JURNAL KARTIKA KIMIA

J. Kartika Kimia, May 2025, 8, (1), 11-24
Journal homepage: http://jkk.unjani.ac.id/index.php/jkk
P-ISSN: 2655-1322 E-ISSN: 2655-0938

Review on Synthesis, Properties, and Performances of Polymer/ Metal Organic Framework (MOF) composites membranes for water filtration application

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DOI: https://doi.org/10.26874/jkk.v8i1.871

Received: 8 Dec 2024, *Revised*: 13 Dec 2024, *Accepted*: 14 May 2025, O*nline*: 6 June 2025

Abstract

Mixed matrix membranes (MMMs) have gained considerable attention as a cutting-edge filtration technology, leveraging the combined advantages of polymer and inorganic fillers. Metal-organic frameworks (MOFs), as a nanoporous materials, are regarded as highly effective fillers in MMM, significantly enhancing molecular separation efficiency. This article provides a comprehensive review of the synthesis, properties, and performance of polymer/MOFs-based MMMs. A comprehensive literature search was conducted using ScienceDirect and Google Scholar with keywords such as metal-organic framework, MMMs, polymers, filler, and membrane filtration. Polymer/MOFs-based MMMs are synthesized using techniques including in situ and layer-by-layer assembly methods. The MMMs exhibit porosity distribution ranges from57 to 78.3%, contact angle ranges from 45° to 75.27°. The MMMs have also demonstrated exceptional performance in water permeability and bovine serum albumin (BSA)/salts rejection reached up to 94.03 L/m^2.h and 99.8%, respectively. These finding highlight the significant potential of polymer/MOFs-based MMMs for advanced water filtration application.

Keywords: Mixed matrix membrane, Performance, Properties, Polymer/MOFs, Synthesis

1 Introduction

Membrane technology is a highly effective method for water treatment, offering key advantages such as reduced chemical usage, energy efficiency, and operational simplicity [1]. It is increasingly regarded as a sustainable and widely adopted solution to address the global shortage of clean water. Due to its low energy consumption and reliable performance, membrane technology has found extensive application in water treatment processes [2]. The structure, pore size, and surface characteristics of the membrane are critical factors influencing the transport of water molecules and solutes. As a result, the development of advanced membrane materials and the refinement of fabrication methods to optimize membrane performance remain urgent research priorities [3]. Polymer-based filtration membranes play a crucial role in wide range of applications, particularly, in separation of molecules with different sizes and molecular weights [4]. However, challenges remain in its application, including the difficulty of controlling pore size and managing membrane fouling [5]. To address these issues and enhance membrane permeablility and selectivity, Metal-Organic Framework (MOF) composites have emerged as a promising solution, significant potential to improve membrane performance.

MOFs are porous crystalline materials composed of a metal-based frameworks linked by organic ligands. Their unique shaft-like structure enables controlled access to target molecules, thereby enhancing separation selectivity [6]. In filtration membranes, MOFs act as effective fillers in the fabrication of composite membranes, significantly boosting molecular separation performance.

Recent studies on the integration of MOFs into composite membranes for filtration applications has demonstrated highly promising results. By leveraging the distinctive porous structure of MOFs, these composites exhibit enhanced retention of salts, organic compounds, toxic substances, and other molecules with specific sizes and weights. Furthermore, MOF-based membranes exhibit excellent mechanical and thermal stability, making it suitable for demanding filtration processes [7]. Moreover, MOFs have been utilized as blending agents to enhance the anti-fouling performance of membranes, addressing a critical challenge in membrane technology [8]. Its uniform pore sizes, high surface area, and exceptional design flexibility make MOFs a valuable component in advancing membrane separation technology [9]. The structural features of MOFs, including tunable pore sizes and diverse topologies, can be tailored to meet specific requirements. These properties highlight the potential of MOFs to in revolutionize membrane-based filtration systems [10].

Recent studies have explored the incorporation of MOFs as fillers in polymer-based membranes. For instance, embedding, TMU-5 MOFs into hydrophilic Polyether-sulfone (PES) ultrafiltration membranes has demonstrated promising results[11]. Additionally, MOFs have been utilized as fillers in composite membranes for CO_2 gas separation, demonstrating g their versatility [12]. The use of chromium-based MOFs (Cr-MOFs) as fillers has further enhanced the membrane performance, resulting in higher water permeability and superior antifouling performance [13].

This article presents a comprehensive review of MOF-based composite membranes for water filtration. The key topics discussed are summarized in **Fig. 1**. The review focuses on membrane composites composed of MOFs and polymers, highlighting recent advancements in their synthesis methods and applications in water filtration. The synthesis of MOF composite membranes can be achieved through in situ synthesis, layer by layer assembly, and post-synthesis modification methods. MOF composite membranes have demonstrated notable potential for various water filtration processes, including reverse osmosis, nanofiltration, and ultrafiltration. Its unique properties, such as high porosity, adjustable pore size, and robust mechanical stability, make it suitable for addressing critical challenges in water purification.

Figure 1. A comprehensive review of the use of MOFs in composite membranes for water filtration

2 Method

A comprehensive literature review was conducted using databases such as ScienceDirect and Google Scholar, utilizing keywords including metal-organic framework, mixed matrix membranes (MMMs), polymers, filler, and membrane filtration. Polymer/MOF-based MMMs are synthesized using various techniques, including the in situ and layer-by-layer methods. In the layer-by-layer technique, the membrane is constructed through the sequential deposition of polymer and MOF layers, resulting in a well-controlled structure optimized for specific applications, such as membrane filtration

3 Results and Discussion

3.1. MOFs/ Polymer based Composite membranes

Polymers are widely used as matrix materials for the fabrication of composite membranes incorporating Metal-Organic Frameworks (MOFs). A composite membrane consists of a polymer matrix reinforced with MOF nanoparticles, which enhance the membrane’s properties and functionalities [14]. Polymers are extensively utilized as matrix materials in the fabrication of composite membranes that incorporate Metal-Organic Frameworks (MOFs). A composite membrane consists of a polymer matrix reinforced with MOF nanoparticles, which synergistically enhance the membrane's properties and functionalities. Polymers serve as a critical component in these membranes, offering a range of advantages [15]. Their inherent mechanical strength and flexibility enable the membrane to withstand diverse operating conditions, including variations in pressure and temperature. Additionally, the polymer matrix plays a vital role in preventing the agglomeration of MOF particles, ensuring their uniform dispersion and stability within the membrane structure

Polymers offer several advantages as matrix materials for MOF-based composite membranes. They provide mechanical strength and flexibility, allowing the membrane to withstand various operating conditions. The polymer matrix also acts as a barrier to prevent MOF particle agglomeration and maintain their dispersion within the membrane. Moreover, polymers can be easily processed into thin films or membranes using techniques such as phase inversion, electrospinning, or solution casting, making them suitable for large-scale production [16].

The incorporation of MOFs into polymer matrices offers additional benefits to the composite membranes. MOFs are highly porous materials with a large surface area and tunable pore sizes, enable efficient molecular sieving and selective transport of gases or liquids [3]. By incorporating MOFs, the composite membranes can exhibit enhanced adsorption capacity, improved separation performance, and high selectivity for specific target molecules [17]. Furthermore, MOFs can introduce functional groups or active sites that facilitate chemical reactions or catalytic processes within the membrane.

The choice of polymer matrix and MOF nanoparticles is dictated by the intended application and desired membrane properties. Various polymers, including polyimides, polyethylene glycol, polysulfone, and polymeric ionic liquids, have been successfully employed in MOF-based composite membranes. Each polymer offers unique characteristics, such as thermal stability, chemical resistance, or hydrophilicity, which can be tailored to meet specific separation requirements. The combination of polymers and MOFs in composite membranes provides a versatile platform for tailoring membrane properties and functionalities to meet the requirements of various separation processes, including gas separation, water purification, and chemical separations. These composite membranes have the potential to improve separation efficiency, enhance selectivity, and enable sustainable and energy-efficient separation processes [18].

Polymer/MOF composite membranes represent a promising innovation in separation technologies. Their ability to integrate the structural and functional benefits of polymers with the superior performance characteristics of MOFs makes them an invaluable solution for addressing challenges in modern filtration and separation processes.

Metal-organic frameworks (MOFs) are a class of innovative crystalline materials composed of metal ions or units connected by organic linkers via covalent bonds [19]. MOFs, consisting of metal ions and interconnected organic ligands, are highly prominent materials in modern research [20]. As a new type of porous material, MOFs are synthesized using multidentatete organic ligands and metal ions. Due to the variety of available ligands and metal atoms, the structure, the,, pore size, functional groups, and coordination sites of MOFs can be tailored to specific needs [21]. In contrast to traditional porous materials such as zeolite and porous carbon, MOFs offer ideal platform for gas absorption and separation, sensing, dye uptake, drug transport and delivery, catalysts, electrode materials, and semiconductors, thanks to their diverse and unique architectures. MOFs have gained remarkable attention as composite membranes for various separation processes. When incorporated into composite membranes, MOFs enhance separation performance and introduce specific functionalities [14]. The combination of MOFs with polymer matrices creates a synergistic effect, merging the mechanical strength of the polymer with the distinctive adsorption and selectivity capabilities of MOFs [14].

Composite membranes incorporating MOFs offer several notable advantages. The high porosity and large surface area of MOFs enable efficient adsorption and molecular sieving, resulting in enhanced separation efficiency [22]. MOFs can selectively adsorb or capture specific molecules or gases, enabling highly targeted separations. Moreover, MOFs can be tailored or functionalized to optimized their adsorption properties for specific target molecules, further improving their performance in separation processes [23]. The selection of polymer matrix is critical in the fabrication of MOF-based composite membranes. The polymer provides mechanical support and stability, maintaining membrane integrity during operation. Polymers such as poly sulfone, polyimide, and polyetherimide are commonly used due to their compatibility with MOFs and their superior mechanical properties [15].

Beyond their versatility, polymer/MOF composite membranes are uniquely positioned to address challenges in specific separation applications by leveraging the customizable properties of both components [24]. Polymers, with their tunable chemical structures, allow the incorporation of functional groups that can enhance interactions with MOFs or target molecules. This facilitates improved compatibility between the polymer matrix and MOF particles, reducing defects at the interface and enhancing the membrane's performance. For instance, hydrophilic polymers like polyethylene glycol can improve water flux, while more rigid polymers such as polyimides contribute to thermal and chemical stability.

On the other hand, MOFs, with their modular frameworks, can be engineered to introduce targeted functionalities, such as hydrophobicity, charge selectivity, or catalytic activity. These modifications open opportunities for multifunctional membranes capable of combining separation with additional functionalities like pollutant degradation, antibacterial activity, or ion exchange. For example, MOFs with metal sites like Fe or Ti can enable photocatalytic activity, making them effective in breaking down organic pollutants during water treatment processes.

Several types of MOFs are widely studied (**Table 1**), including Zeolitic imidazolate framework (ZIF), Material Institute Lavoisier (MIL), Prussian blue analog (PBA) and Universitet i Oslo (UiO) [25]. ZIFs are a class of three-dimensional porous materials composed of imidazole ligands and divalent metal ions, such as Zn^{2+} or Co^{2+}. The nitrogen atoms in the imidazole ligands form tetrahedral coordination bonds with transition metals, resulting in a stable, cage-like topology that is free from interpenetration. [25]. It possesses notable attributes such as high microporosity, exceptional chemical and thermal stability (up to 400 ◦C), and large surface area. The combination of their durability and consistent microporous structure make them highly appealing for gas separations in adsorption and membrane processes [26].

ZIFs have advantages such as their diverse structure, adjustable and porous pore channels, high specific surface area, easy functionalization, and unsaturated sites. [27]. ZIFs are known for their flexibility, porosity, and thermal stability, which can be maintained up to 400℃. These properties make ZIFs highly favorable for gas separation and selective catalysis based on shape and size, owing to their pore size of less than 5 Å. Additionally, ZIFs can enhance the gas separation performance of polymeric membranes that are constrained by the Robeson upper bound. as a result, ZIFs are considered to be an attractive choice as an inorganic filler n the fabrication of mixed matrix membrane (MMMs).

Mixed-matrix membranes (MMMs) are a promising type of membrane for gas and liquid separation. Such membranes can be formed by dispersing metal-organic framework (MOFs) crystals in polymers. Materials of Institute Lavoisier (MILs) exhibit exceptional stability, persistent porosity, and notably large specific surface area. MIL have garnered significant attention due to their large specific surface area and stable structures. Several MIL variants have been formulated, including MIL-53, MIL-100, and MIL-101[28]. Typically, MILs consist of transition metal ions, such as iron, chromium, aluminum, and titanium, combined with rigid polydentate carboxylic acid ligands. These ligands primarily include terephthalic acid (H_2BDC), 1,3,5-benzenetricarboxylic acid (H_3BTC), succinic acid, glutaric acid, fumaric acid and their functionalized monomers [28] [25]. Composites of MIL with polymer have been used for ultrafiltration membranes that can effectively remove methylene blue via adsorption and catalytic oxidation [29]. The fabrication methods for MOF-based composite membranes vary depending on the desired structure and application [30]. Techniques such as solution casting, electrospinning, and layer-by-layer assembly are commonly used to integrate MOFs into the polymer matrix, ensuring their uniform dispersion within the membrane. The applications of MOF-based composite membranes are diverse, including gas separation, such as of carbon dioxide removal from flue gases and natural gas purification [31]. MOFs also show potential in water purification, particularly for removing, heavy metals and organic pollutants. Furthermore, MOF-based composite membranes are being explored for catalytic reactions and chemical separations due to the catalytic properties of MOFs.

For instance, membranes incorporating ZIF-71-type MOF crystals in Torlon (poly(amide-imide)) or Matrimid (polyimide) polymers demonstrated that the polymer crosslinking process did not affect intra-ZIF diffusivity. This conclusion was reached after accounting for and eliminating the effects of molecular that diffusion across or reflection from the crystal boundary [32]. Another study reported the fabrication of novel mixed matrix membrane of Cu-MOF nanocomposite by solvothermal method and combined with solution casting of cellulose acetate (CA)/polyethersulfone (PES) membrane using phase inversion method. [24]. The modified membrane demonstrated outstanding performance, achieving a maximum water flux of 28.5 L m^{-2} h^{-1} and high rejection rates of 85% and 79% for BSA HA, respectively. Additionally, the contact angle decreased from 75.27° to 46.02°, indicating a significant improvement in the membrane's hydrophilicity. Furthermore, the incorporation of Cu-MOF into the membrane material demonstrated remarkable antibacterial properties, effectively inhibiting both gram-positive bacteria (Pseudomonas aeruginosa, Enterococcus faecalis, and Staphylococcus aureus) and gram-negative bacteria (E. coli).

A recent study developed cpolyacrylonitrile-@TiO$_2$/zeolite-8 imidazolate framework (PTZ) hybrid membrane via electrospinning and in situ MOFs synthesis [33]. The optimized PTZ hybrid membrane exhibited excellent performance, achieving a PM2.5 capture efficiency of over 99% with a pressure drop of 34 Pa. The increased specific surface area and pore structure of the membrane improved particle interception and electrostatic interaction, making it highly suitable for PM2.5 filtration.

Furthermore, the uniform coating of zeolitic imidazolate framework-8 (ZIF-8) on the surface of polyacrylonitrile@TiO$_2$ nanofibers facilitated the formation of N-Ti-O bonds, which suppressed electron-hole pairs recombination and enhanced photodegradation efficiency. Compared to the polyacrylonitrile@TiO$_2$ (PT) structure, the PTZ hybrid structure demonstrated a significantly higher PM2.5 degradation efficiency, increasing from 66% to 85%. These results underscore the potential of the PTZ membrane for the effective capture and eco-friendly degradation of PM2.5 particles.

Despite its advantages, the in-situ method also presents certain challenges, such as achieving consistent MOF growth on a large scale and ensuring the long-term stability of the composite membranes in harsh operational conditions. Strategies to overcome these challenges include optimizing precursor formulations, using advanced functionalization techniques, and integrating MOF synthesis with automated membrane manufacturing processes.

3.2 Synthesis of MOF composite membranes

3.2.1 In situ method

The most recent design principles for membranes based on MOFs leverage advanced techniques such as confinement conversion, in situ self-assembly, layer-by-layer assembly, and interfacial polymerization methods in order to enhance separation performance [34]. The in situ self-assembly method involves growing MOFs directly on the surface of an existing membrane, such as a polymer or ceramic membrane. This process is initiated by applying MOF precursor solution to the membrane surface, allowing spontaneous MOF growth through chemical reactions between the precursors. In-situ self-assembly facilitates the fabrication of membranes by enabling the growth of pure MOF films directly on substrates submerged in metal salt and organic ligand solutions [23]. The basic principle of this approach is to promote the direct integration of MOF growth with existing membranes, resulting in hybrid membranes with unique separation properties and enhanced performance.

The in situ self-assembly method has emerged as a promising approach in the synthesis of MOF-based composite membranes, particularly due to its ability to directly integrate MOF crystals onto the membrane surface. This method enables the fabrication of defect-free and uniform MOF films, which are crucial for achieving optimal separation performance. One of the key advantages of this technique is its versatility. The in-situ method can be applied to various types of substrates, ranging from flexible polymeric membranes to rigid ceramic supports. For instance, polymer substrates such as polyethersulfone (PES) and polyvinylidene fluoride (PVDF) are often chosen for their flexibility and processability [29].

This method represents three fundamental steps. First, the polymer membranes undergo hydrolysis or modification, producing a functionalized substrate that facilitates MOFs growth. Second, MOFs precursors are immobilized on the substrate through electrostatic attraction forces. Finally, the substrates are submerged in solution containing a mixture of polymer and organic ligands, where generation occur in situ [35]. This approach provides an efficient and versatile pathway for the fabrication of high-performance MOF-based membranes

Another result on fabrication of ZIF-8 incorporated Polydimethylsiloxane (PDMS) MMMs was carried out through in situ interfacial synthesis. to produce. Zn^{2+} ions were initially dissolved in the aqueous phase and then deposited within the pores of a polyvinylidene fluoride (PVDF) support. Simultaneously, 2-methylimidazole (Hmim) and the PDMS matrix were combined in the organic phase. As Zn^{2+} ions diffused across the phase interface and encountered Hmim, ZIF-8 crystal seeds were primary formed within the PDMS matrix. The resulting ZIF-8 nanoparticles endowed the membranes with enhanced ethanol affinity, hydrophobicity, and thermal stability [36]. A schematic representation of the in-situ synthesis of MOF-based membranes is shown in **Fig. 2** [36].

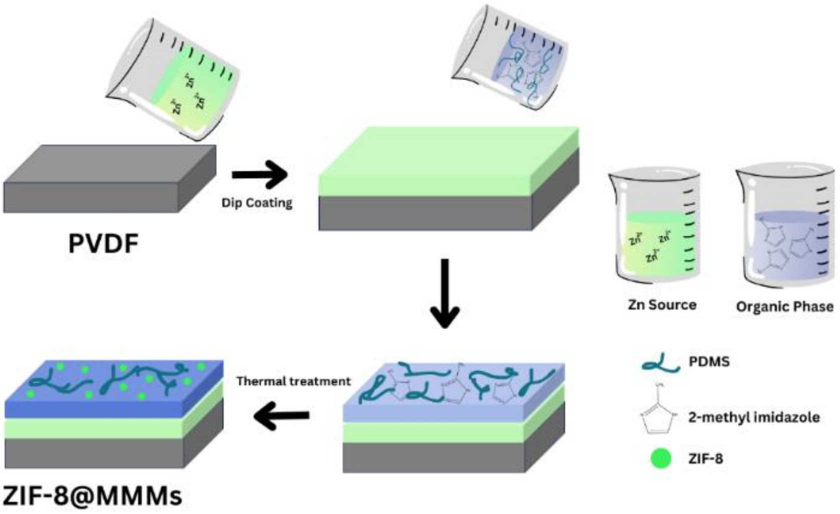

Figure 2. In situ synthesis method of MOF-based composite membrane

Furthermore, the synthesis of polyethylamide (PEI) based membrane grafted on ZIF-8 (PEI-g-ZIF-8). were carried out using in situ using method at room temperature. Zn^{2+} , 2-methylimidazole (Hmmi), and multi-branched PEI [37]. An ethanol solution containing $Zn(NO_3)_2.6H_2O$, Hmim and PEI was stirred and subsequently n centrifuged to isolate the nanoparticles. The results revealed that PEI accounts for 14.40 wt% of the total mass of PEI, Hmim and Zn^{2+}, obviously lower than the actual amount of PEI estimated from the TGA curve. The discrepancy is primary attributed to the preferential coordination of Zn^{2+} with the amino groups in the PEI chains, which take precedence over its interaction with excess Hmim. This preferential coordination accelerates the formation of PEI-g-ZIF-8 [37].

In addition, CNT/UiO-66-NH_2 nano-composites were synthesized via in-situ growth of MOFs on the surface of carbon nanotubes (CNTs).This process was facilitated by the e complexation of zirconium ions with carboxylate functional groups on the CNTs surface and 2-aminoterphthalic acid ligands [38]. The presence of hydrophilic CNTs surrounding the UiO-66-NH_2 nanocomposite effectively prevents aggregation and enhance the dispersibility of the nanocomposite. formation construction of recognition sites but also improves the overall performance of membrane. The synthesis involved dissolving $ZrCl_4$, 2-aminoterephthalic acid, and acetic acid in 50 ml of dimethylformamide (DMF). Then CNT acid was thoroughly dispersed in the precursor solution using ultrasound. The resulting mixture was then transferred to an autoclave and maintainer at 120°C for 24 hours. The nanocomposite was successfully synthesized by separating the slurry via centrifugation, followed by rinsing with DMF and drying under vacuum at 60°C for 24 hours In terms of morphology, in the in situ method of CNT/UiO-66-NH_2 membrane revealed, long CNTs distinctly visible around UiO-66-NH_2, in contrast to the physical mixing method [39].

3.2.2 *Layer by Layer (LBL) Assembly Method*

This method involves the gradual growth of a MOF layer on the membrane surface. In LbL assembly, a selective membrane layer is formed by alternating depositing oppositely charged polyelectrolytes onto a substrate, driven by electrostatic interactions and van der Waals forces [40]. This process involves the sequential deposition of alternating layers of polymer and metal-organic framework (MOF), facilitated by physical or chemical interactions, such as electrostatic interactions, hydrogen bonding, or metal-ligand coordination [9]. MOF layers are interspersed with layers of other organic or inorganic molecules, such as polyelectrolytes or nanoparticles, to create a structured composite. It also allows precise control of the thickness and composition of the MOF layer, as well as the properties of the resulting membrane. This method enables the deposition of ultra-thin films with nanometer-scale control, making it particularly advantageous for creating membranes with tailored thickness, uniformity, and separation performance.

Additionally, the high-performance Polyamide/ZIF-8 membrane has successfully fabricated through LBL assembly method [41]. This method typically begins with the preparation of an activated substrate, followed by alternating immersion in positively and negatively charged polymer or MOF solutions. After each immersion, the substrate is rinsed to remove excess material, resulting in a well-organized thin film. The membrane fabrication scheme using the LBL method is illustrated in the **Fig. 3** [41].

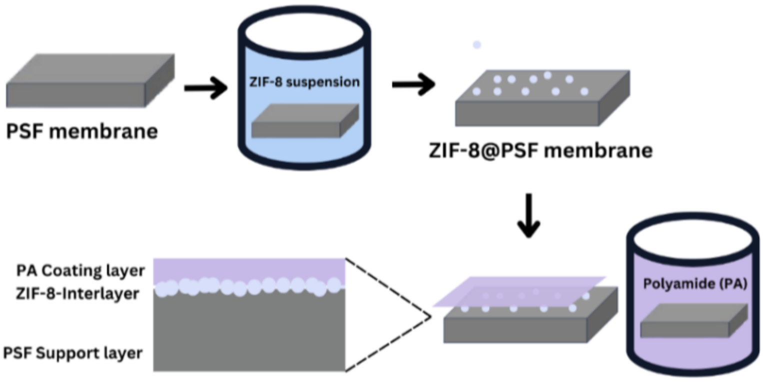

Figure 3. Layer by layer assembly synthesis method of MOF-based composite membrane

The layer by layer (LbL) assembly technique for membrane fabrication allows precise control over surface properties, including thickness, roughness and surface charge [42]. However, this method is a time-consuming. The use of Spin-assisted LbL significantly reduces fabrication time while producing smoother surfaces and more organized inner layers than dip-LbL [43].

The three-layer PAN-MOF-polymer composite membrane was successfully designed by simply coating UIO 66-NH_2-trichloromethane dispersion on the PAN fiber membrane, followed by. PU/PIM solution coating on the UIO66-NH_2 layer to form a polymer layer [44]. Additionally. MOF (UiO-66-$(COOH)_2$/UiO-66-NH_2 membrane was fabricated using twin metal ions and different ligands through seed-assisted in-situ growth By modifying the double-layer UiO-66-based membrane media layer with other functional groups $(COOH)_2$ and -NH_2), the selectivity for Li^+ will be adjusted [45].

Despite its advantages, the LbL method does pose certain challenges. Achieving uniform deposition across large membrane areas and ensuring strong interlayer adhesion for long-term stability remain critical issues. Additionally, scaling up the process for industrial applications requires further optimization and automation. Nonetheless, the LbL assembly method continues to gain attention as a highly adaptable and efficient technique for creating high-performance membranes. Its ability to integrate MOF layers with precise structural control positions it as a key approach in advancing water filtration technologies.

3.3 Properties and Performance of Polymer/MOF composite membrane

The properties and performance of a polymer/MOF membrane can be comprehensively evaluated using key parameters such as contact angle, porosity, water flux, and rejection rate. The performance of polymer/MOF composite membranes is governed by their structural and functional properties, which are critical for achieving optimal filtration and separation efficiency.

These properties are typically evaluated through a combination of parameters, including contact angle, porosity, water flux, and rejection rate, each of which provides specific insights into the membrane's characteristics and performance. The contact angle is a key indicator of the membrane's surface hydrophilicity. A lower contact angle signifies a more hydrophilic surface, which enhances the membrane's affinity for water molecules and improves its anti-fouling properties [13] . This characteristic is particularly desirable for water filtration applications, where the ability to resist fouling and maintain consistent performance over time is crucial. Porosity, on the other hand, reflects the structural features of the membrane, including its pore size and distribution. A highly porous membrane facilitates greater water permeability, allowing for higher water flux while maintaining selectivity [25]. However, the porosity must be carefully controlled to prevent excessive pore enlargement, which could compromise the membrane's ability to reject contaminants. Water flux, defined as the volume of water passing through the membrane per unit area per unit time, serves as a direct measure of the membrane's transport efficiency. Polymer/MOF composite membranes typically exhibit enhanced water flux due to the incorporation of MOFs with well-defined pore structures, which create additional pathways for water molecules [46]. The rejection rate is another critical performance metric, representing the membrane's capability to block specific solutes, such as salts, organic molecules, or heavy metals. The selectivity of polymer/MOF membranes is often enhanced by the MOF's intrinsic properties, such as pore size and chemical functionality, which allow for the precise separation of contaminants based on size exclusion or molecular interactions. These interrelated properties highlight the importance of a balanced design in tailoring polymer/MOF membranes for specific applications. Enhancing one property, such as water flux, may influence others, such as rejection rate or selectivity. As a result, optimizing the performance of these membranes often involves trade-offs and a holistic approach to material design.

Recent advancements in polymer/MOF composite membranes have demonstrated their potential in addressing challenges in water treatment and desalination. The inclusion of MOFs not only improves structural and functional properties but also introduces unique advantages, such as enhanced chemical stability, resistance to biofouling, and the ability to operate under a wide range of conditions.

The detailed comparison of the properties and performance of polymer/MOF membranes is summarized in **Table 1**, which provides a comprehensive overview of key parameters across various studies. This information serves as a valuable resource for guiding the development of next-generation composite membranes tailored for specific filtration and separation needs.

Contact angle measurement evaluate the membrane's surface hydrophilicity, which determines its affinity for water molecules. Porosity reflects the membrane's structural characteristics and pore size, directly impacting its permeability and selectivity. Water flux measures the rate of water permeation through the membrane, offering insights into its transport efficiency. Lastly, the rejection rate represents the membrane's ability to block specific solutes or contaminants, highlighting its separation performance. These interrelated properties and performance indicators are pivotal in tailoring and optimizing polymer/MOF matrix membranes for specific filtration and separation applications. The properties and performance of Polymer/MOF membranes is shown in **Table 1**.

Table 1. Properties and performance of Polymer/MOF membranes

Membranes	Performance		Properties		Ref.
	Water Flux ($L \cdot m^{-2} \cdot h^{-1}$)	Solute Rejection (%)	Porosity (%)	Contact Angle (°)	
PES/ Cu-MOF-Ca	28.5	BSA 85%	62.01	75.27	(24)
PS/ZIF-67	35.39	$NaNO_3$ 50%	57	70	(47)
PS/MIL-53	4.8	Dye 99,8 %	-	63	(48)
PDMS/ZIF 8	17.78	-	-	92	(36)
PVDF/NH2-MIL	94.03	-	63.73	65.58	(49)
PVDF/MOF-ZnL	27.18	BSA 96,5 %	78.3	68.9	(50)
PA/ UiO-66	53.5	Na_2SO_4 99,5% $MgSO_4$ 98.9%	-	45	(51)
PES/TMU-5	18.2	98% protein		57.5	(11)

3.4 *Application of Polymer/MOFs Composite Membranes*

Polymer/ MOF mix matrix membranes have versatile applications in various filtration processes, including reverse osmosis, nanofiltration, and ultrafiltration. In reverse osmosis, these membranes are employed for desalination, effectively removing salts and impurities from seawater to produce potable water. In nanofiltration, they offer selective separation, allowing the retention of divalent ions and small organic molecules while permitting the passage of monovalent ions and water. Additionally, in ultrafiltration, these membranes are utilized for the removal of larger particles (macromolecules). The tunable properties of polymer/MOF mix matrix membranes make them essential tools in addressing a wide range of water purification and separation challenges across these critical filtration processes. The application of Polymer/MOF composite membranes is illustrated in **Table 2**.

Table 2. Application of Polymer/MOF composite membranes

Membrane Materials	MOFs	Application	Ref.
Polyamid	ZIF-93	Nanofiltration	(52)
	UiO-66	Gas Separation	(31)
Polyethilsulfonate	TMU-5	Ultrafiltration	(11)
Polyethylenimine	ZIF-8	Gas Separation	(53)
Polyvinilidin Floride (PVDF)	Cu-MOF-74	Ultrafiltration	(17)
CMC	MIL-53	Nanofiltration	(54)
GO	Al-MOF	Ultrafiltration	(18)
NH_2/PES/PVP	UiO-66	Ultrafiltration	(38)

Reverse osmosis (RO) is a water purification process that uses a semi-permeable membrane to remove impurities and dissolved substances from water. It works by applying pressure to the water, forcing it to pass through the membrane while leaving contaminants behind. This effectively filters out various substances, including salts, minerals, bacteria, viruses, and organic compounds, producing purified water. The semi-permeable membrane used in reverse osmosis has extremely small pores that allow only water molecules to pass through, while blocking larger molecules and ions. As a result, the membrane acts as a barrier, permitting the passage of water while removing the dissolved solids and contaminants.

Reverse osmosis offers several advantages, such as producing clean and safe drinking water, removing contaminants that can affect taste and odor, and providing a reliable solution for various applications, including desalination of seawater and industrial water treatment. However, it has some limitations. The process can be relatively slow, and it requires sufficient water pressure for efficient operation.

In particular, the TFN based RO membrane, with 0.015 wt% of 2D-MOF nanosheets in the aqueous phase, exhibited a remarkable increase of approximately 150.0% in water permeance compared to the benchmark TFC membrane, while maintaining a NaCl rejection rate above 99.0%. Additionally, the as-synthesized TFN membrane demonstrated excellent durability and resistance to fouling

Ultrafiltration is a membrane-based separation process that effectively separates larger particles and solutes from liquid solutions using a semi-permeable membrane. The underlying principle of this technique is size exclusion, where the membrane's pore structure allows smaller molecules, such as solvents and low-molecular-weight solutes, to pass through while retaining larger entities, including colloids, macromolecules, and suspended solids. The pore size of ultrafiltration membranes typically ranges from 1 to 100 nanometers, depending on the specific application and membrane material [55].

The ultrafiltration process typically involves applying pressure or a concentration gradient to the liquid solution, forcing it to pass through the membrane [56]. The membrane acts as a molecular sieve, selectively allowing the passage of molecules or particles below a certain size while blocking larger ones. This size cutoff is usually in the range of 1 to 100 nano meters, depending on the specific membrane used. Ultrafiltration is commonly used in various applications, including water treatment, dairy processing, pharmaceutical manufacturing, and biotechnology.

The advantages of ultrafiltration include its gentle operation conditions, minimal energy requirements compared to other separation techniques like reverse osmosis, and the ability to operate at relatively low pressures. However, it is important to note that ultrafiltration cannot remove dissolved ions or small solutes like salts, which require more advanced techniques such as nanofiltration or reverse osmosis.

Recent advancements in ultrafiltration membranes, particularly those incorporating metal-organic frameworks (MOFs), MOF-polyethersulfone (MOF-PES) composite membranes have demonstrated superior bovine serum albumin (BSA) rejection and higher permeate flux compared to pure PES membranes. Similarly, UiO-66/GO-PES composite membranes have shown excellent separation performance in water filtration applications, offering a balanced combination of high flux and rejection rates [57]. The UiO-66GO/PES membrane shows good rejection in water filtration applications [58]. Another noteworthy development is the polymer/MOF@GO composite membrane, which exhibits enhanced hydrophilicity, resulting in a higher pure water flux of 183.51 $L \cdot m^{-2} \cdot h^{-1}$. This membrane also displays superior anti-fouling properties, as evidenced by a flux recovery ratio (FRR) of 88.13% and a total fouling ratio (TFR) of 40.32%, outperforming polymer/GO membranes. These advancements underscore the potential of MOF-based ultrafiltration membranes to address challenges in traditional systems, such as fouling and limited water permeability, while maintaining high rejection efficiency [62].

In summary, ultrafiltration offers a robust, energy-efficient solution for separating particles and solutes based on size exclusion. The integration of MOFs into polymer membranes further enhances their performance, opening new opportunities for high-efficiency water treatment and other separation applications.

Nanofiltration is a separation process that uses small porous membranes to separate larger particles from smaller particles in a solution (3). Nanofiltration membranes are made of semipermeable materials that have pores of about 1 to 10 nano meters in size. These pores allow water and small ions to pass through the membrane, while larger particles such as salts, organic compounds, and colloidal particles are retained by the membrane. The basic principle of nanofiltration is hydrostatic pressure applied to the solution to be separated. The solution is pressurized to be forced through the nanofiltration membrane. As the solution flows through the membrane, larger particles are blocked by the membrane while water and smaller dissolved compounds can pass through the membrane pores.

The advantages of nanofiltration include high efficiency in separating different compounds, the ability to remove organic compounds, salts, and heavy metals from water, and energy savings due to its relatively low-pressure operation. However, it cannot separate particles of very similar sizes or purify water to ultra-pure levels as can be done by water treatment technologies such as reverse osmosis [59] .

Advancements in NF membranes, particularly through the incorporation of MOFs, have demonstrated remarkable improvements in performance. For instance, The PVP-UiO-66-NH2@polyamide composite membrane showed excellent water permeability of 32.95 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ and a stable Na_2SO_4 removal rate of 99.35%, compared with 17.56 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ and 99.56% of pure polyamide membrane under the same conditions. In addition it showed excellent long-term filtration stability, thermal stability and antibacterial properties [60]. Similarly, the incorporation of ODA-h-NCs into poly(piperazinamide) (PA) membranes has yielded promising results, with a water permeability of 8.97 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ and a Na_2SO_4 rejection rate of 95.8%. These membranes have demonstrated good stability in filtration tests lasting up to 50 hours, highlighting their durability and potential for extended use in industrial applications [61].

The application of two-dimensional MOFs (2D MOFs), such as BUT-203, represents a significant breakthrough in nanofiltration membrane technology. This material has achieved an impressive water permeability of 870 $L \cdot m^{-2} \cdot h^{-1} \cdot MPa^{-1}$ and a rejection rate of 97.9% for anionic dye molecules. In addition, BUT-203-based membranes exhibit excellent long-term operating stability, high dye desalination efficiency, and anti-fouling properties, further emphasizing the role of MOFs as high-performance fillers in NF membranes [62].

In conclusion, the integration of MOFs into nanofiltration membranes has significantly enhanced their separation performance, water permeability, and stability. These advancements underline the potential of MOF-based NF membranes to address critical challenges in water purification and broaden their applicability in diverse separation processes.

4 Conclusion

Metal organic framework (MOF) can be used as a filler material in the fabrication of composite membranes to enhance molecular separation performance. This review explores polymer/MOFs composite membranes, in highlights recent advancement in their synthesis method of composite membrane, and their applications in water filtration. The synthesis of polymer/MOF composite membrane can be achieved through various methods, including In situ, layer by layer, and post-synthesis modification. The composite membranes are applicable in different types of water filtration processes, including forward filtration, nanofiltration, and microfiltration. The incorporation of MOF into composite membrane presents a promising approach for developing high performance water filtration systems.

Acknowledgements

We gratefully acknowledge the excellent support provided by UPI International grant (327/UN40.LP/PT.01.03/2024) and Riset Kolaborasi Indonesia (RKI) grant (788/UN40.LP/PT.01.03/2024).

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