



Metal-organic frameworks-membranes for energy intensive liquid separation

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ABSTRACT

Metal-organic frameworks (MOFs) materials with tunable structures and functionalities have demonstrated great potential as promising membrane materials, and play a crucial role in various industrially important chemical, energy, and environmental processes. Due to their well-defined pore systems, unique chemical versatility, and abundant chemical functionalities, MOFs have garnered interest for various energy intensive separation applications. Formulating them into structured configurations is a key step toward their scale up and successful implementation at the industrial level. This review focuses on the latest development on MOF-based membranes for liquid separations and highlights recent progress on design strategies, criteria for screening MOFs, fabrication methods, the most recent breakthrough in the areas of pervaporation, water treatment, and organic solvent nanofiltration. Additionally, this study also discusses the possible applications of MOF-based membranes in the removal of micropollutants, in decay processes and exhibiting antibiotic properties. The remaining challenges, prospects and guidance on the rational design and fabrication of high-performance MOF-based membranes and transferring technology from laboratory scale towards practical applications are discussed.

1. Introduction

The need for energy-efficient liquid separations is becoming increasingly important as the global demand for energy and fresh water continues to grow. Energy-intensive separation processes, such as distillation, crystallization, reverse osmosis (RO), and condensation currently dominate the industry but are not sustainable in the long term [1–6]. The separation of liquids plays a vital role in various industries, including food production, pharmaceutical, and chemical [7,8]. However, typical separation methodologies require substantial energy consumption and have a considerable environmental impact. As a result, there is a growing interest in developing new separation techniques that are more energy-efficient and environmentally friendly. One of the emerging technologies for liquid separations is membrane-based separation [9–12]. Membrane technology has several advantages over traditional methods, including high selectivity, low energy consumption, and ease of operation [13–17]. It has the potential for diverse applications, including water treatment [18–21], purify acidic solutions [22], gas separations [23–28], desalination [29–32], and solvent recovery [33–36]. A recent study investigated the development of a ceramic hollow fiber membrane with photocatalytic properties for water purification purposes and reported impressive findings. The membrane successfully eliminated over 90 % of endocrine-disrupting chemicals in 180 min [37,38].

The utilization of cutting-edge materials in liquid separations, specifically porous materials such as metal-organic frameworks, is currently a topic of increasing interest [40–44]. For instance, Seoane et al. have created a mixed-matrix membrane by incorporating a MOF as a filler material, which effectively separates water and ethanol [39]. The MOF-based membrane showed excellent separation performance and low energy consumption compared to conventional separation methods. Similarly, Wang et al. demonstrated the use of MOFs for the removal of organic pollutants from wastewater [40]. The study showed that the MOF substances exhibited exceptional adsorption capabilities towards the pollutants and could be conveniently regenerated, indicating its viability as a substitute to conventional methods of water treatment. In addition to experimental studies, there have been several computational studies exploring the potential of MOFs for energy-efficient separations [41,42]. In a recent study, molecular simulations were used to fabricate new polyamide membranes based on novel sulfonated monomers [43–45], and the simulation study revealed the contributions of rigid nature and steric effect to higher free volumes; as a consequence, water permeability and salt rejection of these membranes were found to surpass the conventional counterparts. These findings provide valuable insights for the design of MOFs for energy intensive liquid separation applications [46,47].

MOFs, consisting of metal ions and organic ligands as bridges, have gained significant attention in recent years as a promising platform for

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host-guest chemistry[48–50]. MOFs possess a highly tunable pore structure and a vast diversity in secondary building units, making them superior to typical permeable substances, for instances aluminosilicates, microporous minerals and carbonaceous compounds[51,52]. These advantages allow MOFs to exhibit improved adsorption properties and perform precise and rapid separations[53,54]. MOFs are also being considered as additives in composite membranes for filtration process[55–57]. Unlike rigid inorganic particles, the organic nature of MOFs enables better compatibility with polymers, leading to enhance permeability and potential selectivity in MOF-based membranes compared to pristine membranes. Additionally, MOFs have high capability to control porosity at molecular level as compared to other materials such as graphite, perovskite etc. This makes them an encouraging contestant for utilization in separation applications [58–60].

Formerly, researchers investigated the potential of MOFs as a foundation for separation membranes primarily in the realms of gas storage and separation. This is because of tunable pore size, porous nature, and active regions present in MOFs that allow for effective differentiation of interactions with gas molecules[61]. Although significant focus has been directed towards the utilization of MOFs in gas separation, there is an increasing volume of scholarly work exploring their prospects in liquid separation. This shift towards liquid separations highlights the exceptional advantages that MOFs offer and the escalating significance of MOF-based membranes system in many liquid separation applications. To enhance durability of these membranes has effectively mitigated challenges pertaining to steam sensitivity that were previously encountered with traditional MOFs. However, these developments are still in their early stages, demanding additional research efforts to explore rational design strategies (RDS) and prototype applications more comprehensively. The aim is to effectively construct MOF-based membranes and separate targeted components from liquid mixtures.

To date, there have been several studies focused on water purification using MOF-based membranes. Nevertheless, these studies have not provided the comprehensive overview of the RDS route. Moreover, these investigations have primarily centered on the uses of MOF-based membranes in separation techniques, without considering the latest development in water purification process like, organic solvent nanofiltration (OSN), ultrafiltration (UF), and forward osmosis (FO). Considering these gaps, the objective of this study is to present a meticulous examination of the present advancements in the domain of MOF-based membranes. Subsequently, an overview of the selection process concerning the uses of MOF in water purification applications also discussed. Additionally, we summarized the main challenges associated with design and opportunities for the MOF-based membranes in water purification techniques.

1.1. Current status of Membrane- based liquid separations

The efficiency of liquid separation through membrane-based technologies has garnered considerable interest because of their ability to reduce energy consumption and cost. These technologies are widely employed in separating liquids, such as water, wastewater, organic solvents, biochemicals, and oil separation[62]. The increasing demand for separation processes that are both sustainable and efficient has led to a notable surge in the adoption of membrane technology in recent years, driven by various technological advancements. Table 1 highlights the importance of membrane technology in separation science. Advanced membranes are currently being developed using new materials and fabrication techniques that offer better separation performance, selectivity, and stability. For instance, in the pharmaceutical industry, these techniques are used for separating bioactive molecules like proteins and peptides, as well as food components such as milk proteins and lactose. The polymer membranes are popular due to their low cost and high processability, they still face challenges, including low stability under harsh conditions, poor selectivity, and low permeability. Striving

Table 1

List of MOF based membranes used for different separation applications.

Sr. No.	Name of MOF	MOF based Membrane	Pore Size of Membrane (nm)	Applications	References
1	ZIF-8	Matrimid membrane	~ 50	Water desalination	[63,64]
2	MIL-101	Thin-film composite Membrane	~ 1	Gas separation, water purification	[65,66]
3	UiO-66	Mixed matrix membrane	~ 10	Gas separation	[67]
4	MOF-5	Polymer/MOF composite membrane	~ 20	Hydrogen separation, CO ₂ capture	[68,69]
5	IRMOF-1	Sol-gel derived membrane	~ 1	Gas separation, water purification	[70]
6	NOTT-101	Polysulfone/MOF composite Membrane	~ 1	Gas separation, CO ₂ capture	[71]
7	ZIF-7	Polyacrylonitrile/MOF composite membrane	~ 20	Gas separation, water desalination	[72]
8	HKUST-1	PVDF/MOF composite membrane	~ 20	Gas separation, water purification	[73]
9	MOF-177	Polyimide/MOF composite membrane	~ 2	Gas separation, CO ₂ capture	[74]
10	MOF-520	Zeolite-based membrane	~ 10	Gas separation, CO ₂ capture	[75]
11	NU-100	Polymer/MOF composite membrane	~ 50	Gas separation, water desalination	[76]
12	MIL-53	Ceramic/MOF composite membrane	~ 100	Gas separation, water purification	[77]

for high permeability in these membranes often results in decreased selectivity, and vice versa. However, ongoing advancements in polymer materials and fabrication techniques have led to the creation of advanced polymer membranes with improved separation performance and stability.

1.2. Obstacles in developing liquid separation membranes

One of the primary challenges in fabricating advanced liquid separation membranes is the permeability-selectivity trade-off, which arises from the nature of the membrane materials and separation mechanisms. When the permeability of the membrane increases, selectivity decreases, and vice versa[78,79]. However, the development of advanced materials and fabrication techniques has resulted in the formation of membranes with improved permeability and selectivity. Modifications to membranes, such as the introduction of nanoparticles and surface functionalization[80], have been shown to improve separation performance without sacrificing stability[81,82]. Stability is a crucial factor that impacts membrane performance and lifespan during liquid separation processes, influenced by various factors like temperature, pH, and chemical and mechanical stresses. Therefore, producing stable membranes with superior separation performance remains a crucial goal for the membrane separation field, which is being addressed by advances in materials science and fabrication methods. The Fig. 1 illustrates the number of publications within the past twenty years, based on literature data sourced from the Web of Science [83].

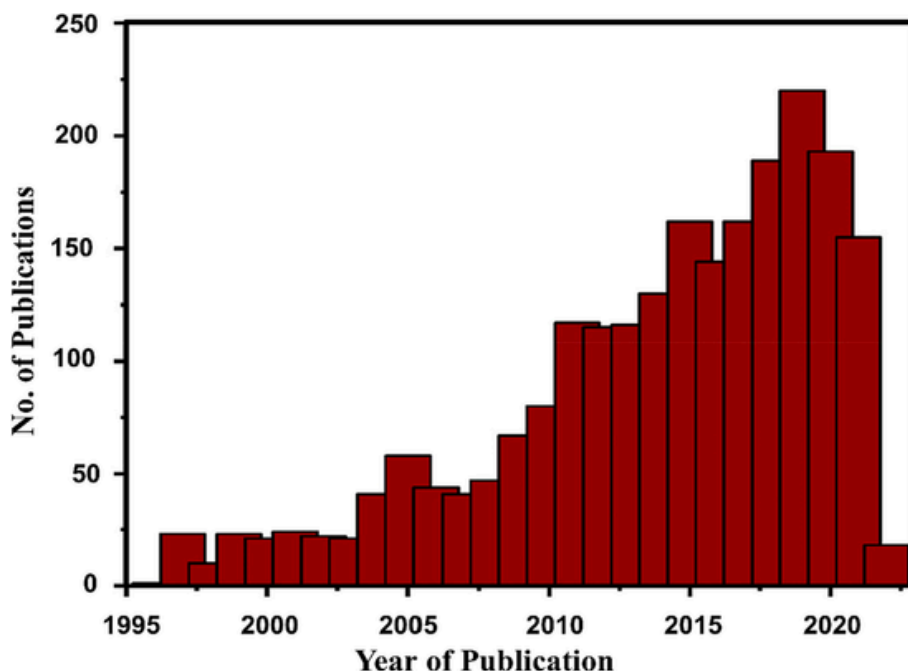


Fig. 1. Number of articles associated to membrane based liquid separation.

2. Designing techniques for fabrication of MOF-based membranes for liquid separation

The implementation of RDS in the fabrication of MOF-based membranes has proven essential for enhancing separation performance. By leveraging unique structural properties and adjustable pore size of MOFs, researchers can tailor these materials for specific separation applications. This approach enables the optimization of factors such as hydrophilicity, hydrophobicity, and chemical functionality to effectively target desired separation outcomes. Furthermore, these design strategies pave the way for the development of highly efficient, stable, and selective MOF-based membranes, resulting in a significant impact on the future of liquid separation technologies. The following strategies will be discussed in detail in this section.

RATIONAL DESIGN STRATEGIES	MOF Structure
	Mechanism of MOF Formation
	Unsaturated Metal Sites in MOFs
	Gating Effects and Structural Flexibility in MOFs
	Postsynthetic Modification of MOFs (PSMM)
	MOF-based membranes for liquid separation
	RDS approach
	In situ synthesis approach
	Blending method
	Interfacial polymerization process
	Alternative approaches

2.1. MOF structure

MOFs are a class of porous materials consisting of inorganic nodes (metal ions/clusters) linked by organic ligands. The Table 2 presents materials that share similarities with MOFs, such as metal-organic polymers (MOPs), covalent organic frameworks (COFs), and covalent triazine networks (CTNs). These materials possess distinct characteristics, along with their respective advantages and disadvantages. Notably, they also demonstrate potential suitability as separation membranes.

MOF structures are generally classified into several categories based on the topology of their underlying nets. For example, MOFs with the same net topology are assigned the same topology symbol. The topology of a MOF is determined by the type of inorganic node, the geometry of the organic ligand, and the bonding mode between the two. The structural diversity of MOFs is a result of the numerous combinations of inorganic nodes and organic ligands. There are many types of inorganic nodes, including metal ions such as zinc (Zn), copper (Cu), and nickel (Ni), as well as clusters, like aluminum-oxo clusters and zirconium-oxo clusters. The organic ligands can be simple carboxylates or more complex, multidentate ligands. The bonding mode between the inorganic node and the organic ligand can also vary, ranging from monodentate to multidentate coordination.

MOFs are synthesized through reticular synthesis, where inorganic and organic units are connected through strong bonds. Due to the ability to alter the size, geometry, and functionality of the constituents, over 20,000 MOFs have been studied and reported in the last decade. The organic units are negatively charged molecules such as ditopic or polytopic organic carboxylates, which combine with metal-containing units to form architecturally strong MOF structures. These structures typically possess porosity greater than 50 % of the MOF crystal volume and surface areas ranging from 1000 to 10,000 m²/g, which is higher than traditional porous materials.

MOF-based membranes were first extensively used for gas storage and separation. This is understandable, as MOFs can have extremely high porosities, along with tunable pore sizes and functional sites to maximize their sieving effects and to differentiate their interactions with gas molecules. For example, HO W.H. et al. reported the synthesis of a new MOF, V₁₀O₂₈@NU-902 as shown in the Fig. 2, with the highest surface area of any known MOF (2075 m²/g) [88], and results showed that V₁₀O₂₈@NU-902 material can transfer electrons between different forms and can catalyze the oxidation of dopamine in the presence of an electric current. Moreover, in 2018, Bao-Xia Dong et al. reported the synthesis of a 3D highly stable porphyrin-based MOF with large channels (3.7 nm) and a high degree of symmetry, which showed enhanced adsorption selectivity for CO₂ [89,90]. Moreover, much attention in the MOF community has been devoted to adsorption and purification of gases, there is now also a vast body of data on the capability of MOFs to separate liquid mixtures. Compared with gas separation, liquid separa-

Table 2

Comparative analysis of MOF and related material family.

Sr. No	Materials	Advantages	Disadvantages	applications	References
1	MOFs	-High surface area, porosity, and tunable pores -High adsorption capacity and selectivity -Versatile metal-ion and organic ligand combinations -Wide range of applications	Synthesis challenges and stability issues	Gas and liquid separation	[84]
2	MOPs	-Good stability and processability -Tailorable properties for specific applications Ability to incorporate functional groups. -Potential for improved mechanical properties	Limited porosity and surface area	Gas and liquid separation	[85]
3	COFs	-High chemical stability Porous and crystalline structure -Covalently bonded organic units -Potential for molecular sieving applications	Limited structural diversity	Gas and liquid separation	[86]
4	CTNs	-High thermal and chemical stability -Unique triazine-based structure -Potential for gas storage applications -Electron-rich backbone for catalytic activity	Low porosity and limited scalability	Molecular separation	[87]

tion is in fact more prominent in the application areas of membrane processes for industrial separation. Utilizing the advantages that MOFs offer, this extension to liquid separations may provide an indispensable platform to adequately exploit the unique features of MOFs. Performance Evaluation of few different membranes are given in Table 3. [17, 91–93].

2.2. Mechanism of MOFs formation

The mechanism of MOFs framework formation involves the coordination of metal ions or clusters with organic ligands to create a three-dimensional network of repeating units, forming the MOFs structure. Fig. 3 is a general schematic representation of the formation of a MOF structure. The formation of MOFs can occur through several pathways, depending on the specific synthetic conditions used [94]. Here, we will discuss a general mechanism for MOF formation. The first step in MOF formation is metal ion ligand interaction. Typically, the ligands used in MOF synthesis are carboxylic acids or nitrogen-containing compounds, such as amines or pyridines. The metal ions or clusters can be introduced in a variety of ways, including by solvothermal synthesis, hy-

drothermal synthesis, or sonochemical synthesis [95]. Once the metal ions or clusters and ligands are brought together in the same solution, they begin to coordinate with one another through the formation of metal–ligand bonds. This process is facilitated by the presence of a solvent or other additive that can help to bring the components into proximity. As the metal–ligand coordination occurs, the MOF structure begins to take shape. The next step in MOF formation is the self-assembly of the metal–ligand complexes into the final MOF structure. This self-assembly process is driven by weak interactions, such as van der Waals forces, hydrogen bonding, and pi-pi stacking. As the metal–ligand complexes assemble, they form the repeating units of the MOF structure. The final step in MOF formation is the removal of any solvent or other additives used in the synthesis process. This step can be accomplished through various techniques, such as washing with a solvent or heating to remove volatile components. The removal of these components leaves behind the solid MOF structure. The formation of MOFs is a complex process that can be influenced by a variety of synthetic conditions, including the choice of metal ion or cluster, ligand, solvent, and other additives [96].

2.3. Unsaturated metal sites in MOFs

Unsaturated metal sites (UMS) are an essential feature of MOFs. They are metal coordination sites that are not fully occupied by coordinating ligands, and therefore are available for binding to small molecules such as gases, catalytic substrates, or other functional moieties. UMS can be formed in various ways, such as by postsynthesis modification (PSM), and thermal, or chemical activation. One common approach for creating UMS in MOFs is through the removal of the coordinated solvent molecules or exchangeable ligands from the metal centers. For example, In Fig. 4, the $(\text{Cu}^{\text{II}})_2$ paddlewheel carboxylate MOF-11 has an open metal site formed after removal of the coordinated water molecule from the $(\text{Cu}^{\text{II}})_2$ [74,97]. Similarly, IRMOF-3 and UMCM-1- NH_2 were also functionalized by removing the amine functionality to create UMS [98]. Another method for creating UMS is through PSM, which involves the covalent functionalization of MOF linkers or surfaces. For example, the organic linker of a MOF, POST-1, was modified by N-alkylation of the pyridyl functionalities, leading to the formation of UMS [99]. However, the presence of UMS is a crucial characteristic of MOFs in the context of membrane technology for liquid separation. UMS can significantly influence the performance and selectivity of MOF-based membranes in various liquid separation applications. In addition, MOF-based membranes with UMS can be engineered to selectively remove heavy metal ions from contaminated water sources. These UMS sites can act as binding sites for specific metal ions due to their affinity for metal coordination. For example, a MOF-based membrane featuring UMS with a high affinity for lead (Pb^{+2}) ions can be used to efficiently remove Pb^{+2} from industrial wastewater, thereby providing a sustainable solution for water purification. Furthermore, in the pharmaceutical industry, MOF-based membranes with UMS can find applications in the separation of organic solvents used in drug synthesis and purification processes. Certain MOFs with UMS can preferentially adsorb and separate specific organic compounds from solvent mixtures. For instance, a MOF-based membrane containing UMS with an affinity for a particular organic compound can be employed to purify and separate that compound from a solvent mixture, contributing to more efficient and environmentally friendly pharmaceutical processes. MOF-based membranes with UMS can be designed to address environmental challenges such as oil–water separation. UMS can play a crucial role in selectively adsorbing hydrophobic organic compounds (e.g., oil) from water, offering a sustainable and efficient solution for oil spill cleanup or industrial wastewater treatment. These membranes allow water to pass through while capturing and separating the oil phase due to the affinity of UMS for hydrophobic molecules. The various methods used to create UMS in MOFs include thermal, chemical, and PSM meth-

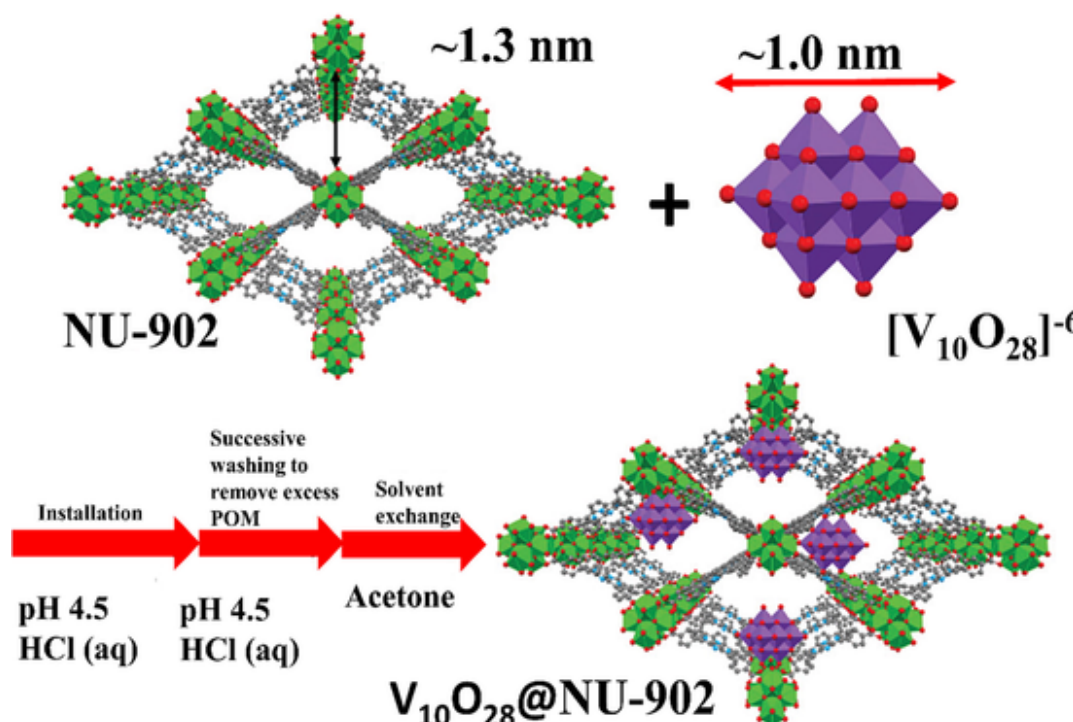


Fig. 2. Illustrates how decavanadate was incorporated into a Zr-based metal–organic framework called NU-902. The colors represent the different elements: green for Zr, red for O, purple for V, grey for C, and blue for N. Hydrogen atoms were not included in the figure to improve clarity. . Adopted from [88]

Table 3
Performance Evaluation of few different membranes.

Property	UiO-66	MIL-101	ZIF-8
Pore Size	Microporous	Mesoporous	Ultra microporous
Permeability	High	Moderate	Low
Selectivity	Excellent	Good	Moderate
Stability	Good	Moderate	High
Structural Diversity	Limited	High	Limited
Surface Area	Large	Moderate	Small
Separation Efficiency	High	Good	Moderate
Chemical Compatibility	Excellent	Good	Limited
Scalability	Limited	High	Moderate
Potential	gas and liquid	Liquid separation,	Liquid
Applications	separation, catalysis	catalysis	separation

ods, and they can be used as active sites for various catalytic reactions. Therefore, utilization of UMS in MOFs can lead to significant developments in liquid separation applications and renewable energy applications.

2.4. Gating effects and structural flexibility in MOFs

One of the exceptional characteristics of MOFs is their structural adaptability, which pertains to their capacity to undergo alterations in their crystal structure as a response to external stimuli like temperature, pressure, and guest molecules. This structural adaptability enables MOFs to display gating effects, where the framework experiences conformational modifications to permit the selective absorption and release of guest molecules. The gating effects in MOFs are governed by a variety of factors such as the dimensions and configuration of the guest molecules, the intensity of the interactions between the guest molecules and the framework, and the inherent characteristics of the framework itself. For example, MIL-53 (Al) is a well-known MOF that exhibits a reversible gate-opening behavior in response to temperature and pressure

changes, allowing for the selective adsorption applications [101,102]. The intrinsic properties of MIL-53(Al) cause a remarkable temperature hysteresis, as evidenced by its structural transition. Specifically, the transition from the open-pored to closed-pored structure occurs at approximately 125 to 150 K, while the transition from the closed-pored to open-pored structure takes place around 325 to 375 K. Notably, this is the first time that such a significant temperature hysteresis has been observed in MOFs.

Another example of a MOF with unique properties is ZIF-8, which demonstrates gate-opening behavior when exposed to guest molecules. ZIF-8's zeolitic imidazole-based structure features large cavities interconnected by narrow windows, allowing for molecular sieving [103]. The structural flexibility of MOFs is closely related to their mechanical properties. MOFs with high mechanical flexibility can undergo large structural changes without breaking, while MOFs with low mechanical flexibility may fracture under stress. The mechanical flexibility of MOFs has been studied both experimentally and computationally and can be tuned by various factors such as the size and shape of the ligands, the nature of the metal ions, and the type of intermolecular interactions present in the framework [104,105]. The structural flexibility of MOFs also plays a key role in their catalytic properties. For example, the catalytic activity of some MOFs can be enhanced by their ability to undergo structural changes in response to the reactants or products of the reaction. This can lead to changes in the size and shape of the pores, which can improve the accessibility of the active sites and enhance the catalytic activity [73].

2.5. Postsynthetic modification (PSM) of MOFs

MOFs have become a popular material for liquid separation due to their tunable and highly porous structure. One technique that has been utilized to improve the performance of MOFs for liquid separation is PSM, which involves modifying the MOF structure after it has been synthesized. PSM can alter the size and functionality of the MOF pores, which in turn can improve the selectivity and permeability of MOF-based membranes. A recent study explored the use of PSM for improv-

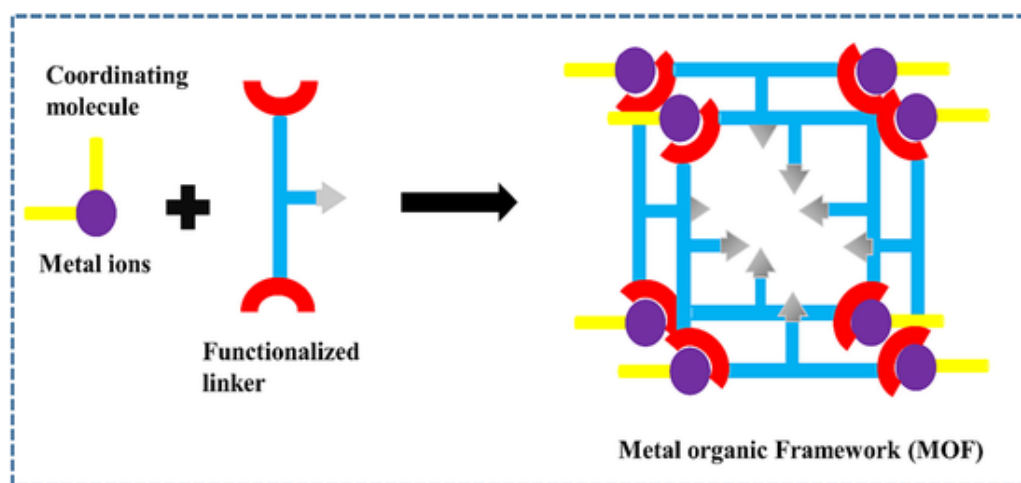


Fig. 3. Schematic representation of the formation of a MOF structure.

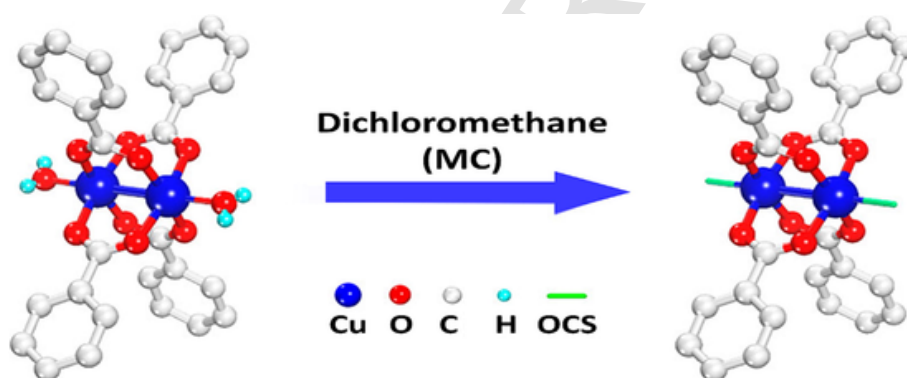


Fig. 4. Schematic illustration of chemical activation of the paddle-wheel-like (Cu^{II}_2) node within HKUST-1. . Adopted from [100]

ing the performance of MOF-based membranes in water purification. In a study conducted by Joshua et al. a membrane surface ligand exchange method (MSLE) was employed to prepare post-synthetically modified ZIF-8 membranes[76]. The modified membrane demonstrated a remarkable improvement in propylene/propane selectivity, reaching 40–70 % during the initial 30 min and continuing to increase while minimizing propylene permeance losses to just 10–20 %.

Also, Zhang et al. used PSM to improve the stability of a ZIF-8-H membrane in the presence of water [106]. He introduced hydrophobic alkyl chains onto the surface of the membrane through PSM, which improved the hydrophobicity of the membrane and prevented water-induced degradation. The resulted membrane demonstrated excellent stability and selectivity for the separation of water and organic solvents. Overall, these studies demonstrate the potential of PSM as a powerful tool for improving the performance of water purification in membranes. By tailoring pore size and functionality in MOF using PSM, researchers can develop membranes with improved selectivity and stability, suitable for various liquid separation purposes.

2.6. Incorporating MOF in membranes

Incorporation of MOF in membranes for water purification have made significant advances over the past decade. This has been achieved through the optimized combination of MOF synthesis techniques and development of membrane through different methods [107–110]. There are two main types of membranes that utilize MOF, including continuous MOF-based membranes and mixed matrix membranes (MMMs). The fabrication of continuous MOF-based membranes involves the production of a pure MOF layer on a supporting base to form

an uninterrupted membrane. In these types of membranes, the porosity of MOF provides exceptional high selectivity for water purification. However, the mechanical instability of thin-film MOFs hinders the formation of large-surface-area membranes, necessitating the use of mechanically stable porous supports. The presence of intrinsic or extrinsic defects can hinders in industrial liquid purification applications. Therefore, to overcome these challenges the durability and robustness of the materials in extensive and harsh conditions are crucial consideration for the large-scale application of continues membrane.

Subsequent type of membrane is comprised of a combination of MOF and polymers. By merging MOF s and polymers, there is an opportunity to blend the ease of handling and shaping of polymers with the exceptional MOFs pores. In contrast to the former membranes, MMMs are frequently self-supported and do not apply on a substrate for structural integrity. The presence of organic linkers in the MOF structure promotes interaction with the polymer matrix, minimizing the occurrence of tiny gaps. The uses of extremely porous and nanostructured MOFs have the potential to enhance liquid permeation performance. However, the presence of glossy polymer may lead to reduced permeability, which can be a challenge. To address this constraint, one possible approach is to augment MOF concentration which can shift composition towards a dominance of MOFs. Also, clustering of particles and inadequate dispersion in MMMs can lead to the formation of defects and voids in the membranes. Conclusively, atomic level comprehension of surface properties of MOF and inners boundaries are crucial to address these issues and improve the incorporation of MOFs and polymers.

2.7. RDS approach

The implementation of a methodical approach in constructing MOF-based membrane is essential to meet the need for accurate and efficient water purification. The effective routes for high-performance liquid separation in MOF-based membranes are centered on RDS approach. The process of rational design begins with a comprehensive scientific definition of the problem at hand. The process involves various considerations, including the careful selection of suitable MOFs for the specific liquid mixtures, comprehensive understanding of the chemical binding characteristics of both the MOFs and membranes, and the development of strategies to optimize the benefits of MOFs in water purification. Considering this precisely outlines issue, RDS are envisaged with the goal of imparting multi-functional synergies to the MOF-based membranes to effectively address the liquid separation challenge. This iterative process of problem definition and rational design continues until a well-aligned solution is achieved. In comparison to an empirical approach, the RDS aims to enhance separation efficiency by employing a systematic approach and to control or maximization of performance parameters. RDS enables the uses of diverse fabrication methods for MOF-based membranes, such as in situ preparation, blending and interfacial polymerization methods.

2.8. In situ synthesis approach

In situ synthesis for membrane fabrication refers to a method where the synthesis of materials, such as MOFs, takes place in direct conjunction with the membrane substrate or inside the membrane's pores. This approach allows for the fabrication of membranes with tailored properties and structures, as the synthesis occurs within the same environment where the membrane will be used. By integrating the synthesis process with the membrane fabrication, in situ synthesis enables precise control over the material composition, morphology, and functionality of the resulting membrane. This technique is commonly employed to enhance MOF membrane performance in various applications, including gas separation, water purification, and liquid filtration. In literature, there are three different routes have been investigated for the

formation of continuous MOF layer on the support namely, direct growth [111], secondary growth [112], and liquid phase epitaxy (LPE) respectively. Although these techniques have been shown to be highly effective in development of MOF layers on base material. However, it is important to recognize that despite their individual characteristics, these methods can be grouped together as part of the in-situ synthesis approach. This approach serves as a conventional strategy for creating continuous MOF membranes specifically designed for liquid separation. The in-situ growth process shows the occurrence of crystallization, development, and interlacing simultaneously as shown in the Fig. 5 (A).

Awang et al. employed this mechanism in their fabrication of a nanocomposite membrane comprising PA and ZIF-8, which was achieved by combining direct growth of ZIF-8 with interfacial polymerization (IP) [114]. Initially, a ZIF-8 intermediate layer was cultivated on the permeable exterior of a PSf-UF membrane by iterative ZIF in situ development. Thereafter, a PA coating was administered on the ZIF-8 intermediary layer to produce a PA/ZIF-8 discerning layer using IP, as is demonstrated in the Fig. 6. During the initial process of direct growth, the ZIF-8 crystals can potentially serve as breeding grounds that can encourage more in the process, thereby resulting in the creation of an ZIF-8 layer on the membrane. This assertion is supported by the SEM images shown in Fig. 7. In addition, the interior pore structure of the substrate can serve as a basis for cultivating an even more unbroken MOF phase. This technique was employed by adapting the porous configuration of the asymmetric polyimide P84 UF membranes using the in direct growth method for organic solvent nanofiltration, to incorporate HKUST-1 [115].

The polymer membrane was submerged into a blend of $\text{Cu}(\text{NO}_3)_2$ and trimesic acid ($\text{C}_6\text{H}_6\text{O}_6$) to prepare the membranes as shown in Fig. 8. The findings showed that the presence of HKUST-1 was evenly distributed both on the surface and within the cross-section of the membranes. To overcome the hurdle of inadequate substrate adhesion during MOF membrane manufacture, the technique of modifying the supports chemically can be employed to enhance divergent nucleation and promote the growth of MOF [116]. Chemical modification was achieved by utilizing trimellitic anhydride ($\text{HO}_2\text{CC}_6\text{H}_3$) as the modifying agent,

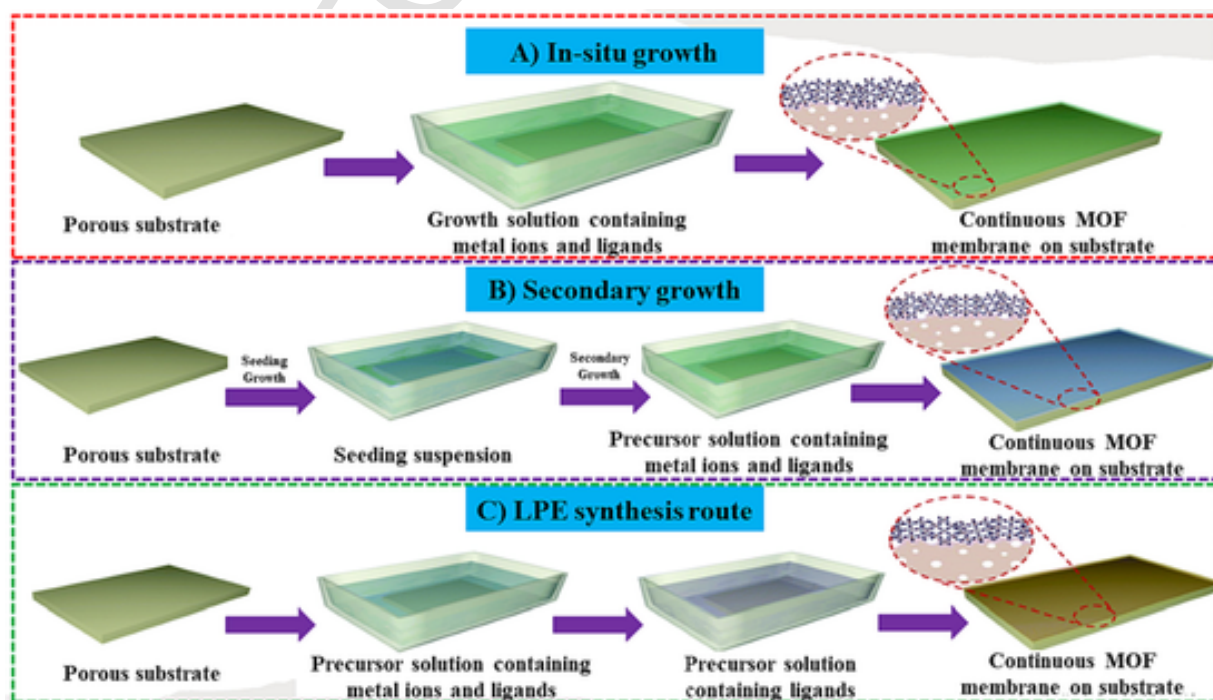


Fig. 5. In-situ synthesis approach for MOF based membranes. . Adopted from [113]

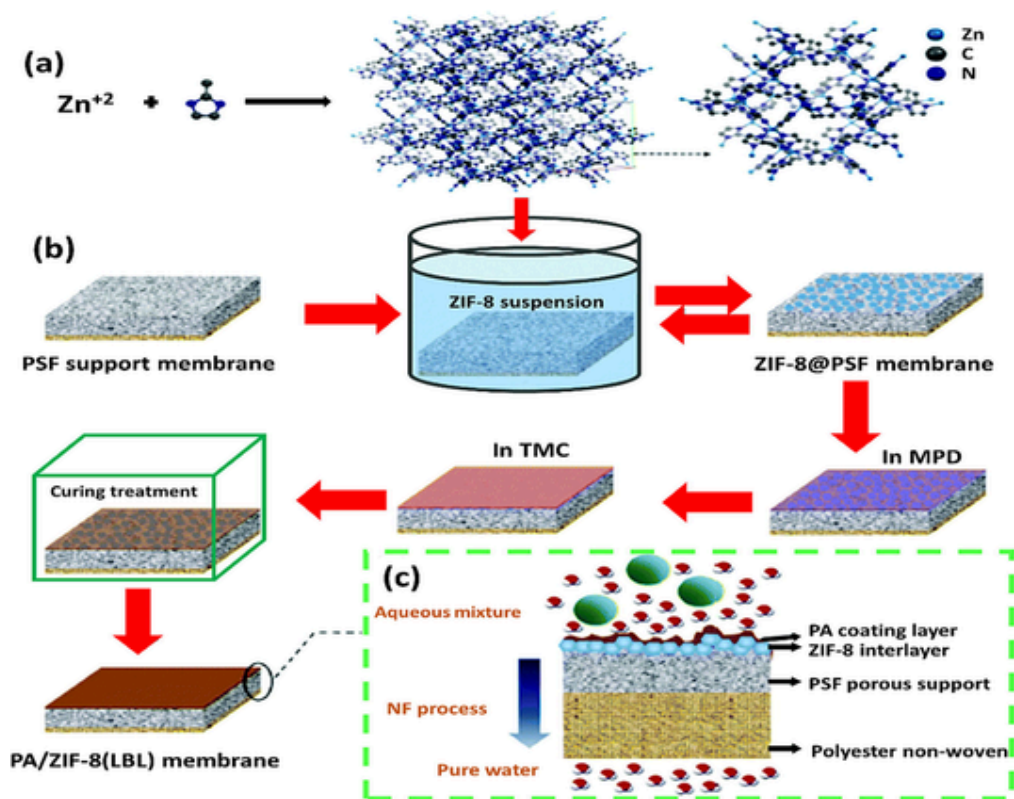


Fig. 6. Designing continuous PA/ZIF-8 MOF membranes using in direct growth. . Adopted from [114]

followed by crosslinking to form carboxylate functional groups that react with Cu^{+2} to initiate the direct growth formation of HKUST-1.

The Fig. 5(B) described the preparation of continuous MOF-based membranes, which can also be achieved through secondary growth, in which pre-attached seed crystals are utilized to facilitate membrane growth. Although secondary growth is more intricate than in direct growth, it offers enhanced regulation over the ultimate alignment of the membrane and permits the emergence of a compact and uninterrupted membrane devoid of deformations like fissures or openings. In the year 2019, a subsequent growth technique was used to fabricate a consistent and compact ZIF-8 covering on imbalanced $\alpha\text{-Al}_2\text{O}_3$ microfiltration circular membranes which acted as a selective layer for pervaporative separation[117] ZIF-8 membrane thickness was determined to be roughly 15 μm , as verified through scanning electron microscopy (SEM), and illustrated in Fig. 9A. Since, MOF synthesis involves coordination bonding between organic and inorganic moieties in solution, creating the hybrid organic-inorganic framework. Therefore, substrates made of the same metal as the MOFs are particularly favorable for directly reacting with the organic linkers to grow as a seed layer for secondary growth. The metal on the substrates can provide the nuclei and enhance the adhesion between MOF layers and substrates. Taking inspiration from this strategy, a facile reactive seeding method was developed to prepare continuous MIL-based MOFs membranes for pervaporation on alumina porous supports, in which the porous support acted as the inorganic source reacting with the organic precursor to grow a seeding layer. For effective secondary growth, substrates composed of the same metal as the MOFs are preferred as they can provide nuclei for the seed layer and enhance adhesion between the MOF layers and the substrates. A simple and straightforward approach was employed in a research experiment to produce seamless MOFs membranes using reactive seeding technique. The membranes were designed for pervaporation and mounted on porous alumina supports, which acted as the inorganic foundation for the seed layer as portrayed in Fig. 9B[118]. Similarly, another study was conducted which showcased the creation of an

organophilic ZIF-71 film for the purpose of pervaporative separation. The porous ZnO base was employed to create the initial layer of the seed. Afterward, a solvothermal reaction involving zinc acetate and dcIm was carried out to develop a continuous ZIF-71 film with a width of approximately 10 μm and no other substances except for leftover ZnO[119] as depicted in the Fig. 9C.

The third approach is the LPE, which has been used to fabricate the MOF-based membranes for liquid separation (Fig. 5 C). The LPE technique is a versatile and widely employed for membrane fabrication, particularly for continuous MOF-based membranes. This approach offers a strategy for precisely designing and creating MOF membranes with controlled properties and structures. This process involves a cyclic procedure where a substrate is alternated between solutions containing metal ions and ligands, followed by intervening cleansing procedures. This controlled cycling allows for the gradual formation of continuous layers of MOFs on the substrate surface or within its pores. By carefully selecting the metal ions and ligands, as well as controlling the solution conditions and cycling parameters, the LPE technique enables the synthesis of MOF membranes with tailored characteristics. One of the significant advantages of the LPE technique is its ability to achieve well-controlled growth of MOF layers. The cyclic process facilitates the formation of uniform and continuous MOF films, ensuring a high degree of structural integrity and surface coverage. Moreover, the transition washing route help remove any impurities or excess reagents, resulting in high-quality membranes. The LPE technique is particularly suitable for synthesizing MOF thin films, often referred to as surface-attached MOFs (SURMOFs). These SURMOFs exhibit excellent adhesion to the substrate and can be tailored to exhibit specific properties such as selectivity, permeability, and stability. By precisely controlling the composition and structure of the MOF layers during the LPE process, SURMOFs with desired functionalities can be achieved for various applications, including gas separation, liquid filtration, and catalysis. However, this process has some shortcomings for instance, tedious operation, intricate fabrication, growth limitations, and potential defects.

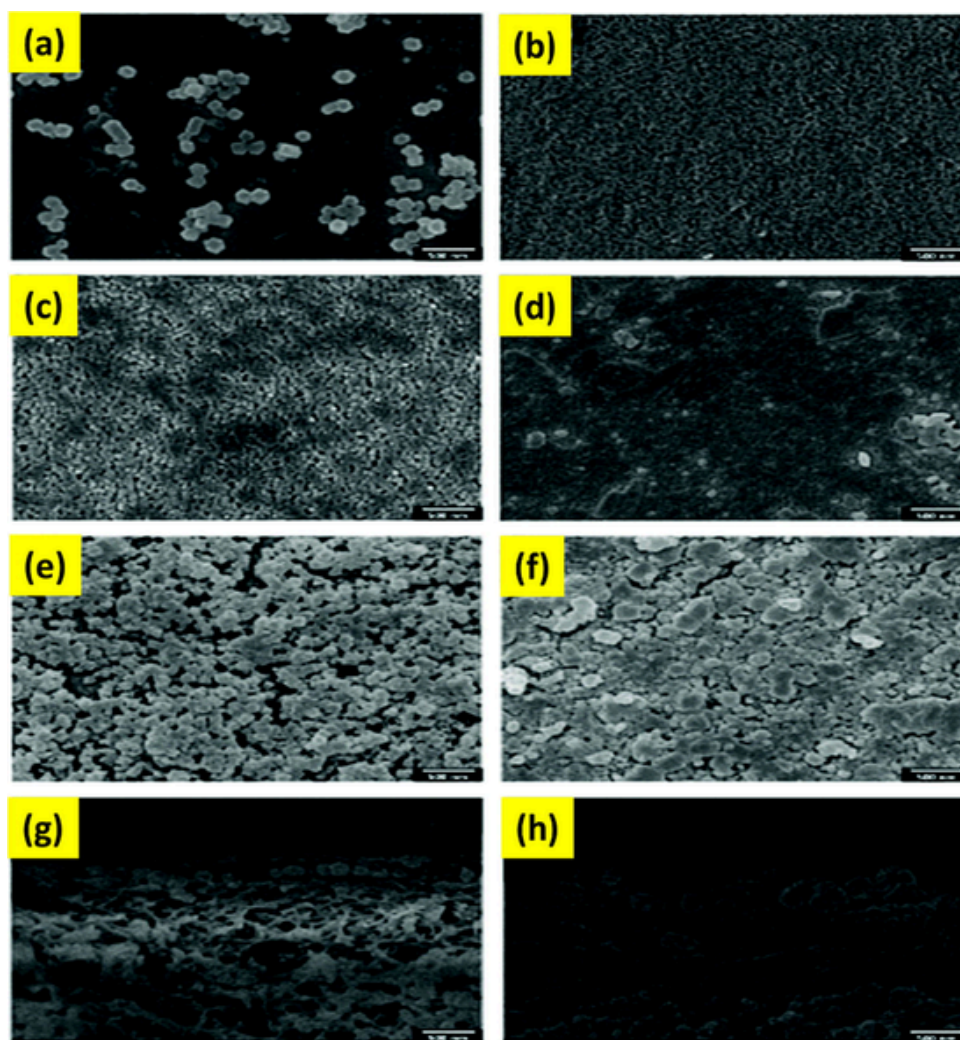


Fig. 7. SEM images of the ZIF-8 nanoparticles. . Adopted from [115]

It is important to address these limitations and continue research and development efforts to overcome these challenges for the widespread application of MOF-based membranes fabricated using the LPE method. For instance, the interfacial synthesis method was used to develop the poly (ether sulfone) (PES) base ZIF-8 membrane[123], as shown in the Fig. 10A. The PES support membrane were submerged in $\text{Zn}(\text{NO}_3)_2$ solution for 24 hrs. Once the extra liquid was eliminated from the membrane, the 2-methylimidazole solution, as previously stated, was cautiously applied onto the surface. After a specific duration the solution was removed. Ultimately, the membranes underwent post-treatment at a temperature of 100°C for the over night. XRD confirmed (Fig. 10B) the formation of ZIF-8 layers on the support. Also, the small peaks were seen on XRD graph that closely corresponded to ZIF-8. Moreover, the Fig. 10 C showed the TEM analysis, which revealed the formation of a continuous ZIF-8 layer. In conclusion, this technique offers a simple scalability, enabling the production of MOF membranes with significant porosity.

2.9. Blending method

Blending is a crucial design strategy for MOF-based membranes, particularly for MOF-based mixed matrix membranes, which have undergone extensive investigations[125,126]. Compared to pure MOF membranes, the reproducibility of synthesis appears to be less of a concern in the case of MMMs, and costly supports are redundant which

suggests that the scaling-up of this type of membrane is relatively easy and inexpensive. Additionally, MOF particles enclosed by polymers are expected to be considerably more robust than bare MOF, and the long term stability of these membranes should not pose an issue. Two approaches were developed for fabricating MOF-based MMMs: substrate-free blending and substrate-based blending. Later method is a common method used in designing MOF-based MMMs for pervaporation[127]. Some porous substrates, such as polymeric membranes[128] and ceramic tubes[129], were used to support the resulting MMMs and improve their stability. The standard procedure comprises the following steps: (1) MOFs and polymers are dissolved in a solvent to form ink; (2) the mixed solution is applied to the porous support through techniques like spin-coating, and (3) the coating is cured or dried to eliminate the casting solvent (see the Fig. 11).

With this method, thin MOF-based MMMs are produced on the surface of porous material, with varying thickness ranging from 0.3 to 20 μm , and applied as a whole.

For example, the solution-blending dip-coating method was used to manufacture pervaporation membranes with an organophilic nature on the inside surface of alumina capillary substrates. The fillers consisted of ZIF-8 nanoparticles, whilst polymethylphenylsiloxane (PMPS) contributed as the polymer matrix[125]. After the heat treatment procedure, illustrated in Fig. 12, exhibited the ZIF-8 nanoparticles were embedded in the PMPS phase homogeneously with no interfacial voids. The upper layer possessed a thickness of approximately 2.5 μm , which

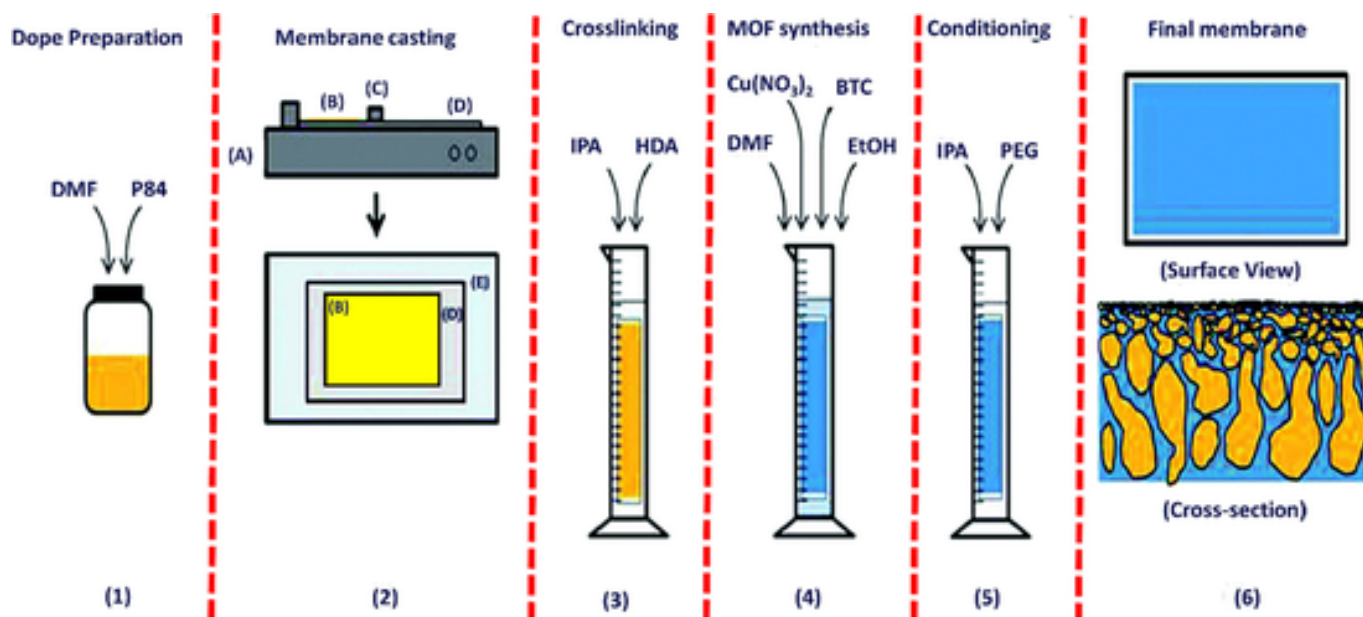


Fig. 8. Method for fabricating MOF-based membranes for in situ growth [116].

may offer excessively high permeability. Furthermore, surface modification of the support broadens the usage of the substrate-based blending method. Recently, a new technique involves pretreating an Al_2O_3 tubular support with a silane coupling agent to enhance adhesion force between the separation layer and the substrate to fabricate a $\text{Co}(\text{HCOO})_2$ -based hybrid membrane suitable for pervaporation [130]. The $\text{Co}(\text{HCOO})_2$ /PEBA hybrid was applied onto the previously treated Al_2O_3 tubular substrate using dynamic pressure-driven assembly and deposited onto the surface to create a hybrid membrane. Finally, the hybrid membrane was crosslinked to obtain the final membrane (as shown in Fig. 13A).

A novel approach for blending using substrate was devised through the integration of RDS and self-assembly. In this approach, a hydrolyzed polymeric membrane serves as the base layer to immobilize MOF precursors via electrostatic forces, producing MOFs on the surface of the modified substrate. This process confers the benefits of low cost and high separation efficacy of MOFs. During this process, the synthesis of MOFs and the fabrication of MMMs are integrated into one multi-component system, which simultaneously presents the advantages of the low cost of the polymer substrate and the high separation potential of MOFs. More importantly, the dispersion of the MOFs and the MOF-to-substrate adhesion are improved. Ping Hu et al. have showcased the practicality of this method in generating MOF hybrid films for desalinating brackish water via an in-situ coordination-driven self-assembly strategy [131].

The initial step involved in the process was the hydrolyzation of a polyacrylonitrile (PAN) ultrafiltration membrane to introduce carboxylate moieties onto its surface. Following its submersion in a methanol-based solution of zinc nitrate $\text{Zn}(\text{NO}_3)_2$ solution, the PAN membrane, together with the Zn^{2+} ions, underwent the subsequent step of filtering a mixed solution of 2-methylimidazole (Hmim $\text{CH}_3\text{C}_3\text{H}_2\text{N}_2\text{H}$) and PSS under a negative pressure environment (as illustrated in Fig. 13B). This method led to in-situ expansion of MOF particles inside the polymer (PSS), and simultaneous bonding of metal ions with both MOF ligands and the modified organic polymer, guaranteeing excellent compatibility and even distribution within the membrane. In addition, a more straightforward and replicable approach called simultaneous spray self-assembly was created to fabricate ZIF-8-PDMS nanohybrid composite membranes for the bioalcohol recovery from water solution [55]. This technique entails pouring the ZIF-8-PDMS suspension and the cross-linking agent and catalyst solution into two self-stirring pressure bar-

rels separately and then spraying them simultaneously onto a PSF ultrafiltration sheet membrane (Fig. 13C). By doing so, this method optimizes the dispersion and loading of ZIF-8 particles, which is expected to have important implications for the preparation of defect-free MMMs for many applications.

Substrate-free blending is a more flexible method for designing MOF-based MMMs, as it does not require a support during the liquid separation process. Unlike the method where the mixture is applied directly on a support, nonporous solid supports (such as glass plates) were used to make sure the mixture separates entirely from the base, creating free-standing MMMs. To ensure both strong durability and good permeability, the membranes typically have a thickness range of 18–30 μm when they are intended for use in pervaporation applications. In case of water treatment, the thickness of MMMs is arranged by a casting knife with a slit larger than 150 μm . Stemming from the interest in the MOF-based MMMs, Perez et al. have described in detail the fabrication procedure of a MIL-53(Al) nanocomposite membrane by using substrate-free blending [55]. The casting solution was obtained by dissolving PMIA polymer and MIL-53(Al) particles in a mixture of *N,N*-dimethylacetamide and LiCl. After casting, the membranes were immediately placed in a vacuum oven and then immersed in distilled water to induce phase inversion. This method is effective and straightforward to introduce MOFs into a membrane matrix, but MOF particle started agglomerate after higher loadings (at a content of 1 wt% and 1.5 wt% for MIL-53(Al)). The covalent polymerization of organic oligomers through a post-synthetic approach is a useful method for achieving good dispersion in MOF-based MMMs. To address this challenge, an alternative and practical method is the post-synthetic technique involving the covalent polymerization of organic oligomers. This approach allows for the creation of MOF-based MMMs with excellent dispersion, presenting a viable solution [92]. Took the synthesized nanosized UiO-66- NH_2 particles and combined them with an isocyanate-terminated polyurethane oligomer in dry chloroform, and thoroughly dispersed this mixture using ultrasound. Once the reaction mixture was transferred into a clean polytetrafluoroethylene (PTFE) container, let the cast membrane air dry at room temperature. Subsequently, applied controlled heating in an oven with air circulation, as illustrated in Fig. 14. These steps led to the formation of free-standing MMMs containing well-dispersed UiO-66- NH_2 , which proved effective in isolating hydrophilic dyes from water and separating dye mixtures based on distinct membrane affinities.

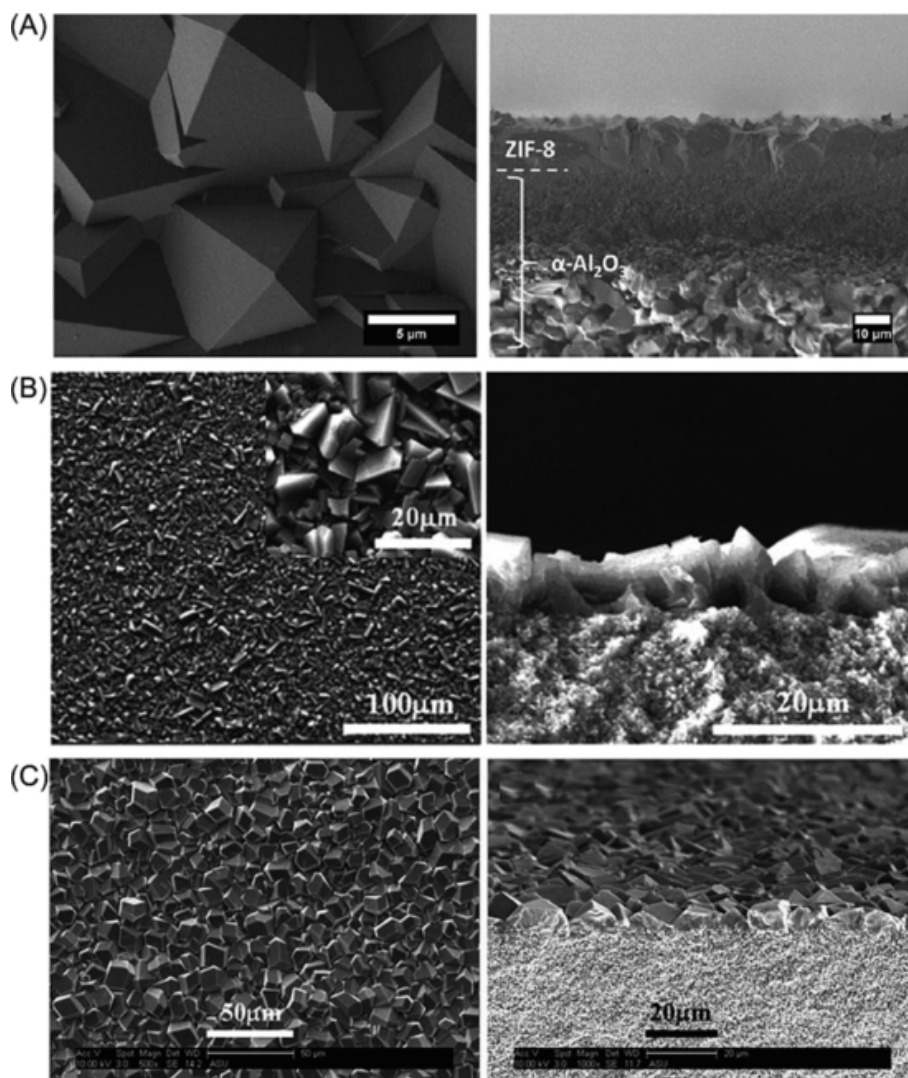


Fig. 9. The top view and cross-section of continuous membranes fabricated by secondary growth methods (A) ZIF-8, (B) MIL-53, and (C) ZIF-71. Adopted From [120–122].

2.10. Interfacial polymerization process

The conventional approach of creating a thin functional layer for nanofiltration (NF) and reverse osmosis (RO) through interfacial polymerization has undergone technical enhancements by incorporating MOFs into the selective layer. By utilizing MOFs, which possess minute particle dimensions, consistent pore sizes, and interconnected porous frameworks, advanced NF/RO composite membranes can be designed with an ideal inclusion of these porous materials. The TFN membranes, produced as a result, exhibit water-like channels that aid in water permeability while obstructing hydrated cations. Consequently, there is an improvement in permeance without compromising selectivity (Fig. 15). The addition of MOFs is achieved through the blending procedure within the separation layer. However, the preparation process entails an interfacial reaction between aqueous and organic phases, establishing a novel approach for creating MOF-based membranes. This strategy is emphasized in the present analysis.

Li et al. utilized interfacial polymerization to add ultra-small MOF nanoparticles with organic monomers into ultra-thin-film composite membrane on the layer on top of porous polymer supports[133]. This approach combined the processability of thin-film composite membranes with the benefits of MOFs. Nanofiltration experiments with the resulting TFN membranes demonstrated a significant increase in per-

meance without sacrificing rejection[134]. The excellent performance of the filtration system was attributed to two main factors. First, the MOFs used in the system had porous structures that allowed solvents to flow through easily, creating preferential flow paths. Second, the nanoparticles were surrounded by a protective layer of PA (Polyamide), which effectively blocked the passage of unwanted molecules. The organic moieties of the MOF particles were also in good compatibility with the PA layer, enhancing the filtration efficiency. In recent times, researchers have shifted away from the trial-and-error method for discovering nanomaterials that improve membrane performance. Instead, they have embraced a rational design strategy to fabricate hybrid nanocomposites.

This approach allows them to intentionally customize the chemistry and functions of the nanocomposites to meet specific requirements before synthesis takes place. By doing so, researchers can optimize the properties of the nanocomposites for targeted purposes. Hybrid nanocomposites utilizing MOFs and other types of nanomaterials have been created and merged with the active layer to fabricate state-of-the-art TFN membranes. An instance of this is the development of ZIF-8@GO composites through in situ growth, which are then integrated into membranes for the production of TFN nanofiltration membranes using interfacial polymerization [93,135]. This is achieved through the coordination between zinc ion and the carboxyl groups of GO. This coord-

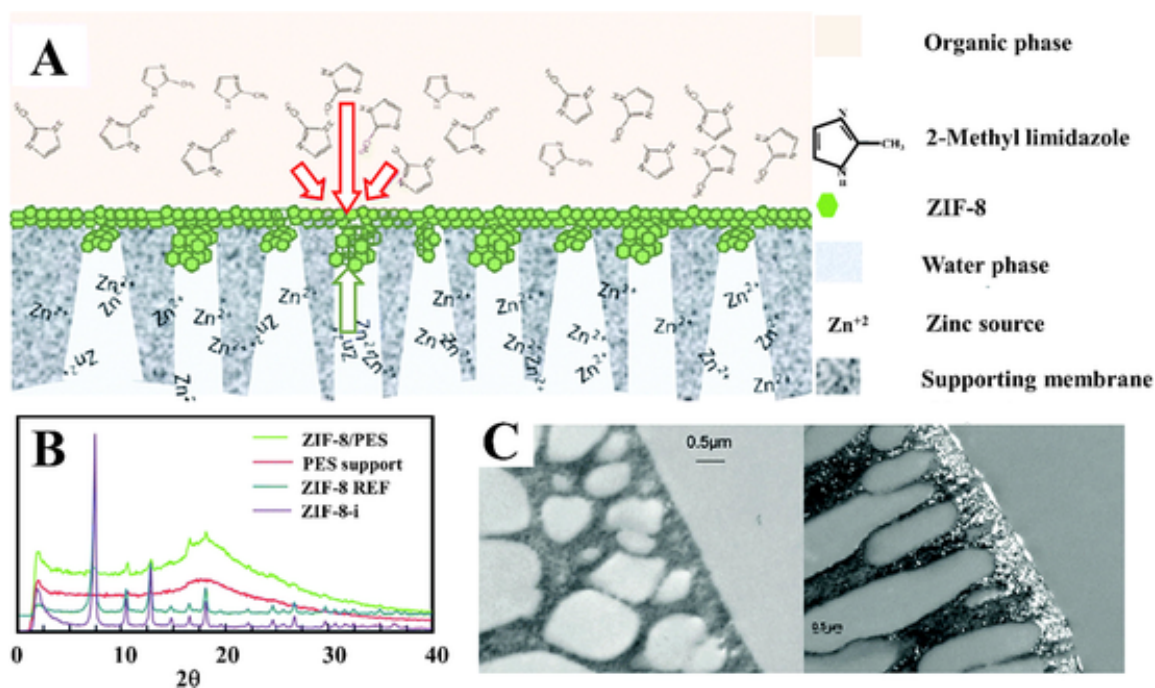


Fig. 10. The interfacial synthesis of ZIF-8 on PES-supported membranes (ZIF-8/PES) is shown in (A); (B) XRD patterns of PES support; (C) TEM images membranes (left) and ZIF-8 films (right). . Adopted from [124]

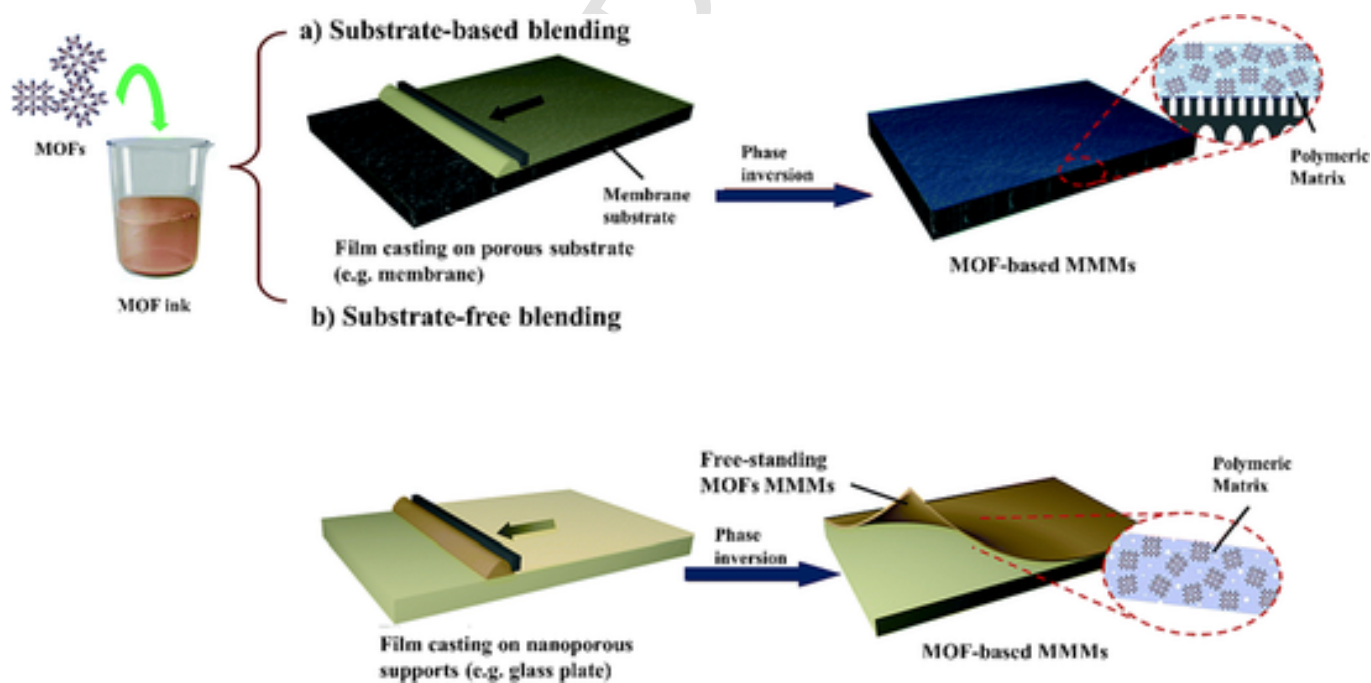


Fig. 11. Blending method for the preparation of MOF-based membranes. . Adopted from [119]

mination allows for the even dispersal of Zn²⁺ ions onto the GO surface, as illustrated in Fig. 16A. The incorporation of hybrid nanocomposites based on MOFs and other nanomaterials greatly improved the permeability of TFN membranes without sacrificing rejection. In one study, ZIF-8/GO hybrid nanosheets were synthesized and incorporated into membranes, leading to effective antimicrobial activity and high hydrophilicity. Another study involved the incorporation of MOF loaded catalytic silver (Ag) nanoparticles for catalytic TFN membrane prepared by interfacial polymerization [136]. The resulted polyamide TFN membranes with high efficiency, sustainable catalytic degradation of

Rhodamine B (RhB), and excellent self-cleaning performance were prepared conveniently. The MOFs template used in the preparation of this new nanocomposite has resulted in unique hybrid nanostructures with sub-100 nm dimensions, due to the reduced nanostructure of the Ag nanoparticles within. Despite their ultra-thin nature, the resulting membranes are remarkably dense and exhibited excellent catalytic behavior, enabling them to both filter contaminants and degrade RhB (Fig-16B) [137]. This innovative approach to design the membranes provides exciting opportunities for the development of next-generation

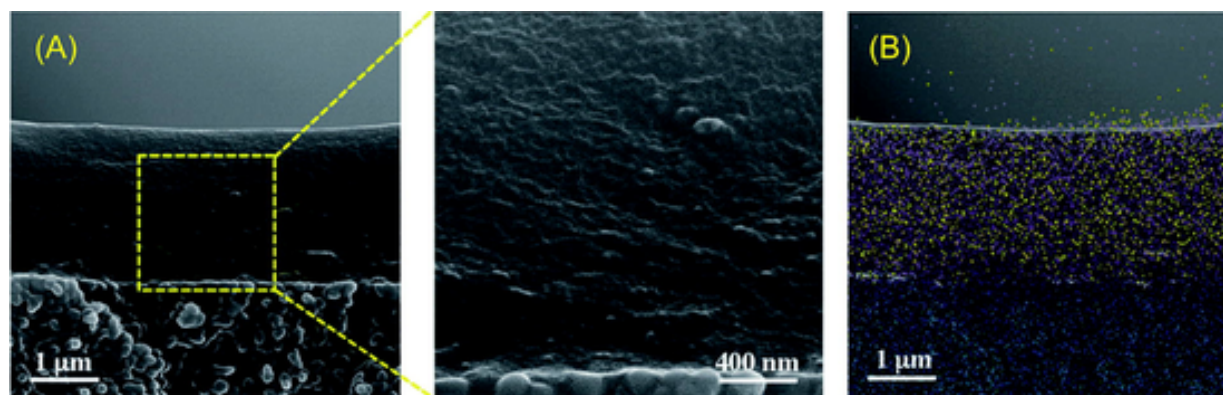


Fig. 12. (A) Cross-sectional SEM images (B) EDXS mapping of the ZIF-8-PMPS membrane. Adopted from [130].

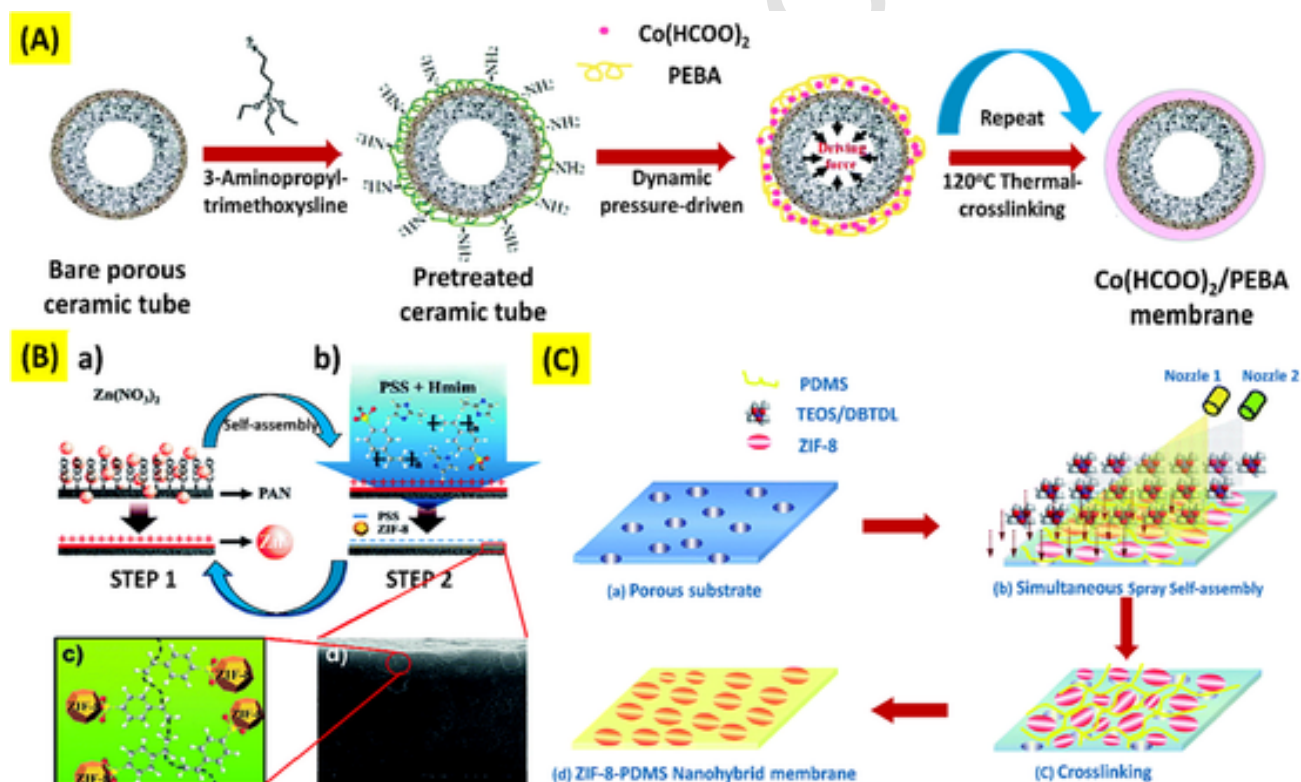


Fig. 13. Designing MOF-based MMMs for liquid separation using a substrate-based blending method. (A) The process of producing Co(HCOO)₂/PEBA membranes on ceramic tubes is shown; (B) ZIF-8/PSS hybrid membranes: (a) Zn²⁺ assembly on the substrate, (b) PSS assembly and ZIF-8 particle formation, (c) proposed membrane structure, (d) an SEM image of the membrane (two layers); and (C) a nanohybrid membrane comprising of ZIF-8 and PDMS is formed via simultaneously sprayed self-assembly. . Adopted from [131,132]

TFN membranes, achieved through careful selection of MOFs framework carriers and encapsulation mechanisms.

2.11. Alternative approaches for fabrication of MOF-based membrane

The effectiveness of MOF-based membranes for liquid separation depends heavily on the development of preparation strategy, which can significantly impact the structure, stability, and actual separation efficiency of MOFs. The efficacy of membranes based on MOFs for separating liquids is heavily contingent on the advancement of manufacturing techniques, which can greatly influence the configuration, durability, and actual effectiveness of MOFs in separation. For example, the graphene acid (GA) membrane was prepared by a novel pressure-assisted self-assembly (PASA) filtration technique [139,140]. The PASA filtration process, operated at a constant pressure difference

DP = 2.0 bar which induced the formation of a MOF@GO membrane (Fig. 17A), and exhibited competitive water permeation for ethyl acetate/water mixtures by the pervaporation. The integration of nano-MOFs into the membrane structure presents a potential application for various composite membranes, providing valuable insights for the development of advanced membranes that enhance the separation efficiency of aqueous organic solutions by modifying the nanostructure of nanomaterials.

To improve the flow rate and minimize hindrance to the transfer of substances, researchers introduced a technique called fine-tuning contra-diffusion. This method involved the preparation of a nanoconfined composite membrane using ZIF-11/PAN. The porous substrate made of hydrolyzed PAN was treated with a solution of zinc ions and benzimidazole (Bim), which penetrated the substrate's pores. Within the restricted area, ZIF-11 crystals were formed through the coordinated reaction be-

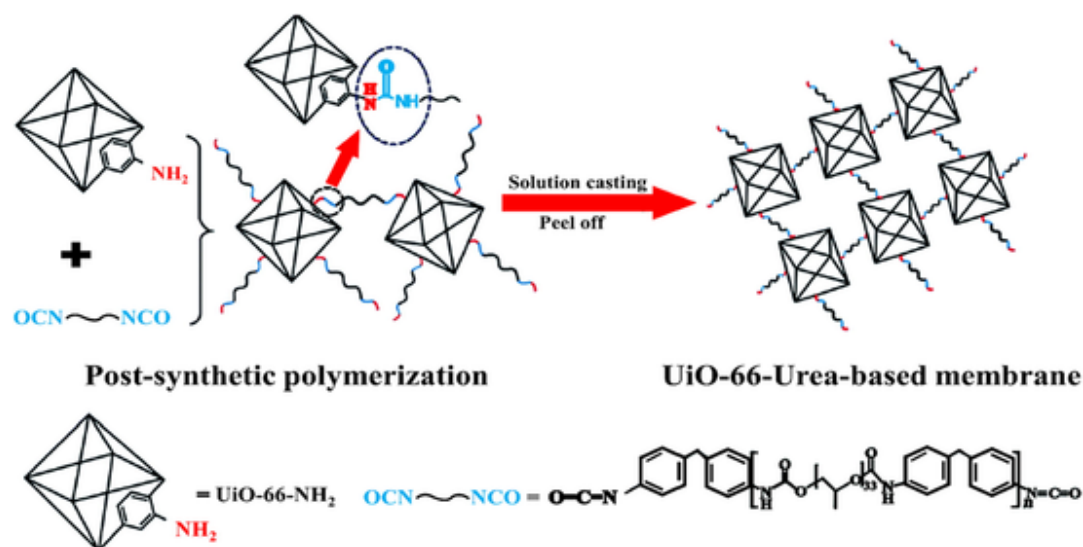


Fig. 14. The diagram shows the process involved in fabrication of UiO-66-urea-based membranes. Adopted from[55].

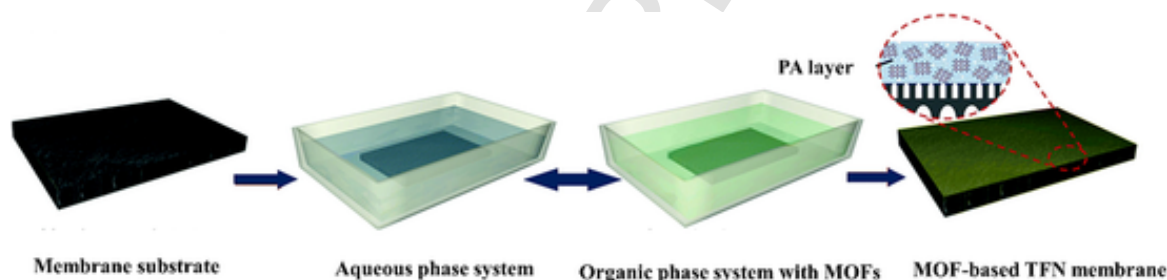


Fig. 15. Interfacial polymerization process for the preparation of MOF-based membranes for liquid separation [120].

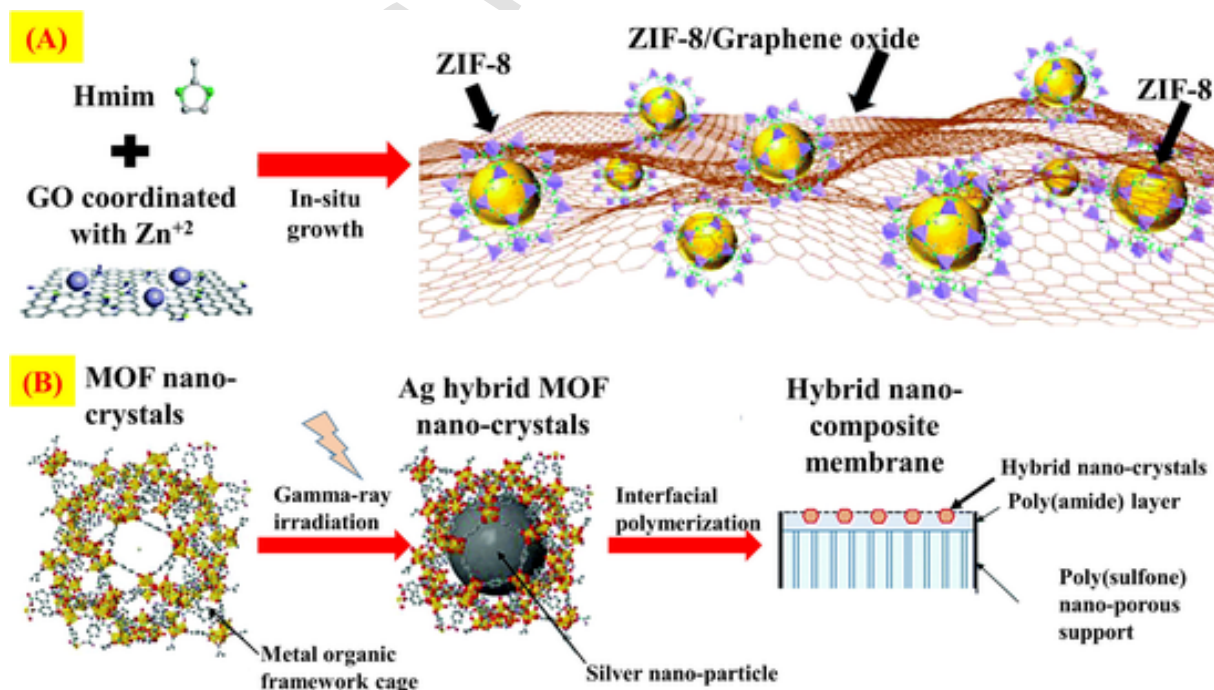


Fig. 16. Hybrid nanocomposites comprising MOFs and other nanomaterials. (A) ZIF-8/GO hybrid nanosheets (B) Hybrid Ag@MOF nanocrystals to design TFN membrane. Adopted from[122,138].

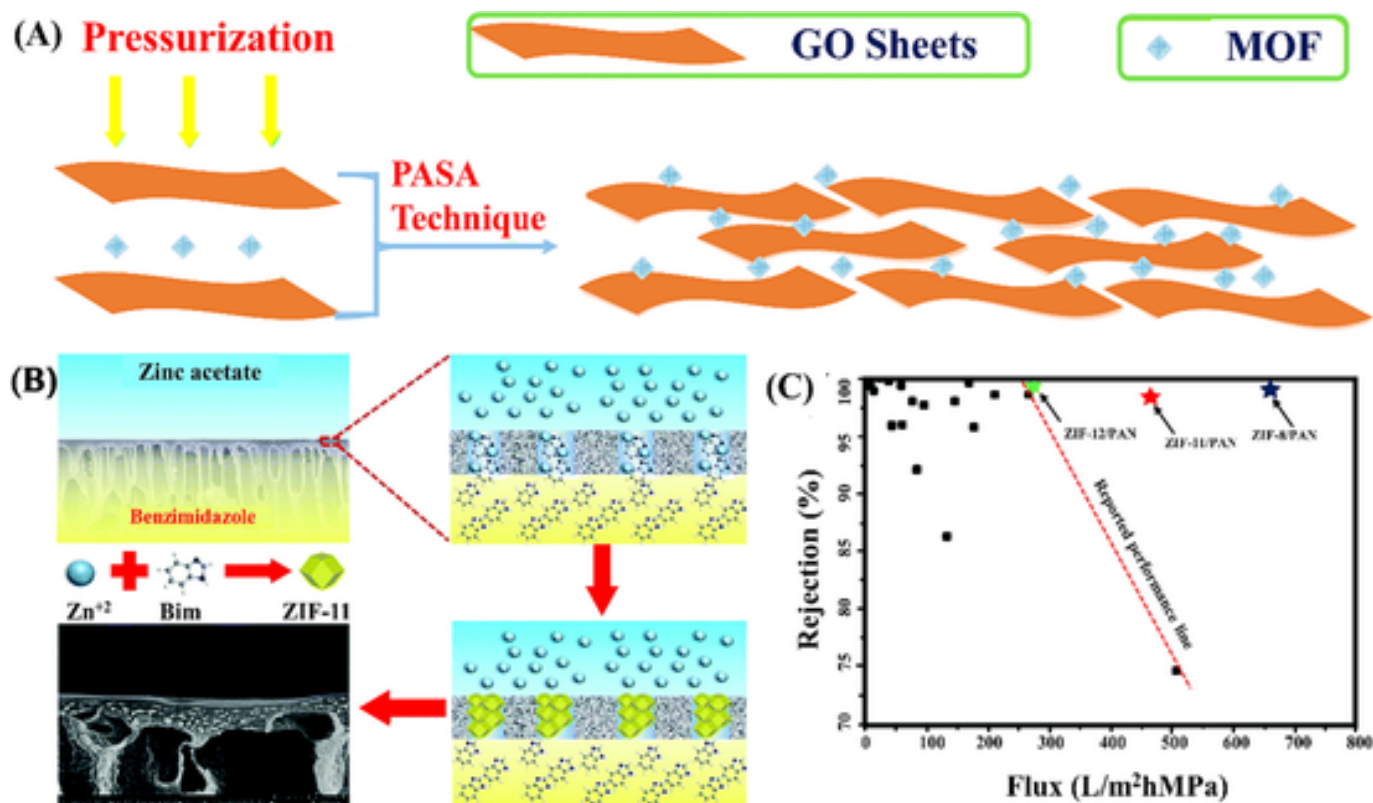


Fig. 17. The schematic illustration showcases (A) PASA Technique (B) Contra-diffusion method. (C) Rejection profile of membrane with literature (C). Adopted From [142,143].

tween zinc ion and Bim (see Fig. 17B). The figure C shows the removal efficiency for MB approximately 99 % [141]. This approach offers a promising route for the effective production of MOF membranes on metal supports with large pores, potentially applicable in the field of liquid filtration.

The development of efficient separation membranes is crucial for various industrial applications such as water purification, food and beverage processing, pharmaceuticals, and petrochemicals. Currently, there is a growing interest in using MOFs as a promising material for liquid separation membranes due to their unique properties, such as high surface area, tunable pore size, and framework flexibility. However, designing MOF membranes for liquid separations requires careful consideration of several key elements. In addition to the selection of appropriate membrane materials and optimal module configuration, factors such as mechanical, chemical, and thermal stability, as well as production scalability and cost-effectiveness, must also be considered. The suitability of MOFs for specific liquid separation applications also depends on their separation characteristics and the type of filtration used. To fabricate the membranes that are efficient, several crucial elements need to be taken into consideration during the design process.

2.12. Fabrication conditions

Compared to other porous materials, the synthesis of Metal-Organic Frameworks requires lower activation energy. In fact, several MOFs such as HKUST-1 and ZIF-71 can be synthesized at room temperature, which has been well documented in the literature [144,145]. The application of these methods offers notable benefits like minimal energy expenditure and the usage of easily accessible and economically viable apparatus. Additionally, it allows for a swift response duration. These factors contribute to the preparation of MOF-based membranes for separating liquids in a gentle and energy-conserving manner, presenting a sustainable and economically feasible resolution. By utilizing

these room temperature synthesis techniques, the production of MOF-based membranes can be made more accessible and environmentally friendly.

2.13. Flexibility

The unique ability of MOF materials to change their unit cell volume, known as “gate opening” or “breathing”, is a key factor in their effectiveness as liquid separation membranes. These changes in unit cell volume, which can range from 40 % to 230 %, occur in response to adsorption or desorption of guest molecules and are influenced by factors such as pressure, temperature, and adsorption. One MOF material of particular interest is MIL-53, which has demonstrated sensitivity to these factors and has been utilized in the development of a MIL-53/polydimethylsiloxane (PDMS) membrane for the separation of ethanol and water mixtures [146,147]. This unique property of MOFs, framework flexibility, provides a valuable tool for molecular sieving in MOF-based mixed matrix membranes. By capitalizing on this feature, MOF-based MMMs have the potential to provide highly efficient and selective liquid separation.

2.14. MOF particle size

The size of MOF particles is a key factor in the performance of MOF-based mixed matrix membrane, and therefore, optimizing their intrinsic properties. The downsizing of MOF particles has been shown to be critical in enhancing their performance in liquid separation processes. MOF nanoparticles have demonstrated a marked improvement in separation efficiency, as they possess increased interior accessibility and a higher external specific surface area. For example, recent research has found that submicrometer-sized ZIF-71 crystals, with diameters (139–429 nm) as the optimal additives for synthesis MMMs [148,149]. Performance of these submicrometer-sized ZIF-71-filled

MMMs surpassed that of both pure polymer membranes and MOFs filled with micrometer-sized ZIF-71 particles. Moreover, liquid separation using MOF-based membranes involves various mechanisms such as solvent selectivity, solute rejection, capillary condensation, and surface diffusion, that contribute to the overall performance of the membrane, (i) Solvent selectivity is the ability of the MOF-based liquid membrane to preferentially allow certain solvents to pass through while restricting the passage of others. This selectivity arises from the unique structure of MOFs, which consist of metal ions or clusters coordinated with organic ligands, forming a highly porous framework. The size, shape, and chemical functionality of the pores in the MOF structure play a vital role in determining solvent selectivity.

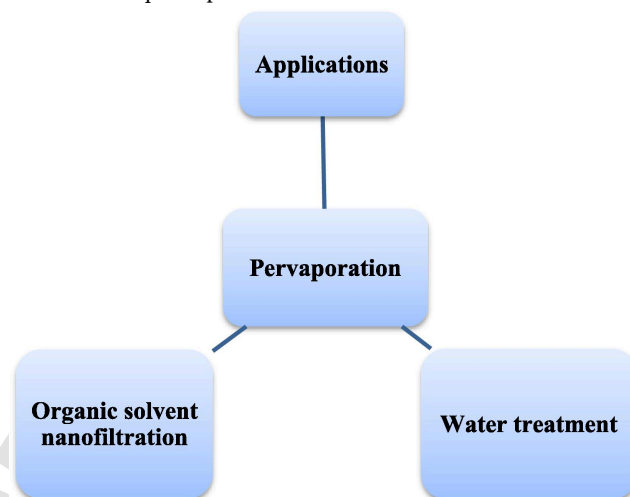
When a mixture of solvents is brought into contact with the MOF membrane, the solvents with sizes and chemical affinities that match the pore dimensions and functional groups of the MOF will be selectively adsorbed or transported through the membrane. Solvents that are too large or lack complementary interactions with the MOF structure will be rejected, resulting in solvent separation. (ii) Solute Rejection: Solute rejection refers to the ability of the MOF-based liquid membrane to block the passage of solutes (e.g., contaminants, impurities, or unwanted solvents) while allowing the desired solvent to pass through. Similar to solvent selectivity, solute rejection is also influenced by the size and shape of the MOF pores. Smaller solutes may be entirely blocked from entering the pores, while larger ones might be partially or completely rejected. Additionally, the surface charge and functional groups present on the MOF pores can contribute to solute rejection through electrostatic interactions and specific adsorption. This selective rejection of solutes is crucial in various separation processes, such as water purification, where the membrane needs to remove harmful ions or pollutants. (iii) Capillary Condensation: Capillary condensation is a phenomenon that occurs in porous materials, including MOF-based membranes, when the vapor pressure of a liquid is reduced in confined spaces (e.g., nanopores or micropores). When the pressure is lowered, the liquid molecules condense and accumulate within the pores, even below the liquid's normal boiling point.

In the context of MOF-based liquid membranes, capillary condensation plays a significant role in enhancing the separation efficiency by promoting the adsorption of specific solvents or solutes. (iv) Surface Diffusion: Surface diffusion is the movement of molecules along the surface of the MOF membrane. When the membrane is in contact with a liquid mixture, the solvents or solutes at the surface can diffuse across it due to concentration gradients. Surface diffusion is more prominent in cases where the MOF pores are partially filled with liquid or in situations involving high surface-to-volume ratios. Surface diffusion can influence the overall separation efficiency by affecting the rate at which solvents or solutes are transported through the membrane. By understanding and controlling surface diffusion, it is possible to optimize the performance of MOF-based liquid membranes for specific separation scenarios. In summary, MOF-based liquid membranes offer a versatile platform for liquid separation due to their unique structural and chemical properties. Solvent selectivity, solute rejection, capillary condensation, and surface diffusion are among the key mechanisms that contribute to their effectiveness in various separation processes. Understanding and harnessing these mechanisms will pave the way for the development of more efficient and tailored MOF-based liquid membranes for practical applications in liquid separation technologies.

3. Applications of MOF-based membranes

MOF-based membranes have become an increasingly popular choice for liquid separation applications due to their tunable compositions and modifiable structures. MOF-based membranes can deliver exceptional separation performance, making them versatile materials for a range of applications[150,151]. In addition to traditional applications such as pervaporation and dye removal, MOF-based membranes are

also being employed in novel applications such as catalytic degradation, fouling-resistance, and oil/water separation. The following chart will discuss the diverse conventional and developing uses of MOF-based membranes for liquid separation.



3.1. Pervaporation

Pervaporation is a highly promising separation technique that has gained significant attention in recent years due to its high selectivity and energy efficiency [152,153]. MOF materials have emerged as a potential candidate for use in pervaporation applications due to their unique properties such as tunable pore sizes, high surface area, and selectivity towards specific molecules. The exceptional separation performance of MOF-based pervaporation membranes has been attributed to their molecular sieving properties and the ability to adjust their pore sizes by altering the framework composition. Moreover, MOF-based pervaporation membranes have been shown to exhibit high flux and selectivity in various liquid separation applications such as the separation of water/ethanol, alcohols, and organic solvents[154,155]. Pervaporation is a membrane separation process that utilizes a semi-permeable membrane to selectively separate a liquid mixture by preferentially permeating one component over the other through the membrane.

In MOF-based membranes, the MOF particles or crystals are used as fillers in the polymer matrix to create a composite membrane. During pervaporation, the liquid mixture is introduced to one side of the membrane, while a vacuum or sweep gas is applied to the other side to remove the permeate component. The MOF-based membrane selectively adsorbs the permeating component, allowing it to diffuse through the membrane, while the non-permeating component is rejected and remains in the feed. The selectivity and permeability of MOF-based membranes can be tuned by adjusting the pore size, surface chemistry, and functional groups of the MOFs. The use of MOFs in pervaporation has shown promise for the separation of various liquid mixtures, including water-ethanol, toluene-cyclohexane, and benzene-cyclohexane mixtures. It is an increasingly popular technique used for separating liquids in various industries, including bio-refinery, petrochemical, and pharmaceuticals. The separation process is based on differences in sorption and diffusion of a liquid mixture[156,157]. To enhance the performance of pervaporation, MOFs have been proposed as an effective additive due to their ability to improve sorption, diffusion, and stability [158,159].

Ongoing research into MOF-based membranes for pervaporation has identified potential applications for both mixed matrix membranes and continuous MOF-based membranes. While MMMs have shown excellent results in pervaporation, research on continuous MOF-based membranes is still in its early stages. Recent studies have demonstrated the effectiveness of continuous ZIF-71 membranes in separating alco-

hols from alcohol-water mixtures, with slower diffusion rates observed for ethanol compared to methanol due to differences in their kinetic diameters [159,160]. Additionally, a new approach for precise measurement of window size in ZIF-8 MOF have been shown for efficient separation of xylenes. The results predicted the 92–95 % removal efficiency was achieved under controlled conditions [154].

Recently, a PVA/Uio-66 MOF mixed matrix membrane fabricated for organic dehydration via pervaporation [96]. The membrane showed excellent separation performance for separating n-butanol (BuOH) from BuOH/H₂O and BuOH/ethanol solutions, with a substantial rise in flux with the increase in feed water concentration and a separation factor decrease considerably. Also, the result indicated that the MMM with 15 %wt Uio-66 provides the very high separation index of 2560 kg/m².h at 343 K (70 °C). Moreover, the Uio-66/PVA film displayed exceptional durability throughout the pervaporation stability examination (240 h), even following exposure to hostile conditions that certain marketable films are incapable of enduring. Another research validated the organic selectivity of Uio-66 films in the pervaporation process, showcasing the enduring nature of continuous Uio-66 films in separating ethanol/water combinations [121]. Additionally, a comprehensive review on Uio-66 membranes was reported to have potential applications in pervaporation [176].

3.2. Water treatment

Water treatment is one of the most crucial applications of MOF-based membranes in liquid separation processes. MOF-based membranes can separate and removing various impurities from water, including heavy metal ions, organic contaminants, and microorganisms. In water treatment, MOF-based membranes can be used in various processes, including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis [161,162]. The separation mechanism of MOF-based membranes is mainly based on size exclusion, electrostatic interactions, and affinity interactions between the membrane and the impurities. Furthermore, the stability and durability of MOF-based membranes make them attractive for long-term applications in water treatment processes. The potential of MOF-based membranes for water treatment has been demonstrated in various studies, and the development of these membranes for large-scale water treatment is a growing area of research [163,164].

3.2.1. Dye removal

MOF membranes are gaining popularity in liquid separations due to their ability to compete with RO membranes [165]. Depending on MOF composition, the pore window of MOFs can vary from 0.3 nm to more than 10 nm, placing MOF-based membranes firmly within the nanofiltration range, allowing them to focus on dye removal. Among various MOF membranes, Karthikeyarajan et al. evaluated the separation performance of a photocatalytic MOF-embedded polysulfone (PSF) membranes for the removal cationic rhodamine B (RhB) and anionic methyl orange (MO) from the water. The final PC-MOF membranes showed a higher flux with good retention for RhB and MO (≈ 90 %) than a bare PSf membrane. In addition, the PC-MOF membranes exhibited remarkable selectivity [170].

Similarly, in another study ZIF-8/PEI hybrid membrane effectively removed aqueous methyl blue solution with the rejection of 97 % [167]. Meanwhile, Xin et al fabricated in situ synthetic modified metal organic framework (MZIF-8) composite membrane for dehydrating ethanol. The membrane flux improved from 0.18 kg/m².h to 4.47 kg/m².h, while separation factor decreases from 318 to 127. The unusual trend in flux and separation factor breaks the trade of law. Moreover, the selectively for water–ethanol mixtures was found to be five times higher than the ideal water/ethanol solution, and under the harsh conditions the MOF-membranes showed good stability [168]. In the meantime, the composite membrane demonstrated efficient removal of Congo red

(CR), methyl blue (Mb), alizarin red (AR), methylene blue (MBA) showed the better removal efficiency in the long run test. The membranes revealed high rejections for all dye solutions (> 99 % for MB, CR, MBA, and AR; > 97 % for MO and IA) [169].

3.2.2. Heavy metal ions removal

MOF-based membranes have shown potential for wastewater treatment applications beyond dye removal. Due to their high surface area and porosity, they have been explored for removing heavy metal ions from wastewater. For instance, an advanced MOF-embedded polyacrylonitrile membrane was developed through a solvothermal reaction and electrospinning process to concurrently separate oil-in-water emulsions and adsorb heavy metal ions with a high adsorption capacity of Cd²⁺ and Cu²⁺. The adsorption effectiveness of Cu²⁺ rose from 68.2 % to 85.5 %, while the adsorption effectiveness of Cd²⁺ climbed from 65.7 % to 81.9 %. The membranes with greater MOF content exhibited enhanced efficiency in heavy metal ion adsorption. However, an overly high MOF concentration led to a reduction in the separation flow rate and the rigidity of the PME membrane [170]. Overall, the membrane is highly effective for wastewater treatment and holds significant potential for real-world applications. Similarly, an embedded membrane made from Ni-Zn MOF was created through phase inversion and sintering techniques to remove Pb²⁺ from aqueous solutions. Various key parameters, such as concentration and pH, were examined to determine their influence on the adsorption process. At a pH of 8 and with the aid of 2 % PVP, the maximum removal rate for Pb²⁺ was found to be 98 % when using a 0.05 % Ni-Zn MOF membrane, with a feed solution containing 80 mg Pb/L [171]. There have been number of works published for metal elimination via membranes [172,173]. However, these MOFs have not yet been utilized in the formation of membranes for water purification.

3.2.3. In reverse osmosis process (RO)

In recent years, MOF-based membranes have gained attention for their potential use in RO processes [174,175]. One advantage of these membranes is their ability to enhance membrane roughness and durability. A study of high performance TFN membrane containing ZIF8/CNT for RO desalination has been reported. These ZIF-8/CNT have shown high rejection rates for NaCl, ranging from 97 % to 100 %, and permeance levels exceed those of commercial RO membranes by one to two orders of magnitude [155]. To enhance the design of membranes, MOFs have been suggested as a possible nanofiller for creating MOF-based thin-film nanocomposite (TFN) structures. In a recent study, ZIF-8 was utilized as a nanofiller in TFN membranes for water desalination, which resulted in a notable rise in NaCl rejection of up to 99.3 % while still maintaining high permeance. These findings showcase the potential of MOF-based TFN membranes as a viable substitute for current commercial membranes [176].

3.2.4. Antifouling membrane

MOFs have been studied for their potential applications in antifouling membranes. The unique features of MOFs, which consist of metal cores and organic ligands, make them suitable for this purpose. A recent study demonstrated the addition of both MOFs to PES and sulfonated PES membranes resulted in a greater reduction of the water contact angle compared to pristine PES membranes. Incorporating MOFs into the PES membrane matrix significantly improved membrane performance, with a notable increase in flux (up to 565 LMH for PES + Uio-66-NH₂) while maintaining a high level of bovine serum albumin (BSA) rejection. The addition of MOFs to the PES matrix also led to a substantial increase in the flux recovery ratio (over 99 % for most mixed matrix membranes). Furthermore, the mixed matrix membranes exhibited greater resistance to protein adsorption compared to pristine PES membranes. Even after immersion in water for 3, 6, and 12 months, both MOFs remained structurally stable [177]. This study provides insight

into the potential of MOFs for developing antifouling membranes for various applications.

3.2.5. Applications in antimicrobial activity and forward osmosis (FO)

MOF-based membranes have also been investigated for their potential antimicrobial activity. Hybrid nanosheets of ZIF/GO have been incorporated into these membranes to achieve a synergistic effect that enhances their antimicrobial properties. Studies have revealed that ZIF-8/GO nanocomposites exhibit greater antimicrobial (84.4 %) activity than ZIF-8 or GO alone, with a minimum inhibitory concentration of 128 mgL^{-1} . Wang et al published their work, which involves gradual release of Zn^{2+} from ZIF-8, in combination with the antimicrobial activity of graphene oxide (see Fig. 18). These findings illustrate the potential of ZIF-8-based nanocomposites as multifunctional antimicrobial agents for various applications[178]. Nanocomposite membranes containing MOFs have shown potential in improving the performance of FO for desalination and wastewater treatment. Researchers have modified membranes with UiO-66 MOFs to reduce transport resistance and internal concentration polarization of the membrane, leading to improved water permeability and maintained salt rejection levels. Mojtaba et al. considered the incorporation of graphene quantum dots (GQD) in the UiO-66- NH_2 MOF to facilitate the water attraction of MOF surface and their affinity with the polyamide layer matrix of forward osmosis membranes[182]. By incorporating GQDs@MOF particles, the water flux and selectivity of FO membranes were altered. Furthermore, the selectivity was approximately 1.5 times greater than that of the control membrane lacking GQDs@MOF particles, demonstrating the importance of membrane design in achieving this goal. Another study incorporated MOF nanocrystals into the thin PA layer of TFC membranes, resulting in a more hydrophilic surface and lower transport resistance, ultimately improving desalination performance without compromising membrane selectivity[183]. These findings demonstrate the potential of MOFs for developing more efficient and effective FO membranes for water treatment applications.

3.2.6. Oil/Water separation

MOF-based membranes have been found to have potential applications beyond desalination and wastewater treatment, including oil/water separation. For example, Wang et al. developed biodegradable

nanofiber membrane of poly (lactic acid) and ZIF-8 with carbon black (ZIF-8@C600) by electrospinning. The PLA/ZIF-8@C600 porous membranes exhibited favorable oil sorption properties for oil–water mixtures and emulsions. In particular, the oil adsorption capacity of the sample containing 1 wt% ZIF-8@C600 was enhanced by approximately 72.59 % in comparison to pure PLA (13.5 g^{-1}), indicating that the PLA/ZIF-8@C600 fibers were effective oil sorbents. Furthermore, the adsorption kinetics of the membranes on paraffin liquid were consistent with pseudo-second order kinetics[184]. Furthermore, MOFs have been also explored for their potential to remove micropollutants for instance, endocrine-disrupting chemicals (EDCs) from water sources due to their high adsorption capacity. Xu et al. focused on the development of an innovative biocatalytic enzyme/MOF composite membrane to enable the efficient and continuous removal of bisphenol A (BPA) from aqueous solutions. The results showed that ZIF-8 incorporation enhanced both the membrane adsorption capacity and water permeability. Moreover, the resulting membrane achieves a new record of 98 % BPA removal efficiency with high permeance ($\sim 33.32 \text{ L/m}^2\text{h.bar}$) in continuous mode. Also, the biocatalytic membrane displays remarkable stability and reusability because of the protective effect of the ZIF-8 exoskeleton, which validates its potential for stable and effective exclusion of micropollutants in water treatment applications[185].

3.3. Organic solvent nanofiltration (OSN)

OSN is a membrane-based liquid separation process that is especially effective for separating small molecules from organic solvents. In an OSN process utilizing MOF-based membranes, a solution containing a mixture of small molecules and solvent is introduced into a membrane module, where it contacts a MOF-based membrane. The small molecules, which are smaller than the membrane pore size, can pass through the membrane and are collected in the permeate stream. Conversely, the solvent, being too large to pass through the membrane pores, is retained in the feed stream. The separation process is driven by a pressure difference across the membrane, with higher pressure on the feed side and lower pressure on the permeate side. This pressure difference forces the solvent and small molecules against the membrane, and as the small molecules pass through the membrane pores, they are collected in the permeate stream. The MOF-based membrane's selectivity in OSN is de-

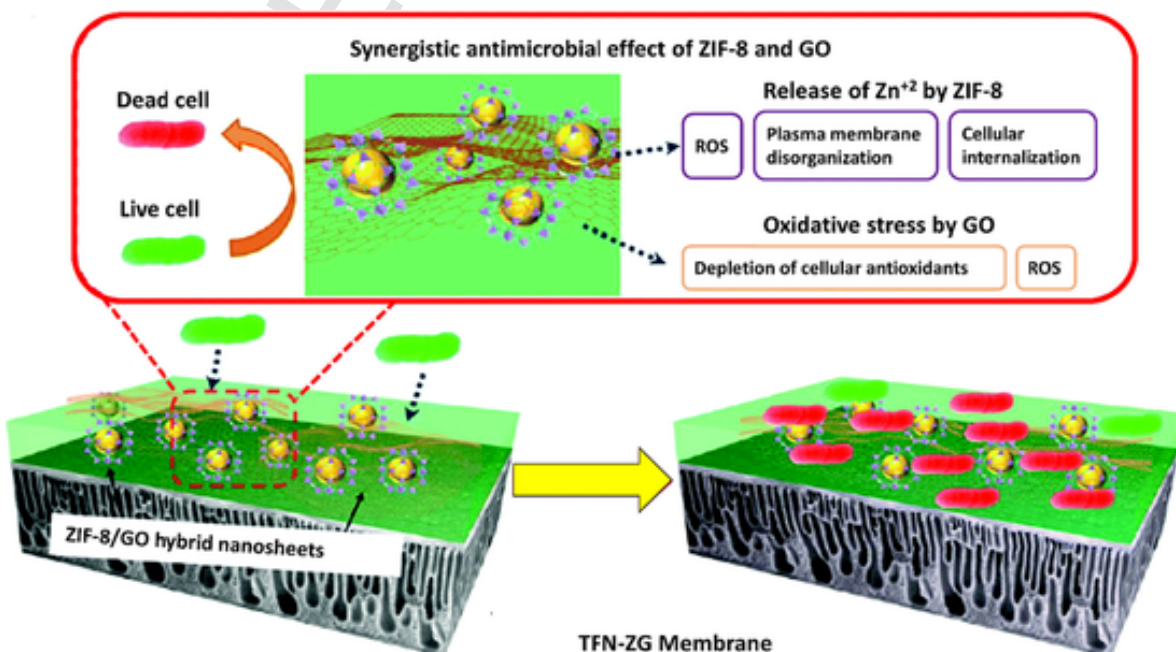


Fig. 18. The Schematic illustration for ZIF-8/GO TFN membranes. Adopted from[2 1 2].

terminated by the size and chemical properties of the membrane pores. MOFs can be tailored to possess specific pore sizes and functional groups, allowing them to selectively separate different types of small molecules. Moreover, the high permeability of MOF-based membranes enables high flux rates and high recovery rates of the permeate stream. Table 4 gives different types of MOFs and ZIFs used in OSN[181].

In addition, the porosity and pore size of MOFs can be tuned to increase solvent flux while maintaining high rejection levels. Li et al. proposed physical and embedding methods of combining MOFs and membranes for OSN to design MOF-based Thin Film Nanocomposite membranes[113]. Karimi et al. demonstrated the potential of mixed matrix membranes by incorporating of ZIF-8 as an additive in the matrix of polyvinylidene fluoride (PVDF) membrane. Incorporating 25 wt% of ZIF-8 into MMMs resulted in a rejection rate of 99.5 % for Rose Bengal (RB) solution in isopropanol (IPA), which is 15 % higher than that of the bare PVDF membrane. During the filtration of RB solution in IPA, blended membranes containing 25 wt% of ZIF-8 experienced a flux reduction of 4.1 %, whereas the bare PVDF membrane experienced a reduction of 16.1 % [95]. Moreover, Shi et al. have recently summarized the progresses in the development of state-of-the-art OSN in their review. This can be improved through chemical modification, which can also enhance OSN performance. One study demonstrated the high rejections and high permeance of an OSN membrane with a molecular weight cut-off of 794 g/mol[186].

Furthermore, Li et al. presented a new category of TFN membranes that contain covalent organic frameworks (COFs) nanoparticles in the polyamide skin layer, resulting in improved solvent permeation flux and high solute rejection for organic solvent nanofiltration[187]. The prepared TFN membranes demonstrated enhanced surface hydrophilicity and reduced skin layer thickness, resulting in a 46.7 % increase in ethanol permeance (up to 79.8 L m⁻²h⁻¹ MPa⁻¹) compared to membranes without COFs. The prepared TFN OSN membranes demonstrated exceptional solvent resistance after static immersion in N, N-dimethylformamide (DMF) at ambient temperature for over 100 days, and after consecutive crossflow filtration using Rose Bengal/DMF solution at ambient temperature for over 7 days, with no significant change in separation performance. Moreover, Echaide-Gorritz et al. investigated the impact of combining two different MOFs (ZIF-11 and MIL-101(Cr)) on the performance of a TFN membrane[188]. The resulting membrane displayed improved rejections compared to bared membrane. These results demonstrate the potential of MOF-based TFN membranes for OSN applications, particularly in the separation of complex mixtures.

4. Conclusion and outlook

The field of MOF-based membranes has a extensive potential for a practical and theoretical applications. With the emergence of MOFs that are stable in water and techniques for modifying them after synthesis, MOF-based membranes have broadened their range of applications to encompass not only gas absorption and catalysis but also liquid separation,

particularly in the field of water treatment. Recent progress in the production of MOF-based membranes has tackled important parameters such as durability, ability to disperse, and hydrophilicity or hydrophobicity, leading to noteworthy enhancements in their overall effectiveness. Furthermore, scientists are acquiring an enhanced comprehension of the formulation mechanisms for MOF-based membranes. They are investigating both traditional and interfacial polymerization techniques to fabricate continuous MOF membranes, as well as MOF-based MMMs and thin-film nanocomposite or thin-film composite membranes. These advancements play a crucial role in propelling the utilization of MOF-based membranes in real-world scenarios and theoretical contexts. Attempts to enhance the utilization of membranes composed of MOFs have resulted in the emergence of numerous techniques, such as self-assembly strategies. Nevertheless, in order to fully capitalize on the benefits offered by these membranes, it is essential to enhance the fusion of MOFs and polymers, as well as the mechanical and processing characteristics of the polymer. An ideal solution would involve a composition that seamlessly integrates MOFs and polymers, while preserving their individual chemical and physical attributes. Despite the advancements achieved so far, certain methods may possess restrictions that impede their potential implementations. For example, the micropores of MOFs may collapse during hybrid processes due to the addition of oxygen in the group, which can limit their use in some applications. Therefore, there is a need to explore new methods that address these challenges and enable the full potential of membrane.

The efficacy relies on the loading quantity of metal ions and the dispersion of MOF. Self-assembly strategies are typically employed to produce composite membranes based on MOF. However, the utmost loading of metal ions in these membranes restricts the number of MOFs utilized. This restriction can be surmounted by judiciously opting for different functional groups and enhancing surface modification techniques. These advancements enhance the concentration of functional groups and the bonding capability between precursors and groups, resulting in elevated loading levels. However, high loading amounts can cause MOF aggregation, reducing separation performance. Achieving a balance between loading amount, MOF dispersibility, and separation performance remains a major challenge in MOF-based membrane design. Advances in MOF-based membrane technology have enabled the separation of single components in liquid environments, as well as synchronous separation of multi-component and multifunctional MOF-based membranes, marking significant milestones in the field of liquid separation.

MOF-derived films possess immense possibilities for various uses, especially in the separation of liquids via adsorption or catalysis processes. To broaden their scope, MOFs have been amalgamated with other nanostructured constituents to create versatile nanocomposites, harnessing the advantages of both materials. Challenges still remain for the future application of MOF based membranes to industrial manufacturing. On the one hand, the experience detailing durability of these membranes when subjected to realistic separation conditions is limited. Additional research is essential in comprehending the stability of such membranes and enhancing their functionality for practical applications. The high cost of MOFs is a significant obstacle to the large-scale production and commercialization of MOF-based membranes. In recent years, researchers have been developing more cost-effective synthesis methods for MOFs that consider economic and environmental considerations, with a goal of avoiding expensive or rare raw materials. Therefore, it is essential to design more cost-effective MOF-based membranes that can reduce production costs and be used in industrial applications. Ensuring the enduring long-term stability of MOF-based membranes in realistic liquid separation conditions should be a topmost concern, alongside investigating their prospective multifarious applications in alternative environmental domains.

Table 4
List of MOFs and ZIFs used for OSN.

Sr. no.	MOF	Metal	Ligand	Window size (nm)	Ref.
1.	HKUST-1	Cu	1,2,4-benzenetricarboxylic anhydride	0.9	[128]
2.	mZIF-8	Zn	2-methyl imidazole	0.64—0.74	[184]
3.	MIL-1019 (Cr)	Cr	terephthalic acid	1.2—1.6	[188]
4.	MIL-1019 (Al)	Al	terephthalic acid	0.6—0.64	[189]
5.	ZIF-11	Zn	benzimidazole	0.3	[190]
6.	ZIF-67	Co	2-methyl imidazole	0.343	[191]
7.	UiO-66 NH ₂	Zr	2-amino terephthalic	0.89	[101]

Uncited references

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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