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**TITULO: TECHNICAL AND ENVIRONMENTAL ANALYSIS
OF "GREEN" MIXED MEMBRANES BASED ON
BIOPOLYMERS AND MOFS FOR CO₂ SEPARATION**

(ANÁLISIS TÉCNICO Y AMBIENTAL DE MEMBRANAS
"VERDES" MIXTAS BASADAS EN BIOPOLÍMEROS Y MOF
PARA LA SEPARACIÓN DE CO₂)

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SUMMARY

Sustainable separation processes are one of the pillars of CO₂ capture and conversion technologies that produce added-value products. The development of sustainable CO₂ separation technologies is crucial to achieve the net-zero transition. Also, the circular economy model proposes a system where materials and waste are continuously reused and revalued, simultaneously reducing GHG. In this sense, membrane technology for CO₂ separation has been accepted as a sustainable and environmentally friendly alternative. Furthermore, it is crucial to do a Life Cycle Assessment (LCA) to evaluate the environmental impacts of emerging technologies as membrane technology, in the early stages of development. However, biopolymers in membrane preparation face challenges as to lower mechanical resistance and separation performance than their oil-based commercial counterparts. This study focuses on the environmental viability of using mixed matrix membranes (MMMs) composed of green metal-organic framework (MOF) nanoparticles and biopolymers for CO₂ separation. The synthesis of these MMMs can also have unforeseen environmental impacts, making LCA essential in identifying environmental hotspots and guiding sustainable material and process selection. The goal is to assess whether these membranes are more environmentally friendly and effective than current alternatives in achieving decarbonization and defossilization goals. The study conducted a technical and environmental analysis of biopolymer-based MMMs with varying percentages of green MOF fillers (UiO-66 and UiO-66-NH₂) in an equivolometric blend of chitosan (CS) and starch (ST). Results showed that increasing the filler content improved CO₂ permeability and the selectivity for CO₂/CH₄ and CO₂/N₂ if mechanical integrity issues are controlled, the 16wt% UiO-66-NH₂/CS:ST composite membrane having the same selectivity as the PDMS commercial membrane used as reference, and 100-fold its CO₂ permeability. The LCA revealed that membranes with higher filler loadings had increased global warming potential (GWP), fossil depletion (FD), and material depletion (MD) impacts. Pristine biopolymer membranes had lower GWP than those with 16 wt.% filler. Nonetheless, biopolymer-based membranes generally exhibited lower environmental impacts than commercial PDMS membranes. In conclusion, biopolymer-based MMMs, particularly those enhanced with UiO-66-NH₂, show promising potential for CO₂ separation with lower environmental impacts compared to PDMS membranes. Achieving optimal performance requires balancing filler content to maintain mechanical integrity and environmental sustainability. This research underscores the importance of developing environmentally friendly membrane materials within the context of a circular economy.

RESUMEN

Los procesos de separación son uno de los pilares de las tecnologías de captura y conversión de CO₂ en productos de valor añadido. El desarrollo de tecnologías sostenibles de separación de CO₂ es crucial para lograr la transición neta cero. Además, el modelo de economía circular propone un Sistema donde materias primas y residuos se reutilicen y revaloricen continuamente, además de reducir simultáneamente las emisiones de gases de efecto invernadero. En este sentido, la separación de CO₂ mediante tecnología de membranas ha sido aceptada como una alternativa ambientalmente sostenible. Además, es crucial realizar un Análisis de Ciclo de Vida (ACV) para evaluar los impactos de tecnologías emergentes en las primeras fases de su desarrollo. Sin embargo, los biopolímeros en la fabricación de membranas se enfrentan a retos como menor Resistencia mecánica y capacidades de separación que las membranas comerciales equivalentes. Este estudio estudia la viabilidad ambiental de utilizar membranas mixtas (MMMs) compuestas de nanopartículas organometálicas “verdes” (MOFs) y biopolímeros en la separación de CO₂. La síntesis de estas MMMs puede dar lugar a impactos ambientales adicionales, haciendo esencial un ACV para identificar los puntos clave ambientales y guiar la selección de materiales y procedimientos. El objetivo de este trabajo es evaluar si estas membranas son más sostenibles ambientalmente y eficaces que las alternativas existentes para lograr los objetivos de descarbonización y desfosilización. Se lleva a cabo un estudio técnico y ambiental de MMMs con cargas variables de nanopartículas de MOF (UiO-66 and UiO-66-NH₂) en una matriz equivolúmica de quitosano y almidón. Los Resultados muestran que al aumentar el contenido de MOF aumentan la permeabilidad de CO₂ y la selectividad de CO₂/CH₄ y CO₂/N₂ si se controla la integridad mecánica. De hecho, la membrana compuesta de 16wt% UiO-66-NH₂/CS:ST tiene la misma selectividad que la membrana comercial de PDMS utilizada como referencia, y 100 veces su permeabilidad de CO₂ permeability. El ACV revela que las membranas con mayor carga aumentan los impactos de calentamiento global (GWP), agotamiento de fósiles (FD) y agotamiento de recurso materiales (MD). Las membranas de biopolímeros sin relleno dieron menor GWP que las que contenían un 16% UiO-66-NH₂. Sin embargo, ambas membranas biopoliméricas exhibieron menores impactos ambientales que la membrana comercial de PDMS. En conclusión, las membranas compuestas de biopolímeros, particularmente las que contienen una carga adecuada de UiO-66-NH₂, revelan un potencial prometedor para la separación de CO₂ con menores impactos ambientales que la membrana de PDMS. Lograr el funcionamiento óptimo requiere equilibrar la carga de nanopartículas para mantener la integridad mecánica y la sostenibilidad ambiental. Esta investigación subraya la importancia de desarrollar materiales de membrana respetuosos con el medio ambiente en el marco de la economía circular.

1. INTRODUCTION

1.1. Climate change and circular economy

The world's energy infrastructure is undergoing significant changes that could considerably impact energy trade and markets due to the profound implications of worldwide energy consumption on socio-economic development. As the energy demand continues to rise and to meet this demand, there is a high implication of the fossil for energy obtention. The energy derived from fossils is crucial because they produce remarkably high energy /weight yield from burning. However, the ongoing use of fossil fuels for industrial purposes poses a threat to the atmosphere, as it leads to significant concentrations of greenhouse gases (GHGs) in the atmosphere (Mustafa et al., 2020). Human activities responsible for the main sources of greenhouse gas emissions are electricity production, heat, and transportation (Environmental Protection Agency, 2024). However, the electric power sector is a significant contributor to climate change as it accounts for 38% of GHGs emissions globally (Ganji et al., 2024). The high level of GHGs is causing numerous global effects, and among the environmental problems, global warming is particularly noteworthy and carbon dioxide (CO₂) is the primary culprit. It has been recently reported which sector is the main responsible for CO₂ emission, **Figure 1** illustrates the Carbon dioxide emissions from fossil fuel combustion in Europe in 2022, by sector (in million metric tons).

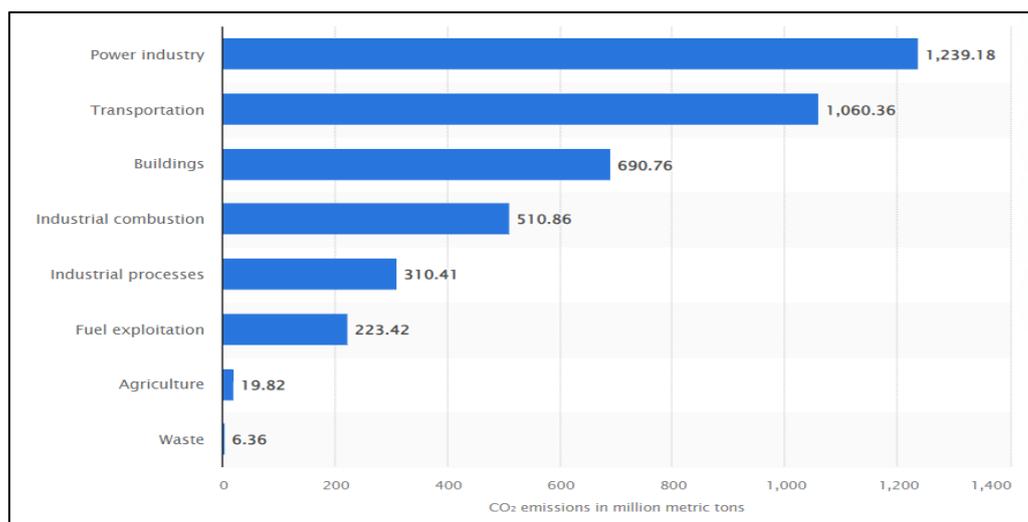


Figure 1. CO₂ emission in Europe by sector in 2022 (Statista, 2024).

The increase in the global average temperature, caused primarily by human activities, has numerous consequences. These include a rise in the frequency of severe weather events and an increase in sea levels either due to the heat-induced expansion of water or the melting of polar ice caps (Broecker, 20009).

Therefore, the Intergovernmental Panel on Climate Change (IPCC) has advised that global warming should be limited to 1.5 °C or 2.0 °C by 2100 to prevent irreversible climate change. In 2015, the UN introduced the Sustainable Development Goals (SDGs), which include 17 specific goals aimed at achieving sustainable development by 2030. SDGs 7 and 13 address climate change by focusing on affordable and clean energy, and climate action, respectively. These goals stress the significance of transitioning to renewable energy sources and mitigating the effects of climate change. Furthermore, the UN emphasizes the implementation of measures

through Conferences of the Parties (COPs), such as the one held in Dubai in November 2023 and the primary aim of this conference was to phase out fossil fuels is a must and also address the increase in GHGs (United Nations, 2023).

The circular economy development model aims to create a system where the flow of materials and waste is circular, allowing for their revaluation throughout the entire production process. This approach can help reducing the supply risk of resources and materials, by increasing the system's ability to respond to shortages in raw material sources (European Commission, 2018). A study of seven European nations found that a displacement to a circular economy model would reduce each nation's GHG emissions by up to 70% and grow its workforce by about 4% (Stahel, 2016).

Furthermore, moving from a traditional linear economy to a circular one requires more than just theoretical and philosophical ideas. It demands the adoption of current technologies or the invention of new ones, as well as a complete rethinking of our connection with raw material resources (Voicu and Thakur, 2023). To increase the sustainability of existing technologies it is essential to integrate the complete life cycle of equipments and processes into the circular economy model. This work deals with this possibility of using membranes made from components selected with sustainability criteria, such as biopolymers and green fillers and solvents, assuring a more sustainable recirculation and reuse of the materials and energy consumption in the context of the circular economy.

1.2. European strategies

Countries around the world are feeling the pressure to take action against climate change by implementing measures aimed at reducing greenhouse gas emissions. The European Union (EU) has emerged as a leader in this effort by developing ambitious strategies and climate goals. The EU is now committed to achieving climate neutrality by 2050, meaning it aims to have net emissions of GHGs. This goal is the cornerstone of the European Green Deal (European Commission, 2021) and is enshrined in law through the European Climate Law (European Parliament 2021). This move toward a climate-neutral society offers a chance to create a more positive future for everyone, ensuring that no one is left behind. Every sector of society and the economy has a role to play in this transition, including energy, industry, transport, buildings, agriculture, and forestry. The EU is poised to lead this global shift by investing in innovative technologies, empowering its citizens, and implementing policies to ensure a fair and equitable transition. These policies will span industrial strategies, financial frameworks, and research initiatives. This commitment to climate neutrality aligns with the EU's dedication to international climate efforts, particularly under the Paris Agreement (United Nations, 2015).

To achieve climate neutrality, it is important to enhance circularity and reduce GHGs emissions, the EU Commission proposes: an analysis of how circular practices impact climate change mitigation, it also advocates improving modeling tools that reflect the benefits of a circular economy on greenhouse gas reduction both at the EU and national levels. Moreover, the Commission highlights that achieving climate neutrality entails not just emission reduction but also carbon removal from the atmosphere. Additionally, the EU Commission also emphasizes the concept of optimizing the life cycle performance of the materials and, therefore, suggests an investment plan to support circular economy-focused projects.

Biomethane, refined from biogas purification, emerges as a premier renewable gas for the future, presenting a substantial opportunity to decarbonize the EU's energy infrastructure.

Biogas typically comprises 35–45%vol. CO₂. The process of upgrading biogas to biomethane primarily involves the removal of this CO₂. Biomethane, which is essentially refined biogas, contains a minimum of 95%vol. methane by volume. It can be used as a fuel for vehicles that operate on compressed natural gas (CNG) or injected into the natural gas grid. Nowadays, adopting biomethane entails ongoing investment in innovative technologies to sustainably upgrade biogas into biomethane and seamlessly integrate it into the existing gas network.

Hence, it is imperative to accelerate the scaling up of biomethane production by 2030, as articulated in the REPowerEU Plan (European Commission, 2022). The European Union aims to achieve a biomethane production capacity, encompassing both biogas and its upgraded variants, of 35 billion cubic meters (bcm) annually by 2030. The projected investment requirement for this endeavor amounts to €37 billion over the specified period. The expansion of biomethane usage requires development of innovative technologies that sustainably convert biogas into biomethane and integrate it into the existing gas network.

1.3. Membrane technology

The development of sustainable CO₂ separation technologies is crucial to achieve the net-zero transition. Sustainable separation processes are one of the pillars of CO₂ capture and conversion technologies that produce added-value products. While CO₂ absorption is a widely used and established technology to separate CO₂ in post-combustion processes in industries, it is an energy-intensive process (3.2 MJ of heat is required to separate 1 kg of CO₂ in flue gas). Membrane technology presents several advantages as small equipment size, cost-effectiveness, small energy consumption, and simple process. In this sense, membrane technology for CO₂ separation has been accepted as a sustainable and environmentally friendly alternative. The advantages of Membrane Technology for Sustainability are energy efficiency, reduction in chemical use, reduction in chemical use, scalability and flexibility, reduced environmental footprint, and improved process efficiency.

However, the extraction of carbon dioxide from flue gases faces several challenges that hinder membrane usage. Flue gases contain low concentrations of carbon dioxide, necessitating the processing of large gas volumes. The elevated temperatures of flue gases quickly degrade membranes, necessitating cooling to below 100 °C before separation. Additionally, membranes must withstand the corrosive chemicals present in flue gases or have these chemicals removed beforehand (Brunetti et al., 2010). Membrane technology has demonstrated several advantages over other methods, particularly for certain gases, with a permeability range conducive to low-volume applications.

Here is an overview of the common types of membrane materials:

Polymer-Based Membranes: These membranes offer advantages such as low cost, easy fabrication technology, operation at low temperatures, and less stringent material requirements for module construction. However, they also face challenges such as limited membrane lifetime, and lower resistance to high temperatures and aggressive chemicals.

Facilitated Transport Membranes: These membranes excel in improving selectivity without compromising permeability. However, they suffer from lower stability, carrier leakage, carrier saturation, and the need for a highly controlled operating environment (Pasichnyk et al., 2023).

Inorganic Membranes: These membranes are known for their long-term stability at high temperatures, resistance to harsh environments, ease of cleaning, and potential for catalytic

activation. They are effective in separating CO₂ from the gas flue, but they come with drawbacks such as high capital costs, brittleness, difficulty achieving high selectivity, and low permeability at medium temperatures.

Mixed Matrix Membranes: Mixed matrix membranes (MMMs) have been widely researched for 20 years as well to improve the thermal, mechanical, and separation properties of all kinds of polymers since one of the seminal works in the 90s of the past century. Mixed matrix membranes consist of a specific nanoparticle filler particle with specific CO₂ preferential adsorption and high surface area into a polymer matrix to provide a novel heterogeneous material with improved properties and the processability and lower cost of polymers. These membranes are known for their high permeability, improved selectivity, ability to remove specific contaminants, and highly functional transport properties. However, they face challenges such as particle sedimentation and agglomeration, interfacial voids, filler-polymer incompatibility, and complex interactions that affect membrane performance. This kind of membrane consists of a small amount of a dispersed phase, consisting of inorganic or organic nanoparticles (zeolites, metal oxides, MOFs, graphene, among others) into a continuous phase, made of a single or blend polymer matrix, thus mixed matrix membranes are reputed by keeping the processability of polymer membranes with synergic properties of the dispersed phases of which a pure membrane would be difficult to fabricate (Casado-Coterillo, 2019).

Metal-organic frameworks (MOFs) are a particular nanoparticle filler widely explored in recent years for mixed matrix membranes due to their organic nature which makes researchers hope for a good adhesion and compatibility with the polymer matrices. However, at the current stage, their environmental performance must be evaluated to boost this technology towards the implementation stage. Among these, UiO-66 (University of Oslo no. 66) nanoparticle synthesis has been recently modified to respond to the green chemistry principles and used in membranes for different applications (Andrades-Rodrigues et al. 2018; Paseta et al. 2019; Chuah et al. 2020).

However, considering its entire life cycle and the aim of circular economy, aspects are characterized by low sustainability, since conventional membrane manufacturing relies on raw materials mainly from non-biodegradable petroleum-based polymers and hazardous solvents, both in the membrane and the module fabrication. These materials are thus associated with the energy and fossil crisis and with disposal burdens at the end of their lifetime, posing risks to workers and the environment (Khaki et al., 2021).

Therefore, research on the development of bio-based environmentally friendly membranes made from biopolymers and non-toxic or non-critical components should be employed within the membrane preparation process and replace traditional ones (Russo et al., 2023).

Biopolymers are a type of polymer that is derived from renewable resources such as plants, animals, and microorganisms. They have gained attention as sustainable alternatives to conventional plastics. Membrane technology is a process of separating components in a mixture, and it finds applications in various industries, including water treatment, food and beverage processing, pharmaceuticals, and energy production. Biopolymer membranes offer several advantages such as compatibility with biological systems, tunable properties, and potential cost-effectiveness (Galiano et al., 2021).

Biopolymer-based membranes have been reviewed recently for CO₂ separation applications due to the intrinsic properties of biopolymers for favoring CO₂ permeability against other gases in flue or biogas or natural gas residual streams, such as flexibility, water resistance, and so on.

However, this hydrophilicity also makes the biopolymer membranes lower mechanical resistance than oil-based polymer membranes. The mixed matrix membrane approach offers a way to improve the potential of biopolymers as sustainable membranes for CO₂ separation applications. Among biopolymers, polysaccharides are mostly studied as base membrane material because of their abundance and variety of renewable resources. The incorporation of a variety of MOFs has been recently reviewed as a means to improve the selectivity and stability of polysaccharide membranes (Musarurwa et al. 2022), especially cellulose acetate (Tanvidkar et al. 2022) or chitosan (Borgohain et al., 2021), but still many practical challenges remain, and therefore the need to analyze the sustainability of the membranes from the earliest stage of preparation to process performance, which has been scarcely analyzed so far.

1.4. Life cycle assessment applied to membrane technology

Life cycle Assessment (LCA) is acknowledged as a potential tool for evaluating the environmental impacts of emerging technologies (Cucurachi et al., 2018). In the field of membrane technology, environmental burdens have been documented, particularly during polymer and filler synthesis, as well as membrane fabrication. These processes entail significant utilization of organic solvents that raise production costs and result in substantial environmental impacts (Goh et al., 2023).

The growing concern for environmental sustainability across the world has encouraged extensive research and development in the use of biopolymers for various applications, including membrane technology. These biopolymer membranes offer a promising alternative to conventional petroleum-based materials due to their renewable nature, biodegradability, and reduced environmental impact (Galiano et al., 2021). However, the environmental impacts of the synthesis process can create unforeseen environmental burdens that have to be evaluated.

The LCA tool aims to evaluate the environmental performance of biopolymer membranes throughout their entire life cycle, from the extraction of raw materials to the disposal of these materials at the end of their life (Goh et al., 2023). Performing an LCA provides identification of potential environmental hotspots between different life cycle stages and makes informed decisions toward more sustainable product development and manufacturing practices. In the specific context of biopolymer membranes, LCA can help quantify the environmental benefits and drawbacks compared to conventional materials, guiding the selection of materials and processes with lower environmental footprints (Razmanm et al., 2022).

Although LCA serves as a valuable tool for assessing environmental impacts, it presents challenges and considerations. Herein lie several crucial factors to contemplate when assessing biopolymer production processes:

- Availability and quality of data on emerging and novel materials.
- Variability in environmental impacts based on factors like location, feedstock sources, and manufacturing techniques.
- Incorporation of uncertainty and sensitivity analysis to account for variability in input parameters and assumptions.
- Addressing trade-offs between environmental indicators (for example, biodegradability vs. energy consumption) and considering potential rebound effects (Beloin-Saint-Pierre et al., 2020).

Given the growing acceptance of membrane technology to tackle environmental and recently, decarbonization issues of industry in the present climate and energy transition emergency, and the challenges posed by conventionally implemented technologies such as chemical absorption or cryogenic distillation, the number of reports addressing the environmental sustainability of all the alternative technologies available have increased in the last decade (Razman et al. 2022; Beloin-Saint-Pierre et al. 2020, Piccino et al. 2016). Besides, **Table 1** collects the most specifically related to this work, regarding the potential of polymers or MMMs in CO₂ separation applications from the environmental point of view. These previous studies addressing membranes just focused on their separation performance. However, there is a recent trend to include fabrication as well, broadening the scope of the LCA studies from gate-to-gate to cradle-to-gate and beyond, in the light of the circular economy.

Khaki et al. (2021) investigated the environmental implications of using PAN, PVIM, and P(AN-co-VIM) polymer membranes for CO₂ capture. Their study focused on specifying the environmental impacts of CO₂ separation using high permselectivity polymeric membranes. The impact factors considered were Cumulative Energy Demand (CED), Global Warming Potential (GWP), marine ecotoxicity, and Human Toxicity Potential (HTP) to identify the use of solvents during synthesis was the main contributor to environmental impacts, explaining the selection of one polymer instead of another.

Luo et al. (2021) explored the fabrication of UiO-66-NH₂ adsorbents for CO₂ uptake. They compared the adsorption process to MEA absorption, with a functional unit of 1 MWh of electricity (tonne CO₂-eq/MWh) supplied to the grid. The impact factor assessed was Global Warming Potential (GWP) and the results reveal that UiO-66-NH₂ production from the aqueous solution-based system is significantly more environmentally and economically feasible than the solvothermal system.

Echarri et al. (2023) studied the potential of ETS-10, ZIF-8, and HKUST-1/chitosan mixed-matrix membranes (MMMs) for CO₂/N₂ separation. Their research emphasized the potential of bio-based membranes in CO₂ separation, using a functional unit of 1000 m² of permeation area. The impact factors included GWP, Ozone Depletion Potential (ODP), Respiratory Inorganics (RI), Ionizing Radiation (IR), Photochemical Ozone Formation (POF), Acidification (AC), Eutrophication (terrestrial, freshwater, marine - EUT, EUF, EUM), Human Toxicity Cancer (HTC), Human Toxicity Non-Cancer (HTNC), Eco-toxicological Effects on Freshwater Microorganisms (ECFM), Land Use (LU), Water Use (WU), Resource Depletion of Minerals (RDM), and Resource Use (RU), concluding that the ETS-10/IL-CS MMM is the one whose manufacture shows the highest impact due to its lower permeability than the rest of the MMMs studied in this work.

Table 1. Summary of scientific publications dealing with LCA studies on MMM and UiO-66 MOF for CO₂ separation used in the present work.

Reference	Membranes	Application	LCA scope	Functional Unit	Impact factors
Khaki et al. (2021)	PAN, PVIM, P(AN-co-VIM) polymer membranes	CO ₂ capture	Specify the environmental impacts of CO ₂ separation using high permselectivity polymeric membranes	Undefined	AD, GWP, ODP, HT, FAE, MEA, TE, HTP, PO, AC, EU
Luo et al. (2021)	Fabrication of UiO-66-NH ₂ adsorbents	CO ₂ uptake	Comparison of adsorption vs MEA absorption	1 MWh electricity (tonne CO ₂ -eq/MWh) to the grid	GWP
Echarri et al. (2023)	ETS-10, ZIF-8 and HKUST-1/chitosan MMMs	CO ₂ /N ₂ separation	The potential of bio-based membranes in CO ₂ separation	1000 m ² of permeation area	GWP, ODP, RI, IR, POF, AC, EUT, EUF, EUM, HTC, HTNC, ECFM, LU, WU, RDM, RU
Goh et al. (2023)	UiO-66-NH ₂ /PIM-1 MMM	Fabrication	Environmental assessment of the production of membrane materials (cradle-to-grave)	1 kg of PIM-1 and UiO-66-NH ₂	GWP, PMFD, TAP, FEP, HTP, WDP

Goh et al. (2023) performed an environmental assessment on the fabrication of UiO-66-NH₂/PIM-1 mixed-matrix membranes. Their cradle-to-grave LCA evaluated the environmental impacts of producing membrane materials, using a functional unit of 1 kg of PIM-1 and UiO-66-NH₂. The impact factors included GWP, Marine Fossil Fuel Potential (MFP), Terrestrial Acidification Potential (TAP), Freshwater Eutrophication Potential (FEP), HTP, and Water

Depletion Potential (WDP), and the study concluded that the P5-Novel synthesis route in PIM-1 production suggested TCTPN is the most environmental-friendly monomer with the lowest environmental burden, while the U5-Solvent-free route in the UiO-66-NH₂ production was determined as the greenest route as it eliminated the requirement for reaction solvents. The LCA results also highlighted the significant impacts of solvent recovery and solvent substitution to water as washing solvent in reducing the environmental burden, where a declining trend was observed on the environmental impacts after applying these techniques.

2. OBJECTIVES

The main aim of this work is to evaluate the environmental feasibility of CO₂ separation by mixed matrix membranes based on green MOF nanoparticles and biopolymers from a life cycle perspective. Our goal is to assess the benefits of these membranes compared to existing alternatives to meet decarbonization and defossilization targets, highlighting the need for membrane and gas separation industries in the light of the circular economy.

Other specific goals are:

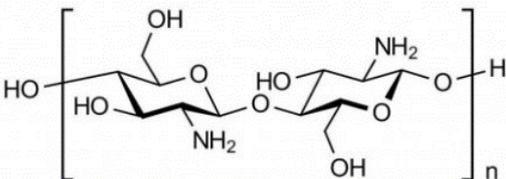
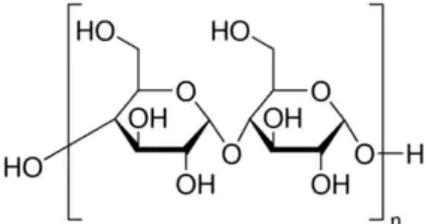
- ✓ **Synthesis and characterization of biopolymer-based mixed matrix membranes:**
 - the biopolymer matrix used is a blend of chitosan and starch, along with dispersed UiO-66 green MOF nanoparticles that have been synthesized using different ligands, with and without NH₂ modification. Once the membrane is prepared, it is characterized its physical and chemical properties.
- ✓ **Evaluation of CO₂ separation performance:**
 - the N₂, CH₄ and CO₂ single gas permeability is measured to assess the permeability and selectivity of the MMMs for CO₂ separation and to conduct rigorous testing to evaluate their effectiveness in separating CO₂ from gas mixtures, compared with commercial membranes.
- ✓ **Life cycle assessment (LCA) analysis:**
 - A cradle-to-gate Life Cycle Assessment (LCA) is performed to evaluate the environmental impacts of biopolymer-based MMMs fabrication throughout by comparison with a commercial oil-based membrane.
 - For this, the impact categories selected are: Quantify the Global Warming Potential (GWP) (kg CO₂-eq), Fossil Depletion (FD) (kg oil-eq), and Mineral Depletion (MD) (kg Cu-eq), associated with each stage of the membrane's life cycle, and considering factors such as energy consumption, resource depletion, and emissions.
 - Additionally, identifying any areas of improvement and potential environmental benefits offered by the new membrane technology in the context of the circular economy.

3. METHODOLOGY

3.1. Materials

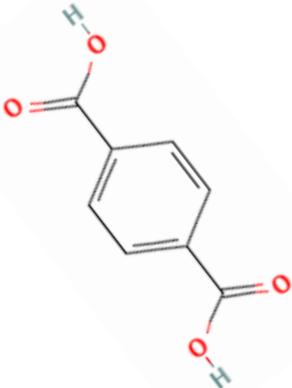
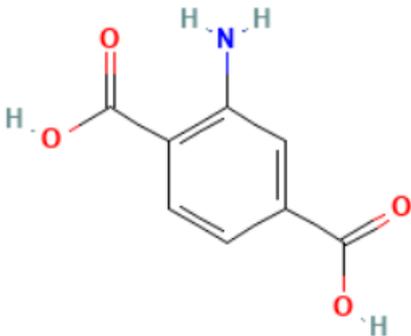
The study employed biopolymer chitosan (CS), produced by deacetylation of chitin, amply present in the crustacean shells and other fish waste, and starch (ST), derived from potatoes, which were sourced from Sigma-Aldrich. Detailed data on their structures and characteristics are outlined in **Table 2**. The mixed matrix membranes (MMMs), however, included metal-organic frameworks (MOFs) as they combined the advantages of high separation performance and ease of processing. For instance, CO₂-philic MOF UiO-66 and UiO-66-NH₂ nanoparticles were synthesized at the University of Zaragoza. The solvents employed in the study were acetic acid glacial (CH₃COOH, M=60.05), purchased from PANREAC, Spain, and deionized water (ElixR technology). Besides, to give mechanical strength to the membrane, a commercial polyether sulfone (PES) membrane with a thickness of 145 μm and a pore size of 0.2 μm as the support material for the composite membranes.

Table 2. Structure and properties of the biopolymers selected in this study.

Polymers	Properties
	<p>Film-forming properties, natural carbohydrate polymer from chitin by diacylation, most abundant organic compound after cellulose, Non-toxic, biodegradable, biocompatible, Good optical structural characteristics, and positive ionic charges (Xie, et al., 2021, Russo et al., 2021)</p>
(a) chitosan	
	<p>Hydrophilicity, film forming properties, mechanical resistance, biodegradable and biocompatible (Raza et al., 2022).</p>
(b) Starch	

In this work, UiO-66 and UiO-66-NH₂ particles were incorporated into the biopolymer matrix as fillers. **Table 3** contains information about the structure and main properties of these fillers.

Table 3: Structure and properties of the UiO-66 fillers (National Centre for Biotechnology Information, 2024).

Ligand	Properties
	<p>High thermal stability, superior chemical resistance towards several solvents, excellent chemical stability against various conditions such as air, water, and chloroform, and exceptional resistance to high external pressure, mainly due to strong Zr-O bond and high coordination number between the Zr clusters and organic ligands. (Ahmadijokani et al.; 2022)</p>
(a) UiO-66	
	<p>High thermal and chemical stability, large accessible pore volume, and the amine groups within UiO-66-NH₂ serving as the coordination sites for metal ions (Timofeev, et al., 2023)</p>
(b) UiO-66-NH ₂	

3.2. Preparation of biopolymer-based membranes of chitosan (CS), starch (ST)

The study utilized flat-sheet composite membranes that were fabricated within our laboratory. In pursuit of the designated objective, a solution with a total volume of 100 mL is considered for this process. Initially, 0.5 g of both CS and ST are weighed and dissolved in 1wt.% acetic acid aqueous solution by stirring under reflux for 24 h at a temperature of 90°C, ensuring that the temperature is maintained at a constant level throughout the process. Afterward, the solution is filtered to obtain the biopolymer-based solution using the vacuum filtration method, in order

to remove residual undissolved impurities. Once the biopolymer-based solution is obtained, the membrane is fabricated using the solution casting and solvent evaporating method.

To fabricate the membrane using the solvent evaporating method involves a 10 mL total volume of membrane, the solution was cast on the PES support and allowed to dry in a covered glass petri dish, for 2 days at room temperature. The glass container was then placed in a controlled environment to ensure that there were no external factors that could affect the drying process. Another way of drying was using an oven without convection at 60 °C for about 8 h. Both approaches are utilized in this study.

3.3. Preparation of mixed matrix membranes

In this scenario, we aim to fabricate a mixed matrix membrane by hybridizing the biopolymer blend with varying weight percentages of Metal-Organic Frameworks (MOFs) nanoparticles, UiO-66 or UiO-66-NH₂, at loadings of 4, 8, 12, and 16 wt.%. The process begins by dispersing the predetermined quantity of MOF nanoparticles into the corresponding volume of polymer solution to obtain a total volume of 10 mL for casting. Subsequently, the mixture is stirred for a certain time to ensure homogenization. The resulting homogeneous solution is then cast onto the PES support followed by solvent evaporation to produce the desired membrane, and the composite membrane is peeled off. **Figure 2** shows a schematic diagram of the membrane fabrication process.

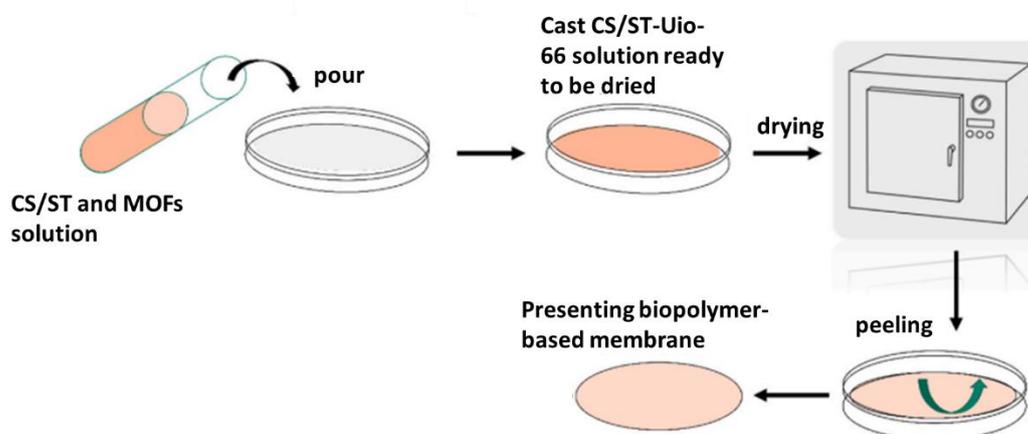


Figure 2. The schematic diagram for the biopolymer-based membrane preparation process.

Figure 3 below illustrates the distinct layers constituting a membrane in both a laboratory-manufactured and a commercially available one, notably polydimethylsiloxane composite membrane Pervap 4060 (PDMS, Sulzer).

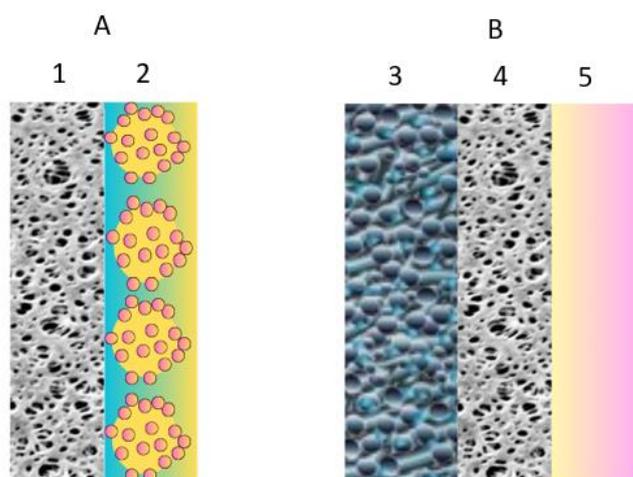


Figure 3. Schematic configuration of membrane layer: A) Biopolymer-based UiO-66 membrane made in the lab, B) PDMS, commercial membrane; (1: support layer (PES); 2: Biopolymer-based UiO-66 layer; 3: Mechanical support; 4: porous support; 5: selective layer)

The compositions of MOF/biopolymer-based membranes for 10 mL volume of casting are given in **Table 4**.

Table 4. The composition of the MOF/biopolymer mixed matrix membranes.

Membrane description	CS (g)	ST (g)	Acetic Acid(g)	Deionized water(g)	UiO-66 or UiO-66-NH ₂ (g)
CS:ST	0.05	0.05	0.1	9.8	0
4% UiO -66 /CS:ST or UiO -66- NH ₂ CS/ST_	0.048	0.048	0.096	9.408	0.004
8% UiO-66 /CS:ST_ 8% or UiO -66- NH ₂ /CS:ST_	0.046	0.046	0.092	9.016	0.008
12% UiO -66 CS:ST_ or CS:ST_ UiO -66- NH ₂	0.044	0.044	0.088	8.624	0.012
6% UiO -66 /CS:ST_ 1or UiO-66- NH ₂ /C:ST_	0.042	0.042	0.084	8.232	0.016

3.4. Membrane characterization

3.4.1. Thickness

In this study, the thickness of the prepared membranes was measured using a digital Mitutoyo digimatic micrometer (IP 65, Japan) with an accuracy of 0.001 mm. Five points of the effective area of the membrane were measured and the average thickness and standard deviation were calculated.

3.4.2. Thermal stability (TGA)

Thermogravimetric analyses (DTA-TGA) were carried out using a thermobalance (DTG-60H, Shimadzu, Kyoto, Japan) in air and N₂ (50 mL/min). Samples of the free-standing membranes, weighing between 1 and 5 mg, were placed in an alumina pan. The samples were then heated at a rate of 10 °C/min in both air and nitrogen until they reached 650 °C.

3.4.3. ATR-FTIR

The Attenuated Reflected Fourier-transform infrared spectroscopy (FTIR) technique was used to analyze molecular interactions on the membrane surface, using a Perkin Elmer, Spectrum 65 FT-IR spectrometer. Therefore, we analyzed membranes of various compositions by measuring absorbance in graph form with a maximum wavelength of 500 cm^{-1} .

3.5. Gas permeation properties

The following is a description of the method used to characterize the performance of the mixed matrix composite membranes. These membranes were cut to an effective area of 15.6 cm^2 . Then, the membranes were introduced in a stainless-steel module which consisted of two stainless-steel components housing a cavity. The membrane was securely placed within the cavity over a microporous stainless-steel disk support with a pore size of $20\text{ }\mu\text{m}$ and sealed using Viton Rings. To test the membrane, pure gas streams of nitrogen (N_2), methane (CH_4), and carbon dioxide (CO_2), were flowed through the membrane module sequentially using a custom-built separation plant shown in **Figure 4**. That order was selected to avoid the plasticization of the polymer by the CO_2 .

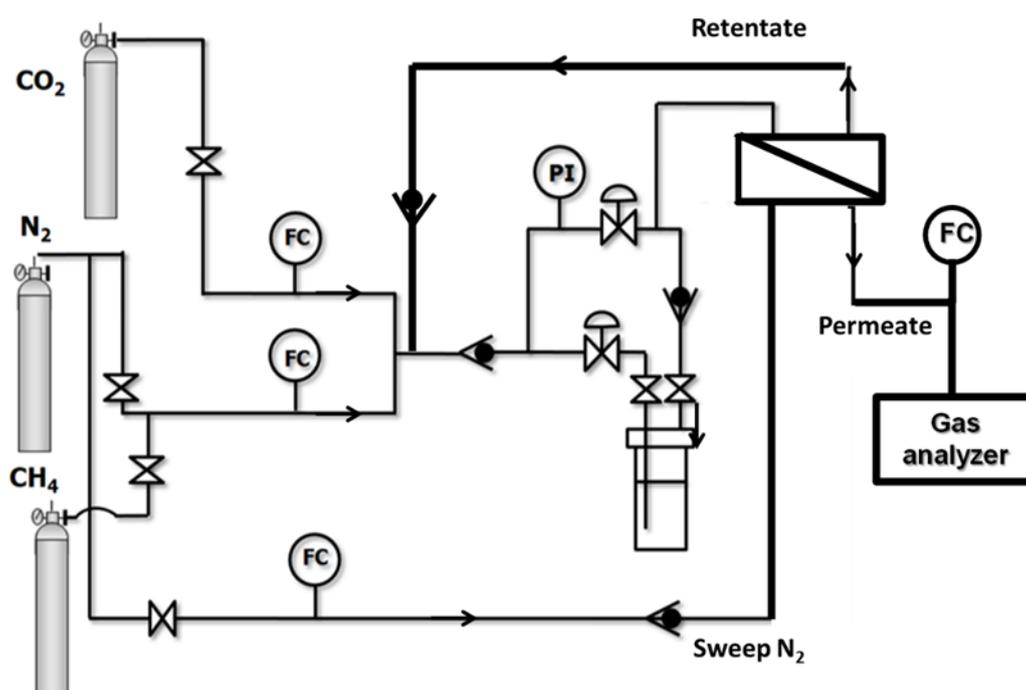


Figure 4. Scheme of the gas separation plant using a Biopolymer-based membrane.

The parameters for the test were controlled. The feed flow rate was set to 50 mL/min and regulated by mass flow controllers (KOFLOC 8500, Sequopro S.L., Madrid, Spain). The permeate flow rate was quantified using a bubble flow meter installed at the outlet of the membrane module. Additionally, the feed pressure was established at 5 bars. Each permeation experiment lasted for 1.5 hours for every individual gas under investigation.

The investigation is centered around evaluating the gas permeance of the Mixed Matrix. The gas permeance, represented by 'i' and measured in GPU units (where 1 GPU is equal to $10^{-6} (STP)cm^{-2} s^{-1} cmHg^{-1}$) is a measure of the pressure-normalized flux of gas passing through a membrane:

$$\left(\frac{p}{l}\right)_i = \frac{Q_p}{(p_r - p_p) \cdot A} \cdot 10^6 \quad (1)$$

- P Indicates the intrinsic permeability of the membrane layer, Barrer.
- p_r and p_p Indicate the retentate and permeate pressure, bar. respectively.
- A Represents the effective area of the membrane, cm^2 .
- l Stands for the thickness of the selective layer utilized for the separation process, cm.
- Q_p Represents the permeate flow rate measured under specific pressure and temperature conditions, $cm^3 (STP) \cdot s^{-1}$.

The selectivity of the membrane is determined by the ratio between the permeability of two gases in the gas pair as the equation.

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (2)$$

- α_{ij} Selectivity, dimensionless.
- P_i and P_j Permeability, Barrer. 1 Barrer = $10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}$.

3.6. Life Cycle Assessment (LCA)

In this work, the International Organization for Standardization (ISO) 14040 a methodological framework has been applied to conduct a Life cycle assessment (LCA). LCA is a crucial methodology for assessing the environmental impact of products, processes, or services throughout their entire life cycle. This methodology encompasses the sequential fundamental steps as outlined in ISO 14040 as shown in **Figure 5** (ISO14040, 2006).

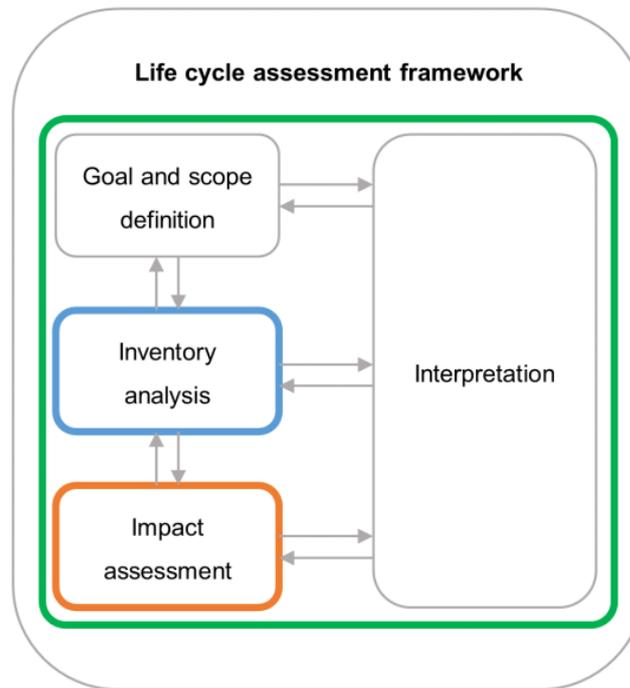


Figure 5. The sequential fundamental steps of the Life Cycle Assessment framework according to ISO 14040.

- The goal and scope definition phase of the LCA is critical as it lays the foundation for the entire assessment. By clearly defining the objectives, functional unit, system boundaries, methodologies, assumptions, and limitations, this phase ensures that the LCA is conducted systematically, transparently, and with a clear purpose in mind. This clarity not only guides the subsequent phases of data collection and analysis but also enhances the credibility and usability of the LCA results.
- The inventory analysis phase: The inventory analysis phase of LCA involves systematically collecting, organizing, and quantifying data on all inputs and outputs associated with the life cycle of a product or system. Following standardized methods and procedures outlined in ISO 14040, this phase provides the data foundation for assessing environmental impacts and supporting informed decision-making.
- The impact assessment phase: The Impact Assessment phase in LCA involves quantifying and evaluating the potential environmental impacts associated with the life cycle of a product or system. By selecting relevant impact categories, characterizing environmental impacts, normalizing and weighting impact scores, and aggregating results, this phase provides valuable insights into environmental performance and supports informed decision-making.
- The interpretation phase: The interpretation phase of LCA involves analyzing, synthesizing, and communicating the results of the LCA. By drawing conclusions, making recommendations, and addressing uncertainties, this phase supports informed decision-making and facilitates continuous improvement in environmental performance. Effective communication of LCA findings is essential for engaging stakeholders and driving positive change toward sustainable development goals.

3.6.1. Scope and goal

This study aims to conduct a comprehensive LCA of biopolymer membrane fabrication from a cradle-to-gate perspective. The interpretation is focused on key environmental indicators such as climate change in terms of GWP, energy resources (non-renewable, fossil) in terms of FD, and material resources (metals and minerals) in terms of MD. The assessment will consider MOFs UiO-66-NH₂ with biopolymers (CS and Starch), and membrane fabrication techniques. The primary objectives include:

- Evaluating the environmental impacts of the manufacturing process of the best performing CO₂-selective MOF-CS:Starch membranes characterized in the prior section.
- Identifying opportunities for improving the environmental performance of biopolymer membranes through optimization of production methods, and resource utilization.
- Comparing the environmental footprint of biopolymer membranes with that of conventional oil-based membranes to assess the overall sustainability benefits.

3.6.2. Functional unit and system boundaries

According to ISO 14040, the functional unit (FU) should quantify the performance of a product being assessed and it is used as a reference unit. Therefore, in this study, the functional unit is defined as the permeation area of the membrane, which is scaled up to 1 m². This FU has been selected to facilitate the comparison with the literature. Meanwhile, the system boundaries for the LCA studies define the scope of the project. Hence the boundary set for this work is cradle-to-gate, as detailed in the schematic diagram depicted in **Figure 6**. The impacts of the raw material and solvents, as well as energy and heat consumption in the fabrication processes, are considered in the environmental assessment.

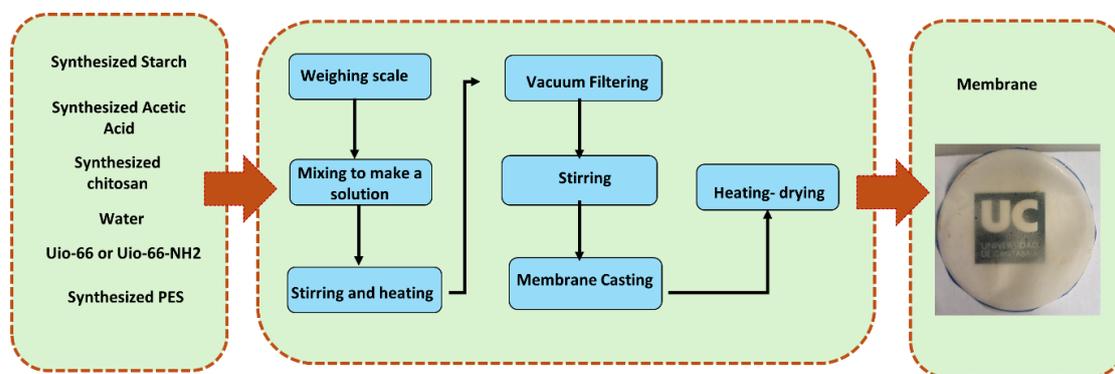


Figure 6. System boundaries for LCA, considering the impact of the raw material and fabrication process.

3.6.3. Life cycle inventory (LCI) and impact assessment (LCIA) method

A comprehensive approach to data collection was followed in this work. The (LCI step involves gathering primary data from the technical section and secondary data (background processes), which was done by utilizing a commercial database. This type of data collection enables the retrieval of existing data according to the specific objectives of the study. Specifically, the

database used to obtain the background processes was Ecoinvent v3.10. (Swiss Center for Life Cycle inventories, 2023), assuming Europe geography.

The calculations of the energy and material consumption upon membrane fabrication are based on the experimental part, a scale-up approach has been applied based on the article by Piccinio et al. (2016). Heat and stirring energy consumption, in this process, aimed to heat the solution to 90 °C stir it for 300 rpm, and maintain it for 24 h. **Equation 3** represents the calculation of the energy for the heating process, considering the Specific heat capacity of the main solvent (water).

$$Q_{heat} = C_p \cdot m_{mix} \cdot (T_r - T_0) \quad (3)$$

Q_{heat} Energy to reach the set point temperature, J.

C_p Specific heat capacity of the main solvent, $J \cdot (kg \cdot K)^{-1}$.

m_{mix} Mass of the mixture, kg.

T_r Temperature of heating, in K.

T_0 Starting temperature, normally it is 294.15 K.

For stirring, **Equation 4** is used to calculate the energy consumption, and the following considerations are considered for its calculation:

- The density of the mixture (ρ_{mix}) is calculated as the ratio of the mass of the mixture (m_{mix}) and its volume (V_{mix}).
- An axial flow impeller, such as hydrofoil type.

$$E_{stir} = \frac{N_p \cdot \rho_{mix} \cdot N^3 \cdot d^5 \cdot t}{\eta_{stir}} \quad (4)$$

T_0 Starting temperature, in K. For this work, the starting temperature is the average experimental temperature in the gas permeation experiments, that is, 294.15 K.

N_p power number, is a dimensionless number according to the theory of dimension analysis.

ρ_{mix} Mixture density, $kg \cdot m^{-3}$.

N Rotational speed of the agitator, $1 \cdot s^{-1}$.

d Impeller diameter, m.

t Time duration of the stirring process, s.

η_{stir} Efficiency value of the process, dimensionless.

Drying of the membrane, this process involves evaporating the main solvent, which in this case it is water. The calculation of energy consumption can be expressed using Equation 5, considering:

- Energy is required to raise the temperature of the liquid to the boiling temperature, 373.15 K.
- Enthalpy evaporation of the solvent (water) at 373.15 K.
- 80% mass of the water is evaporated.

$$Q_{dry} = \frac{C_p \cdot m_{liq} \cdot (T_{boil} - T_0) + \Delta H_{vap} \cdot m_{vap}}{\eta_{dry}} \quad (5)$$

Q_{dry} Heat necessary for the process, J.

C_p Specific heat capacity of the main solvent, $J \cdot (kg \cdot K)^{-1}$.

m_{liq} Mass of the liquid of the solution, kg.

T_{boil} Boiling temperature of the liquid, K.

ΔH_{vap} Enthalpy evaporation of the solvent (water), $J \cdot (kg \cdot K)^{-1}$.

m_{vap} Mass of the liquid is evaporated, kg.

η_{dry} Efficiency of the drying process, %.

Once the required data for the LCI has been collected, the next step is to evaluate the final impacts by processing the inventory data. This can be achieved by selecting impact categories that are relevant to the study's objectives. To accomplish this, a Life Cycle Impact Assessment (LCIA) method is used, which initially classify emissions into different impact categories and secondly characterize them into standard units to allow comparison. The selected impact categories for this work aimed at achieving the goal include Global Warming Potential (GWP), which refers to the measurement of the impact of greenhouse gas emissions on global warming by quantifying their contribution to the rise in temperature in the lower atmosphere over a specific period of time. It measures the impact of emitting 1 kg of GHG compared to the additional radiative forcing resulting from releasing 1 kg of CO₂ during the same time frame, and its measuring unit is kg CO₂-eq. Fossil Depletion (FD) is defined as the ratio between the energy content of fossil resources and the energy content of crude oil also expressed by kg oil-eq. Mineral Depletion (MD) refers to the gradual reduction of non-renewable natural resources, primarily minerals and it is expressed as kg Cu-eq. The ReCiPe Midpoint method was used to calculate the life cycle environmental impacts mentioned above (National Institute for Public Health and the Environment, 2020).

At the end, a sensibility analysis is carried out through a comparison of the operation performance of the selected membranes for CO₂ separation. It is taken into account that their permeability values and maturity level are different. To do that, 20 years are assumed as the overall lifetime of a typical CO₂ capture plant. On the other hand, areas needed to perform the separation with the selected membranes from the experimental part of this work, were calculated using their permeability and considering a flow rate of 20 Nm³/h. It is noteworthy,

that the oil-based membrane is currently commercial and we can assume an expected lifetime ranging between 3-5 years, whereas the lifetime of the emerging biopolymer-based membranes synthesized and characterized in this study is still uncertain. For this reason, different membrane lifetimes will be assumed to evaluate the final category impacts considering a fixed flow rate of gas to be treated.

4. RESULTS AND DISCUSSION

4.1. Characterization of membranes

Thermo gravimetric analyses (TGA)

Figure 7 represents the thermal gravimetric analyses of the unsupported UiO-66/CS:ST MMMs containing the different filler loading contents used in this study. The shape of the curves reveals the main weight losses of CS-based MMMs known previously in the research group (Casado-Coterillo et al. 2015), attributed to the free and bound water in the biopolymer-based matrix, which is not significantly modified by the starch presence in the blend, given its character as a hydrophilic biopolymer itself. The bound water content of the membranes was measured from the weight of the polymer at 392 K and at the temperature showing the maximum heat flow in the DTA curve. This gave water content values of 29.98%, 23.49%, 31.83%, and 35.98% for pristine CS:ST and 4 wt.%, 12 wt.% and 16 wt.% filled MMMs. The thermal degradation of the polymer was calculated as the temperature at which 5 wt.% of polymer weight loss, after the 392 K limit where the loss of weight was attributed to the free water in the polymer matrix. This thermal degradation temperature slightly increased from 473 to 483 K with increasing filler loading.

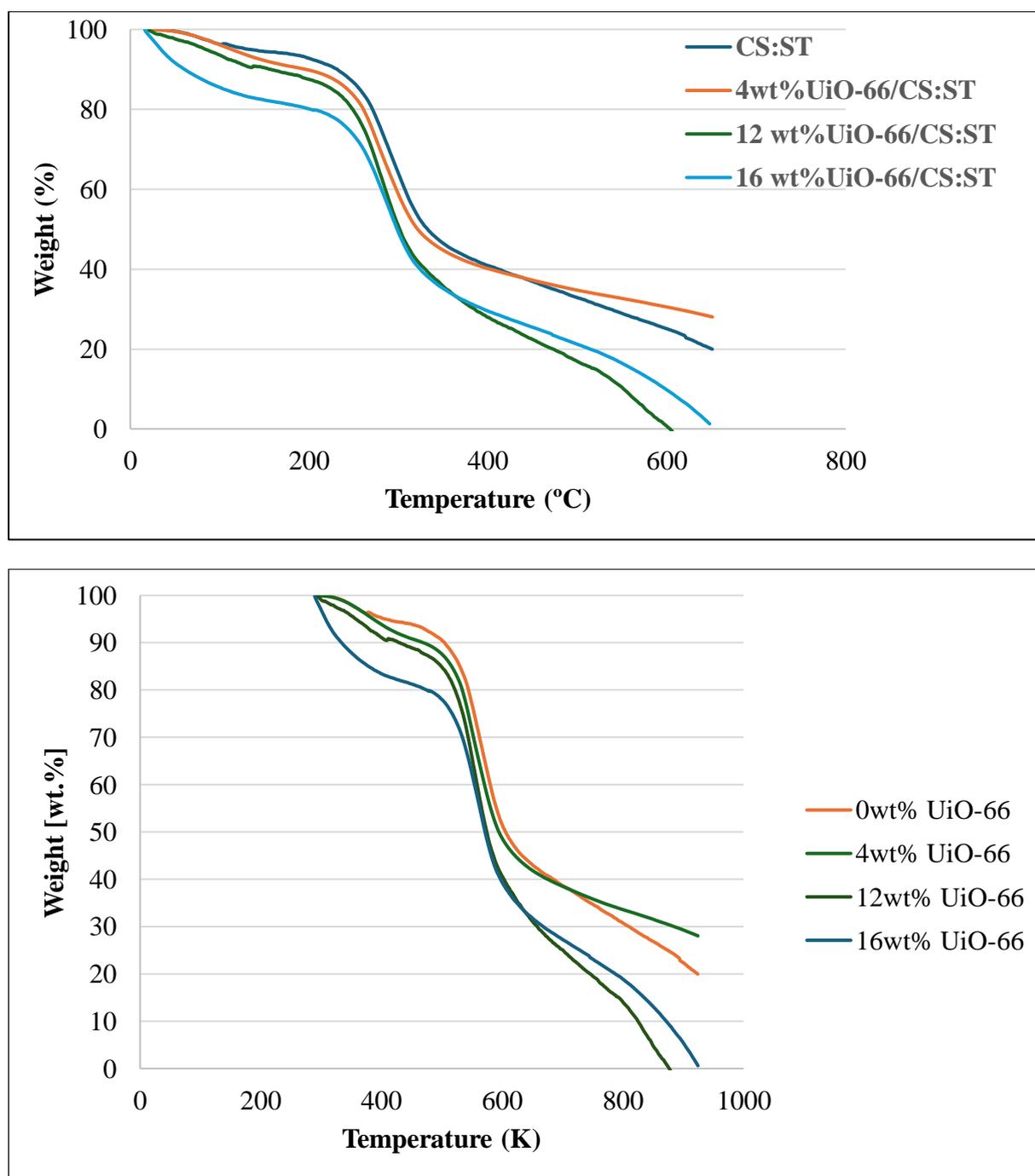


Figure 7. TGA curves of the UiO-66/ CS:ST MMMs.

ATR-FTIR

Figure 8 collects the ATR-FTIR spectra of the unsupported UiO-66/CS:ST MMMs studied in this work. These measurements were measured after gas permeation experiments so they can stand for the stability of the physicochemical properties of the membrane material. The

polyamide I and II bands of chitosan and starch are present in the spectra as well as the bands at 3400 cm^{-1} accounting for the water uptake and hydrophilicity of the CS:ST polymer blend.

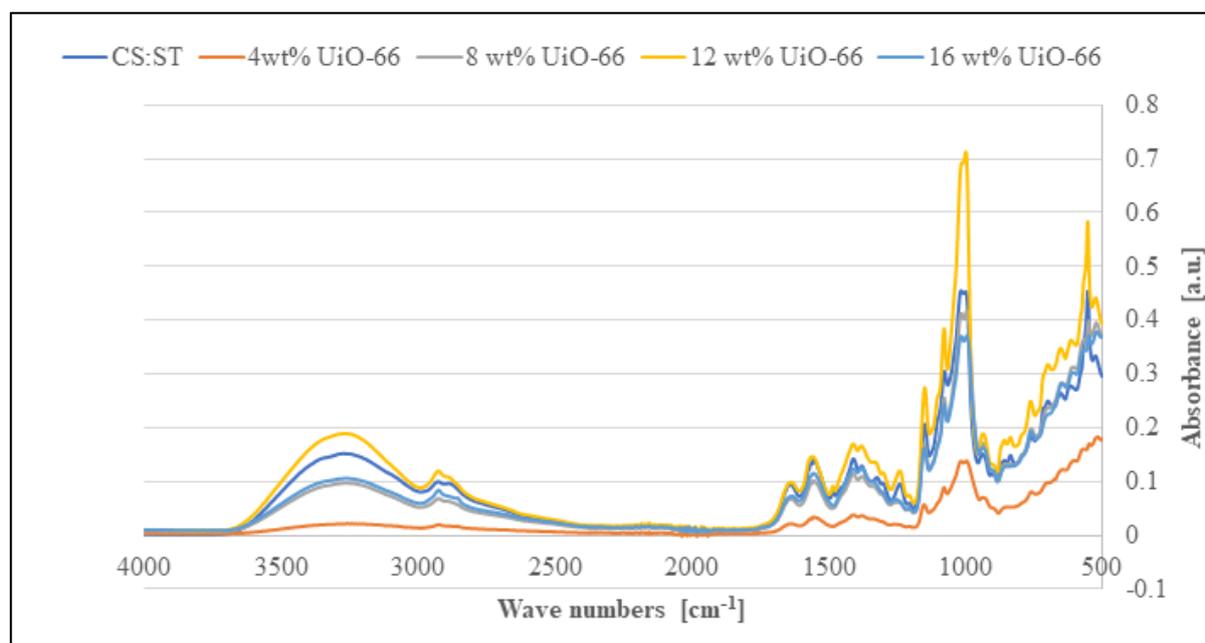


Figure 8. ATR-FTIR spectra of UiO-66/CS:ST MMMs.

Gas Transport and Separation Properties

First, pristine chitosan:starch (CS:ST) blend membranes were characterized as a function of pressure, varying the retentate pressure from 3 to 5 bar, which covers the range in most pilot plant studies for CO_2 separation. **Figure 9** shows the evolution of N_2 permeability as an example since this is the first gas passing through the membrane upon gas permeation characterization experiments. The results obtained for free-standing 4wt.%UiO-66/CS:ST MMM are also shown in comparison. The permeability increased significantly upon UiO-66 nanoparticle addition, and this is attributed to the larger thickness of the active layer of the membrane, 142 and 123 μm , for the pure and mixed matrix membrane significantly. However, the mechanical integrity of the membrane was very difficult to reproduce, so the rest of the membranes were prepared by coating a smaller volume of CS:ST blend solution on microporous polyethersulfone, which had proved compatible with chitosan blend membrane materials. The thickness of the active layer of CS:ST /PES membrane in **Figure 9**, was 17 μm , and the permeability was lower. This is attributed to the high hydrophilicity of the chitosan and starch biopolymers, which facilitate gas transport across the membrane. The thinner membrane was more robust in exchange.

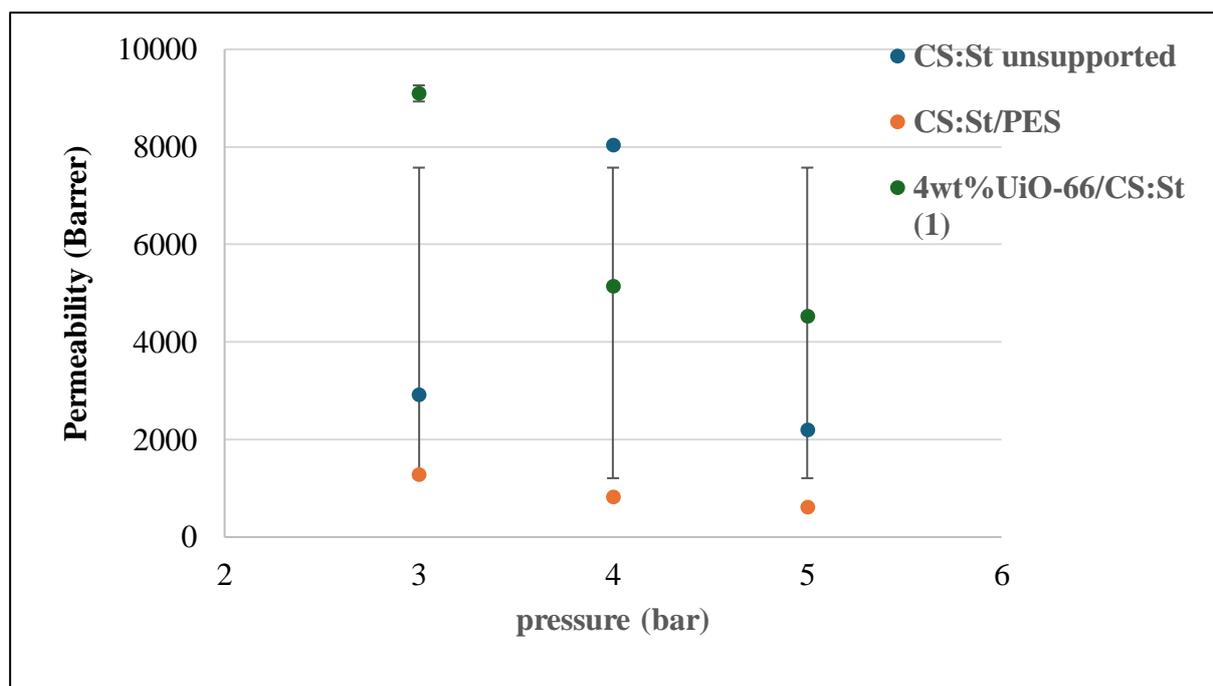
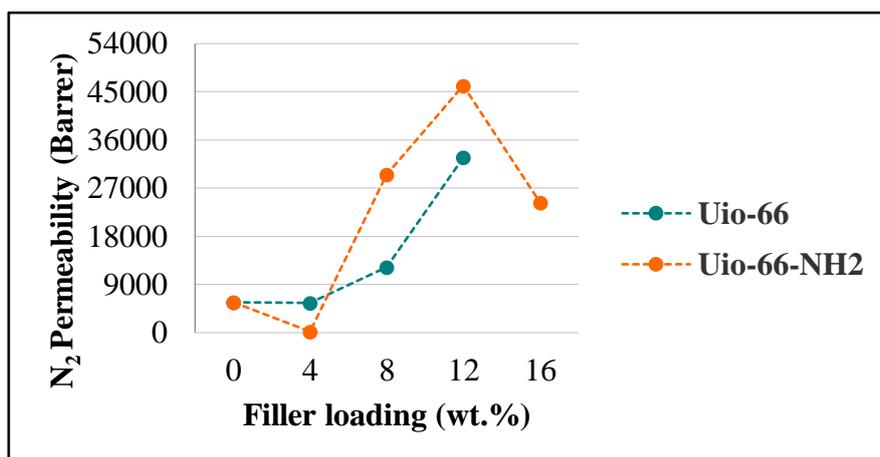
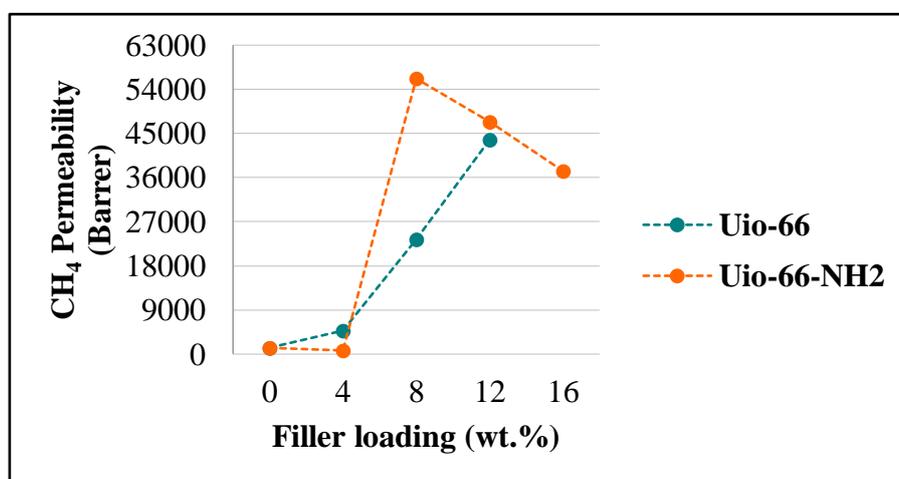


Figure 9. N_2 permeability as a function of pressure for CS:ST free-standing and composite membranes.

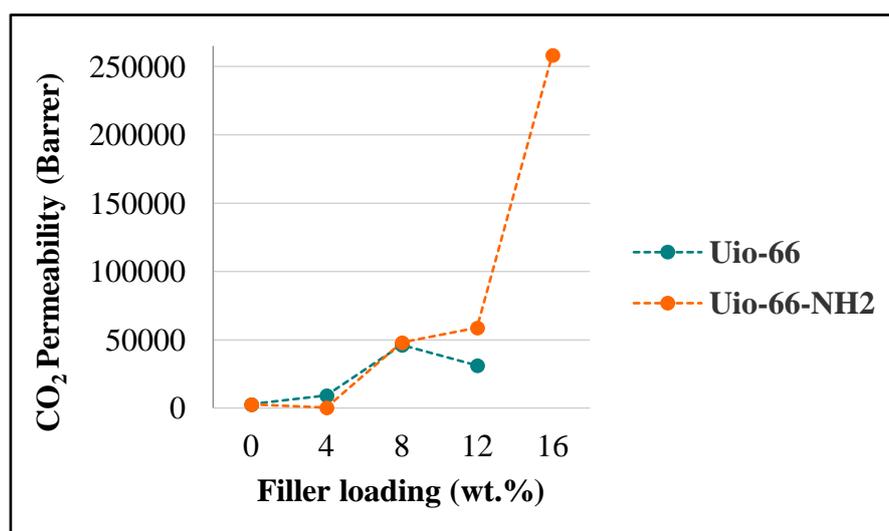
Figure 10 represents the N_2 , CH_4 , and CO_2 permeability measured for the UiO-66 and UiO-66- NH_2 filled CS:ST mixed matrix composite membranes as a function of filler loading. Both N_2 and CH_4 permeabilities increase upon increasing filler loading, then decrease at the highest loading, while CO_2 permeability increases monotonically with increasing filler loading. This agrees with the scarce literature available accounting for the CO_2 uptake capability of UiO-66 and UiO-66- NH_2 MOFs. (Andrade-Rodrigues et al. 2018).



(a)



(b)

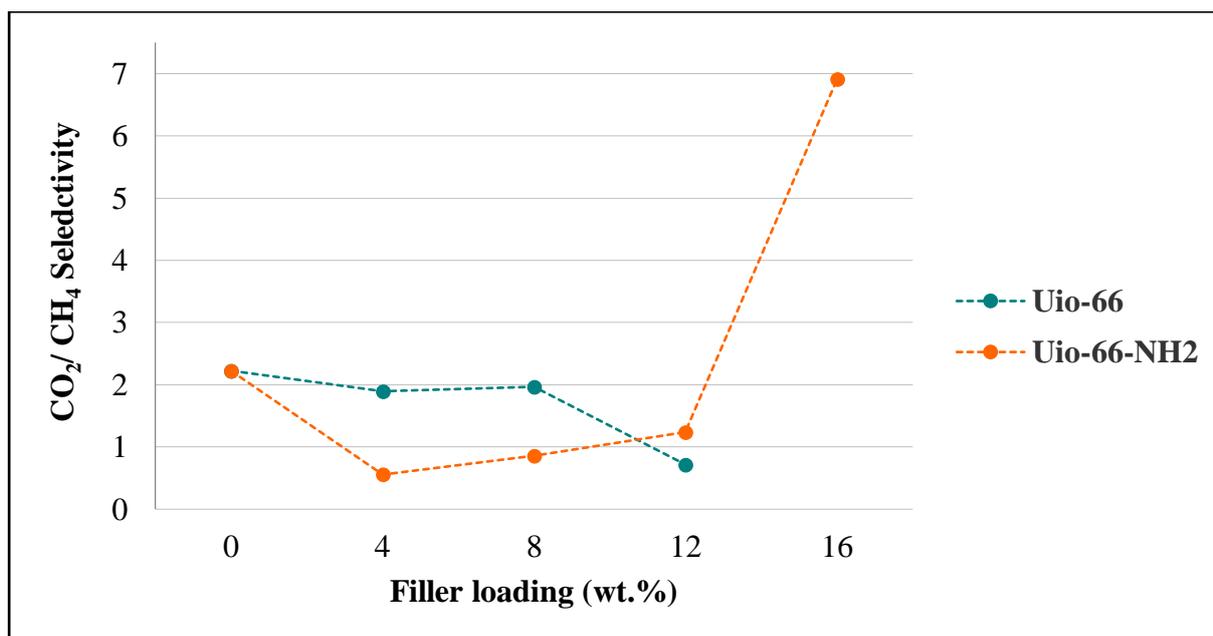


(c)

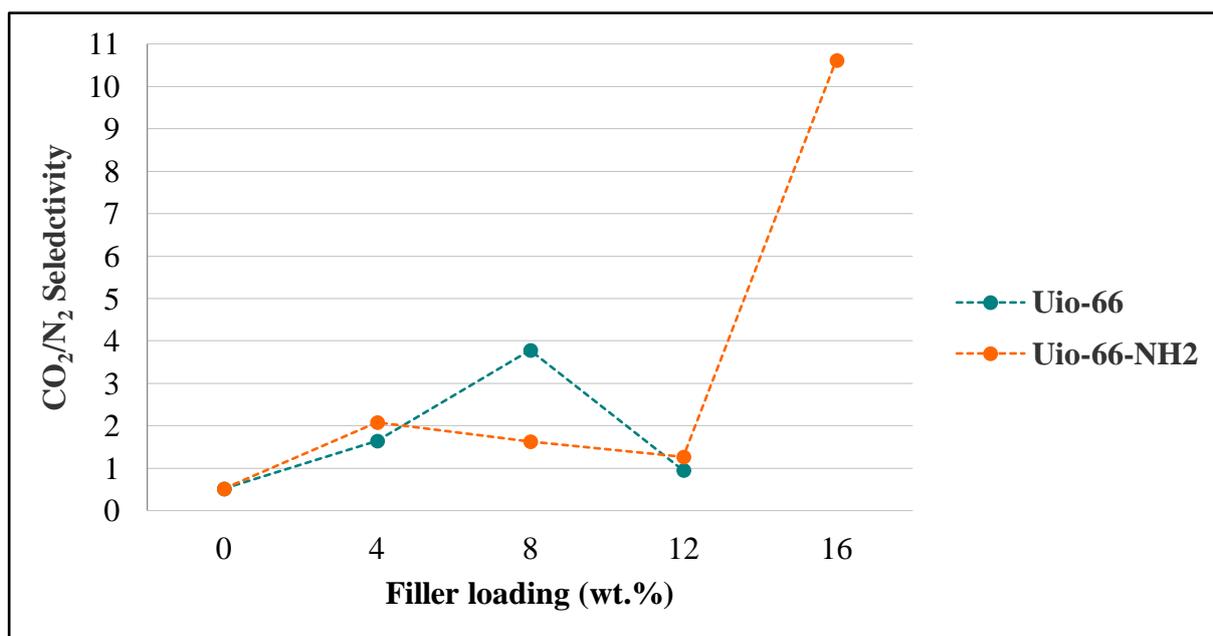
Figure 10. Permeability of N₂ (a), CH₄ (b), and CO₂ (c) through the CS:ST-based MMMs prepared in this work as a function of UiO-66 and UiO-66-NH₂ filler loading.

Table 5 summarizes the selective membranes characterized in this section in comparison with the literature on UiO-66 -filled MMMs for CO₂/N₂ and CO₂/CH₄ separations that have been discussed in this section.

The selectivity of the CS:ST mixed matrix membranes synthesized in this work and calculated by **Equation 5** are represented in **Figure 11(a)** for CO₂/CH₄ and **Figure 11(b)** for CO₂/N₂. The selectivity is generally kept around or below 3-4 for the filler loading contents up to 12 wt.%. Upon increasing the filler loading to 16 wt.%, the UiO-66-filled membrane had its mechanical integrity compromised and it was not possible to measure the series of all the gases to calculate the gas pair selectivity. For the UiO-66-NH₂- filled CS:ST membrane, though, the 16 wt.% highest loading tested gave a gas pair selectivity for CO₂/N₂ and CO₂/CH₄ separation of the same order of magnitude as that of PDMS (Hussain, M., and A. König. 2012). This value was checked by measuring a commercially available PDMS composite membrane (Pervap 4060, Sulzer) under the same conditions and the values obtained agreed with experience and literature, so we used it as reference membrane for the evaluation of the sustainability of the CO₂ separation process including membrane fabrication. For instance, Hussain and König (2012) reported pure PDMS values of 3499 Barrer and CO₂/N₂ and CO₂/CH₄ selectivities of 11.1 and 3.25, respectively. The selectivities of the CS:ST MMMs are lower than some selectivity values reported in the literature for other polymer blends, as collected in **Table 5**. This may be related to the trade-off with the high permeability obtained for the CS:ST membranes as reported for high permeance cellulose acetate blend membranes recently. (Jin et al. 2020).



(a)



(b)

Figure 11. CO_2/CH_4 (a) and CO_2/N_2 (b) gas pair selectivity of the CS:ST MMMs measured in the laboratory.

Table 5. Comparison of the gas permeation properties of the UiO-66-based MMMs in literature.

Reference	Polymer matrix	Filler	Percentage loading (wt.%)	CO ₂ Permeability (Barrer)	CO ₂ /X selectivity	X
Chuah et al. (2020)	OPDA-TMPDA	UiO-66	0	88	33.1	N ₂
			10	142	29	
			20	169	31.9	
	UiO-66-NH ₂	0	88	33.1		
		10	129	36.1		
		20	142	37.1		
Shen et al. (2016)	PEBA	UiO-66	0	71.6	43.2	
			10	96.3	56.6	
		UiO-66-NH ₂	10	87	66.1	
Ahmad et al. (2018)	6FDA-bisp	UiO-66	0	33.9	27.5	
			17	108	41.9	
	6FDA-ODA	UiO-66	7	43.3	57.0	
			8	1728	32.0	
Castarlenas et al. (2017)	Polysulfone	UiO-66-GO	24	21	51	Not available

Reference	Polymer matrix	Filler	Percentage loading (wt.%)	CO ₂ Permeability (Barrer)	CO ₂ /X selectivity	X
This work	CS:ST/PES	0	0	2108.7 1158	± 1.27	1.29
This work	CS:ST	UiO-66	4	5148.99	1.62	3.17
This work	CS:ST/PES	UiO-66-NH ₂	16	258204 170.18	± 10.62	6.91
This work	PDMS (Sulzer)	0	0	1521.55	12.56	4.95

At the end of **Table 5**, we summarize the CO₂ selective membranes prepared in this work from CS:ST biopolymer blend and UiO-66 fillers. hat will be.

It is worth noting that the 16 wt.% UiO-66-NH₂/CS:ST membrane significantly increases CO₂ permeability for a selectivity of the same order of magnitude as the commercial oil-based PDMS membrane. These membranes will be retained for the environmental sustainability analysis below.

For these reasons, these will be the membranes that are kept for the sustainability assessment in the following section, and the pure biopolymer-based membrane for comparison.

4.2. Life cycle assessment

LCA methodology has been used to analyze and evaluate the environmental burdens associated with the production of the membranes previously tested. The data collected from input (i.e. energy and materials) and output (emissions) are categorized based on their impact, with the most significant categories being GWP, non-renewable energy resources, in terms of FD, and material sources like metals and minerals, in terms of MD. These categories are then thoroughly analyzed. After that, the main materials and processes contributing to each impact category are examined separately, identifying the hotspots and potential benefits.

4.2.1. Global warming potential (GWP)

Each composition represents a different scenario in terms of material selection and proportion. The GWP category is influenced by the materials chosen for the membrane fabrication. It is well-known that certain materials may have higher carbon footprints due to factors such as production processes and resource extraction for example polymeric-based membranes such as polyacrylonitrile (PAN) membranes. These polymers are petroleum-based products, and the energy-intensive polymerization process and the extraction of fossil fuels contribute significantly to the carbon footprint. Another example is MMMs such as ZIF-8 and HKUST-1.

The MMMs production process combines polymers with inorganic fillers like ZIF-8 (Zeolitic Imidazolate Framework-8) and HKUST-1 (a copper-based MOF). The production of these materials often requires solvent use, high temperatures, and multiple purification steps, all of which increase the carbon footprint. Regarding resource extraction of these materials, the production of copper for HKUST-1 and zinc for ZIF-8 involves mining and refining processes that are energy-intensive and result in significant CO₂ emissions.

The findings from this LCA show clear differences in the GWP category among the selected membranes, which are attributed to their distinct compositions and fabrication procedures (**Figure 12**). For example, the CS:ST membrane, which contains no fillers, exhibits a GWP of 2.35 kg CO₂-eq/m². Conversely, a membrane containing 4% fillers shows a GWP of 4.09 kg CO₂-eq/m². This pattern persists as the percentage of fillers increases: the membrane with 8% fillers reaches a GWP value of 5.84 kg CO₂-eq/m². Moreover, membranes with 12 wt.% and 16 wt.% fillers demonstrate even higher GWP values of 7.58 and 9.33 kg CO₂-eq/m², respectively. These results establish a direct correlation between the rise in filler content and increased GWP values.

All the membranes analyzed in this study are compared with the commercial membrane. The reference commercial PDMS membrane has a GWP value of 10.23 kg CO₂-eq/m². Despite the trend in the rise of filler content and increased GWP values, the environmental impact of the biopolymer and UiO-66-NH₂-based membranes is less severe than the commercial oil-based membrane.

Figure 11 illustrates the relationship between the composition of MMMs and their associated GWP to identify the contribution of the inputs to GWP. Various types of MMMs, with different percentages of MOFs used in their fabrication, are included in the comparison. Membrane composed of the equimolar biopolymers blend (CS and ST) and 0% percentage of MOF fillers, the inputs that lead to the highest contribution in the GWP are energy and PES with influence percentages on the overall GWP of 64% and 16%, respectively. Coming to the MMMs made by the CS and ST biopolymer blend with UiO-66-NH₂ fillers, firstly, the inputs that significantly interfere with the GWP are DCM, which is a raw material in the fabrication of the UiO-66-NH₂, and energy mainly from the drying process of the membrane. In this analysis, energy consumption encompasses both membrane fabrication and the energy utilized during UiO-66-NH₂ fabrication. Solvent DCM is produced from fossil fuel sources such as natural gas or petroleum. Its production significantly contributes to the GWP, which is estimated at 3.6 kg CO₂-eq/kg. In membranes with 4 wt.% filler loading, the contribution of DCM and energy are 32.4% and 37%, respectively. These numbers increase to 47%, 27%, and 54%, 21% for the MMM prepared with the CS and ST biopolymers and the MOFs at 8 wt.% and 12 wt.% loading, respectively. The MMM composed of biopolymers (CS and ST) with the highest percentage of fillers, 16 wt.%, gives a contribution of the DCM and energy of 59% and 18%, respectively. It seems that DCM is increasing with the percentage of UiO-66-NH₂ loading, and meanwhile, energy is decreasing.

Compared to the commercial PDMS composite membrane, the inputs that provide the highest contribution to the GWP are hexane and polydimethylsiloxane, with values of 53% and 38%, respectively. The reason is that hexane is a hydrocarbon derived from crude oil. The extraction of crude oil is energy-intensive and involves significant greenhouse gas emissions. After extraction, the crude oil undergoes refining and fractional distillation to isolate hexane, which further adds to the environmental impact. The GWP of hexane is notably high because of these factors. For example, the GWP of producing 1 kg of hexane is approximately 3-4 kg CO₂-eq. PDMS is produced through the hydrolysis and polymerization of dimethyldichlorosilane, which

is derived from silicon. The initial step involves the reduction of silicon dioxide (sand) to silicon, a process requiring high temperatures and significant energy. The production of PDMS has a high GWP due to the energy-intensive processes involved in silicon extraction and chemical synthesis. The GWP for producing 1 kg of PDMS can range from 4 to 6 kg CO₂-eq, considering the emissions from electricity consumption, the use of fossil fuels, and the chemical reactions involved.

In conclusion, this study shows that increasing the loading of UiO-66-NH₂ increases the global warming potential of the biopolymer-based CS:ST membrane. Still, this GWP indicator is lower than that of the commercial membrane.

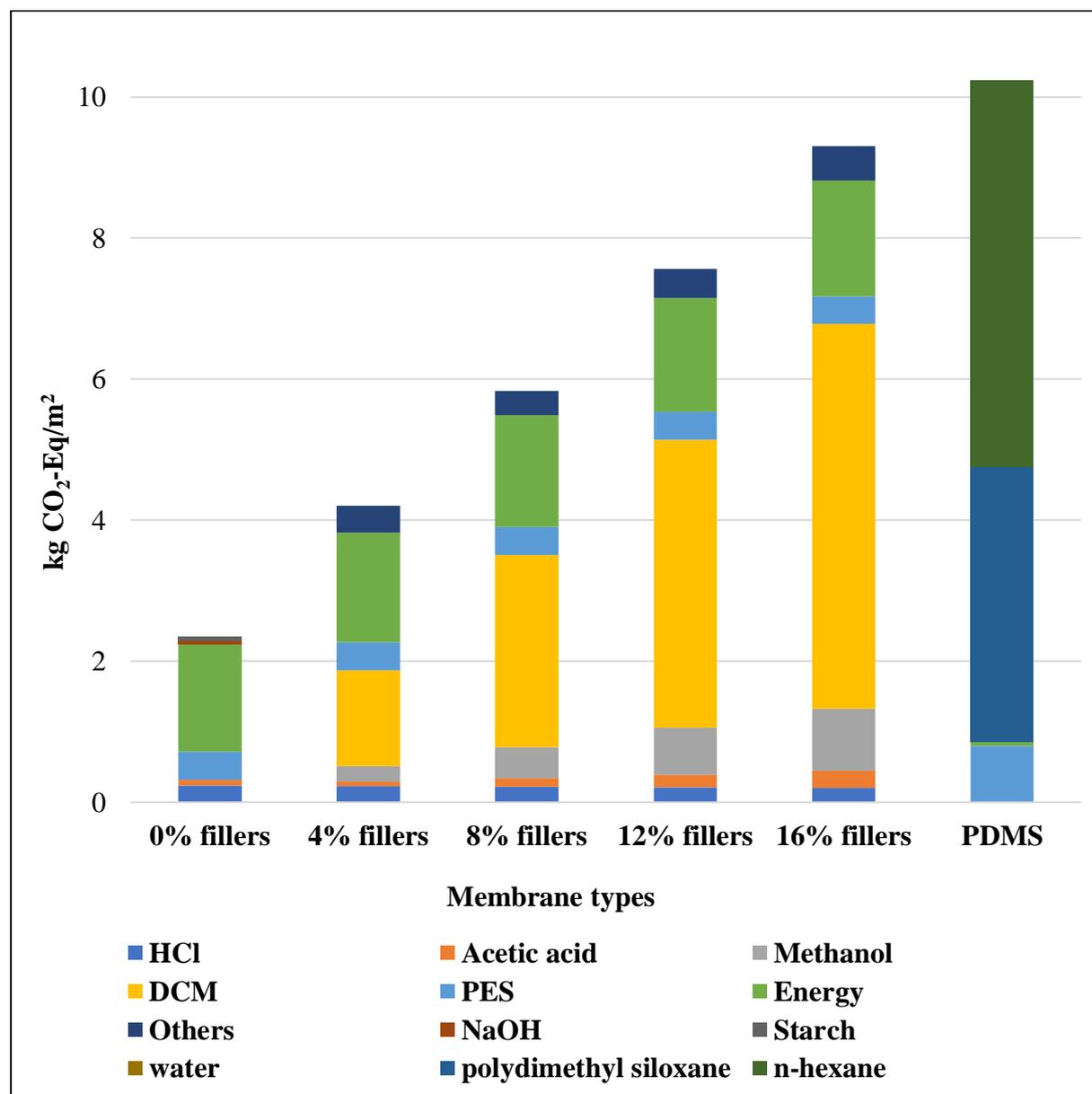


Figure 12. Contribution of the inputs to Global warming potential impacts for the CS:ST membranes assessed in this study, as a function of UiO-66-NH₂ filler loading and the PDMS commercial membrane as reference.

4.2.2. Energy resources: non-renewable, fossils

This section examines non-renewable fossil resources. As we previously discussed, factors such as membrane composition, material selection, and proportion are critical when assessing these impacts. The study found that mixed membranes composed of biopolymers (CS and ST) with 0% MOFs (UiO-66-NH₂) present the minimum impact with 0.79 kg oil-eq/m². The impact increased as the filler percentage increased to 4%, 8%, and 12% at a rate of 1.29, 1.82, and 2.35 kg oil-eq/m² respectively. Also, as the fillers rose to more than the initial amounts by up to 16%, this reached even higher levels at around 2.88 kg oil-eq/m². Alternatively, the commercial PDMS membrane shows the highest impact from non-renewable energy sources at an extent of 6.94 kg oil-eq/m² compared to all other membranes that were synthesized in the study. The reason is PDMS is an oil-based membrane as explained in the previous part, which a higher amount of fossil resources directly involved.

Furthermore, to understand better the inputs that contribute significantly to the impact of non-renewable energy sources, **Figure 13** demonstrates the relationship between the composition of mixed matrix membranes and their associated non-renewable energy sources kg oil-eq/m².

The mixed membranes are composed of biopolymers (CS and ST) without fillers, the inputs energy and PES contributing 55% and 25% respectively to the impact of the non-renewable energy sources. The increase of fillers loading from 4% to 16%, and the impact of the DCM and methanol showed an increase of 300%. DCM is used as a washing solvent in the UiO-66-NH₂ synthesis, it is a halogenated solvent from non-renewable sources. Its contribution to the FD is high due to its manufacturing, which involves industrial processes that require energy for heating and reacting the components, and it has an impact of 0.67 kg oil-eq/kg of DCM. While methanol is also used for the same aim, and it has an impact of 0.87 kg oil-eq/kg of methanol.

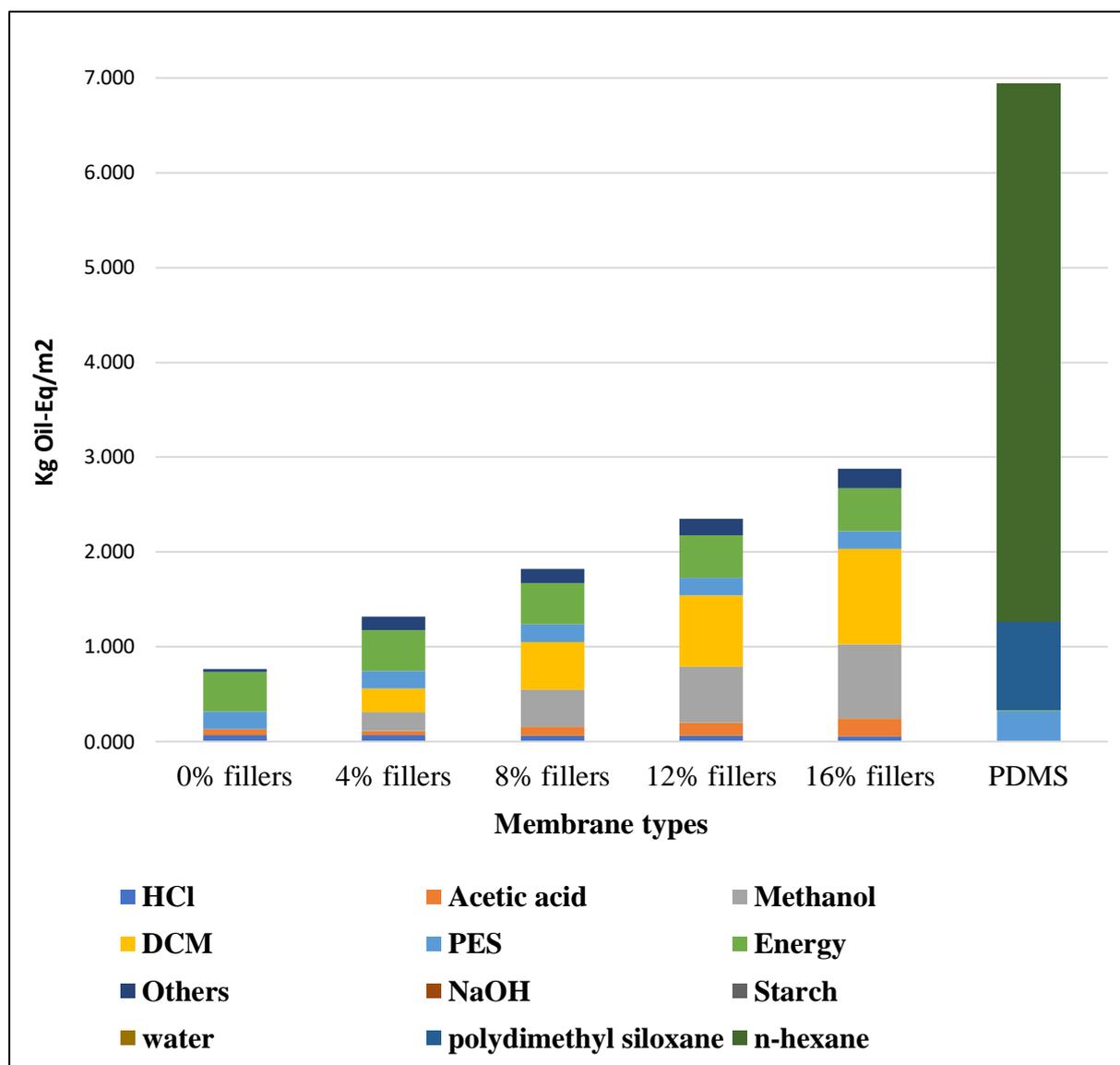


Figure 13. Contribution of the inputs to non-renewable impact, impacts for the CS:ST membranes assessed in this study, as a function of UiO-66-NH₂ filler loading and the PDMS commercial membrane as reference.

As the energy consumption is increasing slightly as the amount of filler loading is increasing, the impact is significantly important.

On the other hand, for the PDMS commercial membrane (shown in **Figure 13**), n-hexane and polydimethylsiloxane are the primary contributors to its impact, accounting for 82% and 13% respectively. n-hexane compound is an organic substance that is derived from fossil fuels, the production of n-hexane involves various processes, each with its energy consumption considerations, and shows that 1 kg of n-hexane has an impact of 0.91 kg oil-eq. Meanwhile, polydimethylsiloxane energy consumption during PDMS production would depend on the specific synthesis method, raw materials, and process conditions. It should be highlighted that 1 kg of polydimethylsiloxane involved an impact of 4.80 kg oil-eq.

4.2.3. Material resources: metals/minerals

The impact of the material resources is also studied, where the pure CS:ST biopolymer membranes with 0% MOFs (UiO-66-NH₂) present the minimum impact (0.063 kg Cu-eq/m²). The impact of material resources increases as the filler percentage rises to 4 wt.%, 8 wt.%, and 12 wt.%, from 0.07 kg Cu-eq/m² to 0.09 kg Cu-eq/m² and further to 0.1 kg Cu-eq/m², respectively.

Meanwhile, the CS:ST membrane with 16 wt. % loading of the UiO-66-NH₂ fillers shows a 0.12 kg Cu-eq/m² of impact. The commercial membrane gives a higher impact of 0.23 kg Cu-eq/m².

Additionally, **Figure 14** illustrates the contribution of inputs to the impact of material resources. The vertical axis represents the kg Cu-Eq/m² of a membrane, while the horizontal axis displays various types of membranes under study. Beginning with the membrane containing 0% fillers, the input with the most significant impact is HCl, accounting for 44%. The remaining components, including NaOH, PES, and energy, contribute collectively 51% to the overall impact. In the UiO-66-NH₂/CS:ST MMMs, the input raw materials HCl, and ZrO used in the synthesis of the UiO-66-NH₂ MOF contribute most significantly to the material resources impact. As the percentage of fillers in the membrane matrix increases from 4 wt.% to 16 wt.%, ZrO exhibits a notable increase of 300%. Meanwhile, HCl displays a slight decrease in the impact of MD by 12.5%, although it remains one of the primary contributors. Other contributors like NaOH, PES, and energy show collectively an important impact.

For comparison, the polydimethylsiloxane polymer material and n-hexane in the commercial membrane, contribute 51% and 41%, respectively. The main contributor is the silicone rubber PDMS polymer, which is a structure that is essentially a silicon-oxygen backbone with methyl groups attached to the silicon.

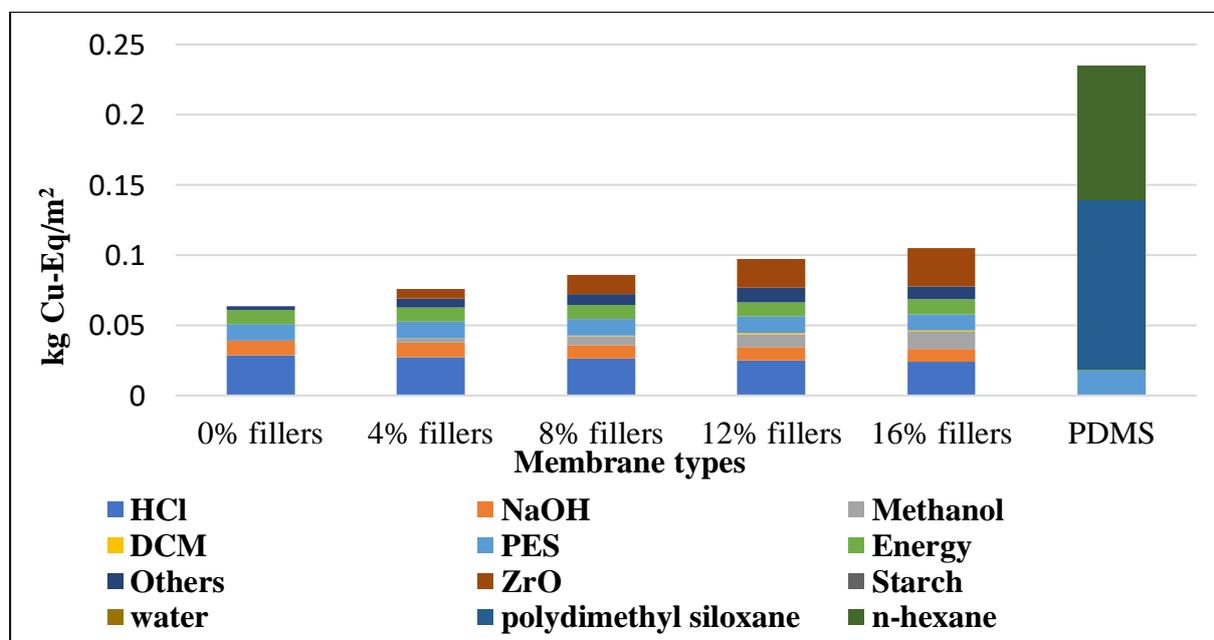


Figure 14. Contribution of the inputs to material resources impact, impacts for the CS:ST membranes assessed in this study, as a function of UiO-66-NH₂ filler loading and the PDMS commercial membrane as reference.

The evaluation of the material resources impact kg Cu-eq/m² reveals that the 16 wt.% UiO-66-NH₂/CS:ST membrane exhibits lower impact levels than the commercial membrane.

The discussions outlined above underscore the critical importance of thoroughly assessing the cradle-to-gate impacts associated with mixed membranes comprised of biopolymers such as CS and ST, particularly when these membranes contain no metal-organic frameworks (MOFs) like UiO-66-NH₂, these materials are assigned for sustainability-centric applications.

Biopolymers, owing to their renewable and biodegradable nature, have garnered considerable attention as promising alternatives in various industries. However, understanding their complete environmental footprint demands a holistic examination that spans from the initial production phase (cradle) to the point of manufacture (gate). This approach, known as life cycle assessment (LCA), offers insights into the environmental burdens associated with different stages of a product's life cycle.

In the domain of mixed membranes, the absence of MOFs, which are often integrated for their exceptional properties, raises questions about the overall sustainability of the material. While MOFs can enhance membrane performance, their environmental implications, are particularly concerning their synthesis and disposal.

In essence, the discourse advocates for a paradigm shift towards a more comprehensive assessment of sustainability-driven materials, particularly mixed membranes comprising biopolymers with or without MOFs. Embracing a cradle-to-gate perspective not only facilitates a deeper understanding of a material's environmental impact but also empowers stakeholders to make informed decisions that align with sustainability objectives. By integrating such assessments into research and decision-making processes, the journey toward achieving true sustainability in material innovation can be expedited.

4.2.4. Environmental performance comparison of membranes for CO₂ separation and sensibility analysis

This section displays the sensitivity analysis results related to the performance of three CO₂ separation membranes selected in the previous section. The composition, permeability, and environmental impacts are compared in **Table 6**.

The permeability obtained in the laboratory, considering a reference value of 20 (Nm³/h) as the flow rate from the residual gas stream from different industrial sources pilot plants with a pressure value of 4 bar, is used to calculate the necessary area (m²) and the environmental impacts. These results show that the MMMs with 0 and 16% loading fillers have higher permeability than the commercial ones, with lower impacts. Knowing that the commercial membranes have a higher durability than the lab-made membranes due to their higher technological readiness level; to justify the results, it is important to do a sensibility analysis of the membranes considering the plant lifetime of 20 years and a range of lifetime of the membranes. Figure 15 shows a comparison between the chosen membranes and PDMS. The 0% and 16% UiO-66-NH₂ membranes are compared with the commercial PDMS membrane to assess their impacts (GWP, FD, and MD) considering the plant's lifetime.

Table 6. Comparison of the environmental performance of membranes used in this work.

Reference	Polymer matrix	Filler	Percentage loading (wt.%)	CO ₂ Permeability (Barrer)	Area (m ²)	GWP kg CO ₂ -eq	FD kg Oil-eq	MD kg Cu-eq
This work	CS:ST/PE S	0	0	2108.7	15.06	30.03	8.94	0.79
This work	CS:ST/PE S	UiO-66-NH ₂	16	258204	0.29	2.75	1.14	0.05
This work	PDMS (Sulzer)	0	0	1521.55	6.14	62.79	42.5 9	1.44

In **Figure 15**, the vertical axis shows the impact, and the horizontal axis shows the years. The time considered starts at less than one year and increases up to seven years. The graphs indicate that at less than one year, the impact is greater. As time progresses, the impacts decrease. The dashed horizontal lines represent the impacts generated by the PDMS membrane replacement at 1, 3, and 5 years within a plant's 20-year lifetime. Below these lines lies the range that is more sustainable than the commercial option. The MMMs with 0% UiO-66-NH₂ show that a 3-year lifetime is required to compete with PDMS in terms of GWP.

When 16% of UiO-66-NH₂ is utilized, it exhibits a significant window of opportunity due to its high permeability, which allows it to achieve the desired performance with a smaller required area. Consequently, this high permeability compensates for its shorter operational lifespan, reducing the lifetime threshold to just 1 year. This reduced threshold makes UiO-66-NH₂/CS.ST membranecompetitive with the commercial PDMS membrane, a material that typically lasts over 5 years. Essentially, despite PDMS's longer lifespan, the efficiency of UiO-66-NH₂ in terms of permeability makes it a viable and competitive alternative in relevant applications.

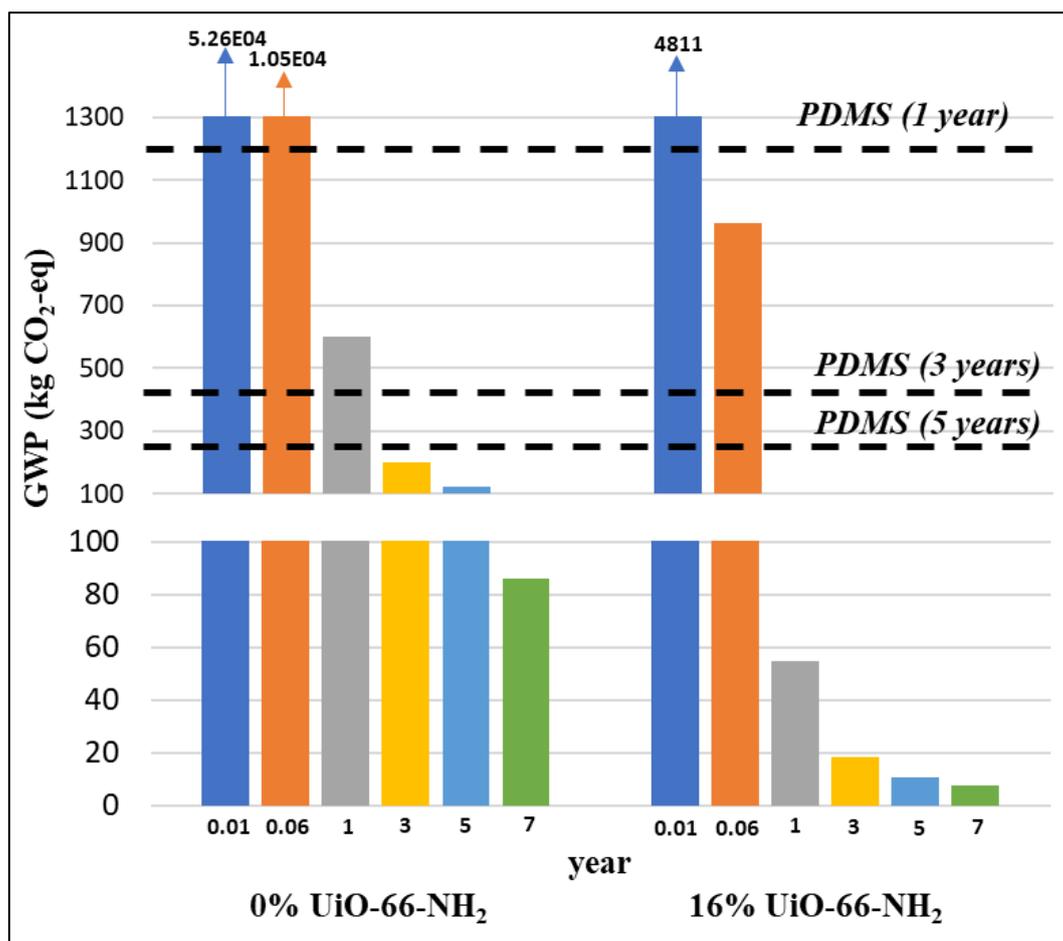


Figure 15. GWP environmental impact comparison between 0 wt.% UiO-66-NH₂ and 16 wt.% UiO-66-NH₂ CS:ST-based membrane with a commercial membrane PDMS, considering the plant lifetime of 20 years and a range of lifetime.

Concerning FD impact, **Figure 16** expresses the same behavior, it illustrates that the impact is highest at less than one year and diminishes over time, the area below these lines represents the range where sustainability is greater than that of the commercial PDMS option. For MMMs containing 0% UiO-66-NH₂, a lifespan of 1 year is necessary to be competitive with PDMS regarding FD. Meanwhile, 16% of UiO-66-NH₂ membrane, it presents a notable advantage because of its high permeability, for the same reason previously mentioned. As a result, this high permeability offsets its shorter operational lifespan, lowering the lifetime threshold to only 1 year. Despite PDMS's durability of over 5 years, UiO-66-NH₂ emerges as a competitive alternative due to its superior permeability efficiency. This characteristic enables UiO-66-NH₂ to offer comparable performance in relevant applications, despite its shorter lifespan.

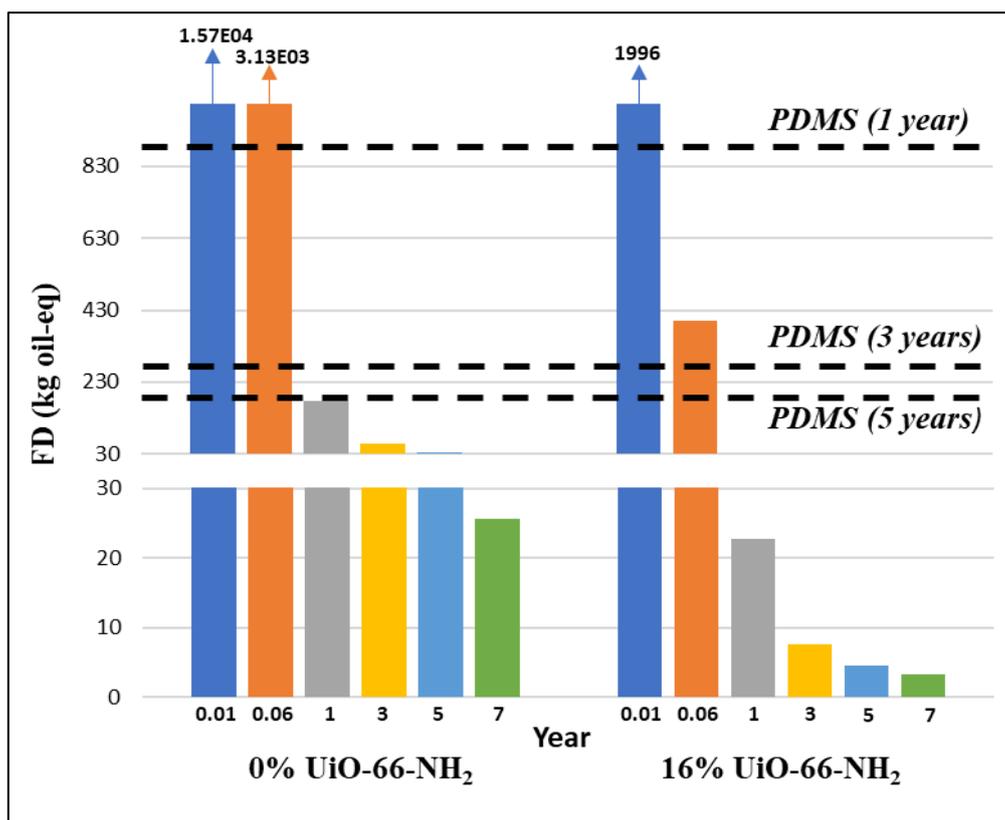


Figure 16. FD environmental impact comparison between 0 wt.% UiO-66-NH₂ and 16 wt.% UiO-66-NH₂ CS:ST-based membrane with a commercial membrane PDMS, considering the plant lifetime of 20 years and a range of lifetime.

Concerning MD **Figure 17** illustrates that the impact is highest at less than one year and reduces over time, For MMMs with filler loading of 0% UiO-66-NH₂, a lifespan of 3 years is necessary to be competitive with PDMS. Simultaneously, 16% of the UiO-66-NH₂ membrane, shows high permeability and therefore a smaller area requires to reach the desired performance. Thus, the high permeability compensates for its shorter operational lifespan, reducing the lifetime threshold to just 1 year. Even though PDMS lasts over 5 years, UiO-66-NH₂ stands out as a strong competitor because it allows substances to pass through it more easily. This feature means UiO-66-NH₂ can perform just as well in important uses, even though it doesn't last as long.

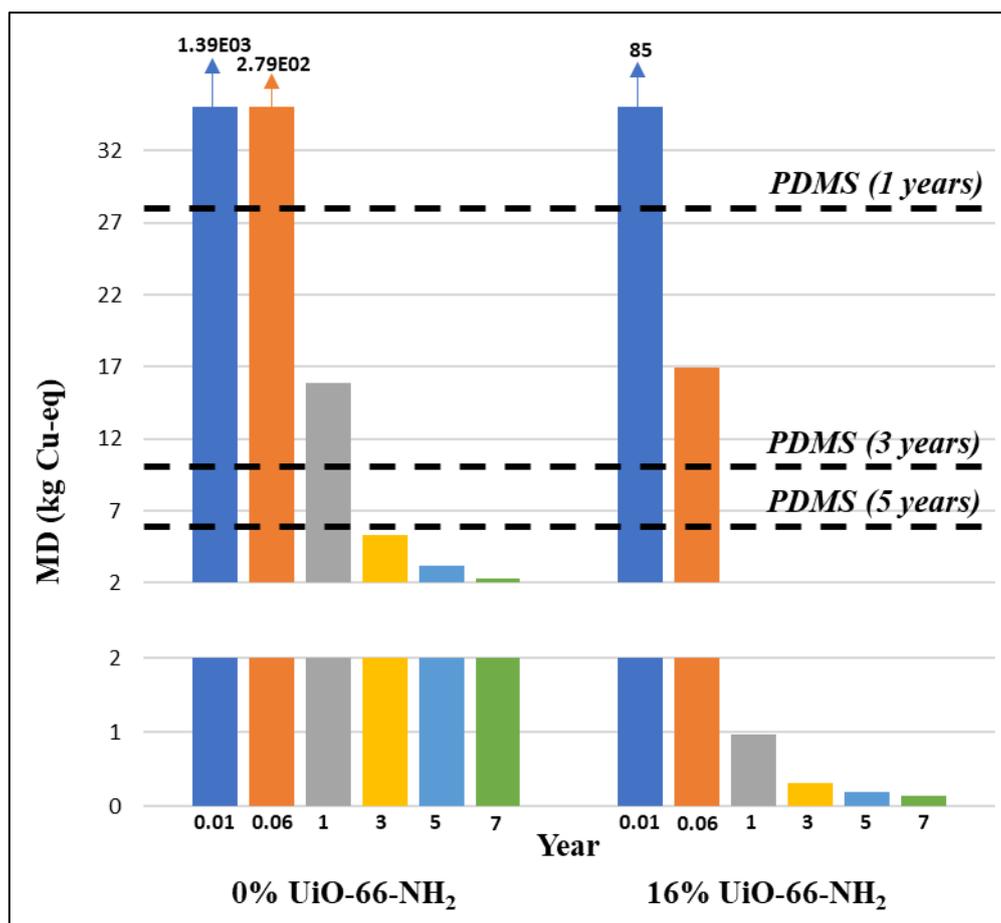


Figure 17. MD environmental impact comparison between 0 wt.% UiO-66-NH₂ and 16 wt.% UiO-66-NH₂ CS:ST-based membrane with a commercial membrane PDMS, considering the plant lifetime of 20 years and a range of lifetime.

To achieve sustainable CO₂ capture from a GWP, FD, and MD perspective, the required lifetime for the 0% UiO-66-NH₂ membrane should be 3 years, while for the 16% UiO-66-NH₂ membrane, 1 year is enough.

5. CONCLUSIONS

This study focuses on the synthesis and characterization of biopolymer-based mixed-matrix membranes (MMMs) using chitosan (CS) and starch (ST), in conjunction with green metal-organic frameworks (MOFs), UiO-66 and UiO-66-NH₂. The study aims to evaluate the gas separation performance, specifically for CO₂, and the environmental impact of these membranes compared to a commercial membrane made of polydimethylsiloxane (PDMS).

In the synthesis process, membranes were developed with varying filler loadings from 0 wt.% to 16 wt.% of MOFs. The gas permeability tests for N₂, CH₄, and CO₂ revealed that both N₂ and CH₄ permeabilities increased with filler loading up to a point and then decreased at the highest loading. In contrast, CO₂ permeability continuously increased with increasing filler content. This consistent increase in CO₂ permeability aligns with the literature, which attributes it to the high CO₂ uptake capability of UiO-66 and UiO-66-NH₂ MOFs. Selectivity measurements indicated that selectivity values generally remained around or below 3-4 for filler loadings up to 12 wt.%. However, at the highest filler loading of 16 wt.%, the mechanical integrity of the UiO-66-filled membrane was compromised, preventing complete gas pair selectivity measurements. Nonetheless, the UiO-66-NH₂-filled CS:ST membrane at 16 wt.% exhibited a gas pair selectivity for CO₂/N₂ and CO₂/CH₄ comparable to that of the commercial PDMS membrane.

Additionally, the study conducted a cradle-to-gate lifecycle assessment (LCA) for the membranes, evaluating the global warming potential (GWP), fossil depletion (FD), and metal depletion (MD) impacts with a functional unit of 1 m². Results showed that increasing the filler loading from 0 to 16 wt.% led to a significant rise in GWP by 297%, mainly due to the substantial impacts from the preparation inputs for UiO-66-NH₂, such as dichloromethane (DCM) and methanol, as well as the energy consumption. Similarly, FD and MD increased by 265% and 58%, respectively.

When comparing the biopolymer-based membranes to the commercial PDMS membrane, the latter exhibited higher GWP, FD, and MD values, despite the increase in environmental impacts with higher filler loadings. This comparison highlights that the biopolymer and UiO-66-NH₂-based membranes, despite their increased filler-related impacts, are still less environmentally detrimental than the commercial oil-based PDMS membrane. The sensitivity assessment demonstrates that lifetimes higher than 3 years could make the CO₂ separation performance of biopolymer membranes more sustainable than that of commercial oil-based membranes.

The study concludes that the laboratory-made biopolymer-based membranes are more environmentally friendly compared to the commercial PDMS membrane. This aligns with the study's objective of creating sustainable and effective alternatives for CO₂ separation. Moreover, the environmental performance comparison involving three chosen scenarios (0 wt.%, 16 wt.%, and PDMS) for CO₂ separation and sensitivity analysis reinforces the potential benefits of the biopolymer-based membranes.

6. CONCLUSIONES

Este estudio se centra en la síntesis y caracterización de membranas de matriz mixta (MMMs) basadas en biopolímeros, utilizando quitosano (CS) y almidón (ST), junto nanopartículas organometálicas “verdes” (MOFs), UiO-66 y UiO-66-NH₂. El objetivo del estudio es evaluar el rendimiento de separación de gases, específicamente para CO₂, y el impacto ambiental de estas membranas en comparación con una membrana comercial hecha de polidimetilsiloxano (PDMS).

En el proceso de síntesis, se desarrollaron membranas con diferentes cargas, desde 0% hasta 16% en peso de MOFs. Los experimentos de permeabilidad de gases para N₂, CH₄ y CO₂ revelaron que las permeabilidades de N₂ y CH₄ aumentan con la carga de relleno hasta cierto punto tras lo cual, disminuyen. Por el contrario, la permeabilidad del CO₂ aumenta con el aumento del contenido de relleno. Este aumento constante en la permeabilidad del CO₂ se alinea con la bibliografía, que lo atribuye a la alta capacidad de adsorción por el CO₂ de los MOFs UiO-66 y UiO-66-NH₂. Los valores de selectividad generalmente se mantuvieron alrededor o por debajo de 3-4 para cargas de relleno de hasta 12% en peso. Sin embargo, en la carga de relleno más alta de 16% wt., la integridad mecánica de la membrana rellena de UiO-66 se vio comprometida, lo que impidió realizar mediciones completas de selectividad de pares de gases. No obstante, la membrana CS:ST rellena con UiO-66-NH₂ al 16% en peso mostró una selectividad de pares de gases para CO₂/N₂ y CO₂/CH₄ comparable a la de la membrana comercial de PDMS.

Además, el estudio realizó una evaluación del ciclo de vida (LCA) desde la cuna hasta la puerta para las membranas, evaluando el potencial de calentamiento global (GWP), el agotamiento de fósiles (FD) y el agotamiento de metales (MD) con una unidad funcional de 1 m². Los resultados mostraron que aumentar la carga de relleno de 0 a 16% wt. lleva a un aumento significativo en el GWP del 297%, principalmente debido a los impactos sustanciales de los consumos relacionados con la preparación para UiO-66-NH₂, como diclorometano (DCM) y metanol, así como al consumo de energía. De manera similar, el FD y el MD aumentaron en un 265% y 58%, respectivamente.

Al comparar las membranas basadas en biopolímeros con la membrana comercial de PDMS, esta última mostró valores más altos de GWP, FD y MD, a pesar del aumento en los impactos ambientales con cargas de relleno más altas. Esta comparación destaca que las membranas basadas en biopolímeros y UiO-66-NH₂, a pesar de sus impactos aumentados relacionados con el relleno, son aún menos perjudiciales para el medio ambiente que la membrana comercial a base de petróleo PDMS. También el análisis de sensibilidad demuestra que vidas útiles superiores a 3 años podrían hacer que el rendimiento de la separación de CO₂ a través de membranas de biopolímero sea más sostenible que el de las membranas comerciales a base de petróleo.

El estudio concluye que las membranas basadas en biopolímeros hechas en laboratorio son más respetuosas con el medio ambiente en comparación con la membrana comercial de PDMS. Esto se alinea con el objetivo del estudio de crear alternativas sostenibles y efectivas para la separación de CO₂. Además, la comparación del rendimiento ambiental que involucra tres escenarios elegidos (0% en peso, 16% en peso y PDMS) para la separación de CO₂ y el análisis de sensibilidad refuerzan los posibles beneficios de las membranas basadas en biopolímeros.

7. NOMENCLATURE

A	Area of the membrane, cm^2 (equation 1).
AD	Abiotic Deple, (Table 1)
AC	Acidification, te/y sulfur dioxide equivalent.
CED	Cumulative Energy Demand, MJ (Table 1).
CNG	Compressed natural gas
COPs	Conferences of the Parties
CS	Chitosan
C_p	Specific heat capacity, $\text{J}\cdot(\text{kg}\cdot\text{K})^{-1}$ (Equation 3).
d^5	Impeller diameter, (Equation).
ECFM	Eco-toxicological Effects on FreshwaterMicroorganisms, kg 1,4-DB-eq. (Table 1).
EUF	Eutrophication freshwater, kg PO_4^{3-} eq. (Table 1).
EUM	Eutrophication marine, kg N-eq. (Table 1).
EUT	Eutrophication terrestrial, kg N-eq. (Table 1).
FD	Fossil Depletion, kg oil-eq. (Table 1).
FEP	Freshwater Eutrophication Potential, kg P-eq (Table 1). (Table 1).
GHG	Greenhouse gas
GWP	Global Warming Potential, $\text{kg CO}_2\text{-eq.}$
HKUST-1	Hong Kong University of Science and Technology-1copper based
HTC	Human Toxicity Cancer, kg 1,4-DB-eq. (Table 1).
HTNC	Human Toxicity Non-Cancer, kg 1,4-DB-eq. (Table 1).
HTP	Human Toxicity Potential, kg 1,4-DB-eq. (Table 1).
IPCC	Intergovernmental Panel on Climate Change
IR	Ionizing Radiation, U235-eq. (Table 1).
ISO	International Organization for Standardization
l	Thickness of the selective layer, cm (Equation 1).
LCA	Life Cycle Assessment

LU	Land Use, m ² (Table 1)
MD	Material Depletion, kg Cu-eq (Table 1)
MEA	Marin Ecotoxicity, kg 1,4-DB-eq. (Table 1).
MMMs	Mixed matrix membranes
MOFs	Metal-organic frameworks
m_{liq}	Mass of the liquid of the solution, kg (Equation 5).
m_{mix}	Mass of the mixture, kg (Equation 3).
m_{vap}	Mass of the liquid is evaporated, kg (Equation 5).
N	Rotational speed of the agitator, 1·s ⁻¹ (Equation 4).
N_p	Power number, dimensionless (Equation 4).
ODP	Ozone Depletion Potential, kg CFC-11-eq. (Table 1)
OPDA-TMPDA	o-Phenylenediamine - Terephthalamide
p	Pressure Barrer, (Equation 1).
Q_{heat}	Heat Flow rate, J (Equation 3).
Q_{dry}	Heat necessary for the process, J (Equation 5).
Q_p	Permeate flow rate, cm ³ (STP)·s ⁻¹ .
PAN	Polyacrylonitrile
PDMS	Polydimethylsiloxane
PEBA	Polyether Block Amide
PES	Polyether sulfone
POF NMVOC-eq. (Table 1).	Photochemical Ozone Formation impact category potential, kg
RDM eq.(Table 1).	Resource Depletion of Minerals impact category potential, kg Sb-
RI	Respiratory Inorganics, kg PM2.5-eq. (Table 1).
ST	Starch
TAP	Terrestrial Acidification Potential, kg SO ₂ eq (Table 1).
t	Time duration, s (Equation 4).

T_0	Starting temperature, K (Equation 4).
T_{boil}	Boiling temperature of the liquid, K (Equation 5).
T_r	Temperature of heating, K (Equation 3).
UiO-66	University of Oslo no. 66
WDP	Water Depletion Potential, m^3 (Table 1).
ZIF-8	Zeolitic Imidazolate Framework-8
ρ_{mix}	Mixture density, $kg \cdot m^{-3}$ (Equation 4).
ΔH_{vap}	Enthalpy evaporation of the solvent, $J \cdot (kg \cdot K)^{-1}$ (Equation 5).
η_{dry}	Efficiency of the drying process for drying process, % (Equation 5).
η_{stir}	Efficiency value of the process, % (Equation 4).
6FDA-bisp	6FDA-Bisphenol
6FDA-DAM	6FDA-Diaminomesitylene
6FDA-ODA	6FDA-Oxydianiline

8. REFERENCES

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