratio of 1.3. Furthermore, when the pH of the inlet piggery wastewater was increased from 7.5 to 12 via NaOH addition, and the COD and VS removal efficiency increased up to 1.2 and 1.5 times, respectively. Total VFA´s removal efficiencies were higher at an inlet pH of 9. The alteration in the archaeal communities seen in the CSTR can be attributed to the rise in pH in the influent SM. It's interesting to note that during the anaerobic digestion of SM this pH rise prevented methanogenic archaea inhibition and improved ammonia removal from the culture broth via membrane extraction.

Previous studies examined the performance of two bioreactors with and without membrane ammonia extraction units using SM as model wastewater, and revealed a 9% increase in CH_4 output when the ammonia extraction unit was implemented (González-García et al., 2021). NaOH was also shown to be a SM pretreatment that increased CH_4 productivity by 13% in batch biochemical CH_4 production experiments (González-Fernández et al., 2008). When using a PTFE tubular gas membrane for NH_3 extraction, Molinuevo-Salces et al., (2018) found that the removal of COD increased from 58% to 68% in a semi-continuous CSTR operating under mesophilic conditions and treating SM at a hydraulic retention time of five days.

Similarly, on previous studies they evaluated the impact of membrane-based ammonia extraction on the treatment of wastewater containing poultry manure (PM) in a CSTR operated at 37 °C and a hydraulic retention time of 15 days. A decrease of 65% in TN and 53.4% in ammonia nitrogen was supported by the membrane-based ammonia extraction module interconnected to the digester, which led to an increase in CH_4 yields from 360 to 574 N mL CH_4 g VS fed^{-1}. Comparably, the removal efficiencies of VS and COD increased from 59% and 57% to 79% and 66%, respectively. Previous works found that CH_4 generation in two poultry manure leach-bed reactors with and without membrane-based NH_3 extraction was 2.3 times greater in the membrane-assisted digester (Bayrakdar et al., 2018). By using a membrane-based ammonia extraction unit interconnected to a leach-bed anaerobic digester treating PM, Bayrakdar et al. (2017) found a progressive drop in TAN concentration to 2 g L^{-1} and achieved a biogas yield of 300 N mL CH_4 g VS fed^{-1} during the dry AD of poultry manure.

Chapter 1

Rivera et al., (2023a) carried out a preliminary economic analysis of the whole expenses of TAN recovery from a CSTR combined with an ammonia extraction system based on membranes for anaerobic poultry manure treatment. Biogas sales (54 tons year $^{-1}$) and ammonium sulfate sales (5413 kg N year $^{-1}$) would provide the plant's income at full capacity. Indeed, 53,983 € would be generated from the sales of biogas (1000 € ton^{-1} of biogas) and 12,775 € (2.36 € kg $^{-1}$ of N as ammonium sulfate (Rothrock et al., 2013)) from the sales of the ammonium fertilizer. In this context, methods for extracting nitrogen from digestates are often expensive. For instance, the process of ammonia stripping can demand as much as 8.65 kWh kg^{-1} of recovered nitrogen. Therefore, membrane-based ammonia extraction emerges as an appealing technology due to its low energy requirements (aproximately 600 € year^{-1}). In brief, optimizing NH_3 extraction to enhance biogas production will be advantageous for the widespread adoption of anaerobic PM digestion processes on large scales.

Thus, the present thesis studies the integration of AD with gas permeable membrane technology to extract ammonia from swine and poultry manure, offering a sustainable solution for nitrogen removal. Gas-permeable membrane technology, known for its compact design and low energy consumption, efficiently separates ammonia from wastewater, enabling in-situ extraction. The process facilitates the production of valuable byproducts such as fertilizers and enhances biogas yields by reducing inhibition of ammonia in the AD process. Across the 4 publications presented in this thesis (**Chapters 4-7**) the main objective which is to enhance the AD process by removing ammonia with membrane technology has been achieved. Overall, this approach presents a promising avenue for environmentally friendly waste treatment and resource recovery. This innovative technology not only produces valuable products like biomethane for sustainable energy and ammonium sulfate for fertilizers but also supports the development of new biorefinery concepts for organic waste management. The validation of these concepts in the doctoral thesis underscores their importance in ensuring efficient resource utilization and expanding the principles of the circular economy.

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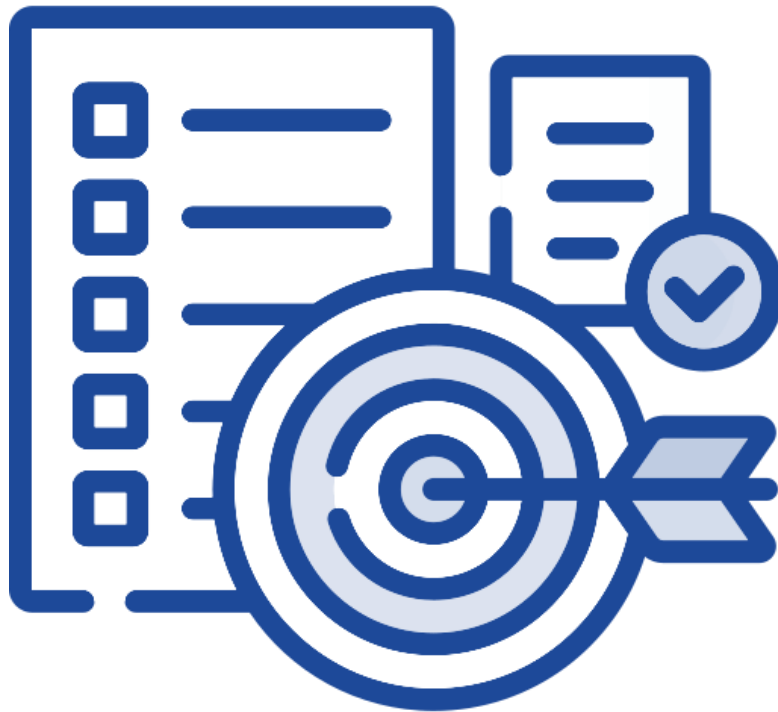
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Chapter 2

Aims and Scope of the Thesis

Chapter 2

2.1. Justification of the thesis

Biogas currently represents the byproduct from the anaerobic digestion of organic waste or wastewaters with the highest potential for valorization. Despite this potential, its utilization as a renewable substitute for natural gas still faces significant limitations, including the presence of contaminants such as CO_2, H_2S, NH_3, and volatile organic compounds. Additionally, the high nitrogen concentration typically existing in the organic waste limits the performance of classical anaerobic digestion processes and the potential biogas production, leading also to fugitive emissions of ammonia during subsequent digestate management. In this context, the recovery of NH_3 from digestates will help preventing the contamination of natural water bodies, which is important because this nitrogenous compound is harmful to fishes, increases the oxygen demand, and contributes to eutrophication. NH_3 also represents a risk to human health, causing respiratory issues and serving as a precursor to N_2O, a potent greenhouse gas. Thus, in-situ NH_3 recovery from digestates is essential for enhancing the environmental sustainability of anaerobic digestion processes and could offer additional economic advantages derived from the production of biofertilizers and the increase in methane productivity mediated by a partial reduction in NH_3 inhibition. Multiple commercial technologies are nowadays available to remove ammonia from wastewater, most of them exhibiting high operating costs and a high environmental impact due to nitrogen conversion and release into the atmosphere. As a result, there is a high demand for the development and implementation of cost-effective and environmentally friendly NH_3 recovery methods for high strength wastewaters like livestock effluents. Therefore, the use of hydrophobic membrane extraction units to in-situ recover ammonia from the anaerobic digestion process represents a novel approach that can contribute to the circular economy through the conversion of livestock wastewaters into valuable products such as biogas and NH_3-based fertilizers.

2.2. Main objectives

The main objective of this PhD thesis is to optimize an innovative operational strategy to enhance the anaerobic digestion process via extraction of ammonia with membrane technology to obtain higher biogas productivities and NH_3-based fertilizers, thereby mitigating the environmental and health hazards associated with untreated discharges. This approach will entail a reduction in the costs for biogas production and favor the implementation of a circular economy model during the management of livestock wastewaters. More specifically, the individual objectives pursued to achieve this overall goal were:

1. To optimize the most suitable design and operational parameters to reduce NH_3 from digestates using selective membrane permeation (i.e., temperature, pH, acid concentration, membranes, and flow rates).

2. To cost-effectively reduce the concentration of NH_3 in the anaerobic digestion broth during the continuous treatment of livestock wastewaters (i.e., piggery and poultry manure) and explore its associated enhancement in biogas productivity and wastewater treatment.

3. To evaluate the total costs of TAN recovery from poultry in an anaerobic digestion plant coupled with a membrane-based ammonia extraction system based on lab scale experiments data.

4. To systematically study the influence of the pH in the influent wastewater on the performance of anaerobic piggery wastewater treatment with membrane-based NH_3 extraction.

5. To identify the changes in microbial population structure of the culture broth mediated by the membrane-based ammonia extraction unit coupled to the anaerobic digester treating livestock wastewater.

2.3. Development of the thesis

In the present thesis, the anaerobic treatment of livestock wastewaters (i.e. piggery wastewater and poultry manure) combined with membrane-based NH_3 extraction was evaluated under different operational strategies and configurations.

Ammonia recovery from synthetic and real anaerobic digestates was carried out using hydrophobic flat sheet membranes operated with H_2SO_4 solutions to convert ammonia into ammonium sulphate. The influence of the membrane material, flow rate and pH of the digestate on ammonia recovery was initially investigated (**Chapter 4**). The impact of suspended solids and pH levels in anaerobically digested piggery wastewater on the extraction of NH_3 using a PTFE membrane was examined through batch tests. Additionally, the effect of NH_3 extraction using membranes on the anaerobic treatment of piggery wastewater was evaluated in a continuous stirred tank reactor connected with different PTFE membrane module configurations (**Chapter 5**). The impact of membrane-based ammonia extraction on the anaerobic treatment of poultry manure wastewater was also evaluated using a continuous stirred tank reactor. This study aimed at improving the efficiency of full-scale anaerobic digestion plants by lowering NH_3 concentration through the implementation of a membrane-based extraction unit. A preliminary techno-economic assessment was conducted to evaluate the economic sustainability of the process (**Chapter 6**). **Chapter 7** investigated the effect of the pH level of the inlet piggery wastewater (modified via NaOH addition) on both ammonia recovery and the performance of anaerobic digestion during piggery wastewater treatment in a continuous stirred tank reactor combined with a membrane-based extraction module. The impact of the pH of the piggery wastewater on the structure of the microbial population of the cultivation broth was also evaluated. Finally, **Chapter 8** summarizes the main conclusions and future work recommendations derived from this work.

Chapter 3

Materials and Methods
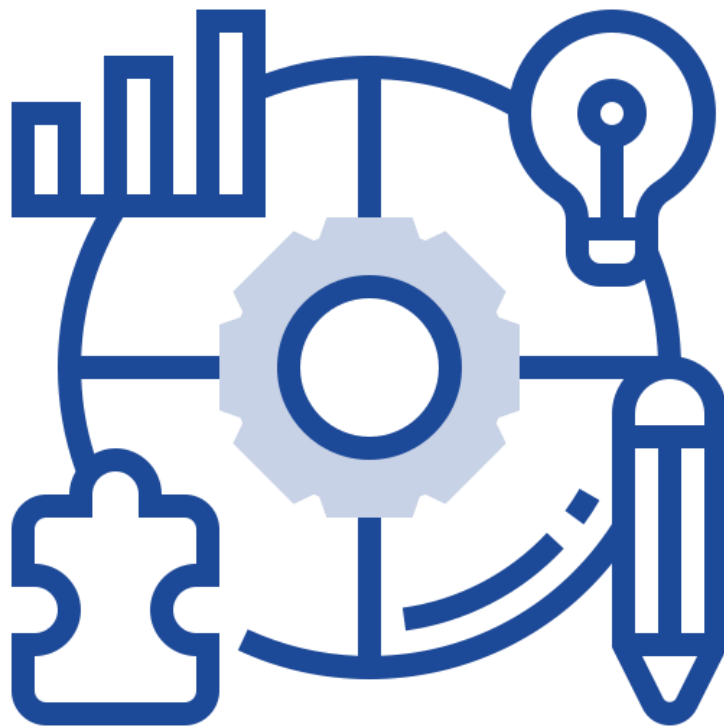
3.1. Materials

3.1.1. Membranes

The membranes used and their main characteristics are shown in **Table 1**. Polytetrafluoroethylene (PTFE) and polyvinylidene difluoride (PVDF) were selected as model commercial membranes based on their ideal properties for the separation of light molecules from water in a gaseous phase.

Table 1. Description of the flat sheet membranes studied.

Membrane	Material	Pore Size	Nominal Thickness (μm)	Contact angle (θ)	Porosity (%)	Wettability	Manufacturer
PVDF-100	PVDF	100 kDa	160	130-135	*	hydrophilic	KOCH
PVDF-0.10	PVDF	0.10 μm	130	130-135	*	hydrophobic	Sterlitech
PTFE-0.20	PTFE	0.20 μm	139	142	*	hydrophobic	Pall Gelman
PTFE-0.22	PTFE	0.22 μm	175	150	70	hydrophobic	Millipore
PTFE-0.45	PTFE	0.45 μm	135	155	*	hydrophobic	Pall Gelman

[*] Information not supplied by manufacturers.

3.1.2. Inocula and substrates

Substrates for **Chapter 4** were synthetic digestate (SD), with a composition mimicking that of a real digestate, consisting of 5.0 g $NaHCO_3$, 0.85 g $C_8H_5KO_4$, 0.73 g peptone from casein, 1.70 g NH_4Cl, 0.90 g $CO(NH_2)_2$, 0.224 g K_2HPO_4, 0.0175 g NaCl, 0.01 Ca_2Cl and 0.005 g $MgSO_4$ (per liter of distilled water) (Torres-Franco et al., 2021). The real digestate (RD) used in this study was supplied by Valladolid WWTP (Spain). This digestate was obtained from the anaerobic digestion of mixed sludge, on-site centrifuged prior to use to eliminate suspended solids. The concentration of NH_3 in SD and RD averaged 605.8 and 678.9 ppm, respectively, while pHs averaged 7.57 and 8.99, respectively.

In **Chapters 5 and 7**, fresh piggery wastewater, previously centrifuged in an industrial decanter, was used as a substrate. It was obtained from a nearby farm (Segovia, Spain) and stored at 4 °C for periods no longer than 45 days. Piggery wastewater exhibited a constant composition: 54.90 g COD L^{-1}, 1.62 g NH_3 L^{-1}, 5.51 g TKN L^{-1}, 31.51 g TS L^{-1}, 21.74 g VS L^{-1} and pH 7.54.

The anaerobic inoculum in **Chapter 5** was obtained from the full-scale digester of Valladolid wastewater treatment plant (WWTP) (Valladolid, Spain). The inoculum composition was as follows: 54.90 g COD L^{-1}, 0.33 g NH_3 L^{-1}, 1.62 g TKN L^{-1}, 13.00 g TS L^{-1}, 7.83 g VS L^{-1} and pH 7.90. The effluent from the experiment in **Chapter 5** (Rivera et al., 2022) was used as the inoculum in **Chapter 7**. The composition of this anaerobic inoculum was pH 8.21, 21.6 g COD L^{-1}, 1.14 g NH_3 L^{-1}, 3.8 g TKN L^{-1}, 23.8 g TS L^{-1} and 13.2 g VS L^{-1}.

In **Chapter 6**, Fresh poultry manure was collected from a poultry farm (Zaragoza, Spain), diluted 1:4 with tap water, sieved by # 20 (0.99 mm) and then stored at 4 °C. Every two weeks new diluted PM batches of 2 L were prepared. The average composition of the diluted PM was: pH 7.4 , 30 g COD L^{-1}, 0.7 g TAN L^{-1}, 3.3 g TKN L^{-1}, 32 g TS L^{-1}, 22 g VS L^{-1}, 10 g TOC L^{-1}, 1 g IC L^{-1}, 5 g acetic L^{-1}, 12 g propionic L^{-1}, 0.1 g isobutyric L^{-1}, 0.5 g butyric L^{-1}, 0.7 g Cl^- L^{-1}, 0.2 g PO_4^{-3} L^{-1} and 0.2 g SO_4^{-2} L^{-1}. The inoculum used was obtained from an anaerobic mesophilic pilot plant treating diluted PM located in Zaragoza, Spain, which generates biogas exclusively from diluted PM in a single stage. The composition of the inoculum was: pH 8.3, 3 g COD L^{-1}, 0.7 g TAN L^{-1}, 3 g TKN L^{-1}, 8 g TS L^{-1}, 3.3 g VS L^{-1}, 3.1 g TOC L^{-1}, 2 g IC L^{-1}, 5 g acetic L^{-1}, 9 g propionic L^{-1}, 0.01 g butyric L^{-1}, 0.2 g isovaleric L^{-1}, 1.4 g valeric L^{-1}, 1 g Cl^- L^{-1}.

3.1.3. Experimental Set-up

Fig. 1 depicts the experimental set-up used in **Chapter 4** for ammonia recovery from digestates. The target digestate (SD or RD) was continuously circulated using a peristaltic pump over the active layer of the membrane in a customized cell module. A sulfuric acid solution was recirculated using a similar peristaltic pump on the support layer of the membrane. Both digestate and sulfuric acid solutions were kept at 35 °C in a thermostatic bath in 0.5 L enclosed Erlenmeyer bottles.
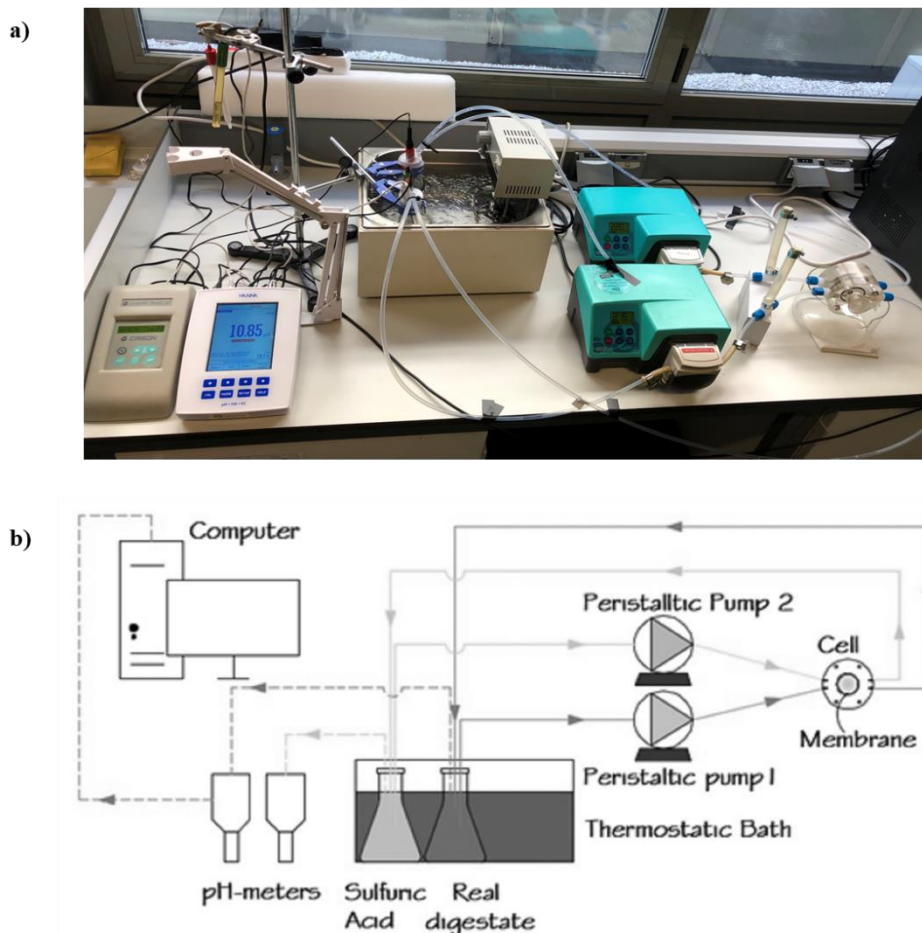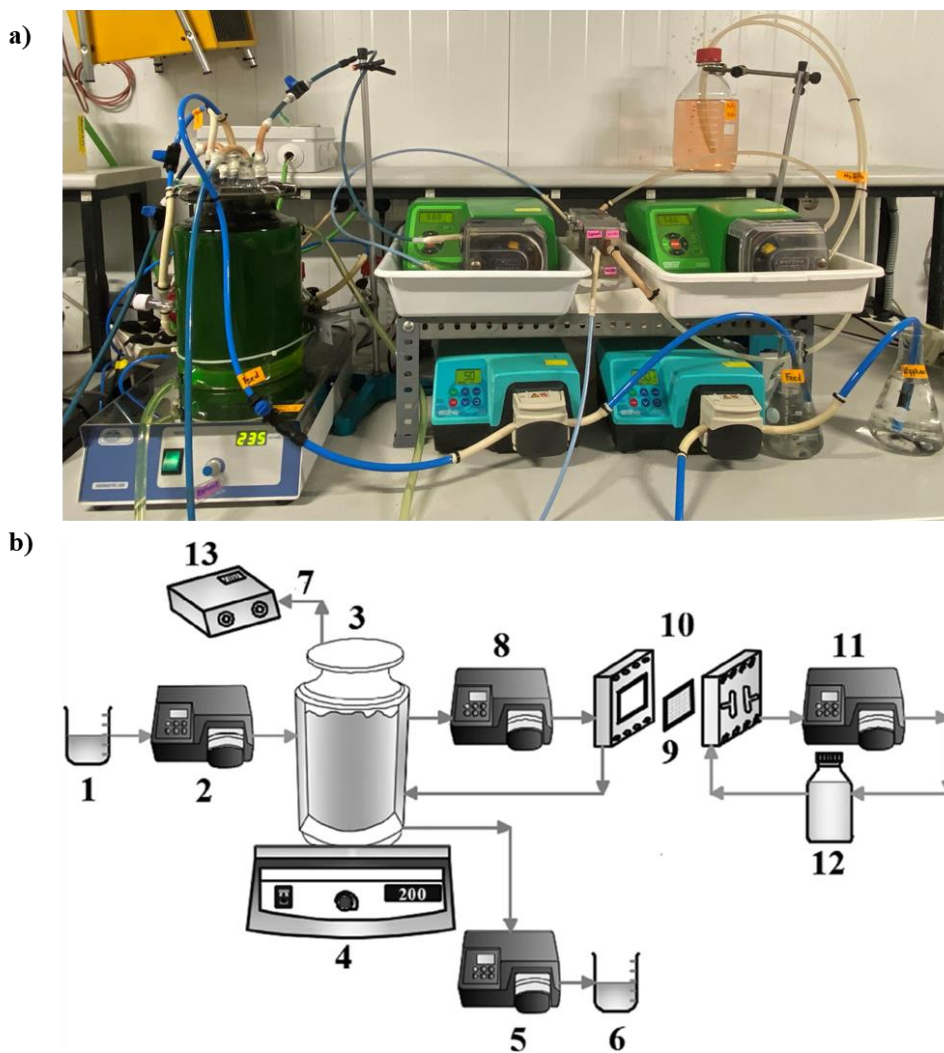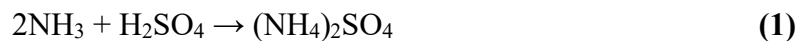
Fig. 1. Photograph (a) and schematic representation (b) of the lab scale ammonia recovery system used in **Chapter 4**.

Fig. 2 depicts the experimental set-up used in **Chapters 5 -7** which consisted of a 3000 mL CSTR magnetically stirred. The culture broth was tangentially recirculated with a peristaltic pump (at $0.25\ \mathrm{L\ min^{-1}}$ over the active layer of a hydrophobic flat sheet membrane holder, with neither spacers nor gaps. The flow inside the membrane holder operated under parallel cross-flow. A hydrophobic gas permeable membrane was herein used to extract NH_3. The use of a microporous and hydrophobic membrane favors the passage of gas since it has a high permeability to gas flows at low pressure. The passage of NH_3 through the membrane will be by diffusion, with NH_3 being captured by the acid solution that recirculates on the other since of the membrane. The extracted ammonia was captured in a 1 M sulfuric acid solution, which was also tangentially recirculated at $0.25\ \mathrm{L\ min^{-1}}$ over the support layer of the membrane with a peristaltic pump. Culture broth and sulfuric acid solutions were recirculated continuously on the membrane. Sulfuric acid recirculation is essential due to the reaction of ammonia with the acid contained in the permeate side of the hydrophobic membrane.

Chapter 3

A commercial fertilizer such as ammonium sulfate (**Eq. 1**) is generated during membrane-based ammonia recovery when using H_2SO_4, which boosts NH_3 diffusion (Darestani et al., 2017). pH and temperature (35–37 °C controlled temperature room) were monitored daily.

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \tag{1}$$

Fig. 2. Photograph (a) and schematic representation (b) of the lab scale CSTR coupled with a membraned-based ammonia extraction system used in **Chapters 5-7**. Influent (1), influent pump (2), CSTR (3), magnetic stirrer (4), effluent pump (5), effluent (6), biogas (7), cultivation broth recirculation pump (8), membrane (9), membrane holder (10), acid recirculation pump (11), acid reservoir (12) and biogas pulse counter (13).

Chapter 3

3.2. Analytical Methods

3.2.1. Digestate Samples

Ammoniacal nitrogen was measured using the Nessler's method at a wavelength of 425 nm in a SPECTROstar Nano spectrophotometer (BMG LABTECH, Germany). Concentrations of TS, VS, COD and TKN were examined according to Standard Methods for the analysis of water and wastewater (APHA, 2005). The determination of TKN and COD concentrations involved a preliminary digestion (Selecta Digestion Bloc, Bloc-Digest Macro 12) followed by distillation (Buchi distiller, Kjelflex K-360) and titration, respectively. pH and temperature were monitored using a Basic 20 pH meter with a 5014 T electrode (Crison Instruments, S.A., Spain). The concentrations of TOC, IC and TN were measured in a Shimadzu TOC-VCSH analyzer (Shimadzu, Japan) equipped with a TNM-1 chemiluminescence module. NO_3^-, NO_2^-, and PO_4^{-3} concentrations were analyzed by high-performance liquid chromatography-ion conductivity (HPLC-IC) (Waters, USA) 515 HPLC pump coupled to a Waters 432 conductivity detector using a Waters IC-Pak Anion HC column (15 cm × 0.46 cm) (Liu and Wang, 2016). VFAs concentrations were determined in an Agilent 7820A GC-FID (Agilent Technologies, USA) equipped with a G4513A autosampler and a TEKNOKROMA NF29370-F packed column (2 m × 1/8″ × 2.1 mm) (Teknokroma, Spain) (Dube et al., 2016). Pretreatment of the samples for VFAs analysis consisted of a centrifugation of 10 min at 7000 rpm. Then, the supernatant was filtered by 0.45 μm, afterwards diluted 1:40 and filtered again by 0.22 μm. The sample was acidified with 20 μL for every mL of sample with sulfuric acid. The standard used for the calibration curve was a mixture of VFAs from Sigma Aldrich (Merck, Germany).

3.2.2. Biogas Samples

Carbon dioxide, hydrogen sulfide, oxygen, nitrogen and methane concentrations were determined using a gas-tight syringe (Hamilton, 1710 SL SYR, 100 μL, United States) in a gas chromatograph with thermal conductivity detection (Varian CP-3800, United States). The GC-TCD was equipped with a CP-Pora BOND Q capillary column (25 m × 0.53 mm × 10 μm) and a CP-Molsieve 5 A capillary column (15 m × 0.53 mm × 15 μm). The gas carrier was Helium (ultra-pure at 13 mL min^{-1}).

3.2.3. Membrane characterization

Surface morphology was analysed by using Atomic Force Microscopy. Images were obtained with a Nanoscope IIIA microscope (Digital Instruments, Veeco Metrology Group, Chadds Ford, PA, USA) using the Tapping mode. Pore size distribution was analysed by the extended bubble point method, or Air Displacement Porometry (ADP), using a Coulter ® Porometer-II manufactured by Coulter Electronics (Porometer, Aptco Invest, Dulles, VA, USA) (Hernández et al., 1996). Samples were first wetted with an electronic liquid FC-43 (FluorinertTM, 3 M, St. Paul, MN, USA) of low surface tension (γ 1.6 × 10−2 N m−1), low vapour pressure (192 Pa) and low reactivity, that can be assumed to fill all the pores given a zero contact-angle with the membrane material. The wetted sample was subjected to increasing pressure, applied by a compressed clean and dry air source. The pressure range for PTFE 0.22 membrane was 0.09 – 0.60 µm.

3.3. Theoretical considerations

3.3.1. Mass transfer

The overall mass transfer coefficient of NH_3 has been calculated with **Eq. 2** according to (Hasanoĝlu et al., 2010).

$$\frac{1}{k_{ov}} = \frac{1}{k_s} + \frac{1}{k_m} \tag{2}$$

Here k_s and k_m are the mass transfer coefficients in the digestate side and within pores, respectively. The resistance in the acid solution side can be considered negligible (i.e., mass transfer coefficient on the acid side is much larger than k_s and k_m). In this context, the mass transfer coefficient on the digestate side can be estimated using **Eq. 3**:

$$k_s = \frac{D_{AW} Sh}{D_H} \tag{3}$$

D_{aw}, Sh and DH are diffusion coefficient of NH_3 in water calculated using the software ASPEN (AspenTech, Bedford, Massachusetts, USA) at 35 °C the Sherwood dimensionless number (Torres-Franco et al., 2021) and the hydraulic diameter, respectively. Similarly, the mass transfer coefficient within pores can be calculated by **Eq. 4** (Malek et al., 1997; Montalvillo et al., 2014):

$$k_s = \frac{\epsilon D_{ij}}{\tau \delta} \qquad (4)$$

τ, δ, D_{ij} and ϵ are the tortuosity, the wall thickness of the membrane, the diffusion coefficient of NH_3 in the air gap within pores and the porosity of the membrane, respectively. Assuming Knudsen regime (Hasanoĝlu et al., 2010) Dij can be calculated in terms of the pore diameter (d_p) and NH_3 molar mass m:

$$D_{ij} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi m}} \qquad (5)$$

The molar theoretical flux of NH_3 across the membrane can be estimated using **Eq. 6** (Guo et al., 2019):

$$J_T = k_{ov} \Delta C \qquad (6)$$

Here ΔC is the difference in NH_3 concentrations between feed and permeate sides. Finally, NH_3 recovery seems to follow first-order kinetics, which can be estimated using **Eq. 7** (Amaral et al., 2016; Mahmud et al., 2000):

$$ln\frac{C_o}{C_t} = k_{ov}\frac{A_m}{V_t}t \qquad (7)$$

k_{ov}, A_m/V_t and t are the overall mass transfer coefficient, the effective ratio of membrane area to feed volume of the digestate and elapsed time, respectively. C_0 and C_t are the concentration of ammonia at time zero and time t in the digestate, respectively. NH_3 recovery (R) ranges between 0 and 1 (**Eq. 8**):

$$R = 1 - \frac{C_t}{C_0} = 1 - e^{-k_{ov}\frac{A_m}{V_t}t} \equiv 1 - e^{-\alpha t} \qquad (8)$$

Here $\alpha = k_{ov}\frac{A_m}{V_t}$ is the rate of concentration decrease and recovery increase. Therefore, the time needed to reach a given R can be estimated using **Eq. 9**:

$$t(R) = -\frac{ln(1-R)}{k_{ov}\frac{A_m}{V_t}} = -\frac{ln(1-R)}{\alpha} \qquad (9)$$

3.3.2. Mass balance

The global mass balance calculation for Nitrogen and Carbon were calculated based on the average concentrations of all their chemical species at the input (PWW) and output (effluent).

Nitrogen mass balance:

$$TKN_{PWW}\, Q_{PWW} = TKN_{EFF}\, Q_{EFF} + N_2 \tag{10}$$

Carbon mass balance:

$$C_{PWW}\, Q_{PWW} = C_{EFF}\, Q_{EFF} + CO_2 + CH_4 \tag{11}$$

where TKN, NH_3 and TC $(g\ L^{-1})$ stand for the concentrations in the influent (PWW) and effluent (EFF). Q_{PWW} stands for the influent PWW flowrate $(L\ d^{-1})$ and Q_{EFF} for the effluent flowrate $(L\ d^{-1})$. N_2, CO_2 and CH_4 represent the molar flow rate $(mol\ d^{-1})$ of each gas estimated according to their compositions (%).

3.3.3. Economic Assessment

The values used in the techno-economic evaluation were based on experimental results and the following assumptions: An annual production of raw PM in a farm of 1200 m^2 and 13,400 chickens would be 1,217 m^3 $year^{-1}$ approximately. The raw poultry manure contains 0.72 g TAN L^{-1}. The digester has a capacity of 150 m^3 with daily feeding of 15 m^3 d^{-1}. PM costs would not be considered because it would be produced in the farm with no transportation costs. The CAPEX (Capital Expenditures) were calculated according to the main equipment, while the Total Investment Cost were calculated as 4.1 × CAPEX (Pérez et al., 2022). The OPEX (Operational Expenditures) were calculated according to the main consumables: energy, water and chemicals. Maintenance costs are estimated as 3.5 % of the CAPEX. For the flatsheet membrane a 10 % of replacement per year was considered. Annual costs of equipment are calculated using a 10-year lifetime and 4 % interest (du Preez et al., 2005).

For the theoretical design of the scaled-up plant, TAN recoveries of 5.475 kg TAN $year^{-1}$ were estimated. A membrane surface area of 220 m^2 is needed in the scaled-up plant to achieve the target TAN recoveries. The total investment cost, considering 4 % interest and 10-year lifetime is 601,291 € (bioreactor, storage tanks, pumps, membrane

module, acid tank, reagents, power and water). The annualized cost 10-year lifetime at 4 % interest is 485,036 €.

The revenues in the full scale plant would be obtained from the sales of biogas (54 ton year^{-1}) and ammonium sulfate (5413 kg N year^{-1}). The sales of biogas would account for 53,983 €. On the other hand, the corresponding fertilizer value accounts for 12,775 € (2.36 € kg^{-1} of N as ammonium sulfate (Rothrock et al., 2013)).

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Chapter 3

Torres-Franco, A.F., Zuluaga, M., Hernández-Roldán, D., Leroy-Freitas, D., Sepúlveda-Muñoz, C.A., Blanco, S., Mota, C.R., Muñoz, R., 2021. Assessment of the performance of an anoxic-aerobic microalgal-bacterial system treating digestate. Chemosphere 270. https://doi.org/10.1016/j.chemosphere.2020.129437

Chapter 4

## A systematic study of ammonia recovery from anaerobic digestate using membrane-based separation
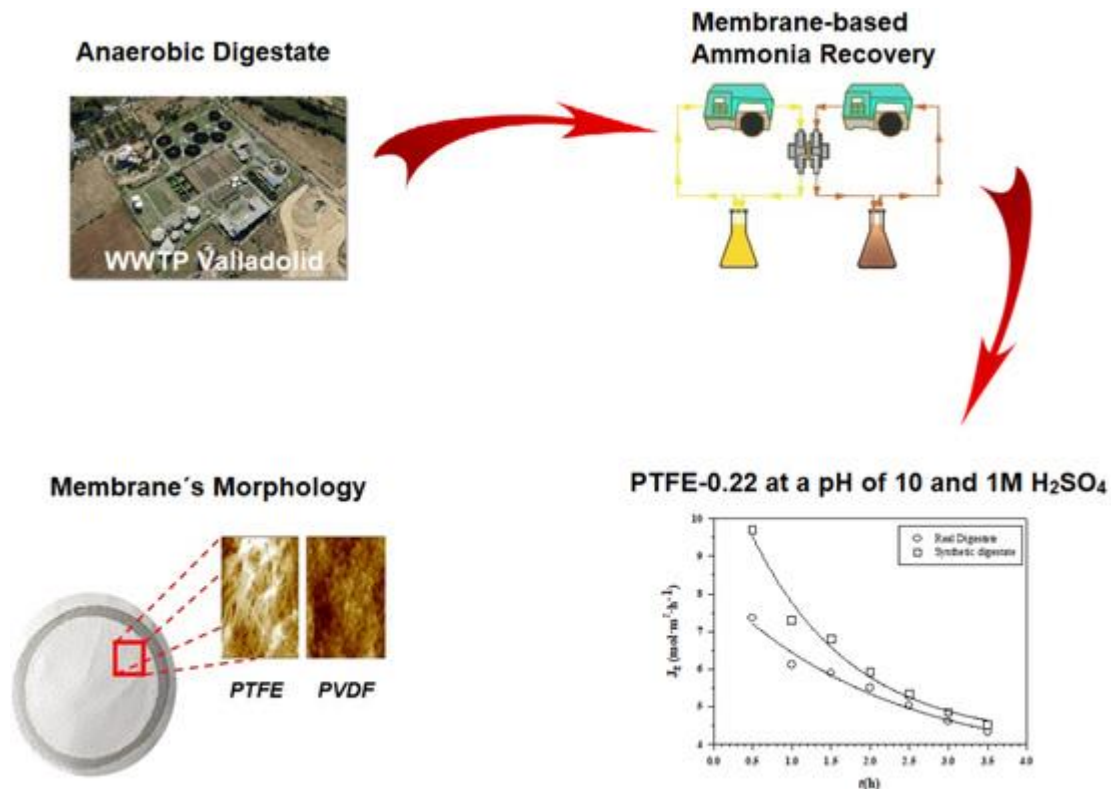
Abstract

Ammonia recovery from synthetic and real anaerobic digestates was accomplished using hydrophobic flat sheet membranes operated with H_2SO_4 solutions to convert ammonia into ammonium sulphate. The influence of the membrane material, flow rate (0.007, 0.015, 0.030 and 0.045 m^3 h^{-1}) and pH (7.6, 8.9, 10 and 11) of the digestate on ammonia recovery was investigated. The process was carried out with a flat sheet configuration at a temperature of 35 °C and with a 1 M, or 0.005 M, H_2SO_4 solution on the other side of the membrane. Polytetrafluoroethylene membranes with a nominal pore radius of 0.22 μm provided ammonia recoveries from synthetic and real digestates of 84.6% ± 1.0% and 71.6% ± 0.3%, respectively, for a membrane area of 8.6 × 10^{-4} m^2 and a reservoir volume of 0.5 L, in 3.5 h with a 1 M H_2SO_4 solution and a recirculation flow on the feed side of the membrane of 0.030 m^3 h^{-1}. NH_3 recovery followed first order kinetics and was faster at higher pHs of the H_2SO4 solution and recirculation flow rate on the membrane feed side. Fouling resulted in changes in membrane surface morphology and pore size, which were confirmed by Atomic Force Microscopy and Air Displacement Porometry.

Chapter 5

## Enhancement of swine manure anaerobic digestion using membrane-based NH$_3$ extraction
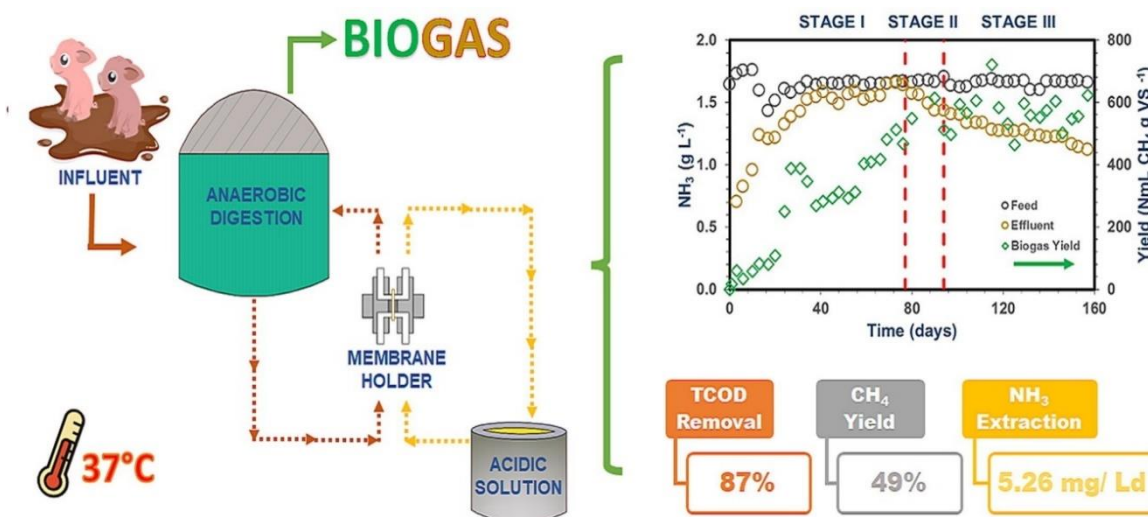
Abstract

The influence of suspended solids and pH in anaerobically digested piggery wastewater on membrane-based NH_3 extraction was evaluated in batch tests. The increase in pH in the anaerobic broth from 8 to 9 resulted in an increase in NH_3 removal efficiencies from 15.8 % ± 0.1 % to 20.9 % ± 0.4 % regardless of the suspended solids. The influence of membrane based NH_3 extraction on piggery wastewater treatment was also assessed in a CSTR interconnected with PTFE membrane modules. The decrease in TKN concentrations mediated by membrane operation induced an increase in CH_4 yield from 380.4 ± 84.9 up to 566.1 ± 7.8 $NmLCH_4$ g VS fed^{-1}. Likewise, COD and VS removal efficiencies significantly increased from 33.0 % ± 2.0 % and 25.7 % ± 2.3 % up to 61.8 % ± 1.3 % and 37.9 % ± 1.8 %, respectively. Interestingly, the decrease in NH_3 concentration entailed a complete assimilation of VFA.

Chapter 6

Side-stream membrane-based NH$_3$ extraction to improve the anaerobic digestion of poultry manure
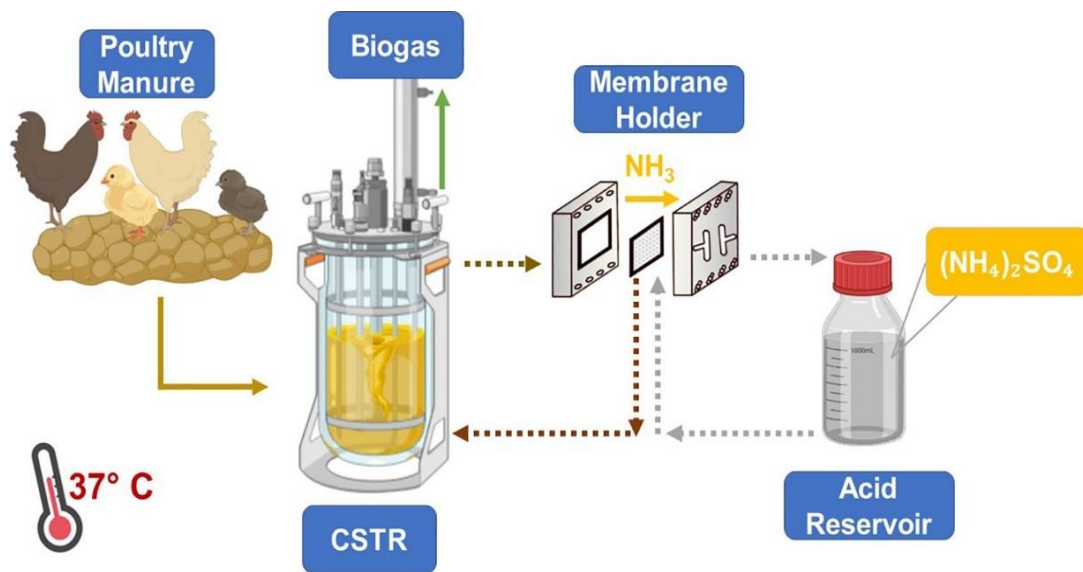
$$\downarrow[NH_3] = \uparrow \text{Biogas Productivity} + \uparrow COD\%_{removal} + \uparrow VS\%_{removal} + \downarrow[VFA]$$

F. Rivera; Joseph Akpan; Pedro Prádanos; Antonio Hernández; Laura Palacio; Raúl Muñoz, Side-stream membrane-based NH$_3$ extraction to improve the anaerobic digestion of poultry manure, J. Water Process Eng. 54 https://doi.org/10.1016/j.jwpe.2023.103990

Abstract

The influence of membrane-based ammonia extraction on poultry manure (PM) wastewater treatment was assessed in a 3 L continuous stirred tank reactor (CSTR). The anaerobic digester operated for 91 days at a hydraulic retention time of 15 days and 37 °C. The flat sheet polytetrafluoroethylene (PTFE) membrane module was interconnected to the CSTR and operated at a recirculation flow rate of 0.25 L min $^{-1}$. The membrane-based ammonia extraction mediated a decrease of total ammonia nitrogen of 64.5 % and of total nitrogen of 53.4 %, which induced an increase in the methane yields from 360 ± 70 up to 574 ± 5 N mL CH_4 g VS fed $^{-1}$. Similarly, chemical oxygen demand (COD) and volatile solids (VS) removal efficiencies increased from 59 % ± 2 % and 57 % ± 3 % up to 79.1 % ± 0.8 % and 65.8 % ± 0.2 %, respectively. This work targeted the enhancement of the performance of full-scale anaerobic digestion plants via reduction of NH_3 concentration with a membrane-based extraction unit.

Chapter 7

Influence of pH on the performance of anaerobic piggery wastewater treatment coupled with membrane-based NH₃ extraction

F. Rivera, Cristian A. Sepúlveda-Muñoz, P. Prádanos, A. Hernández, L. Palacio, R. Muñoz, Influence of pH on the performance of anaerobic piggery wastewater treatment coupled with membrane-based NH₃ extraction, J. Water Process Eng.
https://doi.org/10.1016/j.jwpe.2023.104226
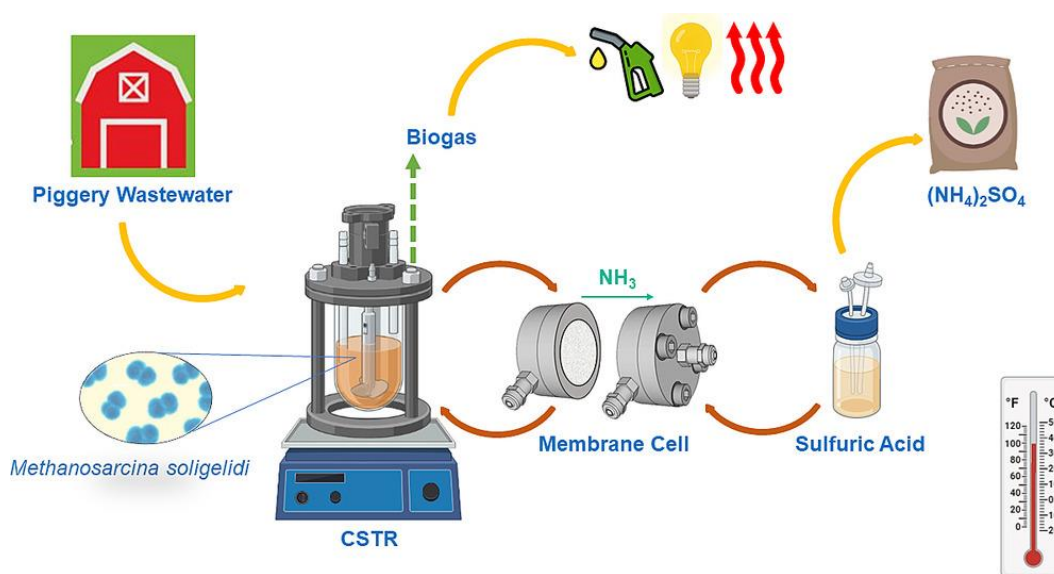
Abstract

The influence of the pH of piggery wastewater (PWW) on both ammonia recovery and anaerobic digestion performance during PWW treatment was evaluated in a continuous stirred tank reactor coupled with a membrane-based extraction module. The anaerobic digester was operated at a hydraulic retention time of 20 days at 37 °C, while the flat sheet PTFE membrane module operated continuously at liquid recirculation rates of 250 mL min^{-1}. The membrane module was able to gradually decrease the total ammoniacal concentration from 1.27 ± 0.01 to 0.62 ± 0.01 g L^{-1} after 360 days of operation. Membrane-based NH$_3$ extraction induced a CH$_4$ yield increase of 1.3-fold. Moreover, COD and VS removal efficiencies increased up to 1.2-fold and 1.5-fold, respectively, along with the increase in PWW pH from 7.5 to 12. Total VFAs removal efficiencies were higher at a PWW pH of 9.

Chapter 8

Conclusions and future work

Chapter 8

The successful implementation of an optimized and innovative operational approach aimed at enhancing anaerobic digestion via interconnection with membrane technology to *in-situ* remove ammonia was here validated. This process results in the simultaneous production of biogas and fertilizers, thereby addressing environmental and health risks associated with untreated wastewater discharges and NH_3 emissions. This thesis confirmed that anaerobic digestion assisted by NH_3-permeable membranes represents a sustainable and eco-friendly method to valorize livestock wastewaters.

This work thoroughly examined the feasibility of several commercially available flat sheet membranes for the recovery of ammonia, along with their susceptibility to fouling, utilizing both synthetic and real digestate samples. PTFE emerged as the most efficient material for ammonia recovery regardless of the type of digestate being used. The highest levels of ammonia recovery were achieved when the pH of the digestate was increased to 10 and 1 M sulfuric acid was employed. Furthermore, it was observed that ammonia recovery rates increased with higher digestate circulation flow rates due to a reduction in mass transfer resistance. The process of ammonia recovery using PTFE membranes was found to follow a first-order kinetics, with faster rates observed under alkaline pH conditions, higher concentrations of sulfuric acid, and increased recirculation flow rates on the digestate side of the membrane. A PTFE-0.22 membrane operating under optimal conditions demonstrated ammonia recoveries of 72% and 85% after only 3.5 hours of operation using real and synthetic digestates, respectively. After 6 hours of operation, ammonia recoveries of 94% were achieved in synthetic digestate under similar operational conditions, in line with the kinetics assumed in the study.

With the results of the optimal operating parameters obtained in batch tests, further experiments conducted in a CSTR were carried out to enhance the anaerobic digestion process and optimize the recovery of ammonia. More specifically, it was demonstrated that enhancing the anaerobic treatment of piggery wastewater can be achieved by reducing NH_3 concentrations in the anaerobic broth through membrane assisted NH_3 extraction. As pH levels rise in the digestate via NaOH addition, an increase in ammonia recovery was observed. The presence of suspended solids in the anaerobic broth did not significantly affect NH_3 extraction during the early stages of the process. The implementation of a membrane module interconnected to the anaerobic digester during the treatment of piggery wastewater resulted in improved removal efficiencies of COD and VS by 87% and 48%

correspondingly, with a complete assimilation of VFA. While the composition of biogas remained stable, methane production experienced a notable increase by 49%. The enhancement of the process was also confirmed when using poultry manure (PM) as substrate. The performance of anaerobic digestion treatment for PM wastewater consistently improved through membrane-assisted ammonia extraction. The continuous extraction of ammonia from the cultivation broth facilitated by NH_3 diffusion through the membrane, leading to a reduction in ammonia concentrations in the cultivation broth. Consequently, methane yield increased by 60% while biogas composition remained constant during the operation of a membrane module interconnected to the digester treating PM. Moreover, an increase in the removal efficiencies of COD and VS, reaching up to 79% and 66%, respectively, was recorded. VFAs were completely assimilated resulting in removal efficiencies of 100%. However, membrane fouling, likely caused by microorganisms, inorganic, and residual organic matter, was detected in the membrane after 20 days of operation. A specific power consumption of 0.48 kWh kg^{-1} of recovered N was theoretically estimated in a full-scale plant.

Subsequently, the effects of pH were studied during the in-situ extraction of ammonia through membrane permeation from the anaerobic broth, with a considerable improvement in the performance of piggery wastewater anaerobic digestion observed at increasing pH values. Higher influent pH levels of piggery wastewater combined with NH_3 extraction led to increased removal of organic matter and biogas production, peaking at an optimal pH of 11. Reducing the concentration of ammonia in the broth from 1.3 to 0.67 mg N L^{-1} resulted in significant enhancements in the removal of VS, COD, and VFAs, achieving efficiencies of 64%, 80%, and 92%, respectively. Furthermore, both the methane content and yield rose from 76% to 84% CH_4 and from 207 to 275 NmLCH4 g COD fed^{-1}, respectively, as a result of NH_3 extraction and pH increase.

Overall, the main objective of this study was to enhance the performance of full-scale anaerobic digestion plants by reducing NH_3 concentration using a membrane-based extraction unit that would also allow to recover ammonia. This innovative technology has the potential to support the production of valuable products such as a sustainable energy vector in the form of biomethane and fertilizers like ammonium sulfate. Despite the advances carried out in the present thesis towards the enhancement of the anaerobic

digestion process via removal of ammonia with membrane technology, further research is still needed to move forward in the implementation of this technology:

- Assessing the energy usage, emissions, and indirect environmental impacts through a life cycle assessment methodology of the anaerobic digestion process couple to membrane-based NH_3 extraction to obtain biogas and fertilizers is essential. This assessment will play a critical role in evaluating both the technical and environmental performance of this technology, aiming to enhance energy efficiency and minimize the carbon footprint.

- The fabrication of customized hydrophobic gas NH_3 permeable membranes designed to withstand elevated levels of acids in their supporting layers and increased recirculation flow rates for this process of in-situ ammonia extraction from the anaerobic digestion process under continuous operation.

- The complete automatization of the anaerobic bioreactor coupled with membrane-based NH_3 extraction process, which would improve the performance of this innovative technology during the valorization of livestock wastewaters.

- The scale-up of the anaerobic bioreactor coupled with membrane-based NH_3 extraction process, which will provide more reliable results due to reduced variability and increased sample size, providing a clearer picture of the ammonia removal, biogas productivity and fertilizers production potentials.

Chapter 9

About the Author

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Biography

Fanny Maritza Rivera Mejía was born in La Ceiba, Atlántida, Honduras. She studied Civil Engineering in the Universidad Católica de Honduras and holds a MSc in Environmental Engineering from the University of Valladolid, Spain (2014). During her master thesis, she conducted a research focused in *Wasterwater Pretreatment with membranes*. She has been awarded several fellowships, a summer course *Environmental Assessment and Sustainability* at Universidad Complutense de Madrid (2012). She has always been committed with the environment, being the environmental coordinator of the Golosón International Airport in La Ceiba, Honduras (2019-2020) and professor of the faculty of Civil Engineering of the Universidad Católica de Honduras (2017-2019).

Fanny joined the VOC and Microalgae group and SMAP research group in 2020, to conduct her thesis project *Optimization Membrane for NH_3 Recovery and Improvement in the Agro-Industrial Wastewater Treatment.* She made a research stay at the department of Earth and Environmental Engineering from the University of Columbia in New York city.

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Publications in international journals:

1. Rivera F.; Sepúlveda-Muñoz C.A.; Prádanos P.; Hernández A.; Palacio L.; Muñoz R., 2023. Influence of pH on the performance of anaerobic piggery wastewater treatment coupled with membrane-based NH_3 extraction. J. Water Process Eng. 55(2023)104226. https://doi.org/10.1016/j.jwpe.2023.104226

2. Rivera F.; Akpan J.; Prádanos P.; Hernández A.; Palacio L.; Muñoz R., 2023., Side-stream membrane-based NH_3 extraction to improve the anaerobic digestion of poultry manure, J. Water Process Eng. 54 (2023)103990. https://doi.org/10.1016/j.jwpe.2023.103990

3. Rivera F.; Villarreal L..; Prádanos P.; Hernández A.; Palacio L.; Muñoz R., 2022. Enhancement of swine manure anaerobic digestion using membrane-based NH_3 extraction, Bioresour. Technol. 362 (2022) 127829. https://doi.org/10.1016/j.biortech.2022.127829

4. Rivera F.; Muñoz R.; Prádanos P.; Hernández A.; Palacio L., 2022. A Systematic Study of Ammonia Recovery from Anaerobic Digestate Using Membrane-Based Separation, Membranes (Basel). 12 (2022) 19. https://doi.org/10.3390/membranes12010019

5. T.A. Nascimento, F.R. Mejía, F. Fdz-Polanco, M. Peña Miranda, Improvement of municipal wastewater pretreatment by direct membrane filtration, Environ. Technol. (United Kingdom). 38 (2017) 2562–2572. https://doi.org/10.1080/09553330.2016.1271017.v

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Conferences:

1. <u>Rivera F.;</u> Prádanos P.; Hernández A.; Palacio L.; Muñoz R "Effect of the pH on the performance of anaerobic piggery wastewater treatment coupled with membrane-based ammonia extraction". Oral Presentation, XIV Latin American Workshop and Symposium on Anerobic Digestion. Querétaro, Mexico, October 2023

2. <u>Rivera F.;</u> Prádanos P.; Hernández A.; Palacio L.; Muñoz R "Membrane-based Ammonia Extraction to Enhance the Anaerobic Digestion Process of Poultry Manure". Oral Presentation, 3rd International Conference on Pollution Prevention and Clean Technologies, Institute of Technology and Business, České Budějovice, Czech Republic, September 2023

3. <u>Rivera F.;</u> Prádanos P.; Hernández A.; Palacio L.; Muñoz R ¨Improvement of the anaerobic digestion of piggery wastewater using membrane filtration¨ Oral Presentation, WasteEng2022, Copenhagen, Denmark, June 2022

4. <u>Rivera F.;</u> Prádanos P.; Hernández A.; Palacio L.; Muñoz R ¨Improvement of the anaerobic digestion of piggery wastewater using membrane filtration¨ Oral Presentation and poster, Jornada de Jóvenes Investigadores Iberoamericanos, Tordesillas, Spain, March 2022

5. <u>Rivera F.;</u> Muñoz R; Prádanos P.; Hernández A.; Palacio L. ¨Eliminación de NH_3 de digestato anaerobio mediante membranas planas y el estudio de su ensuciamiento¨ Oral Presentation, Investigadoras de Castilla y León. La aventura de la Ciencia y la Tecnología, Valladolid, Spain, June 2021

6. <u>Rivera F.;</u> Muñoz R; Prádanos P.; Hernández A.; Palacio L. ¨Eliminación de NH_3 de digestato anaerobio mediante membranas planas y el estudio de su ensuciamiento¨ Oral Presentation and poster, Jornada de Jóvenes Investigadores Iberoamericanos, Tordesillas, Spain, October 2020

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Research stay:

Earth and Environmental Engineering Department, Columbia Engineering, Columbia University, New York, New York (United States of America). September to December 2023. Supervisor: Professor Ngai Yin Yip.

Fellowships:

1. Erasmus plus Internship grant for Columbia University, New York, New York, United States of America (2023).
2. Uva- Internship grant for Columbia University, New York, New York, United States of America (2023).
3. Uva- Travel and accommodation grant for Congress WasteEng2022, Copenhagen, Denmark, June (2022).
4. UVa-Predoctoral researcher Fellowship (2021).
5. ISP researcher Fellowship (2020).
6. Master´s fellowship; Masters in Environmental Engineering; Máster Oficial/Iberoamérica +Asia Universidad de Valladolid- Banco Santander (2013-2014).
7. Summer Course; Environmental Assessment and Sustainability/ Escuela de Verano; Iberoamérica +Asia Fundación Carolina/Universidad Complutense de Madrid (2012)

Professional Membership:

- Member of the Institute of Sustainable Processes (ISP) of the University of Valladolid since 2020.
- Colegio de Ingenieros Civiles de Honduras (CICH): 7270 since 2016.

Reviewing for scholarly journals:

- Journal of Environmental Management (Elsevier)

Teaching:

- Academic year 2023/2024: 1.58 ECTS in Técnicas Experimentales en Física II, Universidad de Valladolid

- Academic year 2022/2023: 2.26 ECTS in Técnicas Experimentales en Física II, Universidad de Valladolid

- Academic year 2021/2022: 1.29 ECTS in Técnicas Experimentales en Física II, Universidad de Valladolid

- Academic year 2019: 3 ECTS in Ecología, Universidad Pedagógica de Honduras

- Academic year 2018: 6 ECTS in Ecología, 3 ECTS in Ingeniería Ambiental, 1 ECT in Laboratorio de Física, 3 ECTS in Física Médica,1 ECT in Laboratorio de Física Médica, 3 ECTS in Ingeniería Sanitaria, 3 ECTS in Estática, 3 ECTS in Mecánica de Sólidos, 4 ECTS in Bioestadística, 4 ECTS in Matemáticas, Universidad Católica de Honduras

- Academic year 2017: 3 ECTS in Ecología, 3 ECTS in Ingeniería Ambiental, 3ECTS in Física, 3ECTS in Hidráulica I, 1 ECT in Laboratorio de Hidráulica I, 3 ECTS in Hidráulica II, 3 ECTS in Ingeniería de Riegos, 6 ECTS in Mecánica de Sólidos, 4 ECTS in Precálculo,4 ECTS in Matemáticas, 3 ECTS in Química, Universidad Católica de Honduras

Certifications:

- Pedagogical Studies and training for Higher Education, Universidad Pedagógica Nacional Francisco Morazán, 2019
- Virtual Teaching, Uniminuto, 2017
- Climate Change, World Bank, 2015
- Environmental Assessment and Sustainability Universidad Complutense de Madrid, 2012

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Students Mentoring:

- Co-supervisor of undergraduate student in Chemical Engineering at University of Valladolid. Student: Luis Villarreal Heras (march-september 2023)
- Co-supervisor of a Master Thesis in the Master of Environmental Engineering at University of Valladolid. Student: Joseph Akpan (october-december 2022)
- Co-supervisor of undergraduate student in Chemical Engineering at University of Valladolid. Student: Luis Villarreal Heras (may-august 2021)

Bachelor Theses Dissertation Committee:

- Richard Gough, Defensa de Práctica Profesional, Universidad Católica de Honduras, 2018
- Franklin Hernández, Defensa de Práctica Profesional, Universidad Católica de Honduras, 2018
- Nilda Medrano, Defensa de Práctica Profesional, Universidad Católica de Honduras, 2018
- María Edith Rodríguez, Defensa de Práctica Profesional, Universidad Católica de Honduras, 2017
- Mirtha Acosta, Defensa de Práctica Profesional, Universidad Católica de Honduras, 2017
- Arnold Núñez, Defensa de Práctica Profesional, Universidad Católica de Honduras, 2017

Attended Courses and Seminars:

1. Jornadas de Investigadoras de Castilla y León, La aventura de la Ciencia y la Tecnología, Universidad de Valladolid, 2024
2. Workshop Biorrefinerías: Redefiniendo la manera en la que gestionamos los residuos, Universidad de Valladolid, 2024
3. Iniciación a la escritura de propuestas de proyectos de investigación, Universidad de Valladolid, 2024
4. Can we use biology to solve problems in chemistry? The case of forever chemical by Carla Ng from University of Pittsburgh, Columbia University, 2023

5. Sustainably scaling up critical metals production by Karan Bhuwalka from Massachusetts Institute of Technology (MIT), Columbia University, 2023

6. New frontiers in resource recovery coupled to carbon transformations for a sustainable climate, environment, and environmental future by Greeshma Gadikota from Cornell University, Columbia University, 2023

7. Science, engineering, and technology in energy transition by Marko Topic from University of Ljubljana, Columbia University, 2023

8. Advancements in nano-enabled membrane distillation for sustainable water - energy environment nexus by Alicia An from Hong Kong University of Science and Technology (HKUST), Columbia University, 2023

9. Rethinking Water: Solutions Now for America's Water Infrastructure, Columbia University, 2023

10. Graduate student symposium, Columbia University, 2023

11. Introducción al diseño de experimentos, Universidad de Valladolid, 2023

12. Elaboración de una propuesta de proyecto, Universidad de Valladolid, 2023

13. BIP course Biological Carbon Capture Technologies, Universidad de Valladolid, 2023

14. Realización de figuras de calidad para artículos científicos, Universidad de Valladolid, 2023

15. Procesos Térmicos de Valorización de residuos, Universidad de Valladolid, 2023

16. Taller de divulgación científica para personal investigador, Universidad de Valladolid, 2023

17. Introducción al diseño de experimento, Universidad de Valladolid, 2023

18. El arte de ser profesional, Universidad de Valladolid, 2023

19. Elaboración de una propuesta de proyecto, Universidad de Valladolid, 2022

20. Valorización de resultados de investigación y creación de EBTS, Universidad de Valladolid, 2022

21. Workshop Polymers for Environmental Preservation and Remediation, Universidad de Valladolid, 2022

22. Como orientar tu carrera académica, Universidad de Valladolid, 2022

23. Valorización y tratamiento de residuos, Universidad de Valladolid, 2022

24. Análisis de datos con SPSS (nivel inicial) Primera edición., Universidad de Valladolid, 2022

25. Tratamiento de datos personales en la investigación, Universidad de Valladolid, 2022

26. Talleres de técnicas analíticas, Universidad de Valladolid, 2021

27. Curso de oratoria para la preparación del concurso 3MT, Universidad de Valladolid, 2021

28. Workshop Anaerobic Digestion Quo Vadis', Universidad de Valladolid, 2021

29. Curso de Análisis de Ciclo de Vida, Universidad de Valladolid, 2021

30. Ética y Buenas Prácticas en la Investigación, Universidad de Valladolid, 2021

31. Bibliometría en la evaluación de resultados de la investigación. Segunda edición, Universidad de Valladolid, 2021

32. Gas Liquid Modeling, Universidad de Valladolid, 2021

33. Iniciación a la escritura y publicación de artículos científicos (Ingenierías y Arquitectura), Universidad de Valladolid, 2020

34. Formación en Comunicación y Soft Skills, Universidad de Valladolid, 2020

35. Successful Research Grant Applications- Getting it Rights, ELSEVIER, 2020

36. Writing Skills, ELSEVIER, 2020

37. Structuring your Article Correctly, ELSEVIER, 2020

38. How to prepare your manuscript, ELSEVIER, 2020

39. Finding the Right Journal, ELSEVIER, 2020

40. Fundamentals of Publishing, ELSEVIER, 2020

41. Book Writing, ELSEVIER, 2020

42. Technical Writing Skills, ELSEVIER, 2020

43. Funding Hacks for Researchers, ELSEVIER, 2020

44. How to Secure Funding-ECR Edition, ELSEVIER, 2020

45. Trabajando con los Resultados, Scopus/FECYT Fundación Española para la Ciencia y Tecnología, 2020

46. Búsqueda Avanzada, Scopus/FECYT Fundación Española para la Ciencia y Tecnología, 2020

47. Fundamentals of manuscript preparation, ELSEVIER, 2020

48. How to write an abstract and improve your article, ELSEVIER, 2020

49. Funding, ELSEVIER, 2020

50. Professional Development, Universidad de Valladolid, 2020