Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29319

286 (2023) 29–39
February

Preparation and application of metal–organic framework-based mixed matrix membranes for water treatment

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Received 24 October 2022; Accepted 24 January 2023

ABSTRACT

Membrane technology has been widely used in the field of water treatment, and the synthesis of membranes with better separation effects and better anti-pollution performances is also the focus of current research. Metal–organic framework materials (MOFs) have attracted extensive attention in many fields in recent years, especially in the synthesis of membranes with excellent water treatment and purification functions. Mixed matrix membranes (MMMs) prepared by adding MOFs to a polymer matrix can improve the performance of the membranes more effectively. In this paper, the advantages of representative MOFs and the preparation method of MOFs-based composite membranes are introduced. Compared with other traditional fillers, MOFs-based MMMs have more advantages in the separation process. It has been successfully integrated with the MOF membranes prepared, and various membrane processes are used in wastewater treatment or seawater desalination processes, for example, forward osmosis, ultrafiltration, nanofiltration, and reverse osmosis. At last, insights and viewpoints are put forward on research contents and development directions in the future. The membrane based on MOFs has excellent separation properties, low biological contamination, and high-water permeation flux, so it is expected to become the leading water treatment technology (in particular, desalination and wastewater treatment).

Keywords: Metal–organic frameworks; Mixed matrix membrane; Water treatment

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1. Introduction

The process of turning a mixture into two or more different substances is called a separation process [1]. Analytical separation methods developed in recent decades have been widely used, which include but are not limited to adsorption, distillation, extraction, crystallization, and membrane separation. Membrane separation technology stands out among these separation technologies due to its high energy efficiency, low investment, environmental friendliness, and other advantages, and has sparked widespread concern. Membrane separation technology has been widely used in various fields, including the petrochemical industry [2], environment protection [3], biorefinery [4], desalination water treatment [5], etc.

The membrane can essentially be seen as a physical wall that isolates two different phases and inhibits the transfer of different chemical substances in the process of individual selection [6]. There are many types of membranes, which can be liquid or solid [7], symmetric or asymmetric, and homogeneous or heterogeneous (based on their structure) [8]. According to pore size, the pressure-driven separation membranes are divided into four types: microfiltration (50–500 nm), ultrafiltration (2–50 nm), nanofiltration (≤2 nm), and reverse osmosis (0.3–1 nm) [9]. Finding a balance between selectivity and permeability is the key to develop advanced membranes with good performance [10]. High permeability and high selectivity are the advantages of the separation membrane. The most important factor that affects membrane performance is the properties of the membrane itself [11]. Polymer macromolecules, such as polyethersulfone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), and other materials, have been used due to their respective advantages [12]. However, since the performance of the membrane is still not ideal, research on the modification of the membrane has attracted extensive attention. Blending modification is one of the most widely used methods. Blending modification refers to the preparation of membrane materials that add a solid phase to the casting solution to form a three-chamber space. The additives mainly include graphene oxide (GO) [13], carbon nanotubes (CTN) [14], metal–organic frameworks (MOFs) [15], etc. MOFs, as a new type of potential nanomaterial, have been widely studied and applied. After modification, the hydrophilicity of the membrane is improved, and the anti-pollution and permeability properties of the membrane are optimized. The advantages of MOFs, the classification and preparation of MOFs-based membranes, and their applications in water treatment, including the desalination of seawater and the treatment of wastewater, are introduced. Overall, MOFs performed better than traditional additives in membranes.

2. MOF membranes

2.1. MOFs

Metal–organic frameworks are considered a kind of potential nanomaterial in the 21st century. The combination of metal ions or metal clusters with an organic binder forms MOF materials [16]. In the 1990s, Yaghi and Li [17] first introduced the definition of MOFs. Since then, research on MOFs has exploded in recent decades, establishing a new field of research. The sub-family of MOF includes, for example, zeolitic imidazolate framework (ZIF) [18], metal azolate framework (MAF) [19], zeolite-like metal–organic framework (ZMOF) [20], and covalent organic framework (COF) [21].

The separation of MOF materials has been a hot topic in the past decade, not only because of their significance and universality but also the inherent properties of MOFs make them particularly suitable for this challenging task. Compared with traditional porous materials, MOF has a stable framework, permanent porosity, pore volume, and enormous surface area. By altering the bond between the organic linker and metal complexes, the pore size/shape, and pore affinity of MOFs can be simply adjusted. The physical and chemical properties of MOFs make them have a wide range of application prospects, so they are considered a multifunctional material for storage, separation, and catalysis among others [22].

2.2. Mixed matrix membranes

2.2.1. MOF-mixed matrix membranes (MOF-MMMs)

Mixed-matrix membranes (MMMs) are composite membranes formed by filling the inorganic dispersed phase in the polymer continuous phase. MMMs can combine the advantages of polymer materials with those of inorganic materials. Mixed matrix membranes first appeared in the 1980s, mainly in gas separation. Later, with the development of membrane separation and the in-depth exploration of MMMs [23], they were developed in the field of water treatment and now have become a hot topic of water treatment membrane research [24]. Various types of filler particles have been reported in many MMMs, such as nonporous graphene oxide [25], zeolites [26], titanium dioxide [27], carbon nanotubes [25], and MOFs [28]. However, the main reasons that the traditional MMM fillers such as zeolite and silica have not been used in industry are their poor compatibility with zeolite polymers and the separation of fillers. In general, MOFs exhibit good membrane selectivity. As a result, the idea of using MOFs as polymer filler particles to improve polymer separation ability has been proposed.

A great deal of effort has been put into developing MMMs for water treatment. Li et al. [29] fabricated the MOF-801/CS mixed matrix membrane by adding hydrophilic MOF-801 crystals into the chitosan (CS) matrix. Meng [30] prepared active BUT-8(A)/polyethyleneimine (PEI) layers on hydrolyzed polyacrylonitrile (HPAN) substrates. The water permeability (396–683 L m^{-2} h^{-1} MPa^{-1}) of the BUT-8(A)/PEI-HPAN membrane and the rejection rate of the dye aqueous solution were relatively ideal. The researchers also concluded that the separation mechanism of the BUT-8(A)/PEI-HPAN composite membrane was that its high-water permeability was due to the convenience of molecules passing through the BUT-8(A) channel.

Of course, MMMs membranes also have good performance in gas separation. For example, ZIFs are used as porous inorganic fillers in many polymer substrates, such as polybenzimidazole (PBI), polysulfone, and polyimide [31], because they possess enhanced CO_2 permeability and a high potential for CO_2/H_2 separation. Ahmad et al. [32] studied the gas separation characteristics of three types of zirconium-based organic framework nanoparticles for 6FDA-DAM mixed matrix membranes (MMMs) at a pressure below 20 bar. The addition of the Zr-MOFs in 6FDA-DAM enhanced the CO_2 permeability and CO_2/CH_4 selectivity of the polymer.

2.2.2. MMMs separation mechanism

Membrane separation is to capture substances larger than the membrane pore size by applying pressure or water inlet pressure, while substances smaller in water are filtered through to achieve separation [33], as shown in Fig. 1. The MOF particles in MMMs are different, and the size of the corresponding sieving particles is different. Selecting the appropriate particles can improve the rejection rate of molecules [34]. Some MOFs can also improve the hydrophilicity [35] and charge property of the material to be separated, as well as the porosity [36] and surface structure of the membrane, and improve the permeation rate of the membrane through different forms.

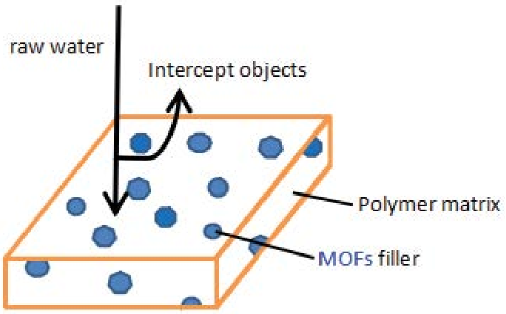

Fig. 1. Schematic diagram of separation mechanism of mixed matrix membrane.

3. MOF-MMMs preparation method

MOFs-based polymer composites have spurred enormous interest in the community of materials primarily due to their stable frameworks, permanent porosities, and large pore volumes and surface areas. Composite membranes based on MOFs have attracted wide attention from scholars, especially in their preparation. This section will also elaborate further.

The preparation methods of MOFs-based composite membranes are generally divided into two categories according to the order of material synthesis and membrane formation. One is to first synthesize the material powder, then add the powder to the prepared casting solution, and finally get the composite membrane. The other is that the synthesis of the material and the formation of the membrane are carried out simultaneously. Table 1 summarises the preparation methods of MOFs-based composite membranes from these two perspectives.

3.1. Layer-by-layer assembly method

Xiao et al. [37] prepared a MOFs-based membrane using polyether sulfone (PES) as a substrate. PES substrate was first immersed in tannic acid (TA) buffer solution and then rinsed with deionized water after 5 min. After rinsing for 5 min, the membrane was immersed in a zinc solution and then rinsed with deionized water, thus obtaining the TA-zinc bilayer. The membrane treated above was immersed in 100 mL 2-methyl imidazole solution to obtain part of the ZIF-8 material, which was then rinsed with deionized water to obtain the ZIF-8/(Ta-Zn^{2+}) N/PES membrane. The performance of the prepared membrane in seawater desalination was tested.

Other researchers combine the self-assembly process with auxiliary methods. Cao et al. [38] first synthesized

Table 1
Summary of the preparation methods of metal-organic framework materials (MOFs)-based membrane

Preparation methods	MOFs	Substrate	Comments	References
Dipping method	ZIF-8; ZIF-67	PA	Simple, the time was short	31
Spin-coating	BUT-8(A)	PAN	High water permeability and rejection rate	30
Dilute solution coating method	ZIF-71	PVDF	Coating optimization, structure, and performance improvement	32
Layer-by-layer assembly	ZIF-8	PES		33
Vacuum-assisted self-assembly	UiO-66-NH_2	PAA	High separation efficiency, good oil pollution resistance, and high stability	34
Spin-assisted layer-by-layer assembly	BUT-8(A)	PAN	Thickness and surface properties of the membrane can be easily adjusted by this method	35
Interfacial polymerization	ICA_D_UIO-66-NH_2	PSf	Elevated separation property, high water flux	36
Interfacial polymerization	HKUST-1	PI	Strong selective permeability, interface defect, and aggregation of MOFs, affect the environment	37
Electrochemical precipitation (EPD) and vacuum-assisted IP process	ZIF-8	PES	Reduce particle aggregation, Control the amount of MOFs deposition and the thickness of the deposition layer	38
Electrochemically assisted interface growth method	Cu-BTC	PES	Good effect on dye rejection	39

UiO-66-NH_2@polyacrylic acid (PAA) nanomaterial, and then prepared MOFs-based composite membrane by a vacuum-assisted self-assembly process. The UiO-66-NH_2@PAA material was deposited on the mixed cellulose ester microfiltration membrane. The prepared composite membrane had high separation efficiency, good oil pollution resistance, and high stability. Meng et al. [39] also prepared BUT-8(A)/PDDA (poly diallyl dimethylammonium chloride) composite membrane using the spin-assisted layer-by-layer assembly method. First, BUT-8(A) hydrophilic nanomaterials were synthesized, and hydrolyzed polyacrylonitrile (PAN) substrate was prepared by hydrolyzed polyacrylonitrile (HPAN) under certain conditions. Then, the BUT-8(A)/PDDA composite membrane was prepared by spin-assisted layer-by-layer assembly method. At a speed of 2,500 rpm, 1 mL of PDDA solution with a concentration of 0.2 $g\cdot L^{-1}$ was dropped onto the surface of the HPAN substrate and rotated for 6 min. Similarly, 1 mL of BUT-8(A) solution at a concentration of 0.2 $g\cdot L^{-1}$ was dropped onto the surface of the HPAN substrate. The BUT-8(A)/PDDA composite membrane with an appropriate number of polymer layers was obtained by adding PDDA solution and BUT-8(A) solution repeatedly. The thickness and surface properties of the membrane can be easily adjusted by this method.

The layer-by-layer assembly process is simple and convenient for adjusting the thickness and surface properties of the membrane. The performance of the prepared MOFs-based membrane is greatly improved, which is mainly attributed to the control of the amounts of alternating deposition between the MOF layer and the polymer layer. The process provides sufficient control for continuous thin layers. However, the nucleation of MOF particles on the substrate surface may not be uniform, which may lead to grain boundary defects.

3.2. Interfacial polymerization

Lin et al. [40] reported a polyamide (PA) thin film nanocomposite (TFN) membrane in which imidazole-2-formaldehyde (ICA) functionalized metal–organic framework (MOF) nanomaterials modified UiO-66-NH_2 (ICA_D_UiO-66-NH_2) nanomaterial was added. The ICA_D_UiO-66-NH_2 composite membrane was prepared by the interfacial polymerization method. The polysulfone (PSf) membrane was used as the substrate during the interfacial polymerization. First, the monomer was prepared: liquid A: 1 wt.% piperazine (PIP) was decomposed in an aqueous solution containing 1 wt.% triethylamine (TEA); liquid B: 1 wt.% 10-camphor sulfonic acid (CSA) dissolved in *n*-hexane (Wako) solution containing 0.15 wt.% trimethyl chloride (TCI). Then, the PSf membrane was immersed in liquid A solution for 60 s. Next, liquid B solution was poured onto the substrate membrane and treated with liquid A for 45 s. Thus, the ICA_D_UiO-66-NH_2 composite membrane was obtained. By injecting the hydrophilic –NH/–NH_2 group, MOFs had a stronger internal polarity, which promoted the transport of water molecules through the TFN composite membrane. Meanwhile, a large number of introduced amine MOFs promoted covalent combining with trimethyl chloride, which enabled perfect fixation of the MOFs without any interfacial defects. When the optimal load mass was 0.08%, the TFN composite membrane exhibited elevated separation properties and high-water flux.

Chen et al. [41] set out the utilization of interfacial polymerization (IP) to prepare a thin film composite (TFC) nanofiltration membrane and *in-situ* growth of the membrane on a polyimide (PI) base layer. The highly porous HKUST-1 was used as the substrate of the intermediate layer to provide a supporting membrane for the ultra-thin separation layer. The inorganic interlayers increased the porosity and specific surface area. The hydrophilic HKUST-1 was also added to the surface of the porous base layer to manufacture a novel TFC nanofiltration membrane. The hydrophilicity and porosity of the supporting membrane were enhanced by the MOFs' intermediate layer.

The TFN film after interfacial polymerization has strong selective permeability, but due to the interface defect between MOFs and matrix and the aggregation of MOFs material, the water flux of the composite membrane decreases, which is a problem that needs to be considered. Second, most of the solvents used in interfacial polymerization reactions are organic, which causes harm to the environment and thus hinders the industrial application of this method.

3.3. Several novel approaches

In recent years, in order to solve the problems of the accumulation of MOFs particles and interface defects and improve the performance of composite membranes, researchers have continuously improved the preparation process of MOFs-based composite membranes. Some novel and efficient membrane preparation methods, such as the combination of the above methods, have been introduced.

For example, Li et al. [42] prepared TFN polyamide (PA) composite nanofiltration membranes using a combination of electrochemical precipitation (EPD) and vacuum-assisted IP process. The preparation of the composite membrane was divided into two steps. The first step was to carry out the EPD process. First, the ZIF-8 solution was synthesized and stirred for 0.5–2 min. The solution was then poured into two electrodes (the cathode was equipped with a polyethersulfone (PES) substrate, and the anode was blank) and then applied with 0.72 $mA\cdot cm^{-2}$ direct current for 0.5–2 min. This resulted in a membrane precipitation by ZIF-8 particles. The second step was to prepare the TFN membrane by the IP method assisted by vacuum filtration. In the process of EPD, the uniform deposition layer was formed in the same electrode direction to reduce particle aggregation, and the quality of MOF particles deposited on the substrate and the thickness of the deposition layer was controlled, the surface structure and performance of the membrane can be improved, and the rejection rate of Na_2SO_4 can reach 96.9% ± 0.7%. Zhang et al. [43] also used an electrochemically assisted interface growth method to grow MOFs *in-situ* on the membrane surface. This membrane preparation process combined the advantages of both anodic dissolution and reverse diffusion of the metal. The Cu-BTC/polyethersulfone (PES) membrane obtained by this method had a good effect on dye rejection.

In addition to combining several membrane preparation methods, He et al. [44] designed a bottom-up synthesis method to grow ZIF-8 directly *in-situ* in the PIM matrix. The precursor of ZIF-8 was dissolved in water and stirred evenly with PIM-1/$CHCl_3$ solution, and the mixture of oil ($CHCl_3$) and water formed a dispersed phase, which made the growth of ZIF-8 slow, reduced the average size of ZIF-8 nanoparticles, then reduced particle agglomeration. The uncoordinated imidazole group on the surface of ZIF-8 nanoparticles interacts with the nitrile group of PIM-1 to form a defect-free matrix filler interface. By precipitating the mixture in pure MeOH, PIM-1, and ZIF-8 can be wrapped and symbiosis in the flocs. After washing, the symbiotic flocs are dissolved in $CHCl_3$, and ZIF-8/PIM-1 MMMs with high content of ZIF-8 can be prepared by evaporating the solvent. This preparation method can accommodate the ultra-high content of MOF loads and improve the problems of poor interface compatibility and packing agglomeration. The ultra-high content of MOF stimulates the ultra-high gas permeability and good gas selectivity of MMMs.

4. Application of MOF-based composite membrane

The application of MOF base membranes is also a research hotspot. MOF-integrated membranes were successfully prepared by different membrane processes and applied in the water treatment process, namely: forward osmosis (FO), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Membrane technology has become one of the major technologies used in various water and wastewater treatment processes due to its efficient removal of contaminants from water bodies. The properties of MOF-integrated membranes for different membrane processes were summarized in Table 2.

4.1. MOFs-based forward osmosis membrane

Forward-osmosis (FO) can be used for desalination when combined with suitable extraction solutions, for other applications such as wastewater treatment and heavy metal separation. This process has received a great deal of attention over the past decade, though these principles have been well established [45]. In the case of desalination, the extracting solution, such as salt water or seawater, and the feed solution are placed in a reservoir but separated by a semi-permeable membrane. The chemical potential of the draw solution is very low, so the water in the brine balances the chemical potential difference through the membrane. Then, water is usually removed from the extract by membrane distillation or medium heat, and the extract is recycled. Fig. 2 illustrates this process briefly.

Mahpoz et al. [46] described the preparation of supporting ZIF-8 membranes on alumina hollow fibers by electroless deposition (ELD) of ZnO, which was then synthesized by the solvothermal method for seawater desalination. The performance of the obtained ZIF-8 composite membrane was measured. When 100,000 ppm NaCl solution was used as extraction and water served as feed solution, the ZIF-8 membrane flux with good symbiosis reached 12.25 $L\cdot m^{-2}\cdot h^{-1}$, and the reverse salt flux reached 0.029 $kg\cdot m^{-2}\cdot h^{-1}$. The prepared ZIF-8 composite membrane was further characterized and analyzed. The high and stable rejection rate of the ZIF-8 membrane in monovalent and divalent high-concentration salt solutions proved that the ZIF-8 membrane was a desalination material with broad application prospects. Bagherzadeh et al. [47] successfully synthesized the GQDs@UiO-66-NH_2 composite and decorated it with *in-situ* surface polymerization on a polyamide repulsive layer. The addition of the GQD@UiO-66-NH_2 particle changed the water flux and separation performance of the FO membrane. When 1 M NaCl and deionized water were used as extraction liquid and feed liquid, respectively, the flux of TFN-0.25 (containing 250 ppm of fillers) membrane was 59.3 LMH in the FO mode. Simultaneously, the separation capacity was about 1.5 times that of the membrane without a GQD@MOF particle.

He et al. [48] proposed a novel forward osmosis (FO) membrane of polydopamine/MOF-801 thin film nanocomposite (PDA/MOF-TFN) for the removal of salt and heavy metal ions. The introduction of MOF-801 provided a lot of water channels and increased the channel curvature of the polyamide (PA) layer, which effectively improved the membrane's water permeability, desalination, and heavy metal removal performance. Compared with the TFC membrane without MOF-801, the performance of the PDA/MOF-TFN membrane was improved, as shown by the fact that the water flux was raised by 30%, the reverse salt flux was decreased by 44%, and the specific salt flux was increased by 56%. The adsorption rates of Cd^{2+}, Ni^{2+}, and Pb^{2+} on PDA/MOF-TFN films were up to 94%, which was attributed to its size exclusion and adsorption properties.

The application prospect of FO is very broad, but it is very difficult to further promote it. It is greatly affected by membrane fouling and internal concentration polarization (ICP) [49–51]. Composite functional nanomaterials are commonly used to improve the water flux and the rejection of a membrane.

Wang et al. [52] successfully fabricated ZIF-8/PDA/PS (polypropylene) composite membrane by immersion strategy. In the FO mode, the high-water flux of the ZIF-8/PDA/PS membrane was 9.6 $L\cdot m^{-2}\cdot h^{-1}$, which was mainly attributed to the good hydrophilicity of PDA and the porous structure of ZIF-8, and the corresponding reverse salt flux was 3.8 $g\cdot m^{-2}\cdot h^{-1}$. In addition, the bacterial killing rate of the composite membrane was studied, and it was found that the killing rate of the composite membrane to *Escherichia coli* was nearly 99%, which was inherently related to the synergistic bacteriostatic effect of ZIF-8 and PDA layer. Pejman et al. [53] prepared a thin-film composite forward osmosis membrane with zwitterions and silver-based metal organic frameworks (Ag-MOFs). They also researched the effect of surface functionalization on improving the antifouling, anti-biofouling, and antimicrobial activity of the membrane. The transmission data showed that compared to pristine membranes, the water flux was significantly increased by about 300%, while the salt reverse flux was similar or slightly decreased. Sodium alginate and *E. coli* were used to evaluate the antifouling performance and biological antifouling performance of the modified membrane. The assays of culturable bacteria showed that there were a large proportion of dead cells when in contact with functionalized membranes containing silver-based MOFs. Seyedpour et al. [54] improved the antifouling and biological antifouling properties by *in-situ* covalently binding Ag-MOF on the active sites of the TFC composite membrane surface. Confocal microscopic analyses revealed that Ag-based MOF made the membrane have

Table 2
Summary of membranes based on metal-organic framework materials (MOFs) in different membrane processes for water treatment

Membrane class	MOFs	Polymer	MOF optimum loading	Membrane preparation method	Key performance	References
FO	ZIF-8			Electroless deposition	- Water flux: 12.25 L·m^{-2}·h^{-1} - Reverse solute flux: 0.029 kg·m^{-2}·h^{-1}	[41]
FO	UiO-66-NH$_2$	PA	250 ppm	*In-situ* surface polymerization	- Water flux: 59.3 LMH - Selectivity was about 1.5 times those of the control membrane without GQDs@MOF particles	[42]
FO	MOF-801	PA		Interfacial polymerization	- Water flux increased by 30% - Reverse salt flux decreased by 44% - High heavy metal ion rejection: >94%	[43]
FO	ZIF-8	PDA; PS		*In-situ* growth	- High water flux: 9.60 L·m^{-2}·h^{-1} - Low solute reverse flux: 3.80 g·m^{-2}·h^{-1} - Bacterial killing ratios with high values of almost 99% against *E. coli*	[48]
FO	Ag-MOFs				- Increased water flux of around 300% compared to pristine membranes - Significant fraction of dead cells upon contact with the functionalized membranes comprising silver-based MOFs	[49]
FO	Ag-MOFs			*In-situ* surface deposition	- Nearly 100% reduction of live bacteria	[50]
UF	TMU-5	PES	0.10 wt.%	Phase inversion method	- Improved the anti-pollution ability of the membranes, especially for filtering solutions with low pollutant concentration	[55]
UF	MIL-101	PVDF	0.10 wt.%	Non-solvent induced phase separation	- 111% PWF improvement, nearly 100% BSA rejection, and 65% FRR enhancement	[56]
UF	hZIF-8	PSf	2.00 wt.%	Phase inversion method	- Improved the water permeability without affecting the rejection performance - Antifouling ability of the hZIF-8 membrane was greatly enhanced	[57]
UF	MIL-53(Fe)	PVDF	67%	Thermally induced phase separation	- Effective capacity of the 67-MIL-PVDF (MIL-53(Fe) with a load rate of 67% in the membranes) membrane increased by 9 times, and the MB removal rate was more than 75%	[58]
UF	ZIF-8	PES	3%	Liquid–liquid phase conversion	- Water flux: 121.50 L·m^{-2}·h^{-1} - High rejection close to 100% for bovine serum albumin - Rejection rates for methyl blue: 82.3% - Rejection rates for Congo red: 98.6%	[59]
UF	UiO-66-NH$_2$	PEI PVDF	2%		- Water flux: 561.00 L·m^{-2}·h^{-1} - Water flux of the BSA-contaminated membrane was restored to 96.13%	[60]
UF	Zr-MOFs				- Removal Cr - At TMP = 0.15 MPa, CFV = 4.0 m·s^{-1}, and T = 35°C, the removal rate of Pb(II) by this process was the highest (61.4%)	[61]

Table 2 (Continued)

Table 2

Membrane class	MOFs	Polymer	MOF optimum loading	Membrane preparation method	Key performance	References
NF	UIO-66-NH_2	PA	0.20 mg·mL^{-1}		- Increased the water flux of the membrane	[62]
NF	Lys@UiO-66		17.13 µg·cm^{-2}	Interfacial polymerization	- Increased by 55% in water flux (18.27 L·m^{-2}·h^{-1}·bar^{-1}) without affecting the selective separation performance - High rejections of divalent cation salts	[63]
NF	UiO-66	PES		Layer-by-layer (LbL) self-assembly	- Pure water permeance: 14.8 L·m^{-2}·h^{-1}·bar^{-1} $MgSO_4$ rejection: 96.3% - Solution flux: 102 L·m^{-2}·h^{-1} - Rejection of Congo red: 99.9%	[64]
NF	NH_2-MIL-125(Ti)	PEI	0.01 wt.%		- High permeability: 12.2 L·m^{-2}·h^{-1}·bar^{-1} - $NiCl_2$ rejection: 90.9%	[66]
RO	ZIF-8		0.30 wt.%	Interfacial polymerization	- Highest water permeance: 1.85 LMH·bar^{-1} - Optimal NaCl rejection efficiency	[71]
RO	UiO-66	PA	0.05%		- The flux of the TFN-RO membrane increased by 50% - UiO-66 TFN membrane was 11% higher than that of the benchmark TFC membrane	[72]
RO	MIL-101(Cr)		0.01%	Interfacial polymerization	- The water flux of the membrane increased from 20.49 to 37.95 L·m^{-2}·h^{-1}, which increased by 85.21%. - Slight increase in the rejection rate of NaCl	[73]

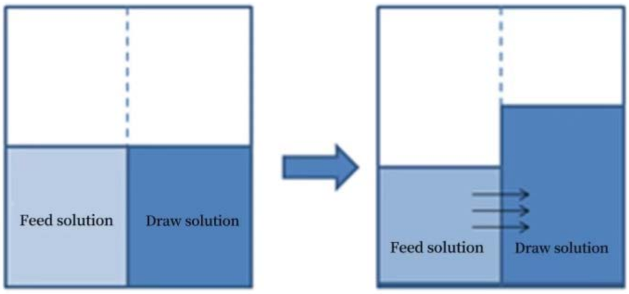

Fig. 2. Forward osmosis phenomenon.

strong antibacterial properties, resulting in viable bacteria decreased by almost 100%.

4.2. MOFs-based ultrafiltration membrane

Membrane fouling is generated by fouling and biological contamination in the feed stream, and membrane fouling is the main problem of separation technology [55,56]. The membrane fouling leads to a significant decrease in permeate flux, which results in the need for more energy and high costs to replace and maintain the membrane's cleanliness. Therefore, it is essential to design a membrane with the best surface properties and a low fouling tendency. Adding hydrophilic additives to the membrane composition can reduce the progress of brigade and fouling because hydrophilic nanomaterials reduce the deposition of pollutants [57,58]. It is found that the metal–organic framework can enhance the anti-pollution ability of the ultrafiltration membrane (UF) by enhancing the hydrophilicity of the membrane surface.

Gholami et al. [59] synthesized a new type of hydrophilic polyethersulfone (PES) ultrafiltration membrane by blending the TMU-5 metal–organic frameworks with the phase inversion method. The results obtained from the study, indicated that the chemical modification of the nanofiltration membrane improved the anti-pollution ability of the membranes, especially for filtering solutions with low pollutant concentrations. This was because TMU-5 nanometer materials had hydrophilic, compared with hydrophobic material modified composite film, TMU-5 membrane was not easy to be contaminated, and even if contaminated also had a strong recovery performance. According to the analysis of hydrophilicity, pure water flux, and antifouling performance of the membrane, MOFs had the best effect when the concentration of MOFs was 0.1 wt.% in the casting solution. In conclusion, a PES membrane with 0.1 wt.% MOF particle concentration obtained higher water flux, higher rejection, and excellent antifouling properties.

Dehghankar et al. [60] succeeded in synthesizing a hydrophilic 1,4-dicarboxyphenyl zirconium (UiO-66) and chromium (III) terephthalate (MIL-101) MOFs and faujasite

(FAU) zeolite nanocrystal. These products were added as nanomaterial additives to a polyvinylidene fluoride (PVDF) matrix, and MMMs were manufactured through a non-solvent induced phase separation (NIPS) process When the mass percentages of UiO-66, MIL-101, and FAU were 0.05, 0.1, and 0.1 wt.%, respectively, MMMs had the maximum pure water flux (PWF) and the highest rejection rate of bovine serum albumin (BSA). According to the results, adding 0.1 wt.% MIL-101 into the PVDF matrix improved PWF by 111%, the BSA rejection rate was close to 100%, and the flux recovery ratio (FRR) was enhanced by 65%.

Sun et al. [61] first synthesized hydrophilic hollow ZIF-8 (hZIF-8) and then prepared a mixed matrix ultrafiltration membrane by phase inversion method. Due to the excellent surface property and nanostructure of hZIF-8, the prepared polysulfone (PSf)/hZIF-8 mixed matrix ultrafiltration membrane significantly improved the water permeability without affecting the rejection performance. At the same time, by adding hZIF-8, the antifouling ability of the hZIF-8 membrane was greatly enhanced. The optimal amount of hZIF-8 additive was 2 wt.%.

4.3. MOFs-based nanofiltration membrane

Nanofiltration (NF) membranes, because of their low energy consumption, high flux, and high repulsion of multivalent salts and certain organic molecules, are widely utilized for effective desalination of seawater and brackish water, as well as other water purification processes. Researchers usually enhance membrane performance by improving membrane permeability and selectivity. Improving the performance of these two aspects specifically manifests in increasing the water transfer channel, the hydrophilicity of the membrane or the surface charge, etc., and the introduction of MOFs nanomaterials can play a vital role. MOFs-modified nanofiltration membranes have been utilized in many water treatment applications, such as seawater desalination, fuel separation, and heavy metal removal.

MOFs-modified NF membrane is widely used in seawater desalination. Gong et al. [62] prepared a TFN composite nanofiltration membrane with a PA/UiO-66-NH_2 active layer on a polydopamine-coated single-walled carbon nanotube (PD/SWCNT) membrane by the interfacial polymerization reaction. In the test of the desalination performance of the TFN composite membrane, it was found that the addition of UiO-66-NH_2 enhanced the hydrophilicity performance of the membrane, thereby promoting the transport of pure water through the membrane hole. Especially, the TFN film, of which the concentration of UiO-66-NH_2 was 0.2 mg·mL^{-1} (TFN-0.2), had the best performance. Gu et al. [63] prepared lysine-modified UiO-66 (Lys@UiO-66) and then fabricated the Lys@UiO-66-based TFN membrane (TFN-LDU) using interfacial polymerization. The water contact angle of the membrane increased slightly as the load density of LysUiO-66 increased. The increase in water contact angle indicated a decrease in the hydrophilicity of the membrane. Under such a high loading density, the decreased surface hydrophilicity may be due to particle agglomerations, which might be caused by the agglomeration of small particles. Therefore, the performance test for the optimal load of Lys@UiO-66 was carried out, and the result was obtained. The optimal Lys@UiO-66 membrane with a capacity of 17.13 μg·cm^{-2}, TFN-LDU8 (Lys@UiO-66 particle was 0.08% w/v) membrane, was increased by 55% in water flux (18.27 L·m^{-2}·h^{-1}·bar^{-1}) without affecting the selective separation performance. The important thing was that the rejection rates of $MgCl_2$ and $CaCl_2$ by the TFN-LDU8 mixed matrix membrane reached 97.81% and 92.81%, respectively. Zhang et al. [64] prepared ultrathin nanocomposite membranes by combining glucose, pDA with Zr-based MOFs through interfacial polymerization. Studies have shown that adding UiO-66-NH_2 MOFs into the pDA-glucose selective layer to obtain pDA-glucose/UiO-66-NH_2 TFN membranes can increase NaCl rejection rate to 92.3%, while simultaneously enhancing water permeance by 114.8% (from 18.3 to 39.3 L·m^{-2}·h^{-1}·bar^{-1}). The selectivity of pDA-glucose/UiO-66-NH_2 membranes to 1,000 ppm of inorganic salts was in the order of Na_2SO_4 (99.9%) > $MgSO_4$ (98.9%) > $MgCl_2$ (97.4%) > NaCl (92.3%). Even in the presence of 3,000 ppm Na_2SO_4, the water permeance of pDA glucose/UiO-66-NH_2 membranes reached 20.9 L·m^{-2}·h^{-1}·bar^{-1}, and the rejection rate was 99%. The addition of stable UiO-66-NH_2 makes the nanofiltration membranes show very stable water filtration performance.

Some scholars have also applied MOF-modified membranes to sewage treatment, and the effect is relatively significant. Wang et al. [65] designed highly permeable composite membranes by layer-by-layer (LbL) self-assembly of polyelectrolytes (PES). The water flow through the NF membrane was accelerated by the incorporation of UiO-66 into other solvent pathways. UiO-66 equipped with a PES membrane had pure water permeability as high as 14.8 L·m^{-2}·h^{-1}·bar^{-1}, which was 160% higher than the original PES membrane. Meanwhile, the membrane exhibited a 96.3% rejection rate for $MgSO_4$, and the molecular weight cut-off (MWCO) was 464.2 g·mol^{-1}. The most interesting thing was that under optimized operating conditions and continuous operation for 240 h, the solution flux of the mixed matrix membrane was upto 102 L·m^{-2}·h^{-1}, and the rejection of Congo red was 99.9%. Gong et al. [66] mixed MOFs into the cross-linking system of polyethyleneimine (PEI) and trimesic acid (TMA) to fabricate a novel positively charged nanofiltration (NF) membrane. The main reason for the increased permeability of the composite membrane was that NH_2-MIL-125 (Ti) provided a preferential water channel. In the performance test, it was found that when the loading amount of NH_2-MIL-125 (Ti) was 0.01 wt.%, the water flux of the composite membrane reached 12.2 L·m^{-2}·h^{-1}·bar^{-1}, and the rejection rate of $NiCl_2$ reached 90.9%.

4.4. MOFs-based reverse osmosis membrane

The reverse osmosis process provides an energy-saving desalination technology to ease the water scarcity crisis due to the doubling of industrial and domestic water consumption [67,68]. In the reverse osmosis process, salt water is passed through the membrane under high water pressure. In this high-pressure water process, water is allowed to pass through the membrane, and the salt ions are repelled [69]. In general, reverse osmosis membrane materials have a remarkable effect on seawater desalination. The new reverse osmosis membrane has excellent results in salt and pollution resistance, which not only reduces operating costs but also provides high water flux and energy requirements. However, the permeability of pure polymer membranes is negatively correlated with water/salt selectivity, which is referred to as the Robeson upper bound [70]. Through the study of organic/inorganic mixed matrix membranes, the introduction of MOF-modified membranes is a promising method for membrane modification.

Wang et al. [71] researched the effect of the size of nanoparticles on the MOFs-doped thin film nanocomposite (TFN) films. They prepared different ZIF-8 materials with average particle sizes of 50, 150, and 400 nm. Compared with the original TFC and other sizes of ZIF-8/PA TFN membranes, the optimal water permeability of TFN-50 membranes was 1.85 LMH/bar and the NaCl rejection efficiency was optimal. Liu et al. [72] suggested incorporating UiO-66 into the PA matrix layer to prepare a nanocomposite (TFN) reverse osmosis (RO) membrane for removing boron from an aqueous solution. The TFN-RO membrane had an inherent porous structure, and its pore size was narrow, so it had a strong boron adsorption capacity. In the desalination test of brackish water, the flux of the TFN-RO mixed matrix membrane increased significantly (50%). At the optimal mixing concentration of 0.05%, the boron rejection rate of the UiO-66 TFN membrane was 11% higher than that of the benchmark TFC membrane, while the water flux and salt rejection rate in the seawater desalination test were not reduced. Song et al. [73] prepared a MIL-101(Cr)@GO reverse osmosis membrane with different doping concentrations by interfacial polymerization and used it for desalination. When the doping concentration was 0.01%, the water flux of the membrane increased from 20.49 to 37.95 $L\cdot m^{-2}\cdot h^{-1}$, an increase of 85.21%, and a slight increase in the rejection rate of NaCl.

5. Conclusion

The enormous surface area, permanent porosity, and adjustable chemical function of MOFs make them promising materials for the fabrication and modification of water treatment membranes. This paper introduces the preparation method of MOFs membrane and their application in water treatment. Numerous studies have shown that different kinds of MOF-integrated membranes can be applied for RO, NF, FO, and UF processes have been reported. Although MMM membrane has achieved good results, its current research and use in water treatment are still relatively few, and there are some insurmountable defects, such as membrane pollution, difficulty in mass production, low practical application efficiency, and a slightly higher price.

MOF-MMM systems have different effects on membrane permeability and selectivity, so the selection of appropriate systems is crucial to membrane performance. The ideal MMMs filler should be evenly distributed and have no gap with the polymer, but the current research level is still difficult to achieve, and the prepared membrane still has some defects, so this will be one of the directions of future research. It has been suggested that the combination of this technique with other separation tools (mixed matrix separation systems) could provide further advantages to this technique. Shortly, the application prospects of forward mixed matrix membranes will be improved through the exploration of the performance of forward mixed matrix membranes by researchers. This article provides insights into the direction of the next step of water purification membranes based on MOFs.

Funding

This research was funded by Shandong Province Natural Science Foundation (ZR2022MB011, ZR2020MB120, ZR2021MB063, ZR2020MB090), Innovation ability improvement project of technology-based small and medium-sized enterprises in Shandong Province (2022TSGC2043, 2021TSGC1358).

Data availability statement

The research data can be found in the cited articles.

References

[1] E. Adatoz, A.K. Avci, S. Keskin, Opportunities and challenges of MOF-based membranes in gas separations, Sep. Purif. Technol., 152 (2015) 207–237.

[2] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Application of membrane separation processes in petrochemical industry: a review, Desalination, 235 (2009) 199–244.

[3] L.C. Tomé, D. Mecerreyes, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho, Pyrrolidinium-based polymeric ionic liquid materials: new perspectives for CO_2 separation membranes, J. Membr. Sci., 428 (2013) 260–266.

[4] I.M. Atadashi, M.K. Aroua, A.R. Abdul Aziz, N.M.N. Sulaiman, Membrane biodiesel production and refining technology: a critical review, Renewable Sustainable Energy Rev., 15 (2011) 5051–5062.

[5] J. Kim, B. Van der Bruggen, The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water treatment, Environ. Pollut., 158 (2010) 2335–2349.

[6] W. Shi, B. He, J. Ding, J. Li, F. Yan, X. Liang, Preparation and characterization of the organic–inorganic hybrid membrane for biodiesel production, Bioresour. Technol., 101 (2010) 1501–1505.

[7] R. Ardito, A. Corigliano, A. Frangi, F. Rizzini, Advanced models for the calculation of capillary attraction in axisymmetric configurations, Eur. J. Mech. A. Solids, 47 (2014) 298–308.

[8] X. Chang, C. Zhang, Y. He, X. Dong, W. Jin, N. Xu, A comparative study of the performance of symmetric and asymmetric mixed-conducting membranes, Chin. J. Chem. Eng., 17 (2009) 562–570.

[9] M. Ulbricht, Advanced functional polymer membranes, Polymer, 47 (2006) 2217–2262.

[10] S. Xiong, L. Li, L. Dong, J. Tang, G. Yu, C. Pan, Covalent-organic frameworks (COFs)-based membranes for CO_2 separation, J. CO_2 Util., 41 (2020) 101224, doi: 10.1016/j.jcou.2020.101224.

[11] E. Saljoughi, M. Sadrzadeh, T. Mohammadi, Effect of preparation variables on morphology and pure water permeation flux through asymmetric cellulose acetate membranes, J. Membr. Sci., 326 (2009) 627–634.

[12] S. Kiani, S.M. Mousavi, N. Shahtahmassebi, E. Saljoughi, Hydrophilicity improvement in polyphenylsulfone nanofibrous filtration membranes through addition of polyethylene glycol, Appl. Surf. Sci., 359 (2015) 252–258.

[13] N. Song, X. Gao, Z. Ma, X. Wang, Y. Wei, C. Gao, A review of graphene-based separation membrane: materials, characteristics, preparation and applications, Desalination, 437 (2018) 59–72.

[14] Z. Rajabi, A.R. Moghadassi, S.M. Hosseini, M. Mohammadi, Preparation and characterization of polyvinylchloride based mixed matrix membrane filled with multi walled carbon nano tubes for carbon dioxide separation, J. Ind. Eng. Chem., 19 (2013) 347–352.

[15] M. Rastgar, A. Shakeri, A. Bozorg, H. Salehi, V. Saadattalab, Impact of nanoparticles surface characteristics on pore structure and performance of forward osmosis membranes, Desalination, 421 (2017) 179–189.

[16] X. Wang, X. Ba, N. Cui, Z. Ma, L. Wang, Z. Wang, X. Gao, Preparation, characterisation, and desalination performance study of cellulose acetate membranes with MIL-53(Fe) additive, J. Membr. Sci., 590 (2019) 117057, doi: 10.1016/j.memsci.2019.04.061.

[17] O.M. Yaghi, H. Li, Hydrothermal synthesis of a metal-organic framework containing large rectangular channels, J. Am. Chem. Soc., 117 (1995) 10401–10402.

[18] H. Hayashi, A.P. Côté, H. Furukawa, M. O'Keeffe, O.M. Yaghi, Zeolite A imidazolate frameworks, Nat. Mater., 6 (2007) 501–506.

[19] J.Y. Lee, J.M. Roberts, O.K. Farha, A.A. Sarjeant, K.A. Scheidt, J.T. Hupp, Synthesis and gas sorption properties of a metal-azolium framework (MAF) material, Inorg. Chem., 48 (2009) 9971–9973.

[20] F. Nouar, J. Eckert, J. Eubank, P. Forster, M. Eddaoudi, Zeolite-like metal-organic frameworks (ZMOFs) as hydrogen storage platform: lithium and magnesium ion-exchange and H_2-(rho-ZMOF) interaction studies, J. Am. Chem. Soc., 131 (2009) 2864–2870.

[21] L. Niu, X. Zhao, F. Wu, Z. Tang, H. Lv, J. Wang, M. Fang, J.P. Giesy, Hotpots and trends of covalent organic frameworks (COFs) in the environmental and energy field: bibliometric analysis, Sci. Total Environ., 783 (2021) 146838, doi: 10.1016/j.scitotenv.2021.146838.

[22] H. Kuringen, G. Eikelboom, I. Shishmanova, D. Broer, A.P.H.J. Schenning, Selective adsorption: responsive nanoporous smectic liquid crystal polymer networks as efficient and selective adsorbents (Adv. Funct. Mater. 32/2014), Adv. Funct. Mater., 24 (2014) 5022–5022.

[23] X. Ai, X. Hu, Research progress of organic-inorganic hybrid membrane, Prog. Chem., 16 (2004) 654.

[24] H. Dong, L. Zhang, H. Chen, C. Gao, Mixed matrix water treatment membrane: materials, preparation and properties, Prog. Chem., 26 (2014) 2007–2018.

[25] J.-K. Wu, C.-C. Ye, T. Liu, Q.-F. An, Y.-H. Song, K.-R. Lee, W.-S. Hung, C.-J. Gao, Synergistic effects of CNT and GO on enhancing mechanical properties and separation performance of polyelectrolyte complex membranes, Mater. Des., 119 (2017) 38–46.

[26] T. Moore, W. Koros, Sorption in zeolites modified for use in organic−inorganic hybrid membranes, Ind. Eng. Chem. Res., 47 (2011) 591–598.

[27] Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, A. Farhadian, A.H. Taheri, Formation of appropriate sites on nanofiltration membrane surface for binding TiO_2 photo-catalyst: performance, characterization and fouling-resistant capability, J. Membr. Sci., 330 (2009) 297–306.

[28] Z. Zhao, X. Ma, A. Kasik, Z. Li, J. Lin, Gas separation properties of metal organic framework (MOF-5) membranes, Ind. Eng. Chem. Res., 52 (2012) 1102–1108.

[29] Q. Li, Q. Liu, J. Zhao, Y. Hua, J. Sun, J. Duan, W. Jin, High efficient water/ethanol separation by a mixed matrix membrane incorporating MOF filler with high water adsorption capacity, J. Membr. Sci., 544 (2017) 68–78.

[30] Y. Meng, L. Shu, L. Liu, Y. Wu, L.-H. Xie, M.-J. Zhao, J.-R. Li, A high-flux mixed matrix nanofiltration membrane with highly water-dispersible MOF crystallites as filler, J. Membr. Sci., 591 (2019) 117360, doi: 10.1016/j.memsci.2019.117360.

[31] V. Nafisi, M.-B. Hägg, Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO_2 capture, J. Membr. Sci., 459 (2014) 244–255.

[32] M.Z. Ahmad, T.A. Peters, N.M. Konnertz, T. Visser, C. Téllez, J. Coronas, V. Fila, W.M. de Vos, N.E. Benes, High-pressure CO_2/CH_4 separation of Zr-MOFs based mixed matrix membranes, Sep. Purif. Technol., 230 (2020) 115858, doi: 10.1016/j.seppur.2019.115858.

[33] D. Zhao, Research progress of mixed matrix membrane for water treatment and separation with metal organic framework, Chem. Ind. Eng. Prog., 40 (2021) 1035, doi: 10.3390/membranes9070088.

[34] T.Y. Liu, H.G. Yuan, Y.Y. Liu, D. Ren, Y.C. Su, X. Wang, Metal-organic framework nanocomposite thin films with interfacial bindings and self-standing robustness for high water flux and enhanced ion selectivity, ACS Nano, 12 (2018) 9253–9265.

[35] R. Dai, H. Guo, C.Y. Tang, M. Chen, J. Li, Z. Wang, Hydrophilic selective nanochannels created by metal organic frameworks in nanofiltration membranes enhance rejection of hydrophobic endocrine-disrupting compounds, Environ. Sci. Technol., 53 (2019) 13776–13783.

[36] J.-Y. Lee, C.Y. Tang, F. Huo, Fabrication of porous matrix membrane (PMM) using metal-organic framework as green template for water treatment, Sci. Rep.-UK, 4 (2014) 3740, doi: 10.1038/srep03740.

[37] Y. Xiao, W. Zhang, Y. Jiao, Y. Xu, H. Lin, Metal-phenolic network as precursor for fabrication of metal-organic framework (MOF) nanofiltration membrane for efficient desalination, J. Membr. Sci., 624 (2021) 119101, doi: 10.1016/j.memsci.2021.119101.

[38] J. Cao, Y. Su, Y. Liu, J. Guan, M. He, R. Zhang, Z. Jiang, Self-assembled MOF membranes with underwater superoleophobicity for oil/water separation, J. Membr. Sci., 566 (2018) 268–277.

[39] Y. Meng, L. Shu, L.-H. Xie, M. Zhao, T. Liu, J.-R. Li, High performance nanofiltration in BUT-8(A)/PDDA mixed matrix membrane fabricated by spin-assisted layer-by-layer assembly, J. Taiwan Inst. Chem. Eng., 115 (2020) 331–338.

[40] Y. Lin, H.-C. Wu, Q. Shen, L. Zhang, K. Guan, T. Shintani, K.-L. Tung, T. Yoshioka, H. Matsuyama, Custom-tailoring metal-organic framework in thin-film nanocomposite nanofiltration membrane with enhanced internal polarity and amplified surface crosslinking for elevated separation property, Desalination, 493 (2020) 114649, doi: 10.1016/j.desal.2020.114649.

[41] K. Chen, P. Li, H. Zhang, H. Sun, X. Yang, D. Yao, X. Pang, X. Han, Q. Jason Niu, Organic solvent nanofiltration membrane with improved permeability by *in-situ* growth of metal-organic frameworks interlayer on the surface of polyimide substrate, Sep. Purif. Technol., 251 (2020) 117387, doi: 10.1016/j.seppur.2020.117387.

[42] J. Li, R. Liu, J. Zhu, X. Li, S. Yuan, M. Tian, J. Wang, P. Luis, B.V. Bruggen, J. Lin, Electrophoretic nuclei assembly of MOFs in polyamide membranes for enhanced nanofiltration, Desalination, 512 (2021) 115125, doi: 10.1016/j.desal.2021.115125.

[43] X. Zhang, Y. Li, C. Van Goethem, K. Wan, W. Zhang, J. Luo, I.F.J. Vankelecom, J. Fransaer, Electrochemically assisted interfacial growth of MOF membranes, Matter, 1 (2019) 1285–1292.

[44] S. He, B. Zhu, X. Jiang, G. Han, S. Li, C.H. Lau, Y. Wu, Y. Zhang, L. Shao, Symbiosis-inspired de novo synthesis of ultrahigh MOF growth mixed matrix membranes for sustainable carbon capture, Proc. Natl. Acad. Sci. U.S.A., 119 (2022) e2114964119.

[45] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: principles, applications, and recent developments, J. Membr. Sci., 281 (2006) 70–87.

[46] N.M.A. Mahpoz, S.N.N.M. Makhtar, M.Z.M. Pauzi, N. Abdullah, M.A. Rahman, K.H. Abas, A.F. Ismail, M.H.D. Othman, J. Jaafar, ZIF-8 membrane supported on alumina hollow fiber with enhanced salt removal by forward osmosis, Desalination, 496 (2020) 114697, doi: 10.1016/j.desal.2020.114697.

[47] M. Bagherzadeh, A. Bayrami, M. Amini, Enhancing forward osmosis (FO) performance of polyethersulfone/polyamide (PES/PA) thin-film composite membrane via the incorporation of GQDs@UiO-66-NH_2 particles, J. Water Process Eng., 33 (2020) 101107, doi: 10.1016/j.jwpe.2019.101107.

[48] M. He, L. Wang, Y. Lv, X. Wang, J. Zhu, Y. Zhang, T. Liu, Novel polydopamine/metal organic framework thin film nanocomposite forward osmosis membrane for salt rejection and heavy metal removal, Chem. Eng. J., 389 (2020) 124452, doi: 10.1016/j.cej.2020.124452.

[49] G.-R. Xu, J.-M. Xu, H.-J. Feng, H.-L. Zhao, S.-B. Wu, Tailoring structures and performance of polyamide thin film composite (PA-TFC) desalination membranes via sublayers adjustment-a review, Desalination, 417 (2017) 19–35.

[50] X. Zhang, L. Shen, C.-Y. Guan, C.-X. Liu, W.-Z. Lang, Y. Wang, Construction of SiO_2@MWNTs incorporated PVDF substrate

for reducing internal concentration polarization in forward osmosis, J. Membr. Sci., 564 (2018) 328–341.

[51] S.E. Kwan, E. Bar-Zeev, M. Elimelech, Biofouling in forward osmosis and reverse osmosis: measurements and mechanisms, J. Membr. Sci., 493 (2015) 703–708.

[52] X.-P. Wang, J. Hou, F.-S. Chen, X.-M. Meng, *In-situ* growth of metal-organic framework film on a polydopamine-modified flexible substrate for antibacterial and forward osmosis membranes, Sep. Purif. Technol., 236 (2020) 116239, doi: 10.1016/j.seppur.2019.116239.

[53] M. Pejman, M.D. Firouzjaei, S.A. Aktij, P. Das, E. Zolghadr, H. Jafarian, A.A. Shamsabadi, M. Elliott, M.R. Esfahani, M. Sangermano, M. Sadrzadeh, E.K. Wujcik, A. Rahimpour, A. Tiraferri, Improved antifouling and antibacterial properties of forward osmosis membranes through surface modification with zwitterions and silver-based metal organic frameworks, J. Membr. Sci., 611 (2020) 118352, doi: 10.1016/j.memsci.2020.118352.

[54] S.F. Seyedpour, A. Rahimpour, G. Najafpour, Facile *in-situ* assembly of silver-based MOFs to surface functionalization of TFC membrane: a novel approach toward long-lasting biofouling mitigation, J. Membr. Sci., 573 (2019) 257–269.

[55] E.F. Barbosa, L.P. Silva, Nanoscale characterization of synthetic polymeric porous membranes: scrutinizing their stiffness, roughness, and chemical composition, J. Membr. Sci., 407–408 (2012) 128–135.

[56] Q. Li, J. Imbrogno, G. Belfort, X.-L. Wang, Making polymeric membranes antifouling via "grafting from" polymerization of zwitterions, J. Appl. Polym. Sci., 132 (2015) 41781, doi: 10.1002/app.41781.

[57] A. Sotto, M. Orcajo, J. Arsuaga, G. Calleja, J. Landaburu-Aguirre, Preparation and characterization of MOF-PES ultrafiltration membranes, J. Appl. Polym. Sci., 132 (2015) 41633, doi: 10.1002/app.41633.

[58] E.M.V. Hoek, A.K. Ghosh, X. Huang, M. Liong, J.I. Zink, Physical–chemical properties, separation performance, and fouling resistance of mixed-matrix ultrafiltration membranes, Desalination, 283 (2011) 89–99.

[59] F. Gholami, S. Zinadini, A.A. Zinatizadeh, A.R. Abbasi, TMU-5 metal-organic frameworks (MOFs) as a novel nanofiller for flux increment and fouling mitigation in PES ultrafiltration membrane, Sep. Purif. Technol., 194 (2018) 272–280.

[60] M. Dehghankar, T. Mohammadi, M.T. Moghadam, M.A. Tofighy, Metal-organic framework/zeolite nanocrystal/polyvinylidene fluoride composite ultrafiltration membranes with flux/antifouling advantages, Mater. Chem. Phys., 260 (2021) 124128, doi: 10.1016/j.matchemphys.2020.124128.

[61] H. Sun, B. Tang, P. Wu, Hydrophilic hollow zeolitic imidazolate framework-8 modified ultrafiltration membranes with significantly enhanced water separation properties, J. Membr. Sci., 551 (2018) 283–293.

[62] Y. Gong, S. Gao, Y. Tian, Y. Zhu, W. Fang, Z. Wang, J. Jin, Thin-film nanocomposite nanofiltration membrane with an ultrathin polyamide/UIO-66-NH_2 active layer for high-performance desalination, J. Membr. Sci., 600 (2020) 117874, doi: 10.1016/j.memsci.2020.117874.

[63] Z. Gu, S. Yu, J. Zhu, P. Li, X. Gao, R. Zhang, Incorporation of lysine-modified UiO-66 for the construction of thin-film nanocomposite nanofiltration membrane with enhanced water flux and salt selectivity, Desalination, 493 (2020) 114661, doi: 10.1016/j.desal.2020.114661.

[64] Y. Zhang, X. Cheng, X. Jiang, J.J. Urban, C.H. Lau, S. Liu, L. Shao, Robust natural nanocomposites realizing unprecedented ultrafast precise molecular separations, Mater. Today, 36 (2020) 40–47.

[65] K. Wang, Y. Qin, S. Quan, Y. Zhang, P. Wang, H. Liang, J. Ma, X.Q. Cheng, Development of highly permeable polyelectrolytes (PEs)/UiO-66 nanofiltration membranes for dye removal, Chem. Eng. Res. Des. 147 (2019) 222–231.

[66] X.-Y. Gong, Z.-H. Huang, H. Zhang, W.-L. Liu, X.-H. Ma, Z.-L. Xu, C.Y. Tang, Novel high-flux positively charged composite membrane incorporating titanium-based MOFs for heavy metal removal, Chem. Eng. J., 389 (2020) 125706, doi: 10.1016/j.cej.2020.125706.

[67] T. Uemura, K. Kotera, M. Henmi, H. Tomioka, Membrane technology in seawater desalination: history, recent developments and future prospects, Desal. Water Treat., 33 (2011) 283–288.

[68] D. Li, H. Wang, Recent developments in reverse osmosis desalination membranes, J. Mater. Chem., 20 (2010) 4551–4566.

[69] M.J. Kotelyanskii, N.J. Wagner, M.E. Paulaitis, Atomistic simulation of water and salt transport in the reverse osmosis membrane FT-30, J. Membr. Sci., 139 (1998) 1–16.

[70] G.M. Geise, H.B. Park, A.C. Sagle, B.D. Freeman, J.E. McGrath, Water permeability and water/salt selectivity tradeoff in polymers for desalination, J. Membr. Sci., 369 (2011) 130–138.

[71] F. Wang, T. Zheng, R. Xiong, P. Wang, J. Ma, Strong improvement of reverse osmosis polyamide membrane performance by addition of ZIF-8 nanoparticles: effect of particle size and dispersion in selective layer, Chemosphere, 233 (2019) 524–531.

[72] L. Liu, X. Xie, S. Qi, R. Li, X. Zhang, X. Song, C. Gao, Thin film nanocomposite reverse osmosis membrane incorporated with UiO-66 nanoparticles for enhanced boron removal, J. Membr. Sci., 580 (2019) 101–109.

[73] N. Song, Y. Sun, X. Xie, D. Wang, F. Shao, L. Yu, L. Dong, Doping MIL-101(Cr)@GO in polyamide nanocomposite membranes with improved water flux, Desalination, 492 (2020) 114601, doi: 10.1016/j.desal.2020.114601.