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Current Trend of MOFs Incorporated Membranes for Advanced Wastewater Treatment

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Abstract. Membrane technology has gained attention in wastewater treatment due to its great potential for producing high-grade water products for reuse. The membrane also effectively removes persistent pollutants in water effluent. However, their application is constrained by low productivity due to fouling formation. Incorporating functionalized nanoparticles into polymeric membranes has attracted much attention due to the improved membrane performance and additional features. Metal-organic frameworks (MOFs) incorporated into polymeric membranes have been widely applied in reverse osmosis (RO), forward osmosis (FO), nanofiltration (NF), and microfiltration (MF) for water and wastewater treatment. This short review presented recent findings, fabrication methods, and a systematic understanding of transport mechanisms under various operating conditions. This study also focused on several important parameters, such as improving physicochemical properties, membrane features, and performance enhancement in wastewater treatment. The reported studies show that MOFs incorporated membranes have reached >95% organic pollutants and 100% suspended solids. The membrane durability was also enhanced up to 140%, and the flux recovery can be maintained at 98% after several cycles. Even some MOFs, such as ZIF-8 and UiO-66, exhibited excellent performance in harsh conditions ($pH < 4$). The prospects and challenges of MOFs-incorporated membranes in industrial applications were also provided in this study.

Keywords: Antifouling, Metal-organic frameworks, Membrane, Wastewater, Water purification

INTRODUCTION

Wastewater treatment using membrane technology has been developed to achieve more advanced treatment. Membrane separation based on advanced polymers has been considered a promising technique for dealing with wastewater treatment containing persistent organic pollutants (POPs) due to their high separation efficiency, relatively low cost, and sustainability (Bai et al., 2021). Currently, many hazardous and emerging contaminants, such as POPs, are discharged from industrial activity that

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tremendously danger the water ecosystem and human health (Wagner et al., 2021; Wibowo et al., 2021). The most commonly encountered POPs in wastewater are synthetic dyes (Shukrullah et al., 2021), agricultural waste such as pesticides and herbicides (Panis et al., 2022), endocrine disruptive chemicals (EDCs) from pharmaceutical waste such as antibiotics, anti-inflammatory, phenols, etc. (Ojha et al., 2021), organochlorine such as polychlorinated biphenyls (PCB) (Yasir et al., 2021), polychlorinated dibenzo-p-dioxins (PCDD), and dibenzofurans (PCDF) (Hashimoto et al., 2021). Advanced membrane separation is a promising and futuristic method for removing these POPs from wastewater due to their flexibility, wide range separation, and adjustable features (Kusworo et al., 2022). However, fouling growth still restricts its application,, resulting in higher operating and maintenance costs due to decreased product recoveries, feed water loss and permeate quality deterioration, shortened operating time, and premature membrane replacement (Esfahani et al., 2019). Membrane fouling is generated by the deposition of rejected particles or compounds on the membrane surface during membrane filtration in either a pressure-driven or temperature-driven process.

There are several techniques that many researchers have developed to mitigate fouling formation in water and wastewater treatment such as surface modification (Ding et al., 2022), filler addition (Yadav et al., 2021), in-situ chemical cleaning (Sun et al., 2019), integrated membrane filtration (Ratman et al., 2020), membrane vibration (Zhao et al., 2018), and ultrasonicated membrane (Qasim et al., 2018). Among these techniques, nanoparticle filler addition to form nanocomposite membrane have driven considerable attention in recent years. Incorporating hydrophilic nanoparticles has been reported to enhance fouling resistance and effectively overcome the trade-off relationship between permeability and solute rejection (Castro-Muñoz et al., 2021). Interestingly, recent studies have attempted to incorporate photocatalyst nanoparticles into polymeric membranes to promote in-situ pollutant degradation into harmless substances (Kusworo et al., 2022). It also enables self-cleaning features that have been claimed as an effective strategy for encounter fouling formation. For example, Penboon et al. (2019) and Lin et al. (2022) have reported the effective removal of dyes in synthetic wastewater using TiO_2 photocatalyst-incorporated polymeric membrane due to a combination of molecular exclusion and in-situ degradation as well as enhanced self-cleaning property. Ariyanti et al. (2021) have reported the performance of TiO_2-incorporated PVDF hollow fiber membrane in a submerged module; they discovered that low TiO_2 loading (0.5 g/L) lowered fouling tendency in the dye removal process. The combination of multiple fillers was also attempted to improve the performance, such as combining ZnO photocatalyst with cellulose nanocrystal, which facilitated the photocatalytic reaction under visible light (Cumba et al., 2022). Despite the excellent performance offered by nanocomposite membranes, the possibility of nanoparticle leaching during filtration is a critical issue that causes another contamination in the treated water. One of the attractive solutions is improving the interaction between nanoparticle and host polymer through a junction of organic ligands by incorporating metal-organic frameworks (MOFs) into the polymer matrix. MOFs are three-dimensional framework porous material consisting of metal ions and self-assembled organic ligands in a rigid periodic network structure that has a large specific area, adjustable pore and topology, and tolerability (Xiao et al., 2019). These excellent characteristics make MOFs the most promising material in fabricating high-performance nano-composite membranes.

There are unlimited combinations of metals and organic ligands to form various structures of MOFs. However, not all MOFs are suitable as membrane filler; some of them have poor stability in water, while others show good stability, such as MOF-74, ZIF-8, MIL-101 (Al, Fe, Cr), MIL-53 (Al, Cr), and UiO-66 (Zr, Ce) (Safy et al., 2020; Yang et al., 2018). MOFs integrated membranes are preferred due to their tunable structure, which exhibits enhanced membrane permeability and selectivity (Aljundi, 2017). Therefore, recent strategies in improving the MOFs structure stability, polymer compatibility, and most recent MOFs incorporation techniques are discussed. Furthermore, this review highlights special features of incorporating MOFs into polymeric membranes, such as enhanced hydrophilicity, photocatalytic properties, antifouling behavior, and self-cleaning ability. The summary of the potential application of MOFs-incorporated membranes for various wastewater treatments is presented. The future trends and challenges of MOFs incorporation into nanocomposite membranes in the field are also provided.

Synthesis Method of Metal Organic Frameworks

MOFs can be synthesized by linking inorganic units such as metal nodes, metal clusters, metal ions, and organic units (organic ligands or organic linkers) through firm bonds to form rigid structures (Qian et al., 2021). Unlimited variations of structural geometry, pore size, and functionality of MOFs can be achieved between metal nodes and organic linkers, resulting in more than 84,000 different MOFs being synthesized in the last two decades (Al Amery et al., 2020). Common metals used in MOFs synthesize alkaline earth metals (Ca or Mg), transition or semiconductor metals such as Fe, Mn, Zn, Zr, Ti, Ce etc. (Rocío-Bautista et al., 2019). Common organic ligands are oxalic acid, dicarboxylic acid, tricarboxylic acid, tetracarboxylic acid, and imidazolate (Sharanyakanth & Radhakrishnan, 2020).

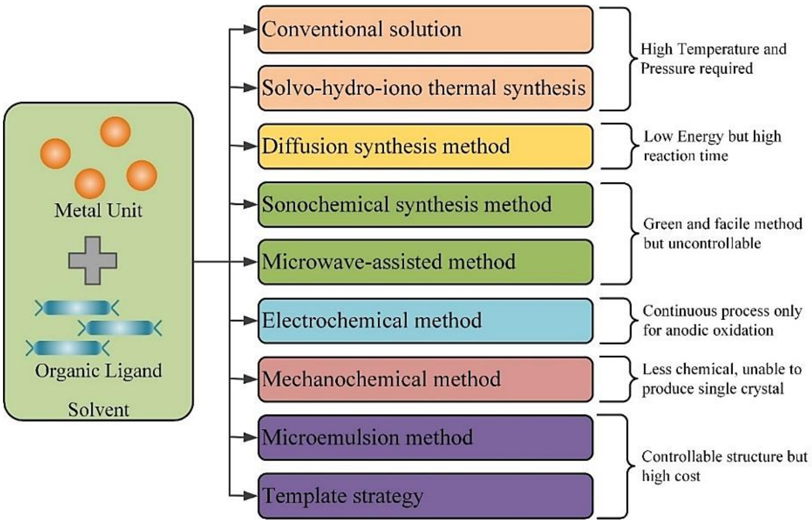

Fig. 1: Synthesize methods for producing MOFs with different approaches

Due to the structural geometry flexibility of MOFs, there are sub-class of MOFs that depend on their structure and constructing materials i.e., Isoreticular Metal-Organic Frameworks (IRMOFs), Zeolitic Imidazolate Frameworks (ZIF), Materials of Institute Lavoisier-frameworks (MILs), Pocket-Channel frameworks (PCNs), and University of Oslo (UiO) (Kusworo et al., 2022). The nature of MOFs produced depends on the type of source materials, the type of energy generated, and the synthesis methods. Several synthesis methods are suitable for large-scale processes, such as conventional solution, solve-hydro-iono thermal process, and electrochemical synthesis. The other methods are facile and green techniques such as sonochemical, microwave-assisted, and template strategies. Figure 1 presents the synthetic methods for producing MOFs.

Conventional Solution Method

This method was classical and the most common method used to synthesize MOFs. Metal sources, organic ligands, and other raw materials are mixed in a solvent by stirring for a specified period at a certain temperature. Then, the precipitate formed during the reaction was separated, and further solvent evaporation was done to obtain pure MOFs crystals. Moh et al. (2011) synthesized ZIF-8 by dissolving an appropriate amount of $Zn(NO_3)_2.4H_2O$ and 2-methylimidazole in dimethylformamide (DMF) as solvent. The mixture was continuously stirred for 30 min and then heated at 120 °C for 24 h to allow the growth of ZIF-8 crystals. The MOFs precipitate is usually washed using methanol to remove the remaining solvent in the crystal pores. Santoso et al. (2021) developed a facile technique to produce ZIF-8 using the acetic acid solution as a green solvent. In this method, they prepared two solutions of Zn^{2+} and 2-methylimidazole in 2% acetic acid and triethylamine. After that, the second solution is gradually added to the first solution in continuous stirring at room temperature for 24 h. However, the crystallinity index of ZIF-8 obtained from acetic acid solvent was lower than that obtained from DMF solvent.

Solvo-hydro-iono Thermal Method

Solvothermal, hydrothermal, and ionothermal are synthesis methods carried out in closed vessels under autogenerated pressure above the solvent's boiling point (Rabenau, 1985). So far, solvothermal and hydrothermal methods are the most common to produce MOFs. In solvothermal, polar solvents such as dimethyl formamide, diethyl formamide, methanol, ethanol, Me_2CO, MeCN, or their mixture are usually utilized. The hydrothermal method uses H_2O as a solvent. The reactions typically take place in a closed vessel (Teflon autoclave) at a temperature range of 50 - 260°C. The elevated temperature is required to facilitate bond formation and to ensure proper crystal growth. UiO-66-BDC, for example, was synthesized via the solvothermal method by reacting the Zirconium (Zr^{4+}) with terephthalic acid as an organic ligand in DMF solvent at a temperature of 100 °C (Lammert et al., 2015). Hu et al. (2020) used a mixture solvent of water and formic acid to synthesize MOF-808 with Hf^{4+} as metal ions and 1,3,5-benzene tricarboxylic acid as an organic ligand. The reaction is carried out at 100 °C for 12 h. In this method, the temperature and reaction time affect the crystal morphology, where prolonged reaction time and raised temperature may lead to decomposition. Lammert et al. (2015) also reported that UiO-66-BDC(Ce) synthesized via solvothermal 30 wt% decomposed at 300 °C. The ionothermal method is a sub-class of solvothermal methods in which ionic solvents are used during the reaction. Ionic solvents are considered environmentally friendly compared to conventional organic solvents. The advantage of the ionothermal method is controlled MOFs physicochemical properties by changing the ionic solvent composition (Bian et al., 2018). However, the presence of ionic residue in generated MOFs crystals becomes one of the major issues in this method.

Diffusion Synthesis Method

In the diffusion method, two techniques were based on conveying the various species into interaction. The first method is solvent liquid diffusion, where two layers of liquid have various density levels, one being the precipitant solvent and the other encompassing the product in a solvent. In this method, MOFs crystals are formed due to the surface contact reaction between metal ions and organic ligands (Tan & Foo, 2021). The second method, the reactants are gradually diffused via physical barriers such as gels (Safaei et al., 2019). The advantage of this method is achieving single crystals that are appropriate for XRD analysis. However, the drawback of this method is a longer reaction time (Sharanyakanth & Radhakrishnan, 2020).

Sonochemical and Microwave-Assisted Method

The sonochemical method is the formation of MOFs crystals from raw reactants with the help of high-energy ultrasound exposure ranging from 20 kHz to 10 MHz. Ultrasound radiation forms acoustic cavitation, creating short-lifetime hot spots with high temperature and pressure (Savun-Hekimoğlu, 2020). The energy from ultrasound radiation is required for bond formation during MOFs crystal growth. The sonochemical method is considered facile, environmentally friendly, energy-efficient, easy to use, and can be applied at ambient temperature. In the microwave-assisted method, reaction heating is generated by dielectric heating instead of external conduction heating (Gabriel et al., 1998). Microwave devices promote an oscillating electric field with the permanent dipole moments of molecules in the medium, causing the molecules' rotation and the liquid's rapid heating. Microwaves can induce uniform and intense heating and thus promote uniform nucleation and crystal growth of MOFs. Cui et al. (2021) successfully synthesized ZIF-67 using a microwave-assisted method where the reaction can be shortened to 30 min at 150 °C under 300 W microwave irradiation. The advantages of this method are the green synthesis, energy efficiency, short reaction time, and the fact that single crystals can be obtained.

Electro-Mechanochemical Method

Electro-mechanochemical method refers to electrochemical and mechanochemical methods. In the electrochemical method, the metal ion is provided by anodic dissolution into a reactant mixture that contains organic ligands. This method can be operated continuously and is suitable for industrial scale. The advantages of this method are mild temperature reaction, extremely fast reaction, and avoidance of anions from metal salts. However, crystal growth occurs in the bulk step due to the in-situ production of metal ions. ZIF-8 (D. Zhang et al., 2021), MIL-100(Fe) (Lestari et al., 2016), and MIL-53(Al) (Millange & Walton, 2018) were examples of MOFs that were successfully synthesized using the electrochemical method. The mechanochemical method is solvent-free and uses mechanical forces to form coordination bonds by either manual grinding of reagents or automatic milling. There are several attractive reasons for MOFs synthesis via mechanochemistry, including room temperature reaction, avoiding any organic solvents, and quick reaction time (10 – 60 min), leading to quantitative yields (D. Chen et al., 2019). ZIFs, HKUST-1, and MIL-78 have been successfully synthesized using the mechanochemical method (Pichon et al., 2006; P. Zhang et al., 2015).

Microemulsion Method

Microemulsions are an isotropic mixture of two or more immiscible liquids in a single phase in the presence of surfactants. Polar and non-polar species simultaneously provide a unique microenvironment for processing chemical reactions to synthesize nano-scaled materials (Ye et al., 2018). The micelles of the microemulsions act as nanoreactors and control nucleation and crystal growth kinetics. The MOFs synthesis using the microemulsion method is considered a simple method, has no energy input, and operates at room temperature, while the major drawback is the use of surfactants that cause environmental pollution.

Template Strategy

Template strategy is the recently developed method for synthesizing MOFs materials with desired mesoporous structure by using structure-directing agents. The common hierarchical molecular templates are the surfactants, coordination compounds, polyoxometalates, block co-polymers, and rarely biomacromolecules are. Kirchon et al. (2018) have reported that meso-structured MIL-53(Al) has been prepared using block co-polymers P123 and F127 as structure-directing agents a hierarchically porous version of HKUST-1 using CTAB as a templating agent. Huang et al. (2012) synthesized MIL-101(Cr) using cetyltrimethylammonium bromide as a supramolecular template. The mesopore diameter of the formed MOFs strongly depends on the hydrophobic volume of templating agent aggregates. The advantage of this method is tunable mesopore structure by varying templating agents.

MOFs Incorporation in Membrane

Due to the superior properties of MOFs and membrane separation performance, MOF-incorporated membranes have been recently developed as a new class in membrane composite for liquid separation. The incorporation MOFs membrane can be either in inorganic ceramic membranes (N. Wang et al., 2016), polymeric membranes (S. Zhang et al., 2020), or self-assembled membranes (Cao, Su et al., 2018). In this review, we focused on reviewing incorporating of MOFs into polymeric membranes due to their high tailorable properties. MOFs are preferred to be combined with polymeric membranes due to their tunable porosity, excellent selectivity, permeability, and better compatibility with polymers, providing special properties such as photocatalytic activity. These special features gave them great potential for practical water and wastewater treatment. MOFs have been involved in the fabrication of MF, UF, NF, RO, and FO membranes for various applications.

MOFs can be incorporated into the polymer matrix in various ways depending on the desired specific structure of the fabricated nanohybrid membranes. Bulk blending is the simplest method for combining MOFs with polymeric membranes. The prepared MOFs powder was dispersed in polymer solvents, such as DMF, DMAc, NMP, Acetone, etc., and followed by polymer powder (PVDF, PES, PSf, etc.,) to form a stable dope polymer solution. The polymer solution can be by either non-solvent, vapor, or thermal induced phase-inversed. Cheng et al. (2019) developed alumina fumarate MOF/PVDF hollow fiber via simple bulk blending followed by dry-jet wet phase inversion. In some cases, ultrasonication is required to avoid MOFs particle aggregation. Ren et al. (2019) incorporated MIL-53(Fe) into PVDF polymer by dispersing MIL-53(Fe) in acetone under ultrasonication for 30 min then the suspension was combined with PVDF solution. The dope solution was then cast and phase inversed via thermally induced. Despite the simplicity of the bulk blending method, the formation of aggregates during dope solution preparation is sometimes inevitable. The aggregates potentially form non-selective voids that deteriorate separation performance. Li et al. (2018) have prepared PAA/ZIF-8/PVDF hybrid ultrafiltration membrane via surface deposition of ZIF-8 nanoparticles. Firstly, ZIF-8 dispersion in 0.5 wt% TMC/n-hexane is ready to, and PVDF membrane substrate is wetted with the same solvent. The ZIF-8 dispersion is then deposited on the membrane surface via vacuum filtration. Finally, the ZIF-8 layer is sandwich-covered using polyacrylic acid (PAA). This incorporation method can prevent the formation of the non-selective void. However, there is a higher possibility of ZIF-8 particle leaching due to the particles being surface localized therefore, a further coating layer, such as PAA, is required. Modi et al. (2022) carried out a different approach where the deposition of MOFs particles is in situ grown on the membrane substrate surface. They prepared a hydrolyzed PAN membrane substrate, and then ZIF-8 was in-situ grown on the active site of the hydrolyzed membrane by incubating the membrane in an aqueous solution of $Zn(NO_3)_2.6H_2O$ for 12 h. Then the membrane was treated using 2-methylimidazole for 1 h. Modi and co-workers reported that the ZIF-8/PAN hybrid membrane has shown great hydro-stability. The incorporation of MOFs can also be decorated to a polymeric membrane substrate via interfacial polymerization, as reported by Xu et al. (2016). They prepared a pre-determined concentration of MIL-101(Cr) in an organic solution of 1,3,5 benzene tricarbonyl trichloride (BTT) and PES membrane substrate coated with m-phenylene diamine (MPD). The MPD-coated PES membrane substrate is immersed in MIL-101(Cr) containing BTT solution for interfacial polymerization. The polymerization between MPD and BTT and MIL-100(Cr) deposition occurred simultaneously. The prepared membrane via interfacial polymerization showed high stability under harsh operation; however, aggregation of nanoparticles, which existed in the dispersed phase and followed by interfacial polymerization, is difficult to avoid. In summary, figures 2 and 3 present a simplified scheme of MOFs incorporation techniques into polymeric membranes.

Strategies for Enhancing MOFs-Membrane Performance

The incorporation of MOFs into polymeric membranes has been well known to give a significant improvement in terms of permeate flux and solute rejection. However, their application limits potential particle release during filtration, hydrolysis, and particle aggregation (Modi et al., 2022; Xu et al., 2016). Several methods have been developed for surmounting the issues above and enhancing performance. Due to the flexibility of MOFs to be decorated by various

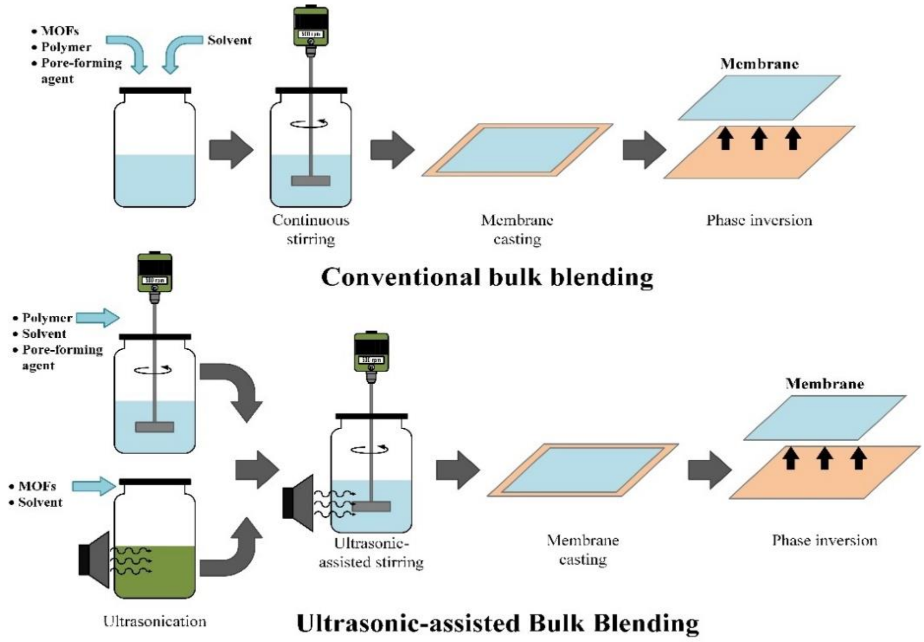

Fig. 2: MOFs incorporation methods via conventional bulk blending and ultrasonic-assisted bulk blending

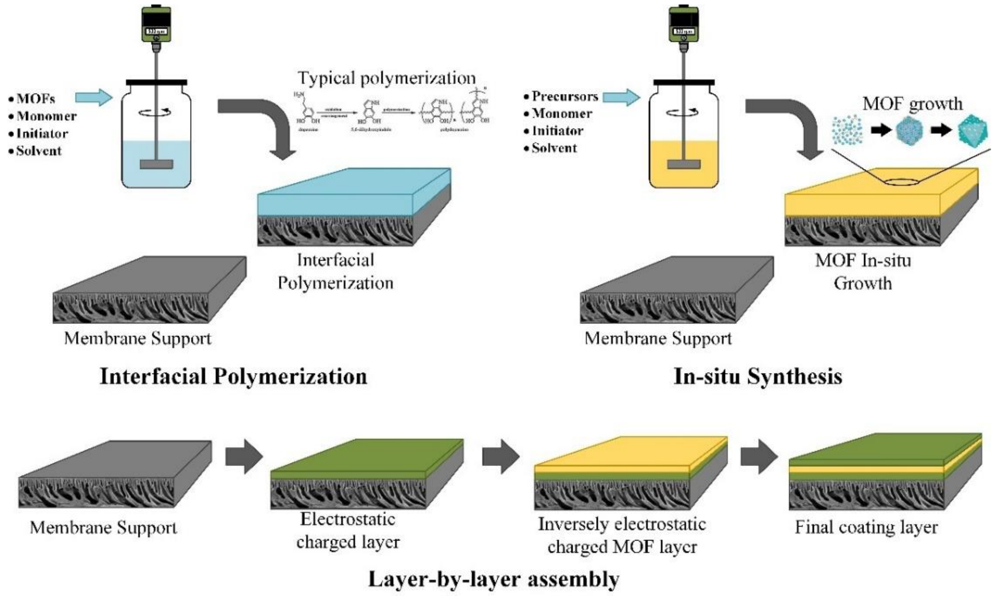

Fig. 3: Simplified schematic representation of various MOFs incorporation techniques into polymeric membrane

types of functions or elements, including organic functional groups, metal ions/clusters, non-metal elements, and carbonaceous material can be performed to enrich the host-guest chemistry where MOFs are host and solute pollutants. Proper modification attempts of MOFs potentially improve structural properties such as crystallinity, porosity, flexibility, stability, and topology (Razavi & Morsali, 2019). Based on our review of recent studies in MOF-s membrane enhancement, there are at least four techniques as follows:

Ligand functionalization

Ligand functionalization can be carried out by attaching organic functional groups into organic ligands of MOFs. The major categories of modifier groups are carbonyl-based (carboxyl, ketone, amide, urea, imide, squaramide), nitrogen-based (ammonium, imidazolium, pyridinium, amine, imine, azines, azoles), oxygen-based (hydroxyl, ethers, azoxy, oxadiazole, oxide), sulfur-based functions (thiol, sulfide, sulfonate), and other functional groups (phosphonate, halide, nitro). Amine and ammonium groups are the most common groups used for MOFs functionalization in membrane fabrication. Ahmad et al. (2020) modified ZIF-8 using amine groups via post-modification to enhance the PES membrane. They reported that amine functionalization induced a positive charge of host material that was beneficial for enhancing antimicrobial properties. Moreover, the presence of the amine group improves the hydrophilicity that significantly enhances permeate flux and flux recovery ratio up to 64% and 84%, respectively. Zhu et al. (2021) also performed a similar strategy in functionalizing MIL-125 with NH_2 group as PAA membrane filler that remarkably improved the separation efficiency of oil and dyes up to 99% with long-lasting membrane usage up to 10 cycles. Gao et al. (2021) also explained that amine functionalization improved the light absorptivity of MIL-88. Other functionalization, such as polyethylene glycol, thiol, and carboxyl, was also successfully performed and showed significant improvement of adsorptivity towards organic pollutants and heavy metal ions (Cheang et al., 2022; Ji et al., 2022; M. Wu et al., 2017). The carboxyl functionalization can involve organic ligands with higher carboxylic degrees, such as H_3BTC and H_4BTEC, as illustrated in Figure 4.

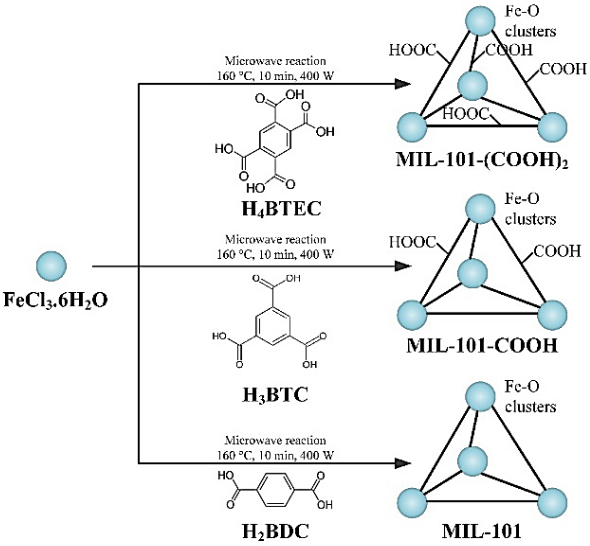

Fig. 4: Schematic illustration of MIL-101 carboxylation using different ligand linkers (Cheang et al., 2022)

Elemental Doping

Elemental doping into MOFs usually aims to improve the catalytic activity of the MOFs due to the strong interaction among the metal atoms and non-metal atoms, would be beneficial for generating more active sites (X. Wang et al., 2016) or acts as a catalyst promotor. In another report, the metal doping into MOFs may affect the electrostatic charge of MOFs and lead to higher attraction toward pollutants (Wibowo et al., 2021). Element dopants can be metal or non-metal atoms such as Fe, K, Cu, Zn, P, S, O, N, C, etc. Co-doping into UiO-66 has been reported to show higher adsorption capacity toward tetracycline up to 224.1 mg.g^{-1} where the photocatalytic activity can be improved about 7.6 times higher than pristine UiO-66 (Cao, Yang, et al., 2018). Min et al. (2019) doped the La atom into pristine UiO-66, significantly increased the phosphate capture due to the reduced coordination number from 7 to 6, exposing more adsorption sites. In other reports, the Mn-doping into UiO-66 MOF has increased the selectivity in removing Congo red dye, while Co-doping into ZIF-8 has significantly enhanced the stability in water exposure (Eltaweil et al., 2021; Taheri et al., 2020). Non-metal doping such as S atom has been successfully doped into MIL-53 and surprisingly enhanced the electro-Fenton catalysis with wide range pH (3 – 9). However, the degradation performance significantly decreased after 5 cycles run.

Semiconductor Metal Oxide/Sulfide Coupling

Many attempts have been made to combine semiconductors with metal oxides or metal sulfides to improve the characteristics and performance of the MOFs. Due to the unique properties of semiconductors, such as photocatalytic activity, the combination of semiconductors and MOFs has been reported to have a synergistic effect in increasing photocatalytic degradation for many organic compounds. Angela et al. (2021) have immobilized TiO_2 nanoparticles in hierarchical porous M-ZIF-8. 5 wt% of TiO_2 loading into M-ZIF-8 has given the highest adsorption and photocatalytic degradation towards crystal violets more than 99%. Kong et al. (2017) also reported that ZnO/CdS composited with ZIF-8 showed higher photocatalytic degradation activity under visible light. They increase the photocatalytic activity, and the semiconductor metal oxides/sulfides enhance the adsorption capacity toward heavy metals. Liu et al. (2019) revealed the increased Hg adsorption capacity of ZIF-8 up to 925.9 $mg.g^{-1}$ after being combined with ZnS. The remarkable adsorption of Hg^{2+} is attributed to the interaction of Hg^{2+} with ZnS to form HgS clusters. In MOFs-polymer hybrid membranes, very few studies reported the incorporation of metal oxides-MOFs composite to enhance the perm-selectivity of the membrane. Zarak et al. (2022) reported the development of a PDMS membrane matrix by embedding TiO_2@ZIF-8 composite for phenol removal. They found that TiO_2@ZIF-8 has good interface interaction with PDMS; moreover, the removal efficiency of phenol could be improved to 177%. Considering the great potential of combining hybrid material of metal oxides/sulfides with MOFs to be incorporated in polymeric membranes, further studies need to be developed to reveal new membrane materials with superior characteristics and performance for practical application in wastewater treatment.

Combination with Carbonaceous Materials

Carbonaceous materials have recently attracted attention for advanced material development due to their special characteristics such as metal-free nature, abundant availability, excellent resistance towards acid and alkali, ultra-high pore volumes, large specific surface area, and flexibility for various modifications. There are many derivatives of carbon materials in the form of distinct allotropic structures such as graphite, diamond, biochar, carbon nanotubes (CNT), graphene, and its derived materials, i.e., graphene oxide (GO), reduced graphene oxide (rGO), functionalized graphene oxide (fGO). Pristine nanodiamonds (NDs) are one of the allotropic forms of carbon with high sp^3-hybridized nanocrystals. Hybrid materials of NDs and UiO-66 have been revealed to have ultra-high adsorption capacity towards anionic and cationic dyes up to 556 $mg.g^{-1}$ in 2 min (Molavi et al., 2020). NDs have a narrow band gap of NDs (2.2 eV) and better light adsorption properties as the results of their unique crystalline structure of hybrid sp^2/sp^3 consequently make the MOFs combined with NDs exhibit narrowed band gap and responsive to visible light (Pan et al., 2022). CNT is the graphite sheet with a rolled-up structure dominated by sp^2 hybridization. The combination of CNT and UiO-66-NH_2 as nanocomposite membranes has been studied by C. Wang et al. (2022). The UiO-66-NH_2 was in-situ grown with CNT and then introduced to PVDF/PVA membrane. The presence of CNT effectively avoids aggregation of CNT/UiO-66-NH_2 NPs, and it can facilitate the selectivity toward sulfamethoxazole up to 2.3 times higher. Another advanced material is graphene and its derivatives (GO, rGO), which possess unique characteristics such as excellent chemical stability, high adsorption capacity, and large surface area and have been demonstrated as environmentally friendly materials. Ahmad et al. (2020) decorated ZIF-8 on a GO nanosheet via solution reaction in alkaline conditions, as illustrated in Figure 5. The ZIF-8@GO nanocomposite was then incorporated into PES hollow fiber membrane. The ZIF-8@GO/PES membrane has shown 64% higher water permeate flux compared to the neat PES membrane. Moreover, the modified membrane showed significant BSA rejection ~95% and a promising antibacterial rate of up to 86% against *E. coli* and *S. aureus*. Another report also found that combining GO with ZIF-67 induced heavy metal ions and photo-reduction of Ag^+ ions (Pei et al., 2021). GO nanosheet acts as mattress-like where MOFs are attached over the nanosheet; thus, it helps the distribution of MOFs in the membrane matrix.

Membrane Morphologies

One of the crucial aspects of membrane fabrication is the assessment of morphological properties. To understand membrane performance comprehensively, it is essential to examine magnified objects visually. In membranes incorporating MOFs, morphological analysis becomes necessary to assess compatibility, distribution, surface structure, internal structure, and any potential defects arising from integrating MOFs into the polymer matrix.

The scanning electron microscope (SEM) stands out as one of the most versatile tools for structural analysis at the micro/nano-meter scale. SEM allows for detailed observations of membrane fouling behavior, particularly concerning surface morphology.

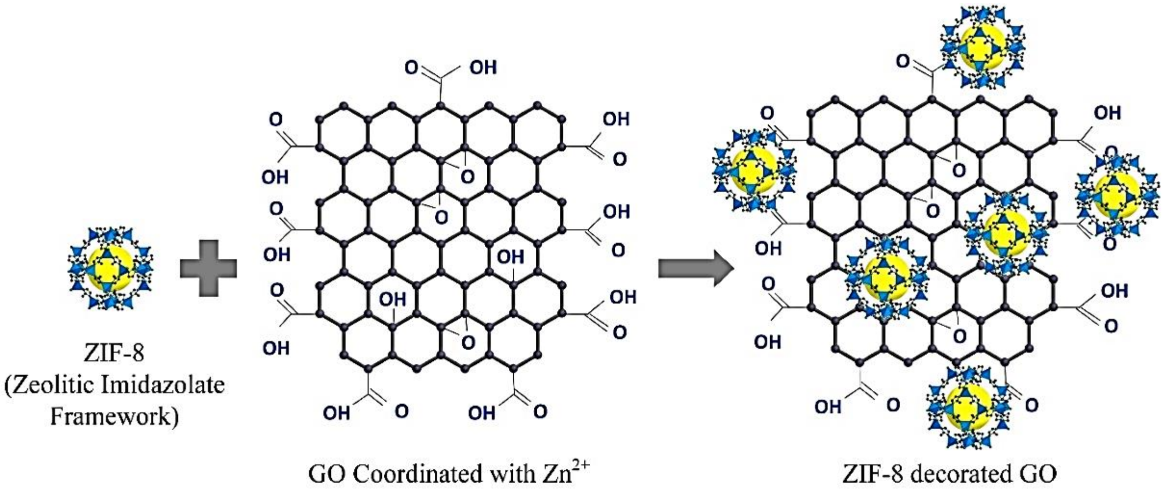

Fig. 5: Schematic reaction of ZIF-8 decoration on GO nanosheets (Ahmad et al., 2020)

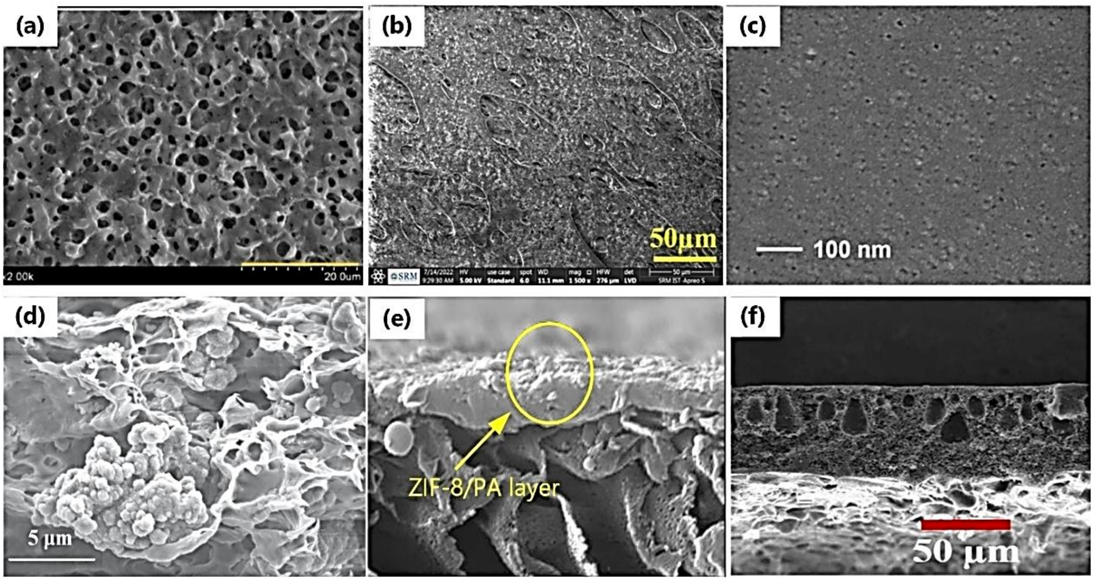

Fig. 6: Surface SEM images of (a) PVDF/NH_2-MIL-68B(Fe) (Xie et al., 2020); (b) ZIF-8@PSf/CS (Gowriboy et al., 2022); (c) HKUST-1@mPES (Lin et al., 2019); cross-section images of (d) MIL-68(Al)/PVDF (Tan et al., 2019); (e) PSF/PA-ZIF-8 (Basu & Balakrishnan, 2017); (f) PSf/UiO-66 (Ahmadipouya et al., 2022) (reproduced with permission)

SEM's exceptional performance in visualizing fouling layers has also been applied to elucidate the formation and structure of dynamic membranes in the presence of MOFs.

As illustrated in Figure 6(a), the introduction of NH_2-MIL-68B into a PVDF membrane formed a porous structure. This can be attributed to the accelerated NMP exchange rate due to the hydrophilic nature of NH_2-MIL-68B (Xie et al., 2020). In contrast, Gowriboy et al. (2022) reported a distinct surface morphology when incorporating ZIF-8 into a PSf membrane, revealing a smooth and dense surface layer (Figure 6(b)). This difference could be due to the increased interaction between ZIF-8 and NMP during the water submersion process, leading to delayed phase separation.

Furthermore, MOFs can serve as sacrificial templates to create uniform surface pores. Lin et al. (2019) employed HKUST-1 (~30 nm) in a PES membrane. After 60 minutes of immersion in water, the preloaded HKUST-1 dissolved, increasing pore size (see Figure 6(c)). This enlargement of pore size induced by MOFs incorporation is not limited to the membrane surface but extends to the inner layers, as evidenced by cross-sectional SEM images. Tan et al. (2019) observed enlarged micropores in PVDF membranes with the addition of MIL-68(Al) and noted that MOF nanoparticles were embedded within the pores of PVDF.

Basu and Balakrishnan (2017) took a different approach, applying ZIF-8 with a polyamide (PA) matrix on the surface of a PSf substrate to enhance membrane separation performance (see Figure 6(e)). By employing this strategy, MOFs can be made more accessible when exposed to treated water. A common intermediate structure found in MOFs-incorporated membranes is a finger-like structure with larger macrovoids, often associated with hydrophilic MOFs like UiO-66. This research underscores the significant role MOFs play in controlling membrane surfaces. Careful selection of the MOF type, loading concentration, and incorporation strategies can lead to the desired membrane structure.

MOFs-Incorporated Membrane Features

MOFs are more flexible than their original metal due to their organic-inorganic structure, resulting in tunable control of the structures and pore size, also allowing the adjustment of their properties. Therefore, MOFs have recently been combined with polymeric membranes to enhance their structural properties, providing new functionalities, and their performance can be improved. The MOFs-hybrid polymeric membrane is one of the fascinating technologies developed to eliminate hazardous contaminants (POPs, heavy metals) from wastewater. Incorporating MOFs into polymeric membranes has been reported to have significant performance enhancement and additional features such as anti-bacterial, photocatalytic, and self-cleaning properties (Gao et al., 2021; Pei et al., 2021).

Hydrophilicity/Hydrophobicity Adjustment

Hydrophilicity and hydrophobicity of the membrane surface are the important membrabe characteristics that influence the separation and permeation properties. The interfacial interactions between a water molecule and foulants with the membrane surface lead to driving water permeation and fouling growth rate. Zhang et al. (2015) have studied the effects of hydrophilicity/ hydrophobicity of membrane surface on membrane fouling. They suggest that designing hydrophilic membranes with high zeta potential and certain roughness can significantly mitigate membrane fouling. The hydrophilicity/hydrophobicity of membranes can be adjusted by incorporating MOFs into membrane polymer. ZIF-8 is considered to be hydrophilic particles, and they have significantly improved PES membrane hydrophilicity. The incorporation of 1.0 wt% ZIF-8 into PES polymer has decreased the water contact angle from 77° to 62°, as reported by Ahmad et al. (2020). Another report showed that 0.5 wt% ZIF-L incorporation into the PES membrane has increased hydrophilicity and reduced surface roughness. These improvements are due to the negative zeta potential nature of ZIF, which exhibits higher electrostatic double-layer repulsion according to Derjaguin-Landau-Verwy-Overbeek (DLVO) theory (Low et al., 2014). The incorporation of UiO-66 also showed excellent hydrophilicity enhancement through large lamellar spacing formation in the CA substrate (Y. Liu et al., 2020). The improvement of hydrophilic properties also helps in rejecting non-polar pollutants such as oil-in-water, as Shen et al. (2022) reported, that incorporating UiO-66-NH_2 into PVDF membrane increased the oil rejection up to ~99%. UiO-66 is an MOFs constructed from Zr ions and terephthalic acid ligand linkers where the nanocrystal is considered super-hydrophilic due to the massive carboxyl group in the organic ligand.

Permeate Flux Improvement

Water permeate enhancement has been reported as the effect of MOFs incorporation due to the formation of additional transport channels for water molecules to promote water penetration (Y. Liu et al., 2020). Wang et al. (2022) found that ZIF-8 incorporation into PES mixed matrix membrane has significantly increased the water permeate flux over 2.5-folds compared with pure membrane and ~90% flux recovery after five cycle runs test. The presence of ZIF-8 induces the formation of a hydration layer that could effectively increase the interaction with a water molecule. Li et al. (2021) developed a hybrid PVDF membrane with aminated MIL-88B/CDs loading via ultrasonic-assisted bulk blending. The presence of NH_2-MIL-88B/CDs has significantly increased the layer spacing and widened the interlayer channel, thus effectively increasing the membrane flux. Cheng et al. (2019) explained that the addition of MOF particles efficiently enlarged the effective porosity of the membrane, thus increasing the flux while maintaining the solute rejection. The cage-like structure of MOFs with aperture size ranging from 3 – 5 Å for small-pore MOFs (Hu et al., 2017), such as zirconium and zeolitic framework, and 14 – 98 Å for large-pore MOFs such as IRMOF-74 (Deng et al., 2012) provide ideal water channel that selective towards pollutants.

Pollutant Rejection Enhancement

Pollutant rejection in the membrane separation process can occur through three main mechanisms: molecular sieving (size exclusion mechanisms), charge exclusion mechanisms, and adsorption (Chang et al., 2012). The MOFs loading into the membrane matrix can enhance the solute rejection through all mechanisms. MOFs provide selective pores due to their tunable cage-like aperture, electrostatic repulsion due to organic functionalities in ligands, and adsorption mechanism simultaneously. Several studies also reported that the removal efficiency was enhanced by in-situ photodegradation initiated by MOFs (Cao, Yang, et al., 2018; Pei et al., 2021). Liu et al. (2021) incorporated ZIF-67 into PVDF ultrafiltration membrane for dye removal in wastewater. They reported that the ZIF-67@PVDF hybrid membrane has achieved high dye removal efficiency of ~ 97% for orange II, ~98% for methylene blue, and ~90% for rhodamine B. Reactive reactive oxygen species (ROS) generation from activated ZIF-67 facilitates this dye removal improvement. Fang et al. (2020) also found that more than 94% of antibiotics, such as tetracycline, oxytetracycline, and ciprofloxacin, were successfully eliminated using UiO-66 incorporated PAN TFC membrane. The rigid cubic structure of UiO-66 held an important role where the diameter of octahedral cavities (1.1 nm) and tetrahedral cavities (0.8 nm) are slightly smaller than the molecular diameter of antibiotics (1.09 – 1.2 nm). Chen et al. (2022) revealed the high adsorption capacity and fast adsorption rate toward heavy metals by a hybrid membrane of β-CD@ZIF-8/PVDF prepared via in-situ synthesis. Membranes adsorbed Pb2+ and Cu2+ ions up to 708.12 $mg.g^{-1}$ and 651.37 $mg.g^{-1}$, respectively, remarkably higher than that of pristine materials. These enhancements are facilitated by the intensified contact within confined spaces and more active sites provided within membrane pores.

Antifouling and Antibacterial Properties

As previously discussed, fouling growth can be mitigated by enhancing surface hydrophilicity and reducing certain surface roughness of the membrane surface. Native polymers such as polyethersulfone (PES), polysulfone (PSf), and polyvinylidene fluoride (PVDF) are considered slightly hydrophobic polymers with static water contact angle range of 70 - 80° thereby, these native polymers are susceptible to fouling tendencies (Kusworo et al., 2021, 2022). MOFs have been proven to improve surface hydrophilicity by providing oxygen-rich and water-attracting groups. ZIF-8 incorporated membrane has increased the flux recovery ratio (FRR) from 26% to 50% during the BSA filtration test (Liu et al., 2021). Ahmadipouya et al. (2022) studied the methanol-activated UiO-66 combined with PSf membrane for wastewater treatment containing dyes. With the UiO-66 loading of 9 wt%, the loss of pure water flux decreased to about 13%, and FRR increased up to ~96%, indicating the highly improved antifouling ability. They also reported that incorporated UiO-66 significantly hindered the formation of irreversible proven by the lowest R_{ir} of 4.38%, lower than pure PSf (R_{ir} = ~45%). Functionalization of UiO-66 using amine groups also improved the antifouling properties due to a hydrophilic amine group (Chen et al., 2022).

Several researchers showed that MOFs also show antibacterial properties such as ZIF-8, ZIF-L, MIL-125(Ti), MIL-53(Fe), MIL-101(Cr), UiO-66 (Ahmad et al., 2020; Cheang et al., 2022; X. Huang et al., 2021; Zhu et al., 2021). The Ag-doping into MOFs crystal also generates antibacterial properties (Q.-C. Chen et al., 2022). Ahmad et al. (2020) studied the antibacterial activity of ZIF-8 embedded PES membrane towards pathogenic bacteria such as *E. coli* and *S. aureus*. The effective antibacterial effect is attributed to the synergistic Zn in the ZIF-8 and imidazole linkers. Antibacterial membranes potentially inhibit biofilm formation on the membrane surface and biofouling. The antibacterial features of MOFs-hybrid membrane sometimes require light exposure to generate oxidative radicals. Through photon energy stimulation, MIL-125(Ti) could impart sufficient antibacterial activity toward *E. coli* in PVDF membrane(Zhou et al., 2020). The photo-activated MOFs promote strong oxidizing species such as hydroxyl radicals, superoxides, peroxides, and sulfate radicals that decompose bacteria cell walls.

Photocatalytic Degradation and Self-Cleaning Properties

Photocatalytic membrane development intends to fabricate advanced membrane material that ca degrade the attached foulant by introducing a photocatalyst. Instead of photocatalyst incorporation in a suspension reactor, embedding photocatalyst into membrane material is preferred based on current trends. The photodegradation in a separated reactor potentially causes particle fouling in membrane pores. Semiconductors metals can provide photocatalytic activity in their atomic state or oxide state. Photocatalytic can be activated by light exposure with an energy equal to or higher than its band-gap energy, initiating the formation of energy-rich electro-hole (e^-/h^+) pairs for redox degradation reaction (Kusworo et al., 2022). The excited electron in the conduction band (e_{CB}^+) and generated holes in the valence band (h_{VB}^+) simultaneously create interfacial charge transfers that generate reactive radical species (OH*, O_2*), as illustrated in Figure 6. Previous studies demonstrated that , MOFs have photocatalytic activity such as zeolitic imidazole, UiO-66, MIL-101, etc. Du et al. (2011) exposed novel MIL-53 as a photocatalyst with sensitivity under UV and visible light. They found that MIL-53(Fe) has the narrowest band-gap energy (2.72 eV) compared with those of MIL-53(Al) and MIL-53(Cr) of 3.87 and 3.20 eV, respectively. The photodegradation experiment showed that MIL-53(Fe) achieved the highest methylene blue (MB) degradation up to ~35% under UV-vis light exposure for 60 min. However, several MOFs, such as zinc- carboxylate-based MOF which undergo a structural transformation in water exposure, are unstable in water. Incorporating MOFs into polymeric membranes by embedding the particles within the polymer matrix is an alternative strategy to improve stability. Choe et al. (2022) developed a sunlight-driven photocatalytic PES membrane by incorporating NH_2-MIL-125 via ultrasonic-assisted bulk blending followed by non-solvent phase inversion. The modified membrane showed photocatalytic degradation activity of Congo red under sunlight irradiation, leading to higher overall rejection efficiency >93%, enhanced FRR ~77%, and promoted self-cleaning ability after several cycle tests. Self-cleaning property is defined as the ability of any surface to readily remove any dirt, foulants, or bacteria on it. Li et al. (2021) developed a self-cleaning membrane by incorporating PDA/ZIF-67 composite on a polypropylene (PP) membrane for dye wastewater remediation. The self-cleaning property is promoted by in-situ photocatalytic degradation by active radical species. The presence of ZIF-67 has activated peroxymonosulfate under visible light irradiation excellently degrading MB and MO dyes up to 95%. Self-cleaning behavior alleviated membrane fouling by simultaneously gaining anti-adsorption properties endowed by hydrophilic membranes and photocatalytic degradation. Liu et al., 2022) reported the high flux (~611 $L.m^{-2}h^{-1}$) and doubled BSA rejection using photocatalytic membrane PES-Ni@UiO-66. They also reveal the developed membrane's remarkable anti-fouling and self-cleaning ability, which was proven by a serial cleaning test under UV irradiation that showed stable FRR at 96%. Zr element in UiO-66 has excellent UV responsiveness that initiates photocatalytic degradation of foulants.

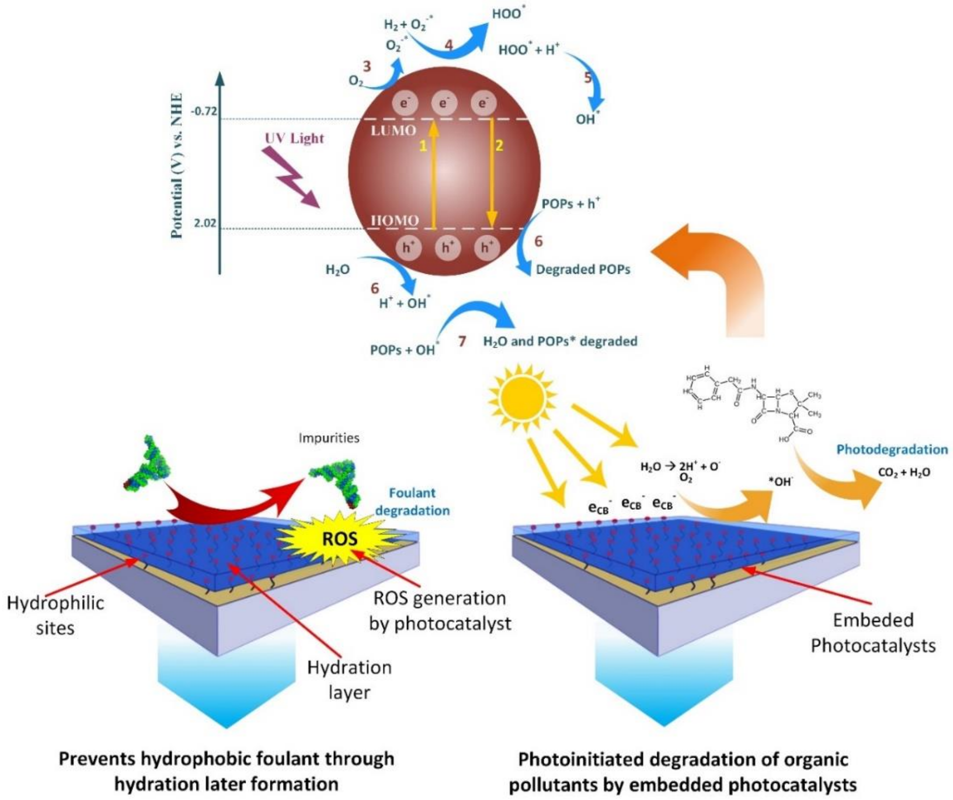

Fig. 6: Simplified mechanisms of photocatalytic activity, antifouling and self-cleaning. Reproduced with permission (Kusworo et al., 2022) copyright 2022, Elsevier.

Enhanced Membrane Durability

A significant challenge in the practical use of MOFs-incorporated membranes lies in developing membranes that can meet the durability requirements of industrial applications. Membrane durability refers to the membrane's ability to maintain its performance over an extended operational period. There are several factors contributing to the failure of MOFs-incorporated membranes in wastewater treatment:

1. Mechanical degradation can occur due to membrane fracture caused by fatigue stresses induced by trans-membrane pressure.
2. Chemical degradation may result from the direct attack of the polymer by radical species generated as by-products of photocatalysis in photocatalytic membranes.
3. MOFs hydrolysis can occur due to reactions between metal ions and water molecules.
4. Membrane swelling can result from the high affinity of the membrane for water molecules.
5. Fouling tendencies can significantly deteriorate membrane performance.

Xie et al. (2020) reported an increase in the tensile strength and strain of NH_2-MIL-88B/PVDF membranes by up to approximately 15% and 40%, respectively, compared to pristine PVDF membranes. This improvement in mechanical strength is attributed to the uniform distribution of NH_2-MIL-88B in the PVDF matrix, facilitating hydrogen bonding between the oxygen-rich and nitrogen functional groups. However, the loading NH_2-MIL-88B at concentrations exceeding 1.5 wt.% slightly decreased tensile strength due to excessive blending in the PVDF matrix. Introducing UiO-66-NH_2 into a thermoplastic polyurethane (TPU)/PSf matrix significantly enhanced mechanical strength by up to 140%, resulting from hydrogen bonds and aromatic diisocyanates (Guo et al., 2020). Aside from MOFs loading concentration, the membrane fabrication method also plays a role in determining mechanical strength. MIL-67/PVDF membranes, obtained through predispersion in acetone followed by thermally induced phase separation, exhibited higher mechanical properties than membranes obtained from nonsolvent-induced phase separation (Ren et al., 2019).

Several MOFs-incorporated membranes have demonstrated stability in response to changes in solution pH. Li et al. (2022) investigated the stability of ZIF-8/PAN membranes at varying pH levels. They found that ZIF-8 began to decompose in extremely acidic and basic solutions, with optimal stability in the pH range of 4 to 10. In another study, UiO-66-NH_2/PVDF showed excellent water stability at pH 2 while effectively removing heavy metal ions (Yu et al., 2023). A consecutive cycle test is commonly employed in durability testing to evaluate membrane stability. ZIF-67@PVDF membranes showed only a small decrease in performance after 5 cycles of testing (Liu et al., 2021). Gnanasekaran et al., (2021) assessed the stability of flux, FRR, and dye rejection of PSf/MIL-100(Fe) membranes through 6 consecutive testing cycles. They observed a slight decrease in flux and FRR but maintained dye rejection at over 98%. The presence of organic ligands in MIL-100(Fe) strengthened the compatibility between the PSF matrix and MIL-100(Fe) nanoparticles, enabling the development of highly stable membranes. Moreover, MOFs-incorporated membranes have demonstrated excellent stability when exposed to organic foulants. Ni@UiO-66/PES membranes have shown antifouling properties against bovine serum albumin, sodium alginate, humic acid, and yeast extract (Liu et al., 2022)

MOFs Membrane Application for Wastewater Treatment

The incorporated water-stable MOFs polymeric membranes have been studied for dealing with wastewater containing various contaminants. Due to their superior characteristics, the number of MOFs-hybrid membranes used in wastewater treatment has increased in recent decades. MOFs-hybrid membranes have proven to eliminate hazardous and persistent organic contaminants in wastewater, even at trace levels (Li et al., 2020). For example, Abdelhameed et al. (2021) used microporous Cu-MOF@cellulose acetate to remove dimethoate pesticides in wastewater selectively. The synergistic ability of adsorption capacity and molecular exclusion has enhanced the dimethoate removal with excellent recyclability. Lu et al. (2020) also developed MIL-100(Fe) embedded cellulose fiber membrane via in-situ synthesis followed by layer-by-layer loading. The prepared membrane shows remarkable dyes and oil removal up to 97.3% and 99.64%, respectively. The membrane also exhibited excellent self-cleaning and long-term reuse capacity under UV-vis and sunlight. Overall, the experimental studies show promising potential for practical application in complex wastewater treatment. Table 1 summarizes wastewater treatment using MOFs-hybrid membrane with various contaminants.

Table 1. The utilization of MOFs-incorporated membrane for wastewater containing various contaminants

Polymeric membrane	MOFs	Incorporation Method	Target contaminant	Performance	Reference
PES	MIL-100(Fe)	Bulk blending	Dyes, TSS, COD (real textile wastewater)	100% TSS removal >92% COD removal >98% dyes ~165.68 L.m^{-2}.h^{-1} flux >90% FRR	(Johari et al., 2021)
Polyamide with PES support	ED-MIL-101(Cr)	Surface deposition	Pharmaceutical residues	> 90% removal of PRs >90% salts rejection ~200 L.m^{-2}h^{-1} permeate flux	(Dai et al., 2020)
Cellulose Acetate	AlFu-MOF	Bulk blending	Real agricultural wastewater	~85% salts rejection >80% water recovery ~18 L.m^{-2}.h^{-1} permeate flux	(Lakra et al., 2021)
PVDF	HKUS-1	Bulk blending	Electroplating wastewater	>99% metal ions removal > 95% COD removal ~99% NH_3 removal ~95% total phosphate removal ~187 Lm^{-2}h^{-1} permeate flux	(H. Wang et al., 2022)
PSF	MIL-100(Fe)	Ultrasonic assisted bulk	Microplastic and dyes	~99% MB and microplastics removal	(Gnanasekaran et al., 2021)

Polymeric membrane	MOFs	Incorporation Method	Target contaminant	Performance	Reference
		blendng		~70 $Lm^{-2}h^{-1}$ PWF ~90% FRR	
Cellulose acetate	MOF-5	Surface aggregation	Dyes	~99% MB removal ~97% CR removal ~3439 $L.m^{-2}h^{-1}$ permeate flux > 85% FRR	(Y. Liu et al., 2022)
PVDF	ZIF-8	Interfacial polymerization	Nickel (II)	~95% regeneration effectiveness ~99% nickel removal	(T. Li et al., 2018)
PP	ZIF-67	In-situ synthesis	Dyes	~75% MB removal ~85% MO removal ~216.8 $Lm^{-2}h^{-1}$ PWF 17% decreased flux decline	(N. Li et al., 2019)
PVDF	ZIF-8	Ultrasonicated bulk blending	Domestic wastewater	~90 $Lm^{-2}h^{-1}bar^{-1}$ water permeance ~87% turbidity rejection	(Ibrahim et al., 2018)
PVDF	ZIF-67	Bulk Blending	Dyes	~99% AO removal ~98% MB removal ~90% RhB removal ~263 90 $Lm^{-2}h^{-1}$ water flux	(D. Liu et al., 2021)
PAN	ZIF-8	Bulk Blending - Electrospinning	Congo Red Pb(II), Cu(II)	~95% CR removal ~35% Cu and Pb removal ~225 $Lm^{-2}h^{-1}$ water flux	(M. Li et al., 2022)
cCS/PVA	UiO-66-NH_2	Ultrasonicated bulk blending	Uranium (IV)	~316 $mg.g^{-1}$ U(IV) adsorption	(Y. Wang et al., 2021)
PA/PSF	UiO-66	Bulk blending	Antibiotics	>99% rejection of antibiotics ~50 $Lm^{-2}h^{-1}$ water flux	(Mu et al., 2021)
PA	UiO-66-NH_2	Layer-by-layer assembly	norfloxacin, ciprofloxacin, and levofloxacin	92 – 96 % rejection ~18 $Lm^{-2}h^{-1}$ permeate flux ~98 FRR	(Fang et al., 2022)
PAN	GO-doped UiO-66-NH_2	Interfacial polymerization	Dyes Antibiotics	~31.33 $Lm^{-2}h^{-1}$ permeate flux >94% rejection efficiencies	(Fang et al., 2020)
TPU/PSF	UiO-66-NH_2	Interfacial polymerization	Tetracycline	>99% TC removal ~64 $L.m^{-2}h^{-1}$ permeate flux	(Guo et al., 2020)
PVDF	MIL-53(Fe)	Ultrasonicated bulk blending	Tetracycline	>99% TC removal ~45 $L.m^{-2}h^{-1}$ permeate flux	(C.-J. Wu et al., 2023)
PES	MIL-125(Ti)/CS	Ultrasonicated bulk blending	Dyes Antibiotics Heavy metals Salts	>99% dyes rejection ~90% Pb rejection 35 – 45% salts rejection > 80% antibiotics removal ~98% FRR ~130 $L.m^{-2}h^{-1}$ PWF	(Khosravi et al., 2022)

Polymeric membrane	MOFs	Incorporation Method	Target contaminant	Performance	Reference
PVDF	NH_2-MIL-88B(Fe)	Bulk blending	Oil/water emulsion	~2000 $L.m^{-2}h^{-1}$ permeate flux ~100% rejection of petroleum ether ~100% FRR	(Xie et al., 2020)
PVDF	MIL-125(Ti)	Bulk blending	Rhodamine B	>99% RhB removal ~321.5 $L.m^{-2}h^{-1}$ permeate flux	(Zhou et al., 2020)

Future Prospects and Challenges

MOFs might be the most powerful material in future research as adsorbent, photocatalyst, and membrane filler for wastewater treatment. Incorporating MOFs into polymeric membranes has been proven to eliminate various hazardous contaminants in wastewater. Several MOFs, such as NH-MIL-101(Al), have shown excellent sensitivity towards heavy metals even in trace concentration (lower than 1 ppb) (X. Liu et al., 2022). Thus, MOFs are materials with great potential for wastewater decontamination in the future. Combining MOFs with polymeric membranes would be the best idea since membranes are fascinating technology. The MOF-hybrid membrane would be easily tailored as a desired structure for a specific purpose. The flexibility of MOFs to be combined with other materials enables researchers to explore the probable development orientations of MOFs-hybrid membranes. Novel multifunctional nanocomposite materials combining MOFs with green carbonaceous materials have great application prospects as an environmentally friendly technology. There is a possibility of developing membrane materials with various abilities such as adsorption, self-cleaning, anti-fouling, and antibacterial besides enhanced pollutant removal. The open functionalization of MOFs with various functional groups would be the solution for low chemical compatibility of nanoparticle filler with polymer matrix, thus preventing particle release during filtration. Despite the high performance of MOFs-hybrid membranes as presented in this review, there are several challenges for future application in wastewater treatment. Water stability of the membrane is a crucial consideration because MOFs are potentially structurally transformed in long water exposure. Therefore, the next studies should focus on maintaining the stability of MOFs embedded membranes in harsh conditions (high temperature, pressure, and extreme pH environment). The MOFs-hybrid membrane fabrication is limited in lab-scale production; facile methods should be studied on a large scale for industrial production. To our knowledge, there are limited studies of MOFs-hybrid membranes for treating real wastewater with complex contaminants. Therefore, future trends should investigate the performance of MOFs-hybrid membranes for real wastewater treatment. The expansion from lab-scale to industrial scale of research findings is required for technology readiness in practical application.

CONCLUSIONS

MOFs are a new class of porous materials with unique properties. Due to their flexible structural tunability, new MOFs are gradually developing for various applications. The synthesis methods of MOFs should be continuously developed to obtain efficient processes and eco-friendly and controllable products. Combining MOFs particles with the polymeric membranes is an attractive idea for achieving synergistic properties of MOFs and membrane separation. Several incorporation techniques have been developed to minimize structural defects that decrease the separation performance. Bulk blending is the most popular technique to embed MOFs into polymeric membranes due to its simplicity and mild operating conditions. The performance enhancement of membranes after MOFs incorporation has been discussed in this review, where the adsorption capacity, photocatalytic property, antibacterial activity, and molecular sieving property of MOFs simultaneously enhanced the overall performance efficiencies. Despite the great potential of MOFs-hybrid membranes for eliminating hazardous contaminants in wastewater, the expansion study from laboratory to industrial-scale is required for the technology readiness in practical application.

CONFLICT OF 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.

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