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Application of Nanoparticle-Doped MOF Composite-Embedded Mixed Matrix Membranes in Carbon Capture

Özge Öztürk Sömek[*a]

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[a,*] Sinop University,
Engineering and Architecture Faculty,
Dept. of Environmental Engineering
57000 - Sinop, Türkiye
Orcid: 0000-0002-1082-7728
e mail: osomek@sinop.edu.tr

[*]Corresponding author:
osomek@sinop.edu.tr

ABSTRACT

Carbon dioxide (CO_2) is released into the atmosphere from both natural sources and human activities. In Türkiye, the largest source of CO_2 emissions from human activities is the energy sector, accounting for 85.4% of total CO_2 emissions in 2020. Over the past 30 years, CO_2 emissions have increased by 173%, making up 86% of total greenhouse gas emissions. This highlights the need for economically viable CO_2 capture technologies. Carbon capture methods are classified into pre-combustion, post-combustion, oxyfuel combustion, and direct air capture. Among these, post-combustion CO_2 capture has been widely studied in recent years. This method involves the separation, capture, and storage of CO_2 from flue gas after combustion. Common techniques include cryogenic separation, selective membranes, electrochemical separation, physical and chemical absorption, and adsorption. Among these, membrane-based CO_2 separation stands out, emphasizing the need for membranes with high CO_2 selectivity and permeability. MOFs are promising candidates due to their high porosity and CO_2 capture capacity. The development of mixed matrix membranes incorporating nanoparticle-doped MOFs into conventional membranes will enhance CO_2 selectivity in gas mixtures. This approach will enable the production of cost-effective, thermally and water-stable membranes with high CO_2 selectivity.

Karbon Yakalamada Nanoparçacık Katkılanmış MOF Kompozit Gömülü Karma Matris Membranların Uygulanması

ÖZ

Karbondioksit (CO_2), hem doğal kaynaklardan hem de insan faaliyetlerinden atmosfere salınmaktadır. Türkiye'de insan faaliyetlerinden kaynaklanan en büyük CO_2 emisyon kaynağı enerji sektörüdür ve 2020 yılında toplam CO_2 emisyonlarının %85,4'ünü oluşturmuştur. Son 30 yılda CO_2 emisyonları %173 artarak, toplam sera gazı emisyonlarının %86'sını meydana getirmiştir. Bu durum, ekonomik açıdan uygulanabilir CO_2 yakalama teknolojilerine olan ihtiyacı göstermektedir. Karbon yakalama yöntemleri; ön yanma, yanma sonrası, oksijenli yanma ve doğrudan havadan yakalama olarak sınıflandırılmaktadır. Son yıllarda, özellikle baca gazından CO_2'nin ayrılması, yakalanması ve depolanmasını içeren yanma sonrası yöntemleri daha fazla araştırılmıştır. En yaygın yöntemler, kriyojenik ayırma, seçici membranlar, elektrokimyasal ayırma, sıvı çözücülerle fiziksel/kimyasal absorpsiyon ve katılar üzerinde adsorpsiyondur. Bunlar arasında membran bazlı CO_2 ayırma öne çıkmakta olup, yüksek CO_2 seçiciliği ve geçirgenliği olan yeni membranlara ihtiyaç duyulmaktadır. MOF, yüksek gözeneklilikleri ve CO_2 tutma kapasitesi ile bu ihtiyacı karşılayabilecek aday malzemelerdir. Nanoparçacık katkılı MOF'lerin geleneksel membranlara katkılandığı karışık matris membranlar geliştirilmesi, gaz karışımlarından CO_2 seçiciliğini artıracaktır. Bu yaklaşım, ısıya ve suya dayanıklı, yüksek CO_2 seçiciliğine sahip daha ekonomik membranların üretilmesini sağlayacaktır.

Anahtar Kelimeler: Sera gazları, CO_2, karbon yakalama, MOF, membran

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1. Introduction

Global CO_2 emissions have surged rapidly in recent years, driven by industrialization and increasing energy demand. As energy consumption rises with population growth, urbanization, and economic expansion, reliance on fossil fuels persists to meet this demand [1]. CO_2 released into the atmosphere from fossil fuel combustion is recognized as one of the major factors of climate change. Climate change threatens the natural balance with effects such as growing global temperatures, sea level increments, and extreme weather events [2,3]. This situation makes reducing CO_2 emissions an urgent priority for a sustainable future.

The distribution of global CO_2 emissions plays a critical role in carbon management strategies. Figure 1 illustrates the total CO_2 emissions and CO_2 emissions per capita across various regions from 2000 to 2023. In the left graph, China's CO_2 emissions show a continuous upward trend, surpassing 12 Gt CO_2 by 2023, indicating that it emits more than other regions. India's emissions are also increasing, although at a lower level. Meanwhile, the European Union, Japan, and the United States exhibit relatively stable or declining emission levels at the same time. In the right graph, the United States has the highest CO_2 emissions per capita, though this value has been on a downward trend since 2000. Japan and the European Union also show similar decreasing trends in per capita emissions. While China's per capita emissions have been rising, they remain lower than those of industrialized nations like the United States. India, on the other hand, has the lowest per capita emissions. Overall, industrialized regions (such as the US, Japan, and the EU) show a decline in per capita emissions, whereas developing countries (particularly China and India) exhibit an increase. This reflects the impact of factors such as industrialization, population expansion, and economic development on CO_2 emissions [4].

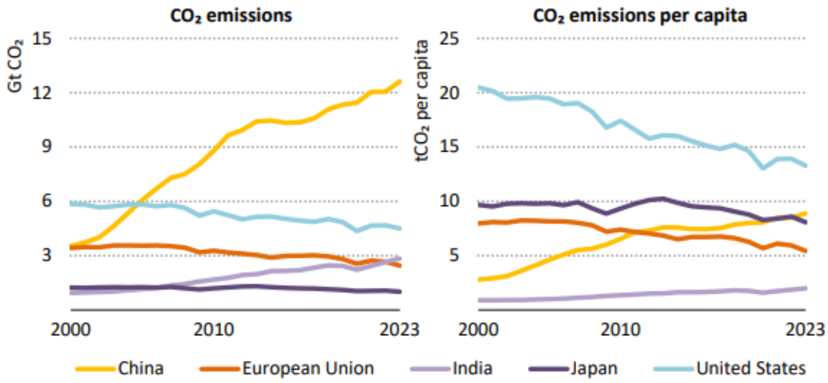

Figure 1. CO_2 total and CO_2 per capita by region [4].

Various strategies and technologies are being developed to reduce global CO_2 emissions. Strategies such as shifting to clean energy sources, optimizing energy efficiency, and utilizing renewable energy significantly contribute to reducing the carbon footprint. Additionally, energy-efficient technologies help lower carbon emissions by enabling less energy consumption in production processes [5]. However, despite these efforts, production processes in carbon-intensive sectors and the use of fossil fuels continue to generate high amounts of emissions. While there is a trend toward clean energy in electricity generation, this transition is insufficient to meet the entire demand, leading to a rise in fossil fuel use to bridge the production gap. The International Energy Agency's (IEA) 2023 CO_2 emissions report supports this situation, noting that emissions from energy generation enhanced by 900 Mt between 2019 and 2023; however, without eco-friendly energy solutions like solar, wind, nuclear, heat pumps, and electric vehicles, this increase would have been approximately three times higher [4]. Therefore, it is understood that clean energy technologies have limited the growth of CO_2 emissions. Yet, the current situation remains inadequate to achieve the net-zero emissions target, indicating that only limited improvement has been possible. In this context, solutions that go beyond existing technologies are needed to achieve more effective results.

At this point, carbon capture and storage (CCS) technologies stand out as a significant solution, directly targeting emissions in carbon-intensive sectors [6]. Carbon capture technologies have the potential to prevent CO_2 emissions originating from coal and gas power plants and industrial sites by capturing CO_2 before it reaches the atmosphere. Specifically, advanced materials such as metal-organic frameworks (MOFs) supported by nanoparticle-enriched mixed matrix membrane (MMM) systems offer a promising solution because of their selective capability to separate and capture CO_2 molecules [7,8]. These innovative carbon capture technologies can capture CO_2 released from carbon-intensive production facilities, reducing environmental impacts and helping achieve carbon reduction goals.

This study aims to reveal the current status in this field by examining the potential of nanoparticle-doped MOF composite-embedded mixed matrix membranes in carbon capture. In this review, the structural characteristics, performance, and advantages of these next-generation membranes used in carbon capture technologies will first be discussed. Subsequently, application examples in the current literature and successful outcomes will be evaluated. Finally, the areas requiring improvement and upcoming development possibilities necessary for the widespread industrial application of these technologies will be discussed. This study intends to further insight into innovative technology with the potential to provide sustainable solutions for enhancing efficiency in carbon capture and achieving carbon reduction goals.

2. CO_2 Emissions, Sources, and Sinks

The escalation of CO_2 emissions has emerged as a pressing global challenge, primarily driven by anthropogenic activities and natural phenomena. The steady increase in CO_2 concentrations in the atmosphere is linked to significant alterations in climate patterns, resulting in severe ecological and socio-economic repercussions. A thorough comprehension of the origins and sinks of CO_2 is imperative for formulating targeted strategies aimed at curbing emissions and fostering sustainability. As industries expand and populations grow, the need to identify and address the specific contributors to carbon emissions becomes increasingly vital in the effort to tackle climate change.

In the study conducted by Liu et al. (2023), global carbon emissions for the year 2022 were analyzed in detail. Figure 2 clearly shows which sectors the emissions originate from and the annual emission trends of these sectors. When examining the sectoral distribution, it is evident that major sectors such as energy production, transportation, and industry provide significant emissions. Particularly, energy production accounts for a large portion of total emissions, playing a critical role in shaping climate policies. The transportation sector is also a significant source of emissions; this sector is directly related to the use of fossil fuels, and thus there is a need to accelerate the transition to alternative energy sources. The industrial sector produces significant emissions due to the energy and raw materials used in production processes. The study also addresses the changes in emissions from these sectors over time. For example, it notes that emissions experienced a temporary decline during the COVID-19 pandemic, but rapidly increased in 2021, approaching pre-pandemic levels. These sector-specific analyses guide policymakers on where more effort is needed to reduce emissions. The data in Fig. 2 also reflects seasonal fluctuations in emissions. For instance, it is observed that emissions rise in winter due to increased energy consumption, while this trend reverses in summer. This situation highlights how emissions are affected by seasonal changes in energy demand [9]. Deforestation and land use changes contribute approximately 10% of global CO_2 emissions. The alteration of forests for agriculture or urbanization not only reduces the planet's capacity to sequester carbon but also releases stored carbon back into the atmosphere. Agricultural practices add around 5% to total emissions, largely through soil management and fertilizer application. Furthermore, waste management practices, including landfilling and incineration, generate approximately 3% of global CO_2 emissions as organic materials decompose or are burned [10,11].

In Türkiye, the biggest contributor to CO_2 emissions from human activities is the energy, industrial processes and product use (IPPU), agriculture, and waste sectors. According to the National Greenhouse Gas (GHG) Emission Inventory Report, which covers the years 1990-2020 submitted as part of the United Nations Framework Convention on Climate Change, the energy sector accounts for 85.4% of total CO_2 emissions in 2020. The remaining 14.2% comes from IPPU, 0.4% from agriculture, and close to zero from waste. Total CO_2 emissions from all sectors have increased by approximately 173% in 30 years. This increase constitutes 86% of total GHG emissions in Türkiye [12].

Despite the challenges posed by CO_2 emissions, various natural and technological sinks exist that can absorb atmospheric carbon dioxide. Forests serve as one of the most significant carbon sinks, with the ability to sequester about 2.6 billion metric tons of CO_2 annually through photosynthesis. Initiatives focused on reforestation and afforestation are crucial for enhancing this capacity [13]. Oceans also play a vital role, absorbing an estimated 2.5 billion metric tons of CO_2 each year. However, elevated CO_2 levels can lead to ocean acidification, which threatens marine ecosystems [14]. Soil is another critical carbon sink, with healthy soils capable of storing approximately 3.3 billion metric tons of carbon each year. Implementing sustainable agricultural practices can significantly enhance soil carbon storage, thereby acting as a buffer against CO_2 emissions [15]. On the technological front, solutions such as CCS aim to sequester CO_2 emissions from industrial processes, currently capturing about 40 million metric tons of CO_2 per year. Additionally, innovations like direct air capture (DAC) are emerging, showing potential for removing millions of tons of CO_2 from the atmosphere annually [16].

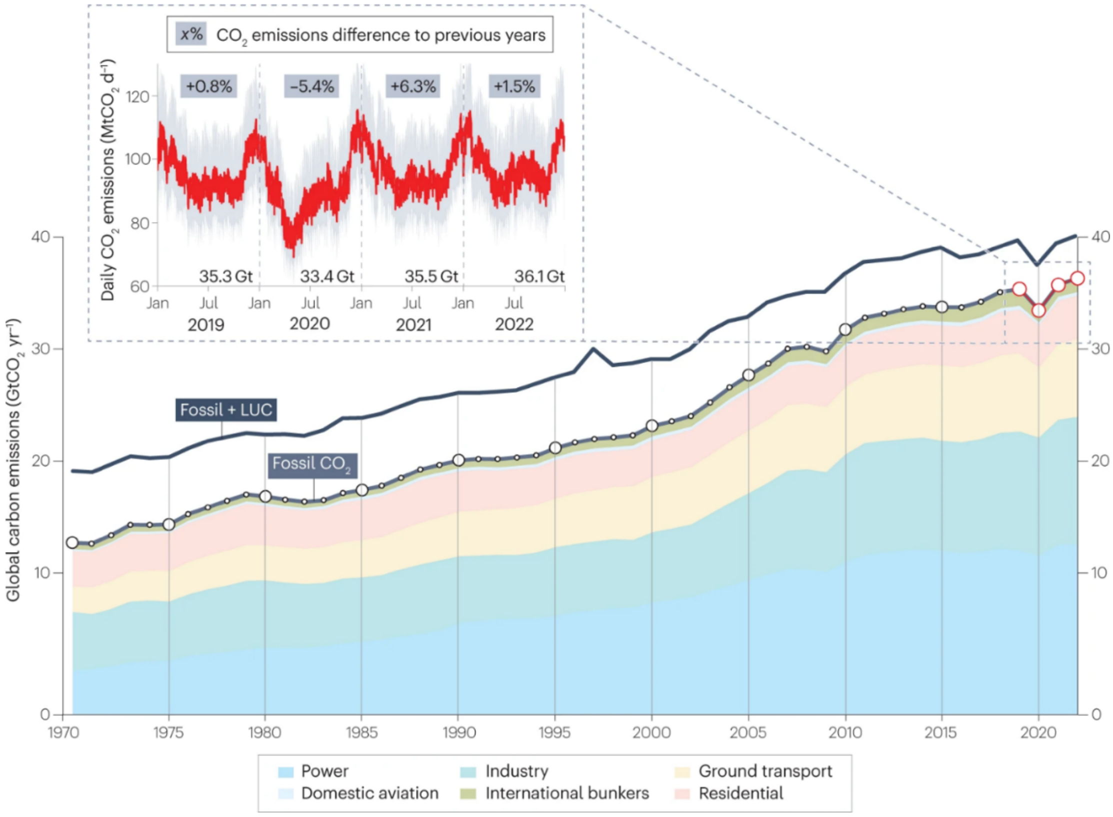

Figure 2. Global CO_2 emissions 1970-2022 [9].

Comprehending the sources and sinks of CO_2 emissions is crucial for creating effective solutions to address climate change. By targeting emissions from fossil fuel combustion, industrial activities, and land use changes, while simultaneously enhancing natural sinks like forests and soils, we can make significant strides toward a sustainable future. These combined efforts will be critical in tackling the multifaceted challenges posed by climate change and in attaining global carbon reduction targets.

3. Capture and Removal of CO_2

As the urgency to address climate change escalates, the development of effective carbon capture technologies has become crucial. These technologies aim to mitigate CO_2 emissions from major sources, such as power plants, industrial processes, and transportation systems [17,18]. Key strategies include pre-combustion capture, which involves removing CO_2 before combustion occurs, typically in integrated gasification combined cycle (IGCC) power plants [19]; post-combustion capture, which captures CO_2 from flue gases after fuel combustion using methods such as chemical absorption and adsorption [20]; and direct air capture (DAC), which extracts CO_2 directly from the atmosphere, presenting a pathway for achieving negative emissions [21]. Recent advancements are increasingly focused on integrating these methods with renewable energy sources to enhance efficiency and sustainability. Table 1 summarizes the principles, advantages, and disadvantages of CCS technologies. Accordingly, Chemical absorption enables the selective capture of CO_2 using amine or solvent solutions and is a method applicable at an industrial scale [22]. However, challenges such as high energy consumption during solvent regeneration, solvent degradation, and corrosion increase the cost and environmental impacts of this method [23,24]. Physical absorption, on the other hand, involves the capture of CO_2 using physical solvents at low temperatures. This method is highly efficient in high-pressure gas streams and has low solvent loss [25]. However, its reduced effectiveness at low pressures limits its large-scale application [26]. When comparing these two absorption methods, chemical absorption offers higher selectivity, while physical absorption has the advantage of reducing solvent costs.

Membrane technologies involve the separation of CO_2 from other gases through semi-permeable membranes. This method is advantageous due to its energy efficiency and modular design [27]. Various CO_2 capture technologies have reviewed the potential of membrane-based systems, particularly in applications such as CO_2-enhanced methane recovery. It is highlighted that membrane technologies when integrated with other CO_2 capture methods, can improve overall efficiency and feasibility in industrial applications [28]. However, limitations such as the chemical and thermal stability of membranes and the need for multi-stage processes to achieve high purity are notable challenges [27]. Nevertheless, innovative approaches such as thin-film composite membranes and graphene oxide modification show promise in enhancing membrane performance [29]. In this context, it was emphasized that novel materials and hybrid approaches, such as incorporating nanoparticles and advanced polymer structures, could improve membrane performance and longevity [30].

Adsorption methods involve the physical or chemical capture of CO_2 using high-surface-area materials [31]. The use of materials like metal-organic frameworks (MOFs) improves selectivity and recovery rates. However, high material costs and long-term stability issues are among the disadvantages of this method [32-34]. Innovations such as hybrid graphene-MOF materials and surface engineering are improving the effectiveness of adsorption technology [35,36]. Cryogenic separation allows producing high-purity CO_2 through liquefaction at low temperatures. The absence of solvent use is a significant advantage [37]. However, the requirement for extremely low temperatures leads to high energy consumption, limiting its economic feasibility [38]. Biological capture involves the sequestration of CO_2 using microalgae or other biological agents. This method offers additional benefits, such as biofuel production [39]. However, challenges such as sensitivity to growth conditions and the need for large areas limit their practical applications [40,41].

Chemical looping CO_2 capture (CLC) is a method that uses metal oxides and enables the direct separation of CO_2 from fossil fuels. CLC is a promising method for decreasing carbon emissions from fossil fuels by enabling highly efficient and direct CO_2 separation [42]. Pilot-scale studies indicate that technology is still in the developmental phase for large-scale commercial applications [43]. On the other hand, the selection of oxygen carriers plays a crucial role in system performance. In this context, it was found that Fe_2O_3/CaO-based oxygen carriers are effective for hydrogen-rich syngas production. Thus, CLC has potential not only for carbon capture but also for hydrogen production [44]. However, despite its high efficiency, its limited commercial adoption and high initial costs are restrictive factors [45]. Moreover, the high reactor design costs were highlighted as a major challenge [46]. With these characteristics, CLC presents a significant opportunity for transitioning to a low-carbon economy by offering sustainable energy production and effective CO_2 emission reduction, but large-scale applicability and cost reduction are needed.

In summary, while chemical and physical absorption methods are among conventional approaches, membrane and adsorption technologies offer innovative solutions. With the latest developments, membrane technologies present a promising pathway for CO2 separation, but overcoming challenges related to multi-stage processing, chemical stability, and thermal resistance is crucial for their widespread adoption in carbon capture applications. Designing mixed-matrix membranes and incorporating advanced nanomaterials with superior properties are essential to addressing these challenges.

Table 1. Carbon capture technologies.

Technology	Principles	Advantages	Disadvantages	References
Chemical absorption	Absorb CO_2 with amine or solvent solutions.	High selectivity, can operate at low temperatures and can be applied on an industrial scale.	Solvent regeneration is energy-intensive, risks solvent degradation and corrosion	[22-24]
Physical absorption	CO_2 is absorbed at low temperatures with physical solvents	Efficient in high-pressure gas flows, low solvent loss.	Poor efficiency at low pressures	[25,26]
Membrane technologies	Separates CO_2 and other gases by semi-permeable membranes	High energy efficiency, modular structure	Requires multi-stage process for high purity, limited chemical and thermal resistance of membranes	[27-30]
Adsorption	CO_2 is physically or chemically trapped in materials with a high surface area	High selectivity and recovery rate, low energy consumption	Material costs can be high, long-term stability can be an issue	[31-36]
Cryogenic separation	Separation of CO_2 by liquefaction at low temperatures	High-purity CO_2 can be obtained, and no solvent is required	High energy consumption for low temperatures	[37,38]
Biological capture	Capturing and converting CO_2 with microalgae or other biological methods	Renewable provides side benefits such as biofuel production	Efficiency is low, requires a large area and growth conditions are sensitive	[39-41]
Chemical looping capture	Capture and storage of CO_2 with metal oxides	High efficiency, direct separation of CO_2 from fossil fuels	Technology is not yet commercially available. The initial cost is high	[42-46]

3.1. Membrane-based CO_2 separation

Membrane-based separation technologies have attracted considerable interest in CO_2 capture because of their potential for high selectivity and energy efficiency. These systems utilize semi-permeable membranes to separate CO_2 from other gases, offering a compact and scalable solution for reducing emissions. Fig. 3 schematically illustrates how gas mixtures are separated using membranes. In the figure, the feed gas, which typically consists of CO_2 and other components, enters the membrane system. The membrane is a semi-permeable structure that exhibits selective permeability to certain gases, allowing some gases to pass through more easily while others are retained. The gases that pass through the membrane are referred to as permeate gas, whereas the gases that are retained by the membrane are called retentate gas. In CO_2 capture processes, the primary goal is usually to separate CO_2 as the permeate gas. In membrane-based CO_2 separation, permeability (P) and selectivity (α) are two key parameters used to assess performance. Permeability indicates the amount of gas passing through a unit thickness of the membrane and is typically measured in Barrer. This parameter reflects how quickly CO_2 can permeate the membrane, which is crucial for achieving high flow rates and efficiency in industrial applications. Selectivity, on the other hand, denotes the degree of selectivity between two gases, often measured for gas pairs like CO_2/N_2, and determines the membrane's ability to separate CO_2 effectively from other gases. Membranes with high permeability and high selectivity allow for the rapid and efficient separation of CO_2 from other gases, making the optimization of these two parameters essential for achieving ideal performance.

Membrane-based CO_2 separation technologies are characterized by several advantages, including energy efficiency, as they typically require less energy than traditional amine scrubbing processes, resulting in lower operational costs [28]. Moreover, the modular nature of membrane systems allows for their deployment in various scales and applications, ranging from large industrial plants to small-scale operations, facilitating ease of integration into existing infrastructures. The various types of membranes employed in CO_2 separation include organic (polymeric), inorganic (ceramic), and nanocomposite (mixed matrix membranes – MMMs) [29]. Polymeric membranes are known for their flexibility and ease of processing, while ceramic membranes offer superior thermal and mechanical stability. Mixed matrix membranes combine the advantages of both polymeric and inorganic materials, leading to enhanced performance characteristics such as increased permeability and selectivity for CO_2 over other gases.

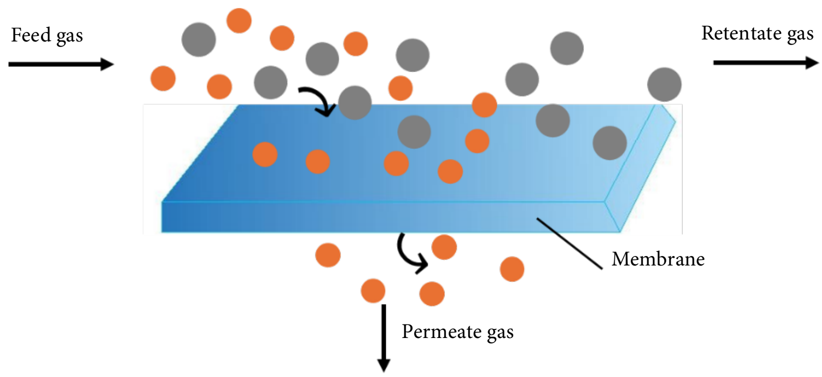

Figure 3. The diagram of gas mixture separation with membranes.

3.2. Design of mixed matrix membranes (MMMs)

MMMs are composite membranes formed by embedding inorganic or organic particles in a polymeric matrix. The particles (e.g. MOF, zeolites, carbon nanotubes) combine with the polymer matrix to further customize and improve the separation properties of the membrane. In this context, the most promising advancement in membrane technology is the development of MOF-based MMMs. These advanced materials combine the beneficial properties of MOFs with nanoparticles, creating a new class of membranes that present superior gas separation characteristics [47,48]. The incorporation of MOFs enhances selectivity for CO_2 due to their high surface area and tunable pore structures, allowing for precise adjustments to optimize gas adsorption properties.

Fig. 4 illustrates the production of a MMM by embedding a nanoparticle-doped MOF composite into a polymer matrix. Initially, nanoparticles and the MOF are combined to form a homogeneous nanocomposite, leveraging the structural and chemical properties of the MOF with the functionality of the nanoparticles to enhance carbon capture performance. The nanocomposite is then added to a polymer solution to achieve uniform dispersion. This step aims to improve the membrane's properties, such as gas permeability and selectivity. The prepared polymer-nanocomposite mixture is cast into a polytetrafluoroethylene (PTFE) mold and then dried and solidified to form the MMM. The casting step is followed by a controlled drying and solidification phase, where solvent removal is carefully managed to prevent defects and ensure the formation of a robust and uniform membrane structure. This process also allows for the fine-tuning of the membrane's porosity and thickness, which are critical for optimizing gas transport and separation. The resulting MMM is optimized for carbon capture applications with enhanced porosity, permeability, and thermal and mechanical stability. These features make the membrane highly effective in capturing CO_2.

3.3. Recent advances in MMMs for CO_2 separation

Table 2 provides examples of MMMs prepared with various polymer and MOF compounds for CO_2 separation applications. In these MMMs, significant increases in CO_2 permeability and selectivity have been observed using MOF fillers like UIO-66, UIO-66-NH_2, MIL-96-(Al), MOF-808, and Mg_2(dobpdc) combined with polymers such as PIM-1, 6FDA-DAM, ODPA-DAM, Matrimid, and PDA [49-54]. The high surface area and porous structures of MOF fillers contribute to the effective capture of CO_2 while facilitating rapid CO_2 transport and maintaining stable selectivity. A high-performance membrane was developed for CO_2/N_2 selectivity by combining 6FDA-DAM polymer with Mg_2(dobpdc), offering significant advantages for industrial applications, especially in CO_2 separation from other gases [51,53]. These studies on membrane selectivity have produced high-performance MMMs using various fillers, with optimized separation parameters. These findings demonstrate that MOFs can enhance CO_2 separation performance in different polymer matrices, and each MOF-polymer combination can be tailored for specific gas separation needs. On the other hand, MMMs obtained by embedding nanoparticle-doped MOF composites in polymer membranes improve the permeability of the membranes by facilitating more efficient pathways for gas transport, leading to a synergistic effect that optimizes both adsorption and diffusion processes. The studies highlighted a range of MOFs, such as ZIF-8 and MIL-53(Al), combined with different nanomaterials, including graphene oxide and porous carbon, within diverse polymer matrices like PSF [55-57]. This results in increased CO_2 uptake while maintaining mechanical stability, which is crucial for consistent membrane performance under diverse operational conditions.

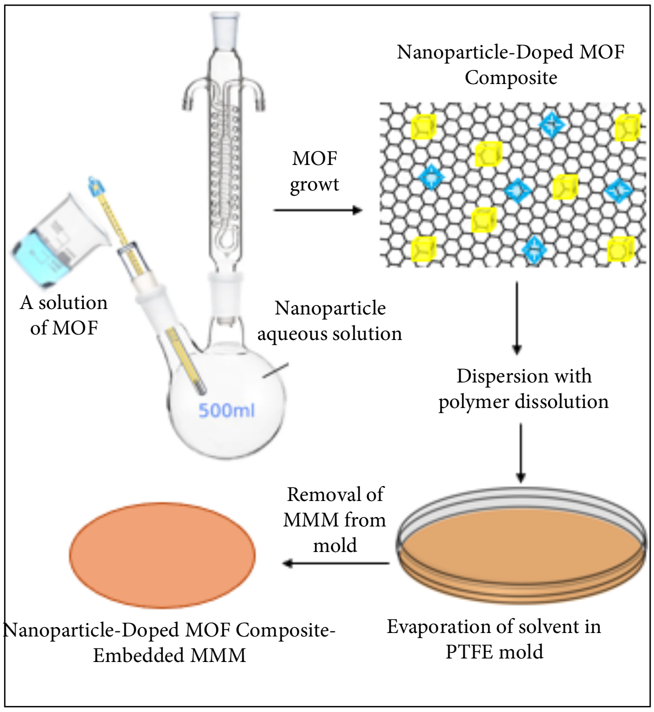

Figure 4. Fabrication flowchart of nanoparticle-doped MOF composite-embedded MMM

Table 2. Application of MOFs as a filler in MMMs for CO_2 capture.

Membrane Materials	Fillers	Application	References
PIM-1	UiO-66-CN	Polymeric membranes with embedded MOF in CO_2 separation	[49]
6FDA-DAM	Mg_2 (dobpdc)	Membranes designed for CO_2 permeability and CO_2/N_2 selectivity	[50]
6FDA-DAM	MIL-96-(Al)	Processing of MMMs for CO_2/N_2 post-combustion separation.	[51]
ODPA-DAM	UiO-66-NH_2 UiO-66-NH_2@PI	High-performance MOF-based MMMs for gas separation	[52]
Matrimid	MOF-808	CO_2/N_2 separation performance of MMMs.	[53]
PDA	UiO-66	CO_2/N_2 and CO_2/CH_4 separation performance of MOF membranes	[54]

Composite membranes contribute to sustainability efforts by utilizing abundant and often environmentally friendly materials in their production. However, challenges remain in scaling these materials for commercial use, necessitating further research into cost-effective manufacturing processes and the long-term stability of these membranes under various environmental conditions. The cost of MOF-based MMMs is primarily influenced by the synthesis of MOF materials, polymer matrix selection, and fabrication processes. Studies have shown that MOF production can contribute up to 60% of the total membrane cost, with solvent-based synthesis being one of the major cost drivers [51,52]. Although MOFs offer superior CO_2 separation efficiency, their large-scale application is often hindered by the high cost of raw materials and complex synthesis routes. Several studies have highlighted the need for cost reduction in MMM fabrication. One approach involves using lower-cost precursors for MOF synthesis while maintaining the structural integrity and performance of the final membrane. For example, solvent-free synthesis and scalable continuous production methods have been explored to reduce costs by approximately 30% [54]. Therefore, it is important to develop alternatives such as solvent-free synthesis and continuous production techniques to make MMMs more economical in the future. Additionally, optimizing polymer-MOF interactions through surface modifications has been suggested to improve compatibility and reduce processing costs [53]. Finally, the use of nanoparticle-doped MOF composites can provide economic advantages in membrane fabrication by optimizing gas migration pathways [55,57].

3.4. Nanomaterials effect on carbon capture performance of membranes

In recent years, nanocomposite membranes obtained using nanomaterials have been frequently used in CO_2 capture. The filler material used in the production of nanocomposite membranes is selected based on the desired performance. Common nanomaterials include metal nanoparticles (Au, Ag, ZnO), carbon-based nanomaterials (carbon nanotubes, graphene oxide), metal-organic frameworks (MOFs), and zeolites. Additionally, functionalization processes can be applied to improve the surface properties of these nanomaterials. Moreover, by combining these nanomaterials, it is possible to produce filler materials with new properties such as high permeability, selectivity, and durability (e.g., MOF-graphene oxide composites). The findings presented in Table 3 provide a comparative assessment of the CO_2 capture performance of nanocomposite membranes. The HKUST-1@Graphene Oxide (GO) membrane was synthesized using the electrodeposition method, achieving a CO_2 adsorption capacity of 194.1 cm^3/g and a CO_2/N_2 ideal adsorption selectivity of 276.5, demonstrating that MOF structures modified with graphene oxide can enhance CO_2 adsorption capacity [58]. The Pebax/ZIF-8/NH_2-MIL-53(Al) membrane exhibited a CO_2 permeability of 488 ± 9 Barrer and a CO_2/CH_4 selectivity of 37.5 ± 0.6, indicating that the incorporation of amine-functionalized ZIF-8 and MIL-53(Al) MOFs improves CO_2 separation properties [59]. Similarly, the PEI-functionalized cerium nanosheet (PEI-F-Ce) mixed with a crosslinked polyethylene oxide (XLPEO) membrane demonstrated a CO_2 permeability of 641 Barrer and a CO_2/N_2 selectivity of 70.1, highlighting that the controlled pore structure provided by amine-functionalized F-Ce nanosheets enhances CO_2 permeability [60]. The Polyethersulfone (PES) blended with polyurethane (PU) and nano-clay membrane showed that the addition of PU and nano-clay fillers increased CO_2 permeability by 7.8 times and CO_2/N_2 and CO_2/CH_4 selectivity by 1.8 and 2.2 times, respectively [61]. The Pebax®1657-MOF-74(Ni)@GO membrane exhibited a significant improvement in CO_2/N_2 separation [29]. On the other hand, during the nanomaterial drop-casting process, some agglomeration occurred within the membrane structure, which could impact gas transport efficiency. Finally, carbon nanotube (CNT) incorporated with NH_2-functionalized MIL-101 and 6FDA-durene polyimide-based mixed matrix membranes (MMMs) demonstrated both high CO_2 permeability and CO_2/CH_4 selectivity, confirming the positive impact of MOF and CNT combinations on CO_2 separation performance [62]. The findings in the table highlight the significant potential of nanomaterial-incorporated membranes in enhancing selectivity and permeability, particularly emphasizing that hybrid membranes based on MOF, CNT, and GO can optimize CO_2 capture efficiency. The integration of nanoparticle-doped MOF composite-embedded MMMs within the wider context of carbon capture technologies and membrane-based separation provides a promising pathway for effective CO_2 removal. By addressing these challenges and leveraging the unique properties of advanced membrane materials, we can enhance the efficiency of CO_2 capture technologies and significantly contribute to global actions aimed at decreasing carbon emissions and addressing climate change.

Table 3. Performance of nanocomposite membranes in CO_2 separation.

Nanocomposite membrane	**Method**	**Findings**	**References**
HKUST-1@GO	Electrodeposition	High CO_2 adsorption capacity of 194.1 cm^3/g and CO_2/N_2 adsorption ideal selectivity of 276.5 at 273 K	[58]
Pebax/ZIF-8/NH_2-MIL-53(Al)	Solution-casting technique	A CO_2 permeability of 488 ± 9 Barrer and a CO_2/CH_4 selectivity of 37.5 ± 0.6	[59]
PEI-F-Ce/XLPEO	Solution-casting technique	Excellent CO_2 permeability (641 Barrer) and outstanding CO_2/N_2 selectivity (70.1)	[60]
PES/PU/nano-clay	Solution-casting and solvent evaporation methods	The combined use of PU and nano-clay as fillers improved the CO_2 permeability, CO_2/N_2, and CO_2/CH_4 selectivity of PES by 7.8, 1.8, and 2.2 times.	[61]
Pebax®1657-MOF-74 (Ni)@GO	One-pot and solvent casting methods.	A substantial increase in CO_2/N_2 separation selectivity,	[29]
CNT-MIL/6FDA-durene NH_2-MIL-101/6FDA-durene CNT-COOH/6FDA-durene	Solution casting method	MMMs containing the synthesized MOF/CNT composite exhibited high CO_2 permeability and CO_2/CH_4 selectivity.	[62]

4. Conclusion

This study underscores the pivotal role of advanced membrane-based carbon capture technologies, concentrating on the integration of nanoparticle-doped MOF composite-embedded MMMs. The innovative use of MOFs within polymer matrices has demonstrated significant potential in enhancing both the selectivity and permeability for CO_2 separation. By leveraging the high surface area, tunable porosity, and customizable properties of MOFs, these MMMs have emerged as promising candidates for effective and efficient carbon capture. However, the application of MOF-composites produced by incorporating carbon-based materials into MOF for use in polymer membranes is critical in enhancing the membranes' thermal and water stability. These materials ensure that the membranes maintain structural integrity under harsh industrial conditions while also functionalizing the membrane pores to make them more CO_2-attractive. The selection of nanoparticles is crucial; they must be carefully chosen to align with the morphological structure of the MOF to achieve optimal synergy. This compatibility enhances the overall performance, as the right nanomaterial can create efficient gas transport pathways, facilitating selective CO_2 adsorption and improving separation efficiency. The use of nanocomposites in membrane production has significantly improved performance, increasing CO_2 permeability by 7.8 times, CO_2/N_2 selectivity by 1.8 times, and CO_2/CH_4 selectivity by 2.2 times. In this context, the amount of filler material incorporated into the membrane is a significant factor. While an optimal filler concentration can maximize CO_2 capture performance, excessive loading of nanomaterials can lead to agglomeration. This agglomeration can block the pores of the membrane, restricting gas flow and thereby diminishing the overall efficiency of the gas separation process. Thus, precise control over the filler amount is essential to maintain a balance between performance and structural stability.

Despite significant advancements in nanoparticle-doped MOF-based MMMs for CO_2 separation, challenges such as scaling up production, economic feasibility, and long-term stability persist. Continued research is needed to optimize material compositions and manufacturing processes for industrial applications. Considering that MOF production can account for up to 60% of the total membrane cost, solvent-free synthesis and continuous production methods could reduce costs by approximately 30%. These findings highlight that MOF and nanoparticle-doped MMMs are promising candidates for cost-effective and efficient carbon capture processes. Progress in this field presents a promising opportunity for reducing CO_2 emissions and contributing to climate change mitigation and global sustainability efforts.

Conflict of Interest Statement

The authors declare that there is no conflict of interest

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