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REVIEW

ZIF-8 membrane: the synthesis technique and nanofiltration application

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Abstract

Membrane technology for water treatment is growing due to the increased demand for clean water and the stringent standard for water quality. Nanofiltration (NF) is widely used in membranes for water treatment due to lower energy consumption and higher flux rates. The application was not limited to only water treatment, yet NF showed excellent potential for solvent nanofiltration application. The utilization of MOF materials for the preparation of NF membranes to produce composite membranes has attracted more attention among researchers due to the advantages offered by the material. Zeolitic imidazolate framework-8 (ZIF-8) membrane has been considered a promising MOF membrane with its capabilities and promising performance due to the small aperture size of the compounds and the stability towards harsh chemical condition. The purpose of this review is to present the synthesis approaches on the preparation of ZIF-8 membranes and the application of ZIF-8 membrane for NF application. The challenges and prospects of ZIF-8 membranes are also discussed to further stimulate the development and the application of ZIF-8 membrane for NF.

Keywords MOF · ZIF-8 · Membrane · Nanofiltration · Organic solvent nanofiltration · Water treatment

1 Introduction

Nanofiltration has been recognized in the late 1980s with the properties that resemble ultrafiltration (UF) and reverse osmosis (RO). The molecular weight cut-off of the nanofiltration membrane is 300–500 Da, with a pore size typically of 1 nm. Nanofiltration membrane has a great potential in the separation of inorganic salts and small organic dye molecules. The difference between NF and RO is that the NF membranes have low rejection on the monovalent ions, yet having high rejection in divalent ions with higher flux in comparison with the RO membranes. The NF system is also able to operate at modest pressure. These attributes have made the NF competitive enough to compare with the traditional approach for water and wastewater treatment application, pharmaceutical and biological processes. Recently, the emerging of the metal–organic framework (MOF) has contributed much to the development of NF membranes.

MOFs are a type of porous, zeolite-like material that combines the qualities of metal and organic compound properties. From the beginning of the twenty-first century, MOF has been studied for their preparation methods and application for the various fields including separation. The MOFs have been introduced as nanofillers in membranes [1], pure MOF membranes [2] and additives in thin-film membranes [3]. Based on their promising potential, in the past 10 years, various outstanding MOF membranes have been successfully fabricated and used including nanofiltration application.

The nomenclature of MOF material is quite random. For example, the zeolitic imidazolate frameworks (ZIFs), a subclass of MOF has almost the same properties with zeolites, in term of its crystallinity, microporosity, large surface area and

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outstanding thermal and chemical stability [4]. The "zeolitic" term was given due to the topology similarity of the material to zeolite [5]. In this class of MOF, nitrogen-containing tetrahedron connected with imidazole rings having different functional groups surround the metal ions. In ZIFs, the metal such as zinc and cobalt coordinate through nitrogen atom of ditopic imidazolate (Im) to build neutral networks with tunable nanoscale aperture. The Zn^{2+} and Co^{2+} are the most common metal ions utilized in ZIF synthesis, whereas imidazole (IM), 1-methylimidazole (mIM), 1-ethylimidazole (eIM) and 2-nitroimidazole are some of the imidazole-type linkers employed in ligands (nIM). ZIF with various features, kinds and structures would be created by combining different metal sites with imidazole organic ligands.

ZIF-8 is a type of MOF compound, produced from the reaction between Zn^{2+} and 2-methylimidazole (Hmim). The material is one of the most researched MOFs due to its promising qualities in harsh conditions, including high acidity and high basicity condition [6] and also exhibit high stability at high temperature [7]. The framework of ZIF compounds is very similar to that of zeolites. In ZIFs, the T-O-T bridges ((T) Si, Al, P) in zeolites are replaced with M-Im-M bridges (M = Zn, Co), and the bond angles are 145° in both structures [5, 6]. The unique properties possessed by ZIF-8, for instance, the ultrahigh porosity, hydrophobicity, thermal and chemical stability and easy synthesis route have made this material become an excellent candidate for adsorption applications [8]. Given the excellent properties and separation performance, researchers have reported on various methods to prepare the ZIF-8 membrane. For the fabrication of pure ZIF-8 membrane, the preparation method include the in situ growth method, secondary seeded method, layer-by-layer technique, dip coating and electrochemical method [9–15]. On the other hand, the mixed matrix membrane (MMM) is usually prepared by distributing the ZIF-8 particles in the polymer matrix [3, 16–18].

Although there are a number of review papers reported on the use of MOF membranes for various applications [2, 19–21], yet a review on ZIF-8 membrane for nanofiltration application is still required to give further insight on the application of the ZIF-8 membrane for water separation. In this review, the synthesis strategies of the ZIF-8 membranes for NF are summarized. The focus is on the current development and the application of the membrane for NF. Besides, the challenges and prospects of the membrane are also discussed.

2 Synthesis of ZIF-8 membranes

2.1 Pure ZIF-8 membranes

The preparation of pure ZIF-8 membrane is developed on a substrate, mainly the inorganic materials or polymer. Therefore, the ZIF-8 membrane can be categorized into two main groups, namely, the pure ZIF-8 membrane on porous substrate and the MMM membranes prepared by mixing ZIF-8 particles with the organic matrix. The preparation techniques of the membranes will be discussed in the following.

Generally, the preparation method for pure ZIF-8 membranes includes the in situ growth method, secondary seeded method, electrochemical growth and layer-by-layer technique.

2.1.1 In situ growth method on non-modified support

The in situ growth method requires only a single-step process to grow the ZIF-8 layer on the non-modified support. The support will be immersed in the ZIF-8 precursor solution, without prior attachment of ZIF-8 seeds. During the fabrication process, the crystal nucleation, crystal growth and intergrowth all take place at the same time on the substrate [22]. However, the lack of chemical bonding between MOF and pristine membrane is the main drawback. The chemical properties of the support's surface, such as the surface charge and acidity are believed to influence the lack of bonding [23]. ZIF-8 layer on alumina support was prepared by using a high concentration gel with a molar ratio of 1:8:75 (Zn^{2+}:Hmim:methanol) [24]. The ZIF-8 synthesis solution and the alumina hollow fibre membrane were placed into the autoclave, then heated for 5 hat three different temperatures (25, 100, and 150 °C). The ZIF-8 layer has grown nicely on the alumina membrane with roughly 6-µm thickness. The cross-section of the ZIF-8 layer revealed several irregularly shaped microcavities in the FIB-SEM image. The SEM micrograph is shown in Fig. 1. Apart from that, Li et al. demonstrated in situ ZIF-8 growth employing an interfacial synthesis technique [25]. A liquid–liquid interfacial coordination approach was used to make ZIF-8 membranes on porous polyethersulfone (PES) substrates. The method requires saturating the support layer with aqueous zinc nitrate, then the 2-methylimidazole solution was poured onto the support layer, forming a layer of ZIF-8 after a certain time of reaction. The SEM imaging exhibited the formation of ZIF-8 layer with a thickness of 250–300 nm.

A dense layer of ZIF-8 film was successfully coated on stainless steel meshes by Ma et al. [26]. The membrane has exhibited high efficiency for oil/water separation. Polyethyleneimine (PEI) acts as a polymer binder to enable the formation of a dense seed layer. After the second growth procedure, the support layer was covered entirely with ZIF-8 film. The thickness of the layer reported is about 1.6 µm. The FESEM image of the fully covered stainless steel mesh is shown in Fig. 2.

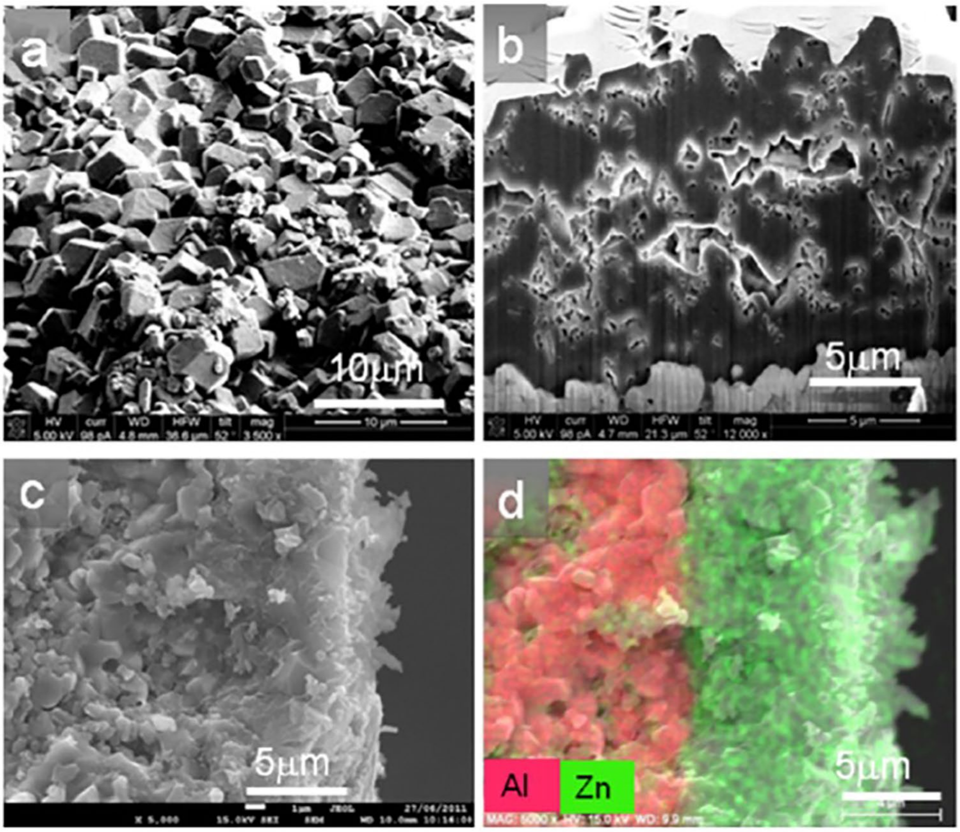


Fig. 1 ZIF-8 membranes mounted on alumina support synthesized from concentrated gel and heat at 100 °C with reaction time of 5 h: SEM images (a) surface, (b) FIB-created cross-section, (c) cross-section and (d) cross-section with elemental mapping image. Adapted from [24]

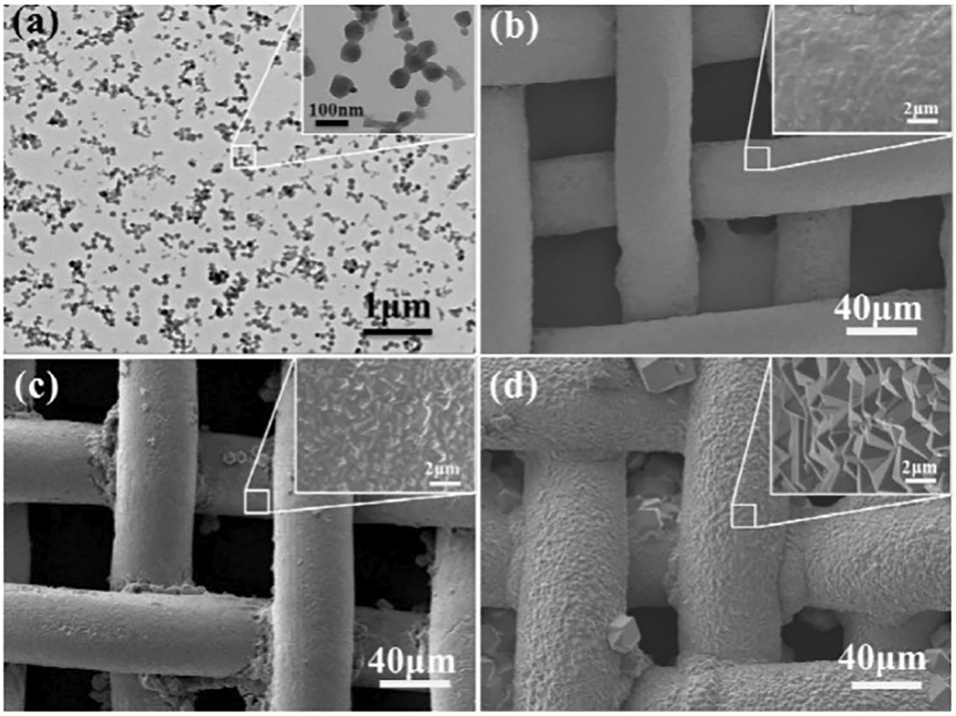


Fig. 2 The TEM image of (**a**) synthesized ZIF-8 nanocrystals; the inset is the magnified view of ZIF-8 nanocrystals. Top and (inset) magnified view of FESEM images of (**b**) neat mesh, (**c**) ZFCM-1, and (d) ZFCM-4 adapted from [26]

2.1.2 In situ growth on modified support

Formation of ZIF-8 layer on pristine supports is usually reported to face various membrane issues, including cracking. As a result, additional support surface modification is occasionally required to generate a uniform and well-grown ZIF-8 membrane. A thermal deposition approach was reported by McCarthy et al. [27] to synthesize ZIF-8 layer by altering the substrate with the 2-Hmim solution. The activation step enables the ligand to bound on the surface of the support membrane. At a temperature of 200 °C, a strong aluminium-nitrogen covalent connection is produced. Furthermore, the existence of sodium formate is required to create a continuous and well-grown ZIF-8 layer, according to the researchers. The deprotonation of surface linkers is spurred by the high pH value, which improves the quality of the membrane created. The imperfect growth of ZIF-8 layer was further improved by the secondary growth procedure with the addition of sodium formate. The research also revealed that zinc chloride was a better metal source than zinc nitrate for developing a continuous ZIF-8 membrane. Yet, after a 36-h synthesis time with zinc chloride and no sodium formate, no film was formed.

Zhang et al. published a method for producing less-defect ZIF-8 tubular membranes that is both easy and scalable, using an ultrathin ZnO layer on the substrate surface. Then the surface was activated with an Hmim solution [28]. Surface moieties and embryonic nuclei-like ZIF-8 SBU are produced when ZnO and Hmim react. These are then used as nuclei for ZIF-8 formation and proliferation on the surface. The activation procedure provides consistent nucleation sites on the surface of the ZnO layer, based on the uniformity of ZIF-8 development. The homogeneity plays the vital role to enhance the reproducibility and scalability of the approach, thus resulting in a membrane with good permeability and selectivity. Furthermore, the high adhesion between ZIF-8 and ZnO can prevent the ZIF-8 layer from delaminating from the support layer. Furthermore, a study reported on the fabrication of ZIF-8 membrane through the in situ growth on alumina and zinc oxide hollow fibre membranes [29]. The membranes possess 5–6 µm of thickness and are crack-free. It is noteworthy that one of the most important features of a good ZIF-8 development is the surface functionalization with Hmim. The Hmim is assumed to react with ZnO, thus promoting the nucleation of ZIF-8.

A bio-inspired technique is also one of the best ways to change organic or inorganic surfaces in order to build a well-grown membrane. The mussel shell adhesion mechanism, for example, has sparked interest among researchers who want to use the same technique to membrane modification. The bio-adhesion property of dopamine enables the polymerization and adhesion on various material surfaces through strong covalent and non-covalent bonds. The polymerization was proposed to occur through self-assembly and a covalent oxidation polymerization of catechol, to form dopamine quinone under aerobic and alkaline conditions. After that, the dopaminequinone is oxidized, and the polymerization reaction is continued via deprotonation and intermolecular Michael addition, resulting in a cross-linked homopolymer. [30–32]. The formation of polydopamine has opened the extensive opportunity for secondary reactions to occur for further modified surfaces. For instance, a ZIF-8 membrane was successfully deposited on alumina support by modifying the membrane with dopamine [32]. The preparation scheme for the formation of ZIF-8 membrane on PDA-modified alumina is shown in Fig. 3. The solvothermal reaction at 85 °C for 24 h produced a well-intergrown rhombic ZIF-8 crystal on top of the PDA-modified alumina support with no crack and pinholes or other defects, with a thickness of ~20 µm. Contrarily, the unmodified support formed a non-continuous layer because of the absence of a chemical bond between the

Fig. 3 Preparation of ZIF-8 layer on PDA-modified supports adapted from [32]

ZIF-8 particles and the alumina support. However, a study by Mahpoz et al. (2019) showed a contradictory result [33]. From the study, when solvothermal synthesis was performed on PDA-modified alumina, the ZIF-8 formed as a non-continuous layer, with isolated and scattered positions throughout the support membrane. The result could be caused by the deficient amount of amino and hydroxyl groups on the support surface after PDA modification which prohibited the continuous growth of ZIF-8 layer.

2.1.3 Secondary growth/seeded growth

The secondary or seeded growth approach, in contrast to the in situ growth method, involves the placing of ZIF-8 seeds on the support [34]. Algieri et al. claimed that his method is preferable since each phase can be controlled independently, resulting in a thinner and less detective membrane [34]. This approach, however, is more difficult than the in situ growth method described before. A few seeding methods were reported from previous literature namely, dip-coating [9], rubbing [9], reactive seeding [10] and immersion [35].

A ZIF-8 membrane deposited on a yttria-stabilized zirconia (YSZ) fibre usinghydrothermal seeded growth method was reported [36]. The process involved dipping a YSZ support in the ZIF-8 solution for 10 s, resulting in a 2.5-m membrane. However, the growth of ZIF-8 is not uniform and unable to cover all the substrate's surface. The seeds are blocked inside the pores of the support, resulting in limited ZIF-8 particle coverage. A study on the effects of different fabrication techniques for the formation of ZIF-8 membrane, namely via secondary seeded growth, rubbing and in situ crystallisation was also reported [37]. The hydrothermal approach was used to prepare the seeding process. Then, the support was calcined at 900 °C for 30 min before the dry ZIF-8 layer was rubbed on the support's surface. In situ growth, secondary growth, rubbing and dip-coating methods were used to fabricate ZIF-8 membranes on alumina by Lai et al. [9]. The crystal size of the ZIF-8 membrane produced by rubbing was between 1 and 4.7 µm, whereas the crystal size produced by dip-coating was between 2.5 and 5 µm. The research also revealed that the improper seeding process will affect the growth of ZIF-8 during secondary treatment, thus resulting to a poor intergrown layer.

Recently, a perfect microporous ZIF-8 membrane was developed via the combination of the dip-coating and secondary growth process [38]. Instead of using methanol as solvent, the precursors in the abovementioned technique uses DI to prepare the precursor solution. The fabrication process was carried out at room temperature for 6 h. From the results obtained, the membrane showed excellent performance to separate propylene from propylene/propane gas mixture.

2.1.4 Microwave-assisted growth

Microwave technology has sparked the interest among researchers owing to its outstanding benefits. Microwave technology is claimed to be a green technology because there is no production of any toxic materials such as gas fumes or require the usage of external energy sources to heat [39]. Using the microwave-assisted seeding method, Kwon and colleague developed a quick and simple way for producing a well-intergrown ZIF-8 layer. The procedure requires three primary steps: first, the saturation of substrate layer with metal source solution, then the substrate will be exposed to the organic linker, and finally, providing microwave irradiation to induce fast crystal formation [40]. Prior to microwave irradiation, it is critical to sustain a high concentration of the solution on the support in order to optimize the heterogeneous crystallization while minimising the impurities on the surface of the substrate. Furthermore, the rapid synthesis of ZIF-8 on both sides of the substrate is aided by the high rate of microwave absorption by metal ions, which raises the local temperature inside the support.

ZIF-8 ultrathin layer was successfully deposited inside the lumen of Matrimid© polymer hollow fibre membrane by the combination of microwave-assisted seeding method and secondary growth method [41]. Firstly, the ZIF-8 particles were seeded on the bore-side of the hollow fibre via microwave-assisted seeding method. The seed crystals were then developed into well-intergrown ultrathin ZIF-8 films, with a thickness of 800 nm, one of the thinnest ZIF-8 membranes developed on polymer hollow fibres, using a microfluidic solvothermal process. The process of secondary growth is shown in Fig. 4. The compact structure of ZIF-8 film formed through this method is contributed by a rapid formation of ZIF-8 due to the high absorption of microwave radiation by the zinc source. Additionally, the controllable position of ZIF-8 growth is another advantage of this microfluid secondary growth method, because the ZIF-8 film can be grown either on the shell or the bore side of the hollow fibre membrane.

A work employing microwave irradiation to prepare mixed metal CoZnZIF-8 with varied Co/Zn concentrations and mixed ligand ZIF-7–8 was recently published [42]. This is the first time a mixed metal ligand, CoZnZIF-7–8, has been effectively synthesized in a single step utilising microwave irradiation. When compared to conventional procedures, crystallisation utilising microwave irradiation achieved a higher yield, used less organic linkers and solvent, and did not require the addition of deprotonators. The ZIF-8 membrane prepared via microwave-assisted method has proved to be better in terms of stability compared to the counter-diffusion process [43].

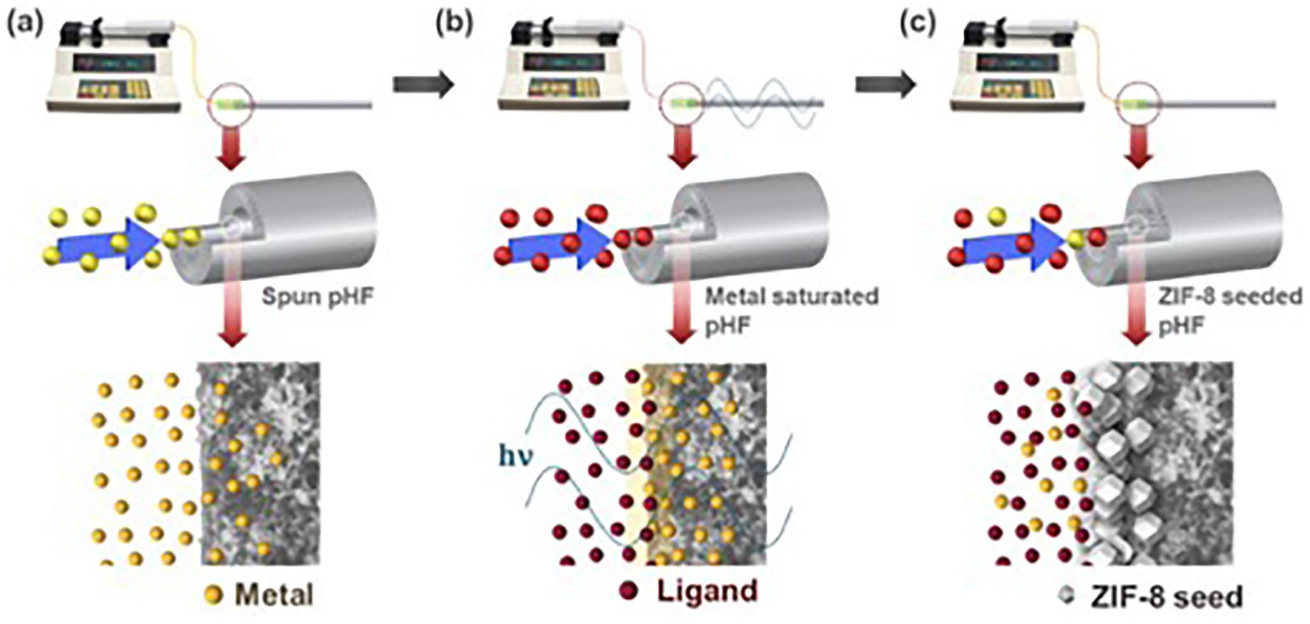


Fig. 4 Microwave-assisted method and secondary growth method growth on Matrimid hollow fiber support (**a**) an as-spun pHF was subjected to metal saturation, (**b**) followed by an injection of ligand precursor solution and microwave irradiation to form densely-packed ZIF-8/pHF seed layers and then, (**c**) the seeded pHF was subjected to the microfluidic secondary growth by flowing growth solution to prepare an ultrathin well-intergrown ZIF-8 membrane on the hollow fiber adapted from [41]

2.1.5 ZIF-8 membrane prepared by electrodeposition method

Another possible approach to deposit ZIF-8 on substrates is through the electrochemical deposition technique. The method does not require the surface activation step, which usually involves the use of non-environmental friendly solvent. Therefore, Wu et al., (2019) reported a successful growth of ZIF-8 on an etched pencil bars via electrodeposition technique [15]. A crack-free and continuous ZIF-8 membrane was able to be produced through this method. The organic ligand, Hmim, was expected to react with the zinc source in this method, resulting in active sites on the surface of the pencil bar, allowing the nucleation and development of ZIF-8 membrane without the need for previous activation. The ZIF-8 membrane exhibited a large surface area and able to withstand at high thermal condition. Therefore, the membrane showed higher adsorption capacity for acidic drugs compared with commercial polydimethylsiloxane/divinylbenzene (PDMS/DVB) adsorbent. The excellent adsorption performance is due to the hydrophobic, hydrogen bonding, and π–π stacking interaction between the membranes and the adsorbates, making it a suitable candidate for adsorption and separation application. Another example of successful electrodeposition of ZIF-8 on zinc electrodes via an anodic dissolution method [44]. The experimental setup was shown in Fig. 5. A heated, de-aerated electrolyte solution containing a linker was used to submerge two Zn electrodes. A fixed potential difference of 2.5 V between the two metal foil electrodes was supplied. A coating of ZIF-8 was successfully generated on the anode.

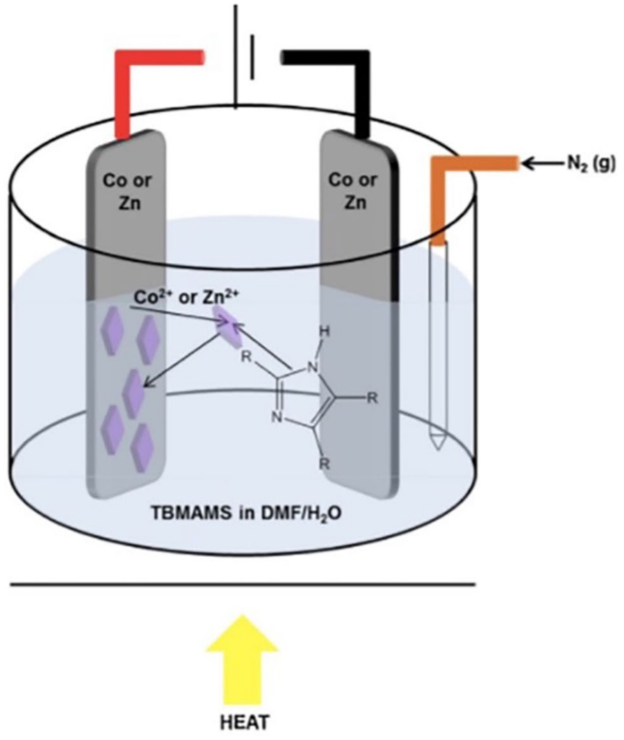


Fig. 5 Electrochemical deposition technique for ZIF-8 membrane preparation adapted from [44]

2.1.6 Other techniques

The contra-diffusion technique was employed by Kwon and Jong [45] to produce the ZIF-8 membrane. The rapid fabrication of continuous and uniformly grown ZIF-8 membranes on alumina substrate with outstanding microstructure was made possible by this simple yet extremely adaptable approach. The synthesis process is based on the counter-diffusion principle, which involves soaking the alumina support in the metal source solution, then performing a fast solvothermal process in the organic linker solution. This innovative technique has a number of advantages, including the ability to mend faulty membranes (i.e., those that are inadequately intergrown) and a large reduction in the use of expensive organic linkers and organic solvents. Figure 6 exhibits a scheme for the synthesis process.

Jang et al. reported on a new counter diffusion method for controlling the diffusion rates of the metal source and organic linker as a solution to enhance the uniformity and promoting well-intergrown ZIF-8 layer problems on the support surface [46]. To reduce the diffusion rates, a small pore size (5 nm) γ-Al_2O_3 layer was placed on top of the α-Al_2O_3 disc. The γ-Al_2O_3 also acts as a shielding layer for the ZIF-8 membranes, preventing thermal and structural damage. The ZIF-8 grains were discovered to be generated mostly inside the γ-Al_2O_3 disc. About 70% of alumina's mesopore was filled with the ZIF-8. Li et al. [47], on the other hand, used a solvothermal technique on a porous alumina support to synthesize the ZIF-8 membrane. The support was first immersed in a 2-methylimidazole melting solution before being infiltrated with a zinc nitrate aqueous solution and heated. After 8 h at 120 °C, a well intergrown and continuous membrane was obtained. The barrier was roughly 12-µm thick, and the maximum zinc concentration was discovered on top, near the surface.

Recently, a SiO_2/ZIF-8 nanofibre membrane was fabricated through the contra-diffusion technique [48]. The as-spun SiO_2 nanofibre was vertically fixed in the middle of a homemade two-cell-diffusion setup. The ultrasonically dispersed ZIF-8 precursors were poured into each cell and let to crystallize for 0.5–2 h at room temperature before taken out and rinsed with methanol. Benefiting from the high surface area of ZIF-8, the composite nanofibre increases in the specific surface area and enhances the number of functional groups Therefore, the particulate matter removal efficiency and formaldehyde capture capacity are also increasing. A group of the researcher also implements the same technique with a slight modification to produce ZIF-8 membrane on porous PVDF [49]. PVDF support membranes were cut into circular discs with a diameter of 12 cm and placed on a customized setup. 2-Methyl imidazole and zinc nitrate solutions were individually poured on two sides of the membranes. The height of the 2-methyl imidazole solution was 4 cm higher than that of the zinc nitrate solution. After diffusion of solutions into the membranes at various duration times of the reaction, the membranes were taken out and dried at room temperature. The results indicated that the membrane prepared at 5 h synthesis time showed excellent performance for dye removal. The modified membranes' improved dye removal performance was owing to improved selectivity and the repulsion effect between the negatively charged membrane and anionic dye molecules. The optimum modified membrane's reusability test with BSA solution revealed only a 36% drop in water flux after three uses. The increased antifouling property of the ZIF-8 modified membranes was substantiated by the observed relative increase in the reversible resistance (Rr) value.

Sonochemical has been one of the favourable methods to deposit nanomaterials on a ceramic surface by forming chemical bonds or chemical interactions with the substrate [50]. A ZIF-8 film was successfully deposited on a Zn metal substrate utilizing the sonochemical technique [51]. Initially, oxidizing agent was used to convert the metal subtrate into metal hydroxide. The ultrasonic irradiation of 100 W was supplied to drive the reaction between the metal ion sourced and the organic ligands for ZIF-8 film formation. The

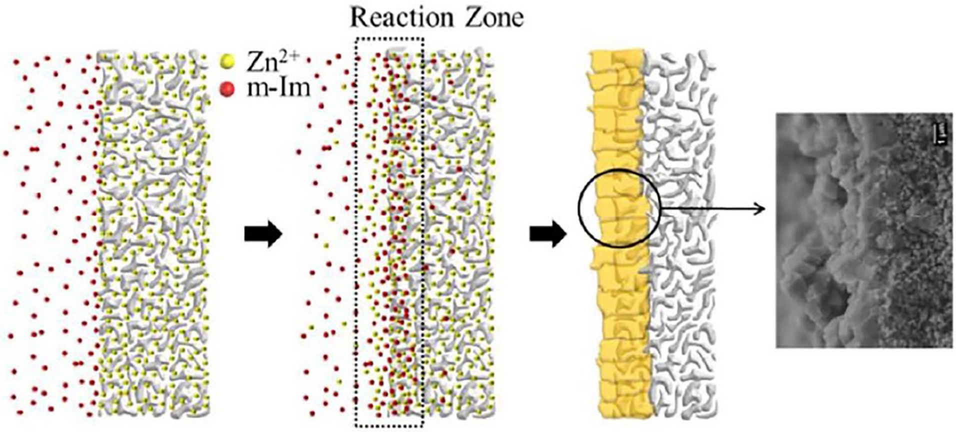


Fig. 6 The in situ growth via counter-diffusion-based synthesis scheme adapted from [45]

temperature was increased steadily with the increment of sonication time. The ZIF-8 films formed then washed with deionized water and acetone and dried in nitrogen before further analysis. From the SEM results, it was observed that the ZIF-8 crystals formed on the substrates have rough surfaces, yet some angles could be spotted. The ZIF-8 crystals can only be seen after 5 min of ultrasonic irradiation, with an average size of 500 nm. However, the ZIF-8 films are not uniform, forming from aggregation of poorly resolved ZIF-8 crystals. Prolonging the reaction duration up to 60 min promotes better ZIF-8 growth on the substrates. The synthesis route of ZIF-8 membrane was shown in Fig. 7.

A thin ZIF-8 layer produced through gel-vapour deposition technique was reported by Li et al. [52]. The scalable and environmentally friendly technique combines both the sol–gel coating and vapour deposition technique, without prior modification, and also solvent-free. This technique was able to produce a controllable thickness of ZIF-8 membrane by modifying the concentration of precursors and the approach for coating process. The method also offers several other advantages including no solvents, and pre-treatment of the substrate is required, outstanding compatibility between the ZIF-8 layers and the support, adjustable location of ZIF-8 layers and also time-effective synthesis process. In the economic point of view, the methods offer greater advantage because the method has the ability to reuse the costly ZIF-8 precursors.

A few years back, a group of researchers reported an approach named interfacial microfluidic membrane processing (IMMP) to fabricate ZIF-8 layer in the inner-side of polymeric hollow fibre membrane [53]. The technique involves three important concepts: (i) the in situ synthesis of ZIF-8 in the membrane module, (ii) an interfacial approach of precursors' solution that is able to tune the position of membrane formation, and (iii) the controllable supply and reusability of reactants. Then a few years later, the same group of researchers published another report on the fabrication of ZIF-8 membrane utilizing the same IMMP technique [54]. The later report further supports that the IMMP technique is able to produce a well-grown ZIF-8 membrane and the membrane showed excellent stability over the long term of operation for gas separation application. A similar approach was also utilized by other researchers, using PBI hollow fibre membrane as support, without seeding process or hydrothermal growth [55].

To further enhance the quality of the membrane produced, for instance, to repair membrane defects due to pinholes or cracks, a layer of the polymer was coated on the ZIF-8 membrane [56][56]. The polymer layer, also known to hinder the flexibility of the ZIF-8 structure, thus contributes to the desired increase in molecular separation [58].

Another MOF deposition method, known as rapid thermal deposition (RTD), was reported to synthesize a well-intergrown membrane of HKUST-1 and ZIF-8 [59]. The RTD is established from the idea of evaporation-induced crystallization studied by Ameloot et al., [60] but RTD is carried out at an elevated temperature. The support layer is soaked in the MOF precursors' solution and heated at high temperatures in this procedure. The flow of the precursors' solution from the inside of the supports to the outside is initiated by the quick evaporation of the solvent from the support. At the same time, crystallization happened at both sides of the support. The RTD process is exhibited in Fig. 8. The microstructure of the membranes prepared via the RTD method displayed a more well-defined structure, in comparison with the membrane prepared via a conventional method. The gas separation performance also significantly improved which is contributed by the improved grain boundary structure.

An electrospray method was reported for the ZIF-8 membrane preparation on a polished disk shape alumina support [61]. The advantages of this approach are as follows: it can

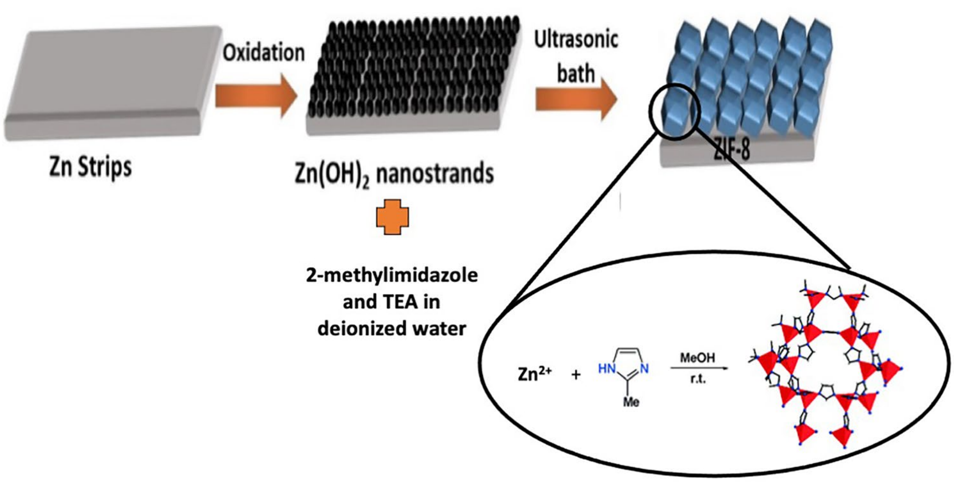


Fig. 7 Schematical diagram of ZIF-8 and MOF-5 membranes on Zn strips adapted from [51]

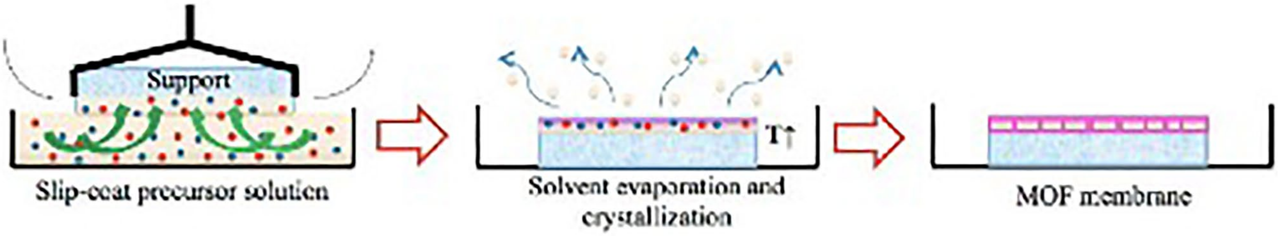


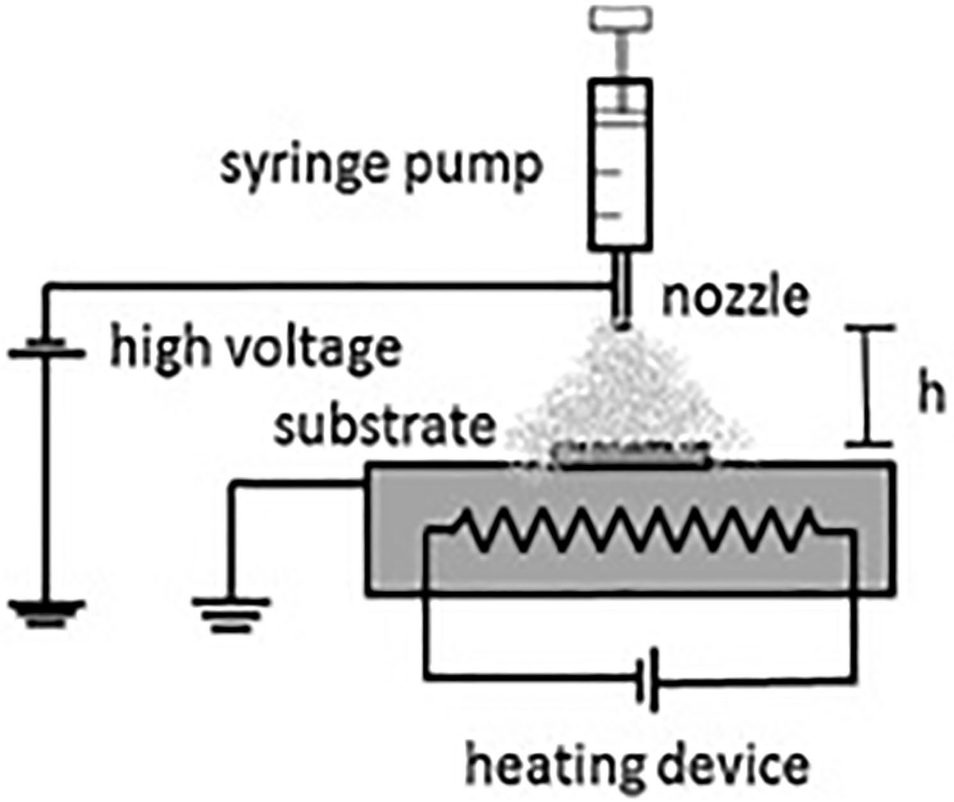
Fig. 8 Schematic illustration of rapid thermal deposition adapted from [59]

reduce reagent waste and duration of the synthesis, apart from the ability to control the thickness of the membrane produced. Therefore, this technique also offered a unique potential for the commercialization of ZIF-8 membranes. The experimental setup is shown in Fig. 9.

Shekhah et al. [62] reported a layer-by-layer technique to produce CU-BTC surface-anchored MOF (SURMOF) membrane. The process was then widely used to generate several types of SURMOF membranes with excellent monolithic properties and high crystallinity, making them ideal for membrane applications. Sanchéz et al. [53] [63] reported the formation of SURMOF ZIF-8 membrane on top of the Au modified alumina support by employing the same technique reported by Shehkah et al. The step was shown in Fig. 10. The functionalized supports were immersed in methanolic precursor solutions and the rinsing solution using a dipping robot in the following order: (i) 10-mM zinc dinitrate hexahydrate solution (300 s), (ii) pure methanol for rinsing (100 s), (iii) 20-mM 2-methyl-1H-imidazole (300 s) as the linker source, and (iv) pure methanol for washing (100 s). This was followed by the next deposition cycle, which began with step (i). The thickness of the SURMOF can be modified by the number of cycles. The dipping approach results in the production of defect-free membranes due to the layer-by-layer deposition process.

A solvent-free and seed-free synthesis technique, known as ligand-induced permselectivity (LIPS) was reported to prepare the ZIF-8 membrane on top of the alumina support [64]. The method is based on the combination of oxide vapour deposition followed by 2-methylimidazole ligand-vapour treatment to form ZIF-8, as shown in Fig. 11. This approach was able to prevent the drawbacks associated with

Fig. 9 Electrospray deposition setup for ZIF membrane preparation adapted from [61]



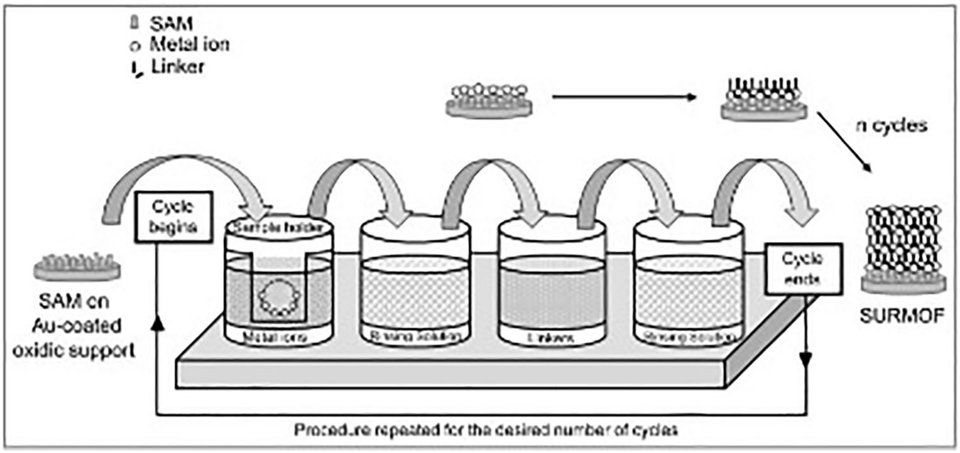


Fig. 10 The layer-by-layer steps for the formation of SURMOF adapted from [63]

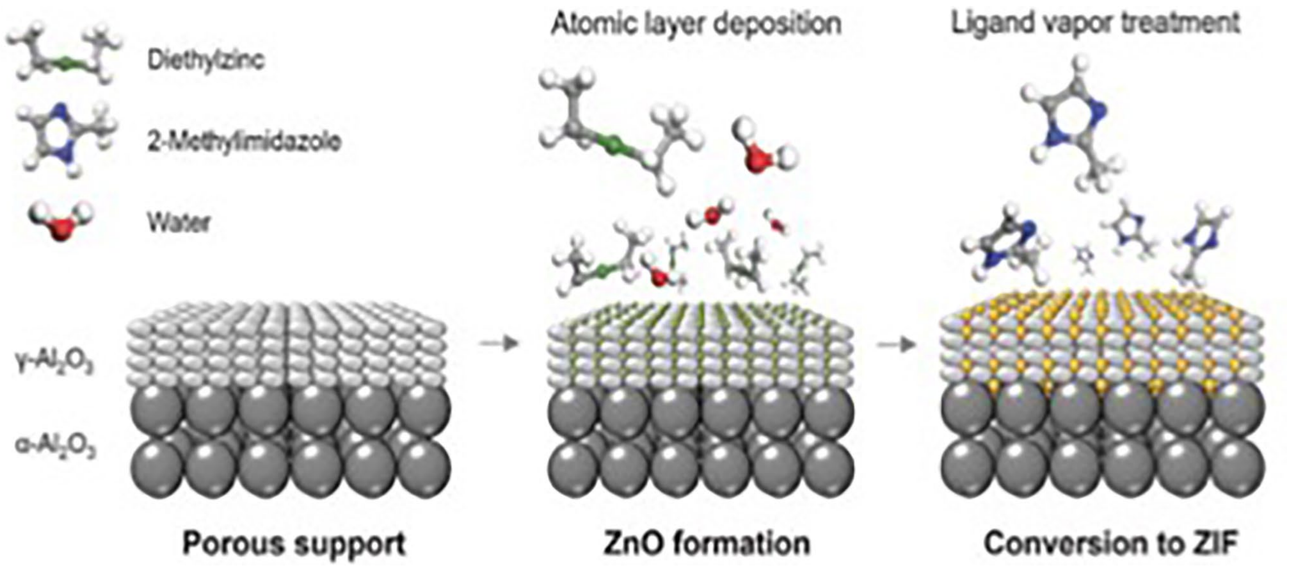


Fig. 11 Illustration of atomic layer deposition technique for ZIF-8 membrane formation adapted from [64]

pore-filling membrane growth such as pinholes and non-selective grain boundaries. As a result, the membrane shows stable performance with a high mixture separation factor for propylene over propane, and high propylene flux. This method has provided a new insight into the preparation of the ZIF-8 membrane with the reliable, scalable and robust approach.

Another interesting approach inspired by the preparation of RO membrane fabrication was reported by Li et al.[25]. ZIF-8 membrane was fabricated on porous PES supports via interfacial polymerization method. The approach started with the immersion of the PES support Hmim solution. After wiping away the excess aqueous solution, the Hmim solution was slowly poured over the surface and rained off after a predetermined duration. Then, the membrane is washed with hexane and methanol and annealed via overnight drying. The SEM image of the ZIF-8 membrane on PES support is shown in Fig. 12.

The research also revealed that the supporting membrane was able to affect the development of the ZIF-8 membrane. Zinc nitrate diffuses toward the water/octanol surface during the interfacial reaction, resulting in a concentration difference. Lower mass transfer resistance causing the zinc nitrate concentration at the interface of the open support is close to the bulk concentration. Therefore, looser packing of ZIF-8 support will be observed at the support surface. On the other hand, the dense support will restrict the transport of zinc nitrate from the bulk of the support to the interface thus resulting to a larger Hmim to zinc nitrate ratio at the interface. As a result, a denser packing of ZIF-8 can be observed. The schematic diagram of the mass transfer was shown in Fig. 13.

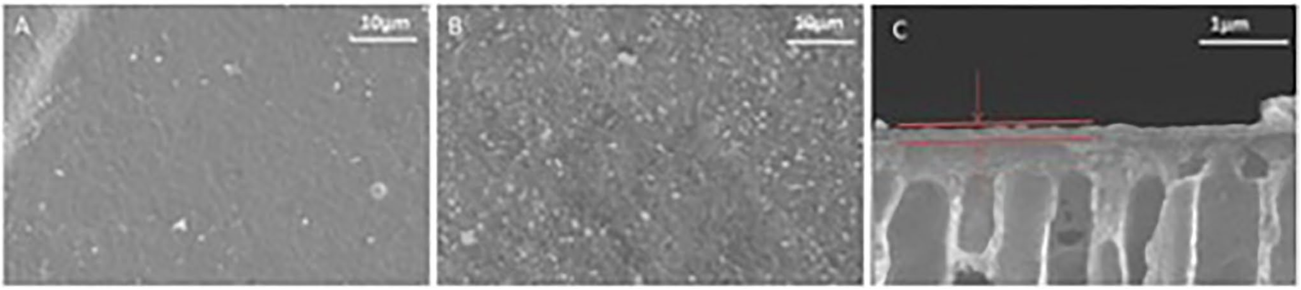


Fig. 12 The SEM images of ZIF-8/PES membranes: (**A**) surface image of the PES support after 3 h octanol treatment, (**B**) surface images of a ZIF-8/PES membrane, (**C**) cross section image of a ZIF-8/PES membrane adapted from [25]

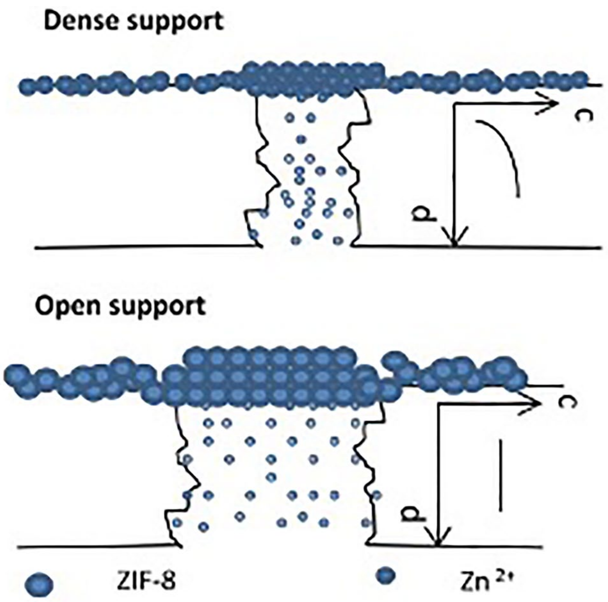


Fig. 13 The schematic diagram of the effect of support layer on the formation ZIF-8/PES membrane adapted from [25]

The support membrane also plays important roles to the long-term application of the membrane. The summary on the advantages offered by different support membranes to the long-term application of the ZIF-8 membrane is tabulated in Table 1.

2.2 Mixed matrix membranes

The pure ZIF-8 membranes suffer from the separation performance issue for practical application apart from their disadvantage on the difficult preparation and high cost. Therefore, to overcome the issue, researchers have made moves to research on the MMMs in recent years. ZIF-8 is in the form of microcrystalline powder, thus it is suitable to act as filler in the polymeric membrane. The implementation of MOF particles as fillers in the TFN is firstly reported by Sorribas et al. in 2013 [71]. The researchers have successfully incorporated few MOF nanoparticles including ZIF-8 in the polyamide thin film layer via in situ IP on top of the crosslinked polyimide support. The research is the breakthrough for the development of MOF MMM membrane for various applications including NF. The synthesis strategy of ZIF-8 membranes will be discussed in the following section.

2.2.1 Blending

The blending of ZIF-8 and polymer materials is the conventional method for the ZIF-8 MMM preparation method. A stable dope solution was prepared by dispersing the ZIF-8 particles in a polymer matrix. Then, the mixture is coated on the substrate via the casting method and dried for the membrane. There are three different types of blending techniques [72]. The first approach is dispersing of nanoparticles in a suitable solvent before adding the polymer to the same solution and continue with the casting process, while the second approach requires the dissolving of polymer in a proper solvent then continue with the addition of nanofillers before the casting. Meanwhile, the third approach involves separate dissolution of filler and polymer, then both of the solutions will be mixed upon the casting process.

Zhao et al. has reported the fabrication of TFN containing polydopamine (PDA) modified ZIF-8 for NF application [17]. The ZIF-8 nanoparticles are modified with the PDA and the preparation of the TFN is employed via the classic IP procedure. Polydopamine (PDA), an extensively used compound for hydrophilic modification of the solid surface, and the good interaction of PDA with the PA monomers improve the dispersibility of the ZIF-8 particles in the polyamide matrix. As expected, the modification using PDA also enhanced the wettability of ZIF-8 and improved the dispersion of the particles in an aqueous solution. The preparation step for the TFN is shown in Fig. 14.

Another study reported on the preparation of the ZIF-8 membrane modified with resin microspheres (ZIF-8@RMs) [73]. The ZIF-8@RMs were firstly fabricated via in situ growth. ZIF-8 nanoparticles were anchored on the outer surface of the RMS to develop the ZIF-8 core–shell

Table 1 The support materials used for the synthesis of ZIF-8 membranes and their advantages for long term applications

Support material	Deposition techniques	Advantages of the support material	References
PES	Interfacial synthesis	The open pores of the support produce continuous growth of ZIF-8 due to nucleation of ZIF-8 in the pores of the support	[65]
PES	In situ growth method	ZIF-8 membrane has better fouling resistance rather than pristine support membrane due to the decrease in surface roughness after ZIF-8 growth on the support membrane	[66]
Tubular ceramic support	Vacuum-assisted assembly method	The ceramic tubular provides better mechanical strength and the ZIF-8 layer improve the dye rejection	[67]
PVDF ultrafiltration membrane	Contra-diffusion method	High stability of PVDF contribute to the good reusability performance of the membrane	[49]
PVDF ultrafiltration membrane	In situ polymerization	High stability of PVDF enable the reusability of membrane with high adsorption capacity for nickel removal	[68]
PI	Interfacial polymerization	Chemically stable support suitable for OSN membrane. The membrane exhibit high RBD rejection (99.1%) and reasonable ethanol permeance (~28 Lm^{-2} h^{-1} MPa^{-1})	[69]
Hyphae	Sonochemical method	Flexible support membrane with abundant functional groups on the cell wall, such as phosphonate, hydroxy and amino group thus improve the formation of ZIF-8 and stability of the membrane	[70]

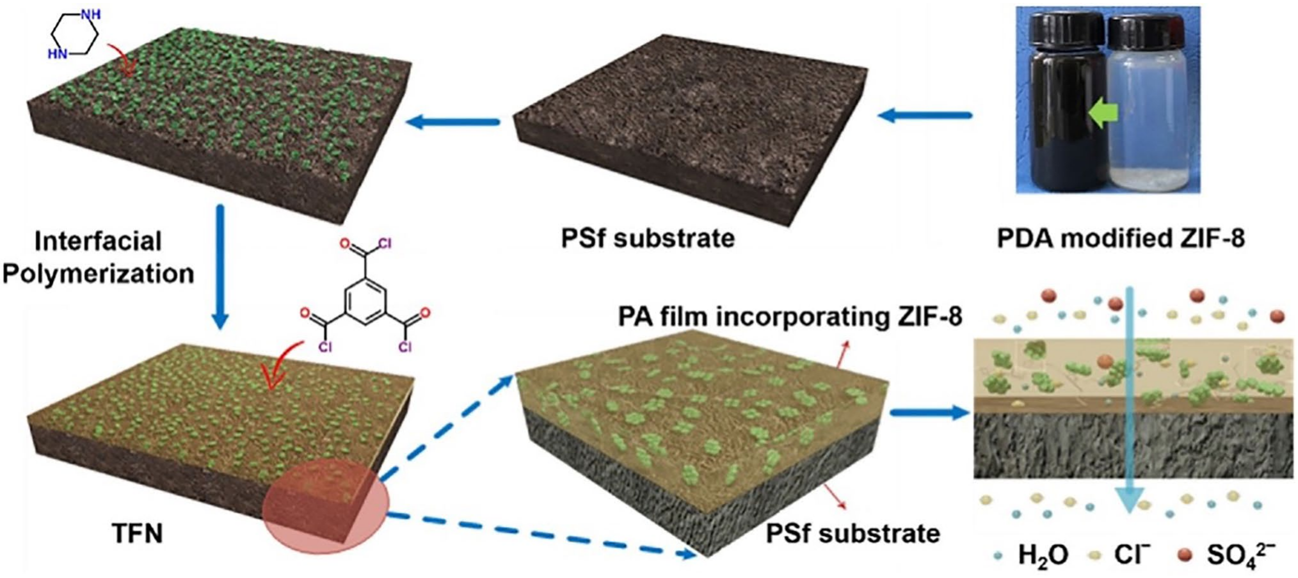


Fig. 14 The preparation step for PDA modified-ZIF-8 TFN adapted from [17]

sphere composite. The MMMs were then made by using the immersion precipitation phase inversion procedure to blend the ZIF-8@RMs as a filler in PPSU. The incorporation of ZIF-8/RMs to the PPSU is expected to increase microporosity in MMMs, reducing ZIF-8/PPSU interface defects. The benefit of RMs' spherical morphology and ZIF-8's outstanding selective micropores is that faults between ZIF-8@RMs and PPSU are reduced. The preparation technique for the ZIF-8@RMs MMMs is shown in Fig. 15.

A new route for the fabrication of nanocomposite ZIF-8 membrane was reported by Li et al. [74]. The researchers have developed an Aramid nanocomposite membrane, by non-solvent induced phase inversion and thermal post-treatment method. The Aramid nanofibre was exfoliated from Kevlar fibre in potassium hydroxide/dimethylsulfoxide. Then, the ZIF-8 was blended in a branched polyethyleneimine (BPEI) and DMSO solution. The coordinative binding of ZIF-8 and BPEI resulted in the good dispersion of ZIF-8 in the ANF dope solution. The results from the study indicated that the steric hindrance of ZIF-8 controls the rearrangement of nanofibres, thus producing a more permeable intermediate layer. Additionally, the non-covalent

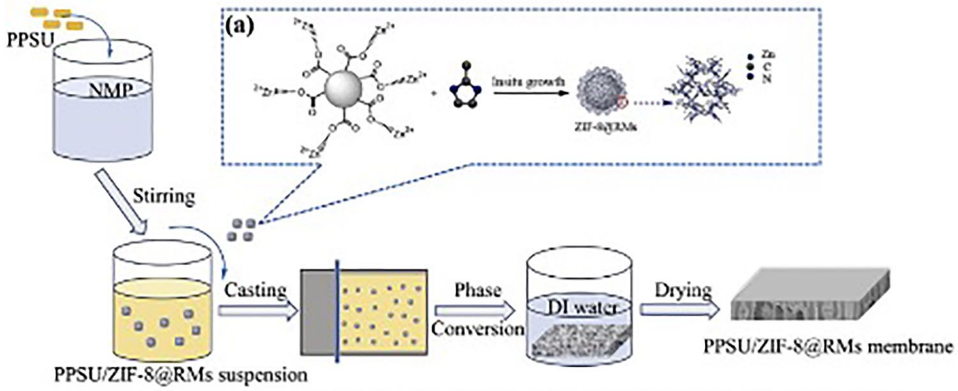


Fig. 15 The preparation steps for PPSU/ZIF-8@RMs membrane (a) Schematic diagram for the fabrication of ZIF-8@RMs adapted from [73]

interactions between the ZIF-8 and ANFs provide considerable mechanical strength to the composite film. Figure 16 depicted the method for the fabrication of the ZIF-8=-modified Aramid nanofibre.

2.2.2 In situ *growth*

Preparation of the MMM membrane by employing the in situ growth technique creates a better dispersion of the ZIF-8 particles within the polymer matrix. A coordination-driven in situ assembly method was reported to develop hybrid ZIF-8/PSS membrane on the polyacrylonitrile (PAN) substrate [75]. In situ formation of ZIF-8 during the membrane fabrication improves the dispersion of the nanoparticles, thus leading to the increase in the compatibility, stability, rejection, adsorption and wettability of the membrane. The improvement can be denoted due to the formation of chemical bonds between the nanoparticles and the polymer. Figure 17 shows the preparation scheme of the process.

Another interesting approach reported by Zhao et al. to improve the performance of membrane is by constructing a ZIF-8 interlayer between PES microfiltration membrane and PA layer [76]. In the study, a modified interfacial synthesis technique was applied by the addition of poly(sodium 4-styrene sulfonate) into the aqueous region to preserve the ZIF-8 layer developed at the water/organic interface. The polystyrene is able to control the dispersal of ZIF-8 on the PES, thus resulting in a thin, uniform and well-grown PA film. The Zn^{2+} was able to coordinate to the PSS polymer via coordination with the oxygen atom of the sulfate. The coordinated Zn^{2+} at the same time coordinates with the nitrogen atom of the Hmim at the water/n-hexane interface, which then induces the initial growth of ZIF-8. Since the ZIF-8 particles formed in between the PSS polymer, thus the connection between the particles was enhanced. Therefore, a stable ZIF-8 layer was obtained due to the strong interaction between the ZIF-8 particles and the polymer. It can be inferred that the addition of PSS is able to improve the dispersion and homogeneity of the ZIF-8 on the substrate. Figure 18 illustrated the mechanism of the ZIF-8 formation through the PSS-assisted interfacial synthesis approach.

2.2.3 Layer by layer

The support layer is soaked in the ZIF-8's precursor solution following the layer by layer (LBL) process. The substrate is cleaned with solvents after each cycle of deposition to eliminate any unreacted precursors and guarantee that a continuous coating of ZIF-8 forms on the substrate. Wang et al. in 2015 have reported on the preparation of the ZIF-8 TFN membrane. The LBL approach includes two steps; first by the growth of ZIF-8 nanoparticles on the porous substrate

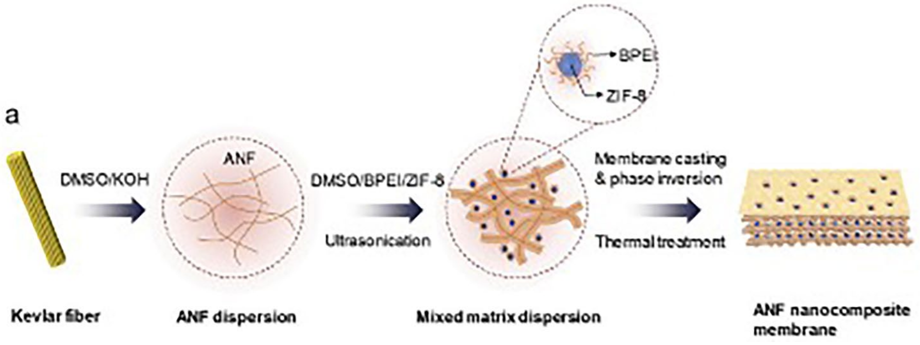


Fig. 16 Preparation of ANF nanocomposite membrane adapted from [74]

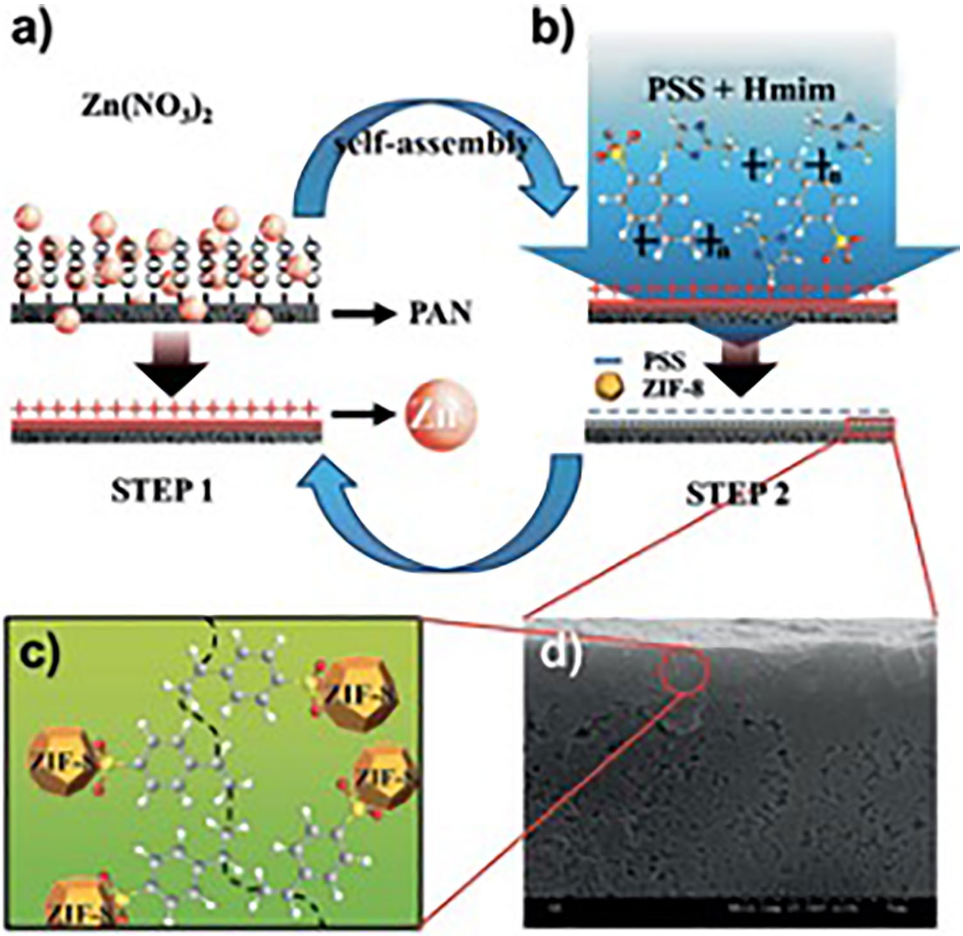


Fig. 17 The coordination driven self-assembly method **a**) Assembly of Zn2+ on the substrate. **b**) Assembly of PSS and formation of ZIF-8 particles **c**) proposed structure of the membrane and **d**) cross-section SEM image of the resulting membrane (two layers) adapted from [75]

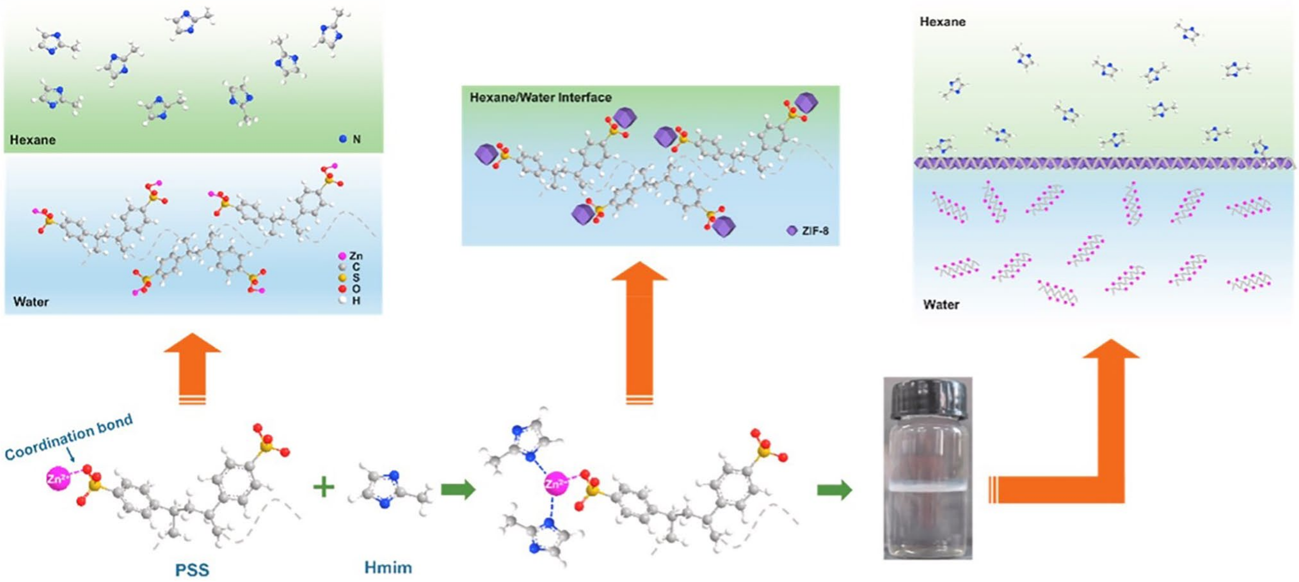


Fig. 18 The synthesis mechanism of the PSS-assisted interfacial method adapted from [76]

via the in situ growth method. The second process required forming an ultrathin PA layer on top of the ZIF-8 layer, followed by IP and curing. The high compatibility of polymers and ZIF-8 allows gaps between ZIF-8 nanoparticles to be filled. Moreover, this method also can overcome the aggregations of nanoparticles because no dispersion of nanoparticles in a polymer matrix is needed. Figure 19 depicted the preparation step for the LBL method.

Basu and Balakrishnan also prepared a ZIF-8 TFN membrane utilizing the LBL technique, as previously employed by Wang et. al. The fabrication steps started with the in situ formation of ZIF-8 on the polymer support [3]. Then, ZIF-8/PA layer was fabricated on the PSF support via layer-by-layer (LBL) technique. Washing process is performed after each cycle by using suitable solvents to remove any unreacted starting materials. The AFM image of the membrane revealed the good formation of PA film on top of the ZIF-8 layer. The well-distributed formation of PA film enhanced the adhesion between the ZIF-8 layer and the PA layer.

In 2020, Huang et al. has reported an interesting method to prepare the prepare ZIF-8-decorated hyphae membrane [70]. The researcher successfully prepared a special phased growth of ZIF-8 on a hyphae (mucor) surface. The layer-by-layer approach successfully avoids the self-aggregation of the ZIF-8 particles and also able to produce the layer-by-layer assembly of the membrane. The preparation technique is shown in Fig. 20.

3 ZIF-8 membranes for NF application

The high-pressure NF membrane process has shown great ability to generate large amounts of high-quality water. The high removal capacity, the decreasing price for the membranes, low energy consumption and enhanced membrane lifetime in comparison with the RO membranes have made the NF membranes being selected in water treatment applications [77]. ZIF-8 has shown a remarkable potential to be developed as an NF membrane due to the promising results

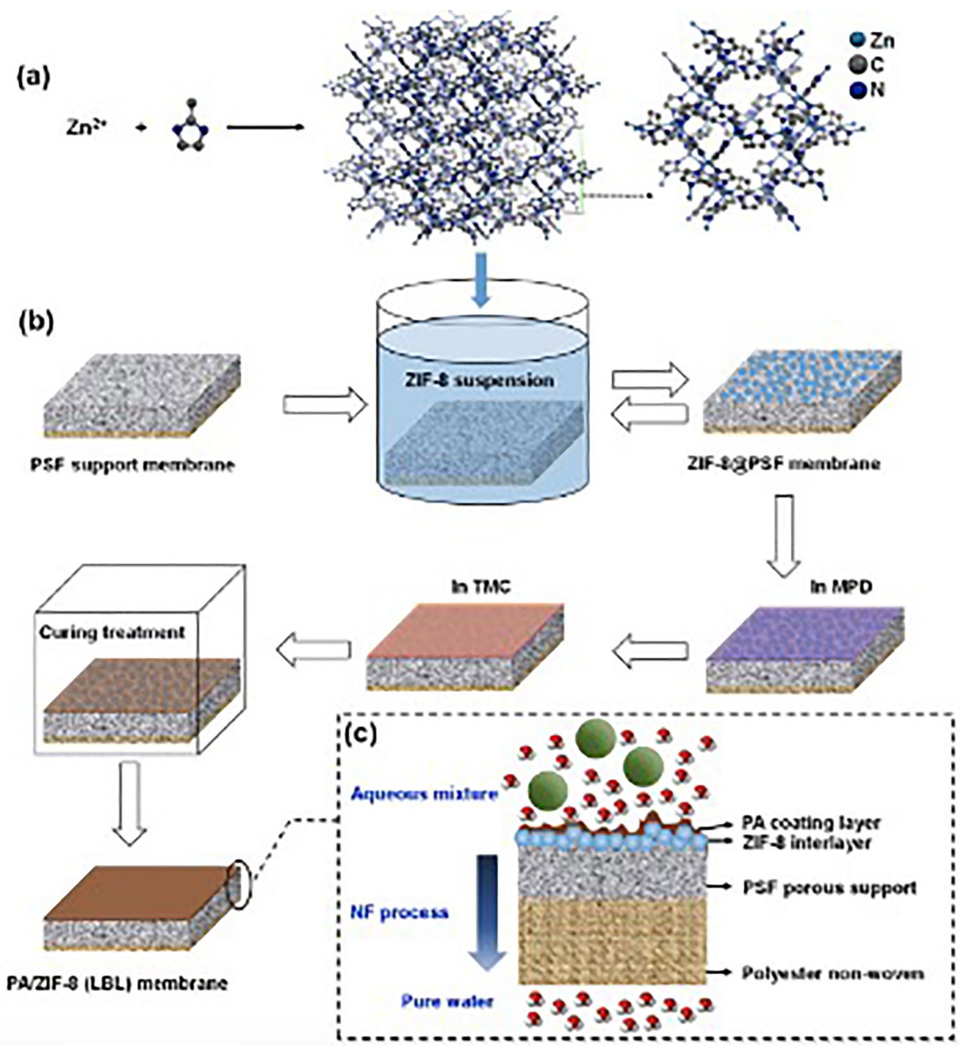


Fig. 19 The preparation step for LBL method (**a**) ZIF-8 synthesis, (**b**) LBL fabrication procedures and (**c**) cross-sectional structure of the PA/ZIF-8 (LBL) membrane adapted from [88]

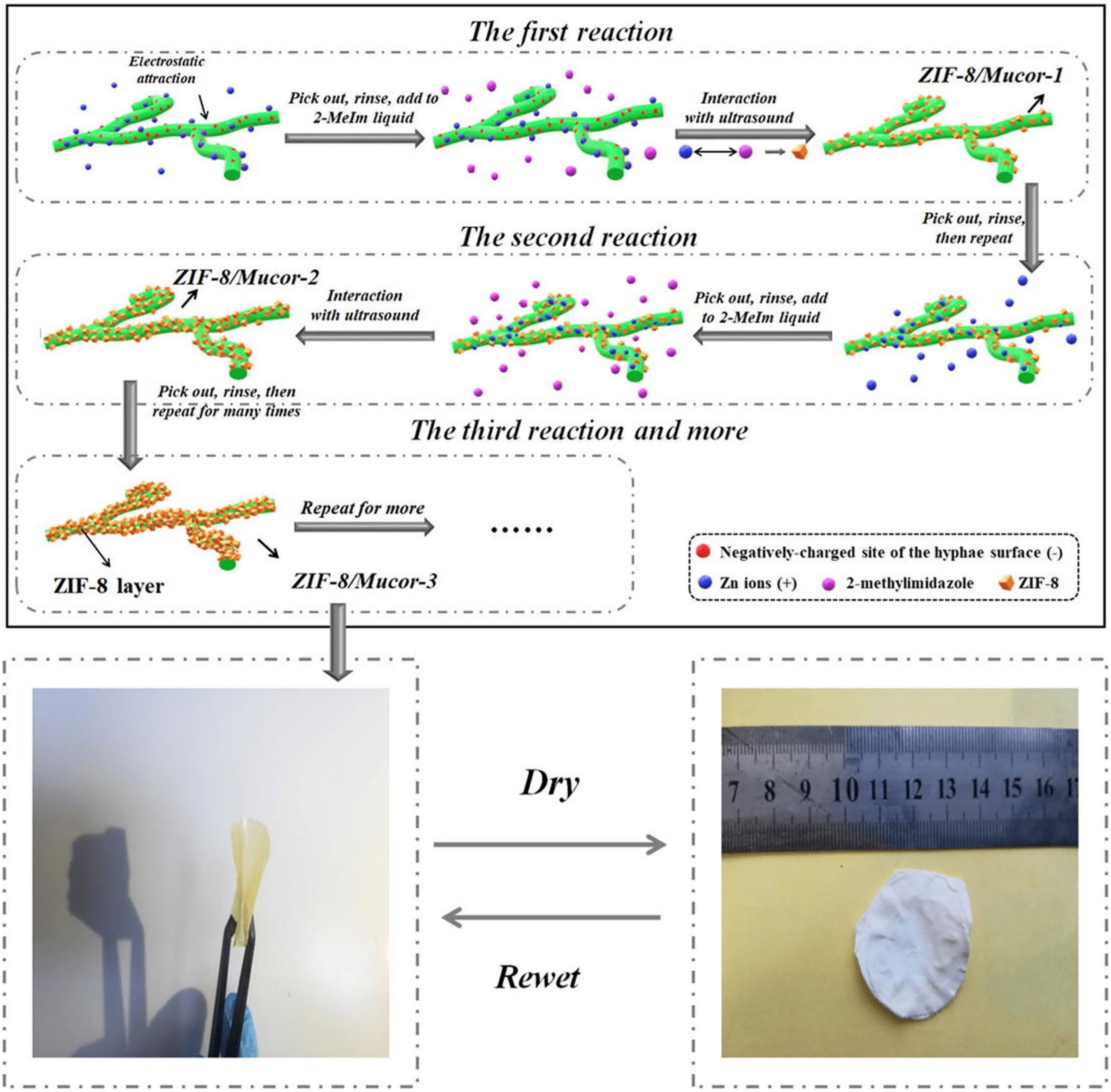


Fig. 20 The preparation step of the ZIF-8-decorated hyphae membrane and the image of the dried and wet membranes

for water treatment. At present, the MMM ZIF-8 membrane is mostly used for water treatment.

The small aperture size of ZIF-8 of 0.40–0.42 nm has placed the ZIF-8 membranes in the NF range, making them comparable with the RO membranes. Mostly, the application of the ZIF-8 is focusing on dye removal. A study reported on the removal of methyl blue in aqueous by using ZIF-8/PSS [75]. The membrane exhibited a flux of 265 $\mathrm{Lm^{-2}\,h^{-1}\,MPa^{-1}}$ and retention of 98.6% at optimum condition, which is higher than the pristine PAN membrane under similar conditions. A thin and uniform ZIF-8/PEI membrane showed almost similar performance for methyl blue removal with permeance up to 33.0 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ with the rejection of 99.6%. The membrane also effectively removes Congo Red, acid fusion (AF), and methyl orange (MO) with stability up to 60-h continuous test. The ZIF-8 membrane also showed excellent ability to remove reactive dyes.

The TFN-mZIF displays high removal of reactive blue 2 (RB2) and reactive black 5 (RB5) [78]. The TFN-mZIF was prepared on top of the HPAN support. The membrane can reject up to 99.2% and 99.0% of the RB2 and RB5, respectively, with the flux of 14.9 $\mathrm{Lm^{-2}\,h^{-1}\,bar^{-1}}$. The TFN-mZIF showed lower dye retention rather than the TFC. Yet, the water flux of TFN-mZIF was enhanced by 199.3% at 4 bar. The great enhancement gives a promising potential for the membrane to be used for dye removal application. A hybrid membrane of poly(sodium 4-styrene sulfonate) with ZIF-8 supported on tubular alumina was synthesized to remove methyl blue dye for an aqueous system [79]. The pristine substrate was found to have dye rejection of 30.4% with a flux of 866 $Lm^{-2}\ h^{-1}\ MPa^{-1}$. When the support was layered with ZIF-8/PSS, the rejection increased to 85.3%, and after seven layers of coating, the rejection increases to 99.4%. Yet, the flux decreases to 92 $Lm^{-2}\ h^{-1}\ MPa^{-1}$ at seven-layer due to the denser layer of the membrane that restricted the flow of water through the membrane. The four layers of the membrane were determined as the optimal layer in this study. The membrane can reject up to 97.4% of the dyes with the flux of 230 $Lm^{-2}\ h^{-1}\ MPa^{-1}$.

Yang et al. reported on the study of the ZIF-8 membrane prepared via in situ methods on the HPAN substrate. The ZIF-8 nanoparticles are embedded within the PEI matrix [80]. The NF performance of the ZIF-8/PEI hybrid membrane indicated that the membrane was able to reject the MB, CR, AF and MO with the rejection percentage of 99.6%, 99.2%, 94.4%, and 81.2%, respectively. The dye with a larger molecular weight has higher rejection rather than the smaller size of dyes. The different permeance towards different dyes is due to the different interactions between dye molecules and membrane surfaces. The higher negative value of zeta potential will lead to the stronger adhesion of the dye with the membrane's surface. The phenome resulted in a thicker dye layer on top of the membrane, and therefore reduced the permeance of the membrane.

Another important application of the ZIF-8 NF membrane is the organic solvent NF application. Numerous studies were conducted to study the performance of the ZIF-8 membrane for OSN application. In 2018, Yang et al. have reported on the ZIF-8@GO composite membrane on ceramic support performance for methanol purification. In this study, the organic dye was used as the solute. The performance study indicated that under optimum conditions, the membrane was able to reject up to 99% of the dye with the methanol flux of 6.1 $Lm^{-2}\ h^{-1}\ bar^{-1}$. The improved flux for ZIF-8@GO/PEI membrane is due to the more well-defined mass transfer channels formed in the membrane. Furthermore, the lower concentration of ZIF-8@GO and PEI used in the vacuum-assisted assembly method also contributed to the higher flux of the membrane. The stability of the ZIF-8 nanoparticles during membrane preparation is one of the important issues that need to be concerned, especially if the membrane is applied for OSN application. Furthermore, a previous study indicated that the linkage between metal and organic linkers of ZIF-8 are dissociated at pH value below than 6 [81–83]. To overcome the limitation, Wang et al. have reported a novel strategy by changing the organic linkers of ZIF-8 into carbon skeleton through direct carbonization of the ZIF-8 [84]. The approach has successfully improved the ZIF-8 stability during membrane preparation contributed by the protonation of acid in acidic condition. Consequently, the CZIF-8/PI MMM exhibits excellent OSN performance with the ability to remove up to 90% of Congo red with the permeance of 16.52, 4.05, and 2.08 $Lm^{-2}\ h^{-1}\ bar^{-1}$in water, ethanol and isopropanol, respectively.

ZIF-8 membrane also showed promising performance for the separation of pharmaceutical waste. In 2017, Basu and Balakrishnan have firstly reported on the performance of the ZIF-8 TFC-NF membrane for the removal of pharmaceutical compounds from wastewater [3]. The ZIF-8 TFC-NF membrane prepared through a layer-by-layer technique was able to produce a defect-free membrane with the ability to reject up to 55% of acetaminophen with the permeance equivalent to the standard PSF/PA membrane. Table 2 summarizes the membrane performance, rejection and application of the previously reported NF membrane.

In comparison with the NF commercial membranes, the ZIF-8 membrane offers several advantages with regard to the properties and performance of the membrane. The commercial inorganic NF membrane, for example alumina, although it has been widely used, the membrane exhibited low rejection towards nanosized molecules [85]. The alumina membranes with a pore size less than 1 nm were fabricated, but due to the low flux, the membrane is not suitable for industrial applications [86]. On the other hand, the ZIF-8 membrane offers good molecular rejection and at the same time, exhibits high water permeation due to the porosity of the material. Whilst the commercial polymeric NF membrane is well-known for its molecules rejection; however, the membrane is not suitable for high temperature applications. Whereas for the ZIF-8 membranes, the material is well known for its thermal stability [7], therefore the ZIF-8 membrane has better advantage to be applied for water separation at high temperature.

4 Challenges and future outlook

A decade ago, the ZIF-8 membranes are well-known for gas separation applications. The expeditious growth of the ZIF-8 membranes can be significantly observed by the tremendous increase in research and publications. However, the utilization and progress of ZIF-8 in other fields are still not well established. This is due to several reasons, related to the characteristics and performance of the produced membrane, for example, the stability, selectivity and pore size. Another relevant issue apart from the aforementioned matter is the compatibility of the ZIF-8 with the support or polymer matrix and the issue of dispersibility of the ZIF-8

Table 2 The summary of previously reported nanofiltration membrane

Polymer matrix	Support	Composite membrane fabrication technique	Flux	Rejection	Application	References
PSS	PAN	Coordination in situ self-assembly	265 Lm^{-2} h^{-1} MPa^{-1}	98.6% for methyl blue	Dye removal	[75]
PA	HPAN	Interfacial polymerization	14.9 Lm^{-2} h^{-1} bar^{-1}	99.2% for RB2, 99.0% RB5	Dye removal	[78]
	PES	Liquid–liquid interfacial coordination	Up to 37.5 L m^{-2} h^{-1} bar^{-1}	> 98% for RB	Dye removal	[25]
	PSF	In situ growth with substrate modification	> 30 L m^{-2} h^{-1} bar^{-1}	> 99% for MB, CR, MBA and AR > 97% for MO and IA	Dye removal	[87]
PA	PSF	Layer-by-layer	27.1 $kg/m^2/h$	99.8% for CR	Dye removal	[88]
	PVDF	Non-solvent induced phase inversion	10.4 L m^{-2} h^{-1} bar^{-1} for water 14.7 L m^{-2} h^{-1} bar^{-1} for IPA 37.7 L m^{-2} h^{-1} bar^{-1} for ethanol	96.1% RB in water, 99.5% RB in IPA 99.2% RB in ethanol	Dye removal	[89]
PEI	HPAN	Self-assembly and interfacial reaction	33.0 L m^{-2} h^{-1} bar^{-1}	99.6% for methyl blue aqueous solutions,	Dye removal	[80]
Chitosan/PVA	PVDF	Blending	78.94 L m^{-2} h^{-1} bar^{-1}	90.32%malachite green	Dye removal	[90]
PEI	Ceramic substrate	Vacuum-assisted assembly	6.1 L m^{-2} h^{-1} bar^{-1} for ethanol	99% of organic dyes	Organic solvent nanofiltration	[67]
PEI	Aramid nanofibre on non-woven PP/PE	Non-solvent induced phase inversion and thermal post-treatment	2.9 L m^{-2} h^{-1} bar^{-1} for ethanol L m^{-2} h^{-1} bar^{-1} for IPA	> 90% EB	Organic solvent nanofiltration	[74]
PA	PI	Interfacial polymerization	~ 28 L L m^{-2} h^{-1} MPa^{-1} for ethanol	99.1% RBD	Organic solvent nanofiltration	[69]
PA	PSF	layer-by-layer	5.5 Lm^{-2} h^{-1} bar^{-1} for 4 layer membrane	55% acetaminophen	Pharmaceutical compounds from aqueous feed	[3]
PSS	PES	Interfacial polymerization	9.6 L L m^{-2} h^{-1} bar^{-1}	91% SO_4^{2-}	Water treatment	[76]
PA	PSF	Interfacial polymerization	4.81 L m^{-2} h^{-1} bar^{-1}	89.9% for SO_4^{2-}	Water treatment	[17]

nanoparticles in polymer or organic matrix which leads to aggregation at high concentration [91]. The improper interfacial interaction of MOF with the polymer system or the substrates may lead to defects of the ZIF-8 membrane, for example, cracking [9] and non-continuous growth [92] for pure ZIF-8 membrane or pore blocking [93], polymer chain rigidification [94, 95] and formation of interfacial voids [96, 97] in the MMM membrane. Apart from that, scalability of the ZIF-8 membrane is another challenge. The weak adherence of the ZIF-8 to the polymer matrix needs to be improved to enhance the stability of the ZIF-8 MMM membrane.

The lower stability of ZIF-8 compared to other fillers such as zeolites [98] especially the water stability and stability towards organic media is another challenge. Most of the pure ZIF-8 membrane and ZIF-8 MMMs require the support layer during preparation. The weak adhesion between the ZIF-8 nanoparticles and the membrane support will cause the peel off of the layers, which leads to the inefficiency of the membrane for separation purposes [33]. Surface modification is one of the possible measures to overcome the delamination issue between the ZIF-8 layer and the substrate. However, the flexibility of the ZIF-8 framework also contributes to the instability of the membrane.

The scaling up of the ZIF-8 membrane for industrial and commercial applications is an interesting issue that needs to be considered. In terms of synthesis route, the ZIF-8 membranes have more advantages rather than the zeolite membranes, for example, the ZIF-8 synthesis can be carried out at room temperature with shorter synthesis duration and lower cost due to the mild synthetic conditions which allow the use of polymer as supports [98]. However, when considering the water stability of the ZIF-8 membrane, the application of the membrane for prolonging filtration time rather becomes the biggest challenge for commercial application.

5 Conclusions and prospects

The application of the ZIF-8 membrane for gas separation has been established due to the high porosity, high surface area and adjustable structure of the material. To further enhance the potential of ZIF-8, researchers have prepared the ZIF-8 membranes either in the form of a pure membrane or mixed matrix membranes. Numerous methods have been developed regarding the preparation of the ZIF-8 membrane. The pure ZIF-8 prepared via in situ growth, secondary growth, microwave-assisted growth, electrodeposition method and other techniques include the contra-diffusion method. Whilst for the MMMs, several methods have been well established for instance the blending method, in situ growth method and the layer-by-layer method.

Over the last few years, the ZIF-8 membranes have been applied for liquid separation including NF. Numerous NF applications have been discussed in this review including water treatment and organic solvent nanofiltration. From the perspective of preparation and application of ZIF-8 for nanofiltration application, future research on ZIF-8 membrane will be focusing on the following outlook:

1. Development of simple and scalable techniques for ZIF-8 membranes
2. Preparation of highly stable ZIF-8 membranes for aqueous and organic media
3. Preparation of high permeation and high separation efficiency of ZIF-8 membranes
4. Low-cost and green approach on the fabrication of ZIF-8 membranes
5. Commercialization of ZIF-8 membranes for wastewater treatment

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Declarations

Conflict of interest The authors declare no competing interests.

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