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Current progress in metal-organic frameworks-embedded membranes for water desalination

Bary Leonard Suwandi[a,b], Laurensia Nadya Widjaja[a,b], Stefani Catherine[a,b], Shella Permatasari Santoso[a,b,*], Felycia Edi Soetaredjo[a,b], Artik Elisa Angkawijaya[c], Adriana Anteng Anggorowati[a], Suryadi Ismadji[a,b,*], Phuong Lan Tran-Nguyen[d], Yi-Hsu Ju[b,c]

[a]*Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, East Java, Surabaya 60114, Indonesia, Tel. +62 31 3891264; Fax: +62 31 3891267; emails: shella_p5@yahoo.com (S.P. Santoso), suryadiismadji@yahoo.com (S. Ismadji), baryleonard10@gmail.com (B.L. Suwandi), laurensianadya@gmail.com (L.N. Widjaja), stefanicatherine99@gmail.com (S. Catherine), felyciae@yahoo.com (F.E. Soetaredjo), adrianaanteng@ukwms.ac.id (A.A. Anggorowati)*
[b]*Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Rd. Sec. 4, Taipei 10607, Taiwan, email: yhju@mail.ntust.edu.tw (Y.H. Ju)*
[c]*Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, 43 Keelung Rd. Sec. 4, Taipei 10607, Taiwan, email: artikelisa@mail.ntust.edu.tw (A.E. Angkawijaya)*
[d]*Department of Mechanical Engineering, Can Tho University, 3-2 Street, Cantho City, Vietnam, email: tnplan@ctu.edu.vn (P.L. Tran-Nguyen)*

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ABSTRACT

Rapid population and economic growth cause severe anthropogenic emissions, which lead to many water pollutions. As a result, the demand for potable water is increasing dramatically in the last decades. Various logical solutions and sustainable developments, such as converting seawater into freshwater, have been explored. Several methods have been employed in water desalination, such as pressure-driven membranes, capacitive deionization, and adsorption desalination. Still, the limitations of the present technologies are low water productivity and quality. Therefore, it is essential to perform further research to design materials and methods with higher salt rejection property and large flux capacity. Recent study and development have pointed out an advanced material called metal-organic frameworks (MOFs) with fascinating chemical and physical properties. Researchers and engineers have been studying MOFs for their potential application in water desalination. This review is aimed to stimulate future research related to the utilization of MOFs for seawater desalination, particularly in the desalination membrane development. Recent advances from the MOF in water desalination are given, starting with outlining various studies of membrane-modified MOF, followed by the application of MOF in desalination technology. Finally, the explanation of the concept of increasing desalination performance by MOF to fill the knowledge gap.

Keywords: Membrane; Nanomaterial; Salt rejection; MOF; Desalination

* Corresponding authors.

1. Introduction

The availability of clean and freshwater is the foremost crucial resource for all life forms on earth. The need for decent water increases with rapid population growth. Ironically, the availability of clean water has become scarce due to the rapid industrialization and urbanization (source of anthropogenic emission). A severe level of emissions caused by anthropogenic activities causes drastic depletion of clean water sources [1]. At present, there are more than 0.78 billion individuals around the globe who do not have access to clean water resources, which have resulted in significant health issues. Reliable access to clean and affordable water is viewed as one of the global problems that require special attention in the 21st century; the sustainable development of water desalination and purification has become a routine agenda for many engineers to overcome the issue. Desalination (Fig. 1) is considered as a sustainable solution in providing freshwater supplies. Attempts to desalinate seawater by using methods such as forward osmosis, reverse osmosis, evaporation, capacitive deionization, adsorption, and distillation to gain freshwater has been made to fulfill this increasing demand [2–6]. At present, reverse osmosis membrane technology has become the most utilized desalination process due to its potentiality to diminish the process cost, without degrading the water quality.

Numerous studies on the desalination process using membrane have been conducted to increase the efficiency of obtaining fresh water from the sea or brackish water. In recent years, nanotechnology and nanomaterials gradually play a vital role in improving desalination technology [7,8]. Membrane constructed from nanomaterials is considered one of the best filtration-materials in desalination [9]. Nanomaterials are described as the material smaller than 100 nm in at least one external dimension; its small size provides a higher surface area to volume ratio [10]. Reviews about nanomaterials for water and wastewater treatment in various applications such as photocatalysis, water purification, adsorption, disinfection, sensing, and monitoring have been written, as summarized in Table 1 [10–15]. The modification of thin-film membranes with various nanomaterials gives us a chance to redefine the standard of water desalination processes.

The blossoming research about water desalination using nanomaterials left us with many choices of process and many choices of material, as summarized in Table 2. A clear insight into the challenges and possibilities of water desalination is the key step to develop better technology for fulfilling the increasing demand for freshwater at a rationally low cost. Lately, the utilization of metal-organic frameworks (MOFs) as new membrane materials in water desalination is gaining much interest among engineers. The enormous pore of MOFs provides a large surface area, making them efficient in water desalination. This review aims to explore and summarize the current development of MOF-embedded membranes and their disadvantages and possible future advances, which yet to be done. This review will provide insight to the reader in seeing the promising role of MOFs in increasing the efficiency of desalination and its current progress. Also, it is noted that membrane modification with MOFs is an attractive approach to improve the membrane properties, which resulted in higher salt rejection and water permeability. We foresee the rapid development of MOFs utilization in different desalination processes and how the incorporation of MOFs can improve membrane performance.

Modification of desalination membranes by embedding MOF has been widely studied, where the addition of MOF provides a notable increase in desalination performance. For example, the addition of MOF can reduce the affinity between water molecules and the pore surface of the membrane, making it easy for water molecules to pass through the pores. Others, the addition of MOF, brings the presence of antifouling or antibacterial properties to the membrane. This article discusses the performance of several MOF-modified membranes, their preparation, and how MOF can improve their desalination performance.

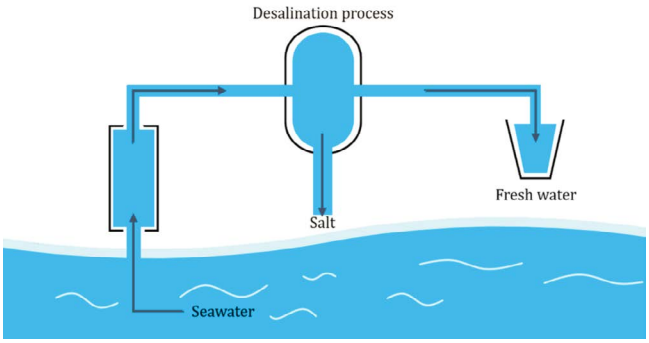

Fig. 1. Schematic diagram of saline water desalination process.

2. Assorted MOF-modified membranes

Based on the size of the materials, the membranes categorize as thin-film nanocomposite (TFN) and thin-film composite (TFC). TFN is the membrane-embedded by nanoparticles, while TFC is embedded with larger particles. Polyamide (PA) thin-film is the most common membrane used in desalination; its fabrication involves the interfacial polymerization (IP) process in which *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) are reacted [29]. In this section, various type of MOF-embedded membranes is presented.

2.1. Simple MOF-embedded membranes

The incorporation of silver-based MOF, namely Ag-BTC (Ag = silver(I) and BTC = 1,3,5-benzene tricarboxylic acid), into the polyamide (PA) thin-film was reported to provide a significant increase in desalination performance. The membrane was prepared by using the IP method, a different concentration of AgBTC was loaded in an organic solution containing 14 wt.% polyethersulfone (PES) and 1 wt.% polyvinylpyrrolidone (PVP) dissolved in DMF. The resulting MOFs, with average diameters of 33.4 nm (nanocrystals), were then embedded into the membrane at various weight percentages. It is reported that TFN-0.04 and -0.08 (TFN membrane with 0.04 and 0.08 wt.% AgBTC loading) was able to enhance the membrane water permeability 1.3

Table 1
Progress on water desalination using nanomaterials

Nanomaterials	Emphasis of review	References
Nanomaterials-polymer composite membranes	Incorporation of carbon-based nanomaterials (CNTs) into polymer composite membranes to form membranes with exceptionally high salt-rejection and permeability.	[9]
Metal-oxide nanoparticle-enhanced membranes, CNT-modified metal-oxide nanoparticles	Development of the coating of hydrophobic membranes with metal-oxide nanoparticles and carbonaceous nanomaterials such as CNT for various applications, including for desalination process. The functionalization of the membrane into hydrophilic to impart its mechanical properties was also discussed.	[16]
Enhanced thin-film composite membranes (TFC)	Incorporation of nanoparticle into a thin-film composite membrane to enhance the low-biofouling and anti-scaling properties of the TFC membrane. The zeolite-embedded membranes exhibit exceptional salt-rejection activity.	[3]
Zeolites, Aquaporin	The use of zeolite and aquaporin for the desalination process.	[1]
Ion exchange membranes (IEMs)	Developments of IEMs include the utilization of nanomaterials such as CNTs, zeolites, silica, TiO_2, and silver nanoparticles to enhance the strength, permeate-selectivity, ion-conductivity, and thermal stability of the membrane.	[17]
Rationally fabricated nanomaterials	The use of specific nanomaterials (graphene 2-D, zeolite, and molybdenum disulfide) for the production of 3-D nanomembrane for application in a solar desalination device.	[18]
Graphene	The use of graphene as nanofiltration materials. The improvement of the membrane structure to enhance the water flux was also discussed in this review.	[19]
Carbon nanotubes, zeolites,	The use of CNTs and zeolite membranes for seawater desalination. Some critical features of CNTs and zeolite as desalination membranes were also discussed.	[20]
Aquaporin membranes, Carbon-based membranes	Utilization of carbon-based materials (CBM), and aquaporin as promising membrane materials. Various aspects of the desalination process using these membranes are also discussed.	[21]
Nano-fiber membranes	The use of nanofiber membranes for removing salt in the desalination process.	[22]
Zeolites, CNT	Various aspects of the application of zeolites and CNT in desalination and water treatment process.	[23]
Nanoparticle oxides, carbon nanotubes, graphene, carbon nanofibers, and nonporous carbon cloth	The synthesize of capacitive deionization electrodes based on electrosorption nanomaterial electrodes for desalination. A comparison with reverse osmosis is also given in this review paper.	[24]
CNT membranes with antimicrobial nanoparticles (silver nanoparticle and TiO_2)	Modification of CNT membranes with antimicrobial nanoparticle for the water desalination process.	[2]
Graphene-based membrane, carbon nanotubes	Modification of carbon nanotubes and graphene by chemical treatment for the desalination process.	[25]
Carbon nanotube	Application of carbon nanotubes (CNTs) as high selectivity desalination membranes.	[26]
Graphene-based nanomaterials	Application of graphene-based nanomaterials as an innovative solution for water desalination.	[27]
CNT, inorganic membrane	Production and application of CNT based and inorganic membranes for the desalination process.	[28]
Metal-organic framework (MOFs)	The desalination process depends on the MOFs' pore size, where water molecules are possible to pass, but salt ions do not pass. The absence of cooperation between water flux and salt rejection depends on MOFs' pore size and surface charges.	[29]

Table 2
Performance of some hybrid membrane in different desalination processes

Desalination process	MOF-layers	Test conditions	Water permeability (L/m^2 h bar)	Solute rejection (%) or permeability	Ref.
RO	ZIF-8/PA	*p*: 15.5 bar *C*: 2,000 ppm NaCl *v*: 0.37 m/s	3.35	>98%	[30]
RO	MOF1/PES/PAN MOF2/PES/PAN	*p*: 5 bar *C*: 7,000 ppm NaCl	36 (5 bar) 41 (5 bar)	93% 97%	[31]
RO	UiO-66/PSU MIL-125/PSU	*p*: 300 psi *C*: 2,000 ppm NaCl	74.9 (300 psi) 85.0 (300 psi)	98.8% 98.6%	[32]
RO	POSS/PA with POSS = • P-8Phenyl • P-8NH_3Cl • P-8NH_2 • P-1NH_2	*p*: 15.5 bar *C*: 2,000 ppm NaCl *v*: 0.37 m/s	33.0 (15.5 bar) 27.1 (15.5 bar) 33.4 (15.5 bar) 3.2 (15.5 bar)	98.2% 98.9% 98.6% 95.9%	[33]
RO	UiO-66/Al hollow fiber	*p*: 10 bar *C*: 0.20 wt.% (of the salt used)	0.28	86.3% (Ca^{2+}) 98.0% (Mg^{2+}) 99.3% (Al^{3+})	[34]
RO	HKUST-1@PA/PES	*p*: 2 or 4 bar *C*: 500/2,000 ppm NaCl	6.94	~98.2% (2 bar) ~97.4% (4 bar)	[35]
FO	Ag-BTC/PES/PVP	*C*: 0.5 – 2 M NaCl *v*: 21 cm/s	~4.3‡	~0.6 L/m^2 h	[36]
FO	CuBDC-NS/PA	*C*: 1 M NaCl *v*: 15 cm/s	3.13	0.317 L/m^2 h	[37]
FO	PMM_{F300} PMM_{A100} PMM_{C300} (PMM prepared from mixture of substrate and active layer(AL))	*C*: 0.5 M $MgCl_2$ (draw solution)	~92 (at given *p*)‡ ~98 (at given *p*)‡ ~107 (at given *p*)‡	~75%‡ ~91%‡ ~93%‡	[38]
FO	ZnO@MOF-5 (magnetic MOF-5)	*C*: 0.5 M Caspian seawater	117 (at given *p*)	–	[39]

Cross-flow filtration	NH_2-MIL-101(Al)/chitosan	*C*: 2,000 mg/L NaCl, 1,000 mg/L $MgCl_2$ or $CaCl_2$	4.0 (NaCl) ~3.8 ($MgCl_2$)‡ ~3.4 ($CaCl_2$)‡	~29.0% (NaCl)‡ 93.0% ($MgCl_2$) 86.5% ($CaCl_2$)	[40]
CDI Electrochemical cell	ZIF-67/PPy	*C*: ~10 mM NaCl *v*: 10 mV/s† *V*: 1.2 Volt	–	11.34 g salt/g (with 1.32)δ	[41]
CDI Electrochemical cell	PC-ZnCo-3	*C*: 750 mg/L NaCl *V*: 1.4 Volt	–	45.62 mg salt/gδ	[42]
Adsorption	CPO-27(Ni)ζ Aluminum fumarateζ MIL-101(Cr)ζ	T_{hot}: 150°C T_{cold}: 25°C Cycle: 700 s Switching: 70 s	–	0.47 g_{H_2O}/g^{δ} 0.53 g_{H_2O}/g^{δ} 1.47 g_{H_2O}/g^{δ}	[43]
Adsorption	MIL-101(Cr)/$CaCl_2$ζ	–	–	0.65 g_{H_2O}/g^{δ}	[44]
MD	AlFu/PVDF	*C*: 3.5 wt.% NaCl	–	99.9%	[45]
MD Ultrafiltration	CA/HKUST-1@GO	*p*: 0.15 MPa *C*: 1.0 g/L BSA	183.51 (0.15 MPa)	95.37%	[46]
MD ultrafiltration	TMU-5/PES	*p*: 3 bar *C*: 40,000 ppm oil-water emulsion	123.212 (kg/m^2 h)	>98%	[47]
MD	Si NPs/PVDF	*p*: 1.2 kPa *C*: 35 g/L NaCl	12,749.6 (g/m^2 h)	~100%	[48]
MD ultrafiltration	hZIF-8/PSU	*p*: 0.2 MPa *C*: 0.5 g/L BSA	579 (0.2 MPa)	>98%	[49]

†Scan rate in millivolt per second;
‡Value approximated from the given graph in cited literature;
δDesalination or adsorption capacity;
ζNon-membrane;
PA = polyamide; PES = polyethersulfonate; PAN = polyacrylonitrile; PVP = polyvinylpyrrolidone; PSU = polysulfone; PPy = polypyrrole; PC = porous carbon; CA = cellulose acetate; BSA = bovine serum albumin; PVDF = polyvinylidene fluoride.
MOF = metal-organic framework; ZIF = zeolitic imidazolate framework; BTC = trimesic acid (1,3,5-benzene tricarboxylic acid); BDC = benzene-1,4-dicarboxylic acid; POSS = polyhedral oligomeric silsesquioxane; UiO = University of Oslo (prototypical of Zr-MOF); MIL = Materials Institute Lavoisier; A100 = Basolite A100 (MIL 53 or aluminum terephthalate); C300 = Basolite C300 (HKUST-1 or copper benzene-1,3,5-tricarboxylate); F300 = Basolite F300 (Fe-BTC); AlFu = aluminum fumarate; Si NPs = silica nanoparticles; hZIF = tannic acid modified ZIF.

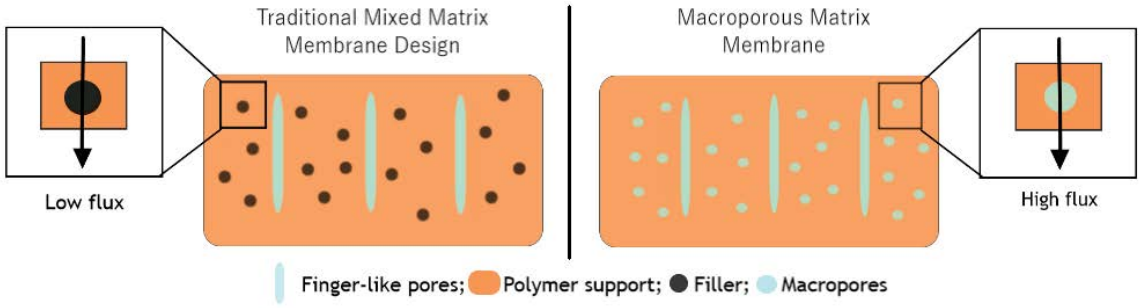

Fig. 2. Schematic representation of PMM compared to traditional MMM (redrawn with slight modification from Lee et al. [6]).

and 2.4 times higher, compared to the polyamide membrane. The MOF loading also led to the enhancement of seawater desalination flux, 34 L/m² h for TFN-0.04, while only 27 L/m² h for TFC [36]. UiO-66 and MIL-125 are other nano-sized MOFs that have been proven to have excellent desalination performance. Significant water permeability of 74.9 L/m² h, with a high salt rejection of 98.8%, was achieved by modifying the TFN membrane with UiO-66. The modification of the TFN membrane with MIL-125 provided higher surface area and pore size. Thereby, higher water permeability of 85 L/m² h and 98.6% salt rejection were obtained [29,32].

Desalination performance of binary and ternary MOFs was reported; namely, MOF1 synthesized from the trivalent cerium cluster in a warm solution of carboxymethyl cellulose (CMC); and ternary complex, MOF2, which is synthesized by the addition of anthranilic acid to MOF1. The implantation of cerium-based MOF (0.1 wt.%) into the TFC can increase NaCl rejection from 69% to 93% (for MOF1) and 97% (for MOF2), from an initial of 7,000 ppm NaCl at a feed pressure of 5 bar. Higher MOF loading helps to increase the water flux 1.2 times from TFC only [31]. Dai et al. [37] embedded copper 1,4-benzenedicarboxylate nanosheets (CuBDC-NS, BDC = benzene-1,4-dicarboxylic acid) inside the PA layer. This study shows that CuBDC-NS embedded inside the PA layer helps in increasing the water flux by nearly 50% (from 1.95 to 3.13 L/m² h bar), and decreasing salt permeability by 25% (from 0.418 to 0.317 L/m² h), compared to the plain membrane. The addition of CuBDC-NS also resulting in the enhancement of antifouling activity due to its hydrophilicity and biocidal ability.

While almost all of the studies used hydrophilic MOFs, Duan et al. [33] introduced a unique approach in utilizing the TFN membrane for water desalination. MOF with hydrophobic properties was used instead of hydrophilic MOFs, specifically the ZIF-8 (ZIF = zeolitic imidazolate framework). The addition of 0.4% (w/v) nano-ZIF-8 (~200 nm) to TFN membrane increases NaCl rejection up to 62%, with water permeability of 3.35 L/m² h bar (higher than BW30). A similar approach has been demonstrated by other researchers, such as hydrophobic-POSS (POSS = polyhedral oligomeric silsesquioxane) implantation to TFN membranes produces a membrane with rigid and bulky cages which effective in increasing the volume of selective membrane layers [33]; incorporation of porous-hydrophobic carbon nanotubes into TFN produces a membrane with ultra-fast water transport [50].

2.2. Multiple MOFs-embedded membranes

Several MOFs can be combined in desalination membranes, such as in preparing mixed-matrix membranes (MMMs). MMMs are a novel material that gains a lot of attention due to their superior thermal stability and mechanical properties. The synthesis of MMMs involves (1) dispersion of MOF-nanoparticles into organic solvent; (2) dissolving polymer materials into the MOF solution with constant stirring to produce a homogeneous mixture; (3) evaporation of water in the casting of the solution. MOF-based MMMs are highly beneficial in the water desalination process due to their tunable and small pore size, which come in handy for adjusting water permeability [38].

An MMM membrane prepares by casting two different MOFs, namely NH_2-MIL-101(Al) and NH_2-MIL-101(Cr), onto a polysulfone (PSU) support sheet. The resulting TFN membrane has a positively charged surface that allows for a higher rejection of multivalent positive ions. In contrast, monovalent positive ions are less rejected—this caused a vast rejection of salt, such as $MgCl_2$ and $CaCl_2$ (93.0% and 86.5%, respectively), whereas the rejection of NaCl and Na_2SO_4 fell drastically. The electrostatic effect makes the salt rejection order to be $MgCl_2$ > $CaCl_2$ > NaCl > Na_2SO_4 [40]. Wang et al. [51] report another notable MMM; however, clay minerals were used instead of MOFs. The membrane is prepared by using polyvinylidene fluoride (PVDF)/cloisite clay composite hollow fibers with the addition of ethylene glycol (EG) and *N*-methyl-1-pyrrolidone (NMP). The resulting membrane has a low heat conductivity, low vapor transfer, high thermal efficiency, and stable mechanical strength. The membrane also has proven to enhance the permeate flux in the MD process, with 100% salt rejection [51].

2.3. Porous MOF-embedded membranes

Unlike MOFs-based MMMs, the porous matrix membranes (PMMs) use water-soluble MOFs nanoparticles as filler, which will be easily washed away by water. The idea is to provide more holes on the membranes, to improve the flux of solvent through the membrane [29]. Fig. 2 shows the difference between MMM and PMM. PMM filled with MOF was developed by Lee et al. [38], it has been used for forward-osmosis processes. In the fabrication of MOFs-based PMM, Lee et al. [38] mixed three different types of MOFs, that is Basolite F300, Basolite C300, and Basolite A100. Polyacrylonitrile (PAN) was used as the dope solution, and

the addition of lithium chloride into the dope solution was conducted at 60°C. The layer-by-layer (LbL) self-assembly process was done by immersing MOFs into polyallylamine hydrochloride (PAH) and polysodium 4-styrene-sulfonate (PSS) for three times to form the rejection layer. Finally, it was immersed in 0.1 wt.% glutaraldehyde (GA) for 30 min to establish the crosslinking of the salt rejection layer, which provides high forward osmosis water flux. PMM can altogether increase water penetrability in a pressure-driven membrane process, perhaps due to the expulsion of MOF particles in the polymer matrix, which expands membrane porosity and interconnectivity. More critically, current researches recommend MOF as a green layout might have great potential for pressure-driven membrane processes as well as for carbonated nanofiber membranes for particular screening and separation of nanoparticles [52], or osmotically driven membrane processes (i.e., osmosis to the front (FO) and pressure-suppressed osmosis (PRO)) [53].

3. MOFs-modified membrane in various desalination methods

3.1. Capacitive deionization

Capacitive deionization (CDI) was first aroused during the 1960s and has multiplied over the past two decades as a promising water desalination innovation [54]. The idea of CDI technology is to temporarily storing salt ions in an electric double layer (EDL) at the interface between the CDI electrode and the salt solution. This technology offers low energy consumption because the voltage utilized is typically lower than the electrolysis potential of water (~1.23 V) [55]. The CDI requires both deionization and capacitive processes. Ions from saline water are removed by applying electrostatic forces onto the solution through positively and negatively charged electrodes. Cations and anions are attracted to their corresponding electrodes, Fig. 3a. The regeneration step is also necessary to desorb the ions from saturated electrodes, which then transferred into wash water by reversing the potential difference between electrodes, as shown in Fig. 3b [24].

The improvement on CDI process can be engaged by changing the properties of the electrodes, such as into (1) high surface region that can be accessed by large-sized ions, (2) high electronic conductivity, and (3) high electrochemical stability [54]. The current interest in research from membrane CDI (MCDI) is focused on structuring new materials with alluring properties, as referred above [42]. The main idea was to combine the high porosity MOFs and high conductive electrode to produce a newly effective electrode. One of the latest attempts on developing high-end electrodes for the CDI system was conducted by Wang et al. [41]. A combination of ZIF-67 with polypyrrole (PPy) nanotubes resulted in a three-dimensional hybrid material with interconnected MOF particles using the nanotubes as bridges; the bridge enables the MOF particles to transfer electrons between them. The well-dispersed MOF particles gave uniform particle size distribution on the hybrid electrode. This ZIF-67/PPy hybrid electrode exhibited a remarkable desalination capacity of 11.34 mg/g and excellent cycling stability [41]. A series of bimetal MOFs (BMOFs) with various Zn to Co molar ratios were successfully synthesized to design the optimal combination of ZIF-8 and ZIF-67, which later be used to create a CDI electrode. The recently arranged BMOFs were coded as BMOF-ZnCo-*n*, and the derived carbon was characterized

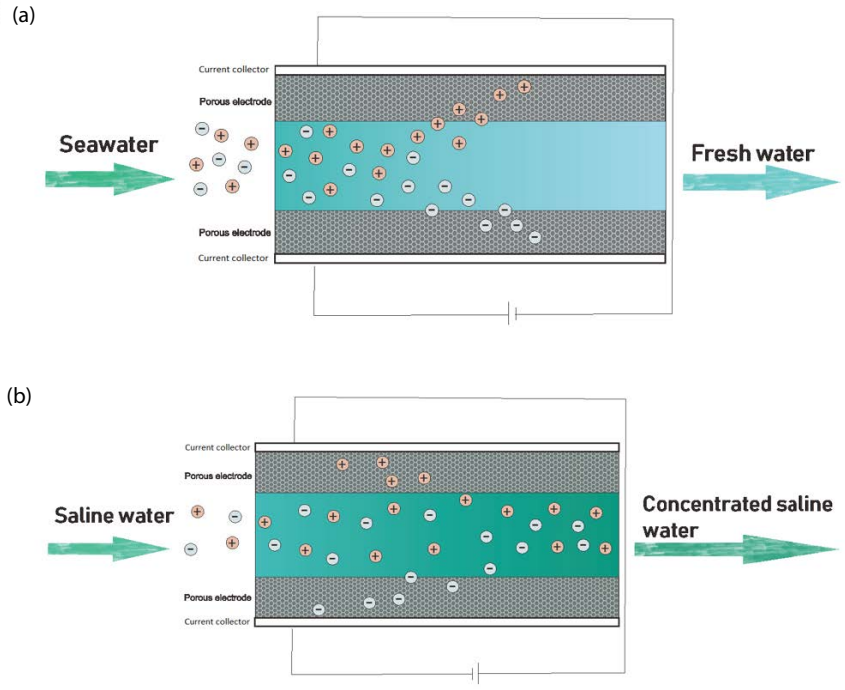

Fig. 3. (a) Deionization of saline water and (b) regeneration of CDI electrodes (redrawn with slight modification from Gaikwad and Balomajumder [24]).

as PC-ZnCo-*n* (*n* = molar proportion of Zn to Co). Among the synthesized PC-ZnCo-*n*, PC-ZnCo-3 demonstrated the highest salt removal capacity of 45.62 mg/g in the membrane CDI system [42].

3.2. Forward osmosis

Among the methods applied for water and wastewater treatment, FO provides an option in contrast to conventional pressure-driven membrane processes (particularly in seawater desalination); that is, minimal cost, high selectivity, and less inclination to fouling contrasted with other membrane methods [56,57]. Membranes with two unique structures are utilized in the FO procedure: (i) robust skin asymmetrical membranes containing layers of skin coordinated over the permeable layer [58], and (ii) thin-film composite (TFC) membranes, which comprise of ultra-slim active layers (AL) over the permeable support layer (SL) [59].

Fig. 4 shows the FO process. Briefly, the water molecules pass through the membrane from the feed water, which has a lower concentration to the draw solution and higher concentration due to osmotic pressure. The membranes utilized in the FO are mainly adopted in a flat sheet configuration [60]. However, most of the flat sheet configurations fold into spiral wounds that form tubular membranes. In maximizing the surface area of the membrane, the configuration of the tubular membrane or hollow fiber must be used. An ongoing research effort concentrated on building a high-performance hollow fiber membrane for the FO procedure [61]. In large-scale FO processes, hollow fiber membranes show more advantages than that of flat sheet membranes. Hollow fiber membranes offer an increase in durability, flow patterns, and packaging density [62].

Lee et al. [38] utilized PMM as SL for the fabrication of TFC FO membranes. The bulk porosity of MOF-based PMM expanded as the membrane tortuosity decreased—this led to the increased mass transfer of water and the well-controlled dilutive internal concentration polarization (DICP) in the FO substrate due to the decreasing membrane fundamental parameter [38]. Another effort for developing this research was made by Arjmandi et al. [39]; a magnetic water-unstable MOFs was used to create pores with various sizes and dispersions throughout the membrane. Zirehpour et al. [36] developed hydrophilic silver-based MOF-embedded TFC to enhance the desalination performance of the FO membrane. The prepared membranes have an improved porosity and pore interconnectivity, which resulted in a high FO flux of 82 L/m^2 h. Furthermore, the hydrophilic surface and high porosity of MOF provide another transport way for water [36].

3.3. Reverse osmosis

The most commonly used water desalination process is RO, with around 20,000 large scale plants worldwide. The concept of RO is the inverse of FO; by giving a more massive pressure than the salinity osmotic pressure of the feed water, the water molecules are forced to pass through a set of semi-permeable membranes and leaving the salt ions behind (Fig. 5). The main advantages of the RO process are high energy efficiency, low operating temperature, and increased productivity [29]. The HKUST-1 MOF has been used to modify the PA matrix with PES and polydopamine (PDA) SL, in a low-pressure RO process. HKUST-1 considers as the potential material because of its fast transport of water molecules, which pass through the flow channels of the organic framework, and highly solute rejection due to its steric exclusion properties [35]. The formed membrane resulted in the high rejection of NaCl, which was 98.2% at 2 bar and 97.4% at 4 bar. For a long term RO operation, the modified HKUST-1 at the PA membrane shows the same durability as the original membrane. The HKUST-1 doped membrane has enhanced surface hydrophilicity, antifouling capability, and water permeability compared to the original membrane. The higher surface hydrophilicity allows the water molecules to be adsorbed into the PA matrix, facilitating the water transport through the porous flow channels. Moreover, the negative surface charges lead to higher fouling resistance [30,33,35].

3.4. Adsorption desalination

AD is an emerging alternative for the water desalination process due to its environmentally friendly, low-cost, and high energy efficiency properties. AD technology mainly consists of two cycles, that is evaporation–adsorption and

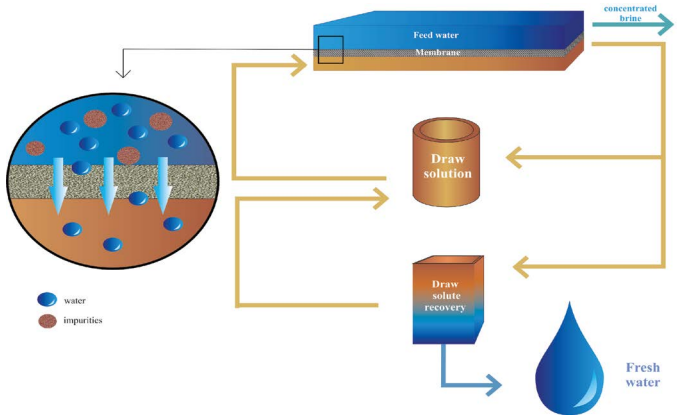

Fig. 4. Forward osmosis schematic diagram.

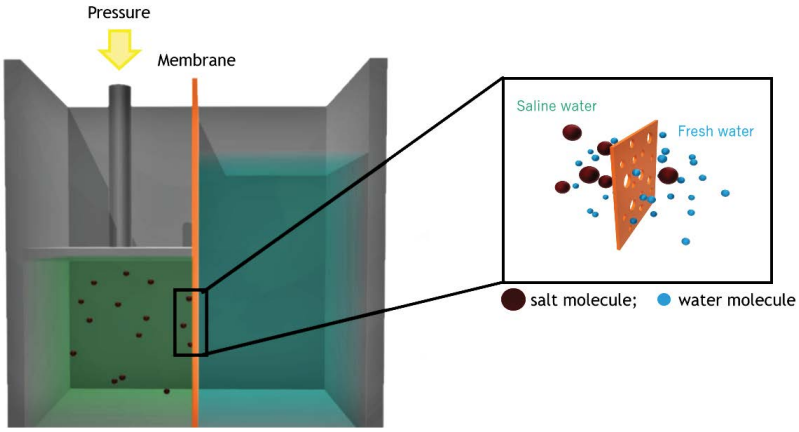

Fig. 5. Reverse osmosis schematic diagram.

desorption–condensation. The first cycle works by evaporating water using a low-pressure evaporator. Adsorbent materials then collect the water vapor in two or more beds containing a finned tube heat exchanger. After the evaporation step, hot water is employed through the heat-exchanger tube to warm the beds so that the water vapor release. Cooling water is supplied afterward into a condenser above the beds, which condense the vapor into collectible potable water [29,43]. The system consists of two adsorption beds packed with MOF, evaporator, and condenser material, as shown in Fig. 6.

AD system with a silica gel bed is the most common one. However, the major disadvantage is the lack of hydrophilicity of this material that causes a low adsorption capacity, which must be covered up by employing high relative pressure. The utilization of porous and highly-hydrophilic MOFs has been an exciting way to cope with the problem. The improvement of AD by incorporation of MOF has been demonstrated by Elsayed et al. [43], in which they are employing three kinds of MOF materials, namely MIL-101(Cr), aluminum fumarate, and CPO-27(Ni). MIL-101(Cr)-employed bed exhibited the highest water uptake and also the highest specific daily water production (SDWP), which outperformed the other two MOFs.

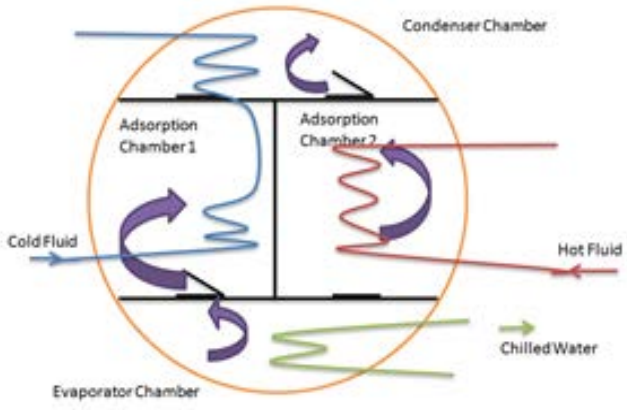

Fig. 6. Adsorption system schematic diagram (Redrawn with slight modification from Elsayed et al. [43]).

3.5. Membrane distillation

MD has been developed for over 40 y, and it is considered a potential application for seawater desalination due to its high productivity and low-cost operation. In particular, membrane distillation involves water evaporation and vapor condensation and mass and heat transfer mechanisms, as shown in Fig. 7. A porous hydrophobic membrane was installed as thermal insulation and physical barrier between the two phases; the membrane allows free transport of water vapor through the pores while preventing the liquid water from getting off the membrane due to its surface tension forces. In the MD process, the membrane must be kept dry so that only vapor diffuse through the pores [41].

The hydrophobic membrane mostly comprises of polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyethylene (PE), or polypropylene (PP); which

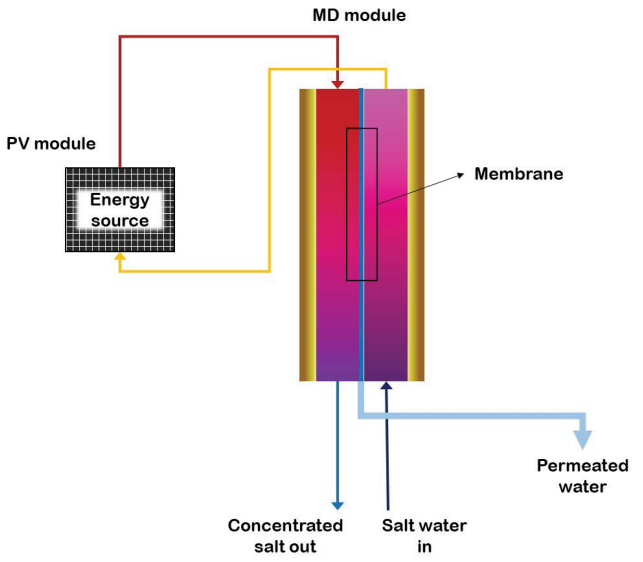

Fig. 7. Membrane distillation (MD) module basic setting (Redrawn with slight modification from Mahmoudi and Akbarzadeh [63]).

have the following properties: high liquid entry pressure, high permeability, low fouling capability, high chemical stability, and high thermal stability [63–65]. The unique properties of the MD process rely on its thermal gradient, which is created across a hydrophobic membrane and functionates to bring the solution to their saturation point without any noteworthy flux-decline. The membrane used in the MD process holds all solid or nonvolatile contaminants and therefore resulting in 100% pure water. A green modification of the MD process has been developed, particularly for its energy source; the solar energy, geothermal energy, and waste grade energy (with low-temperature industrial streams) has been applied to MD technology [65].

Many engineers have studied sustainable development for membrane used in MD technology, where the incorporation of MOF to synthesis a hybrid membrane is the most popular to date. The main goal of the development is to create a membrane with high porosity to achieve an efficient (both thermally and permeability) water desalination. Cheng et al. [45] synthesized a novel hydrophobic hybrid MOF/PVDF hollow fiber membrane (MOF = aluminum fumarate, abbreviated as AlFu). The hydrophobic hybrid membrane was found to improve the permeate flux and thermal efficiency because of the enlarged porosity of the membrane. The prepared MOF/PVDF shows a high salt rejection of 99.9% for 3.5 wt.% NaCl solution, during 50 h MD process. Yang et al. [66] have reported a similar finding; they have proven that incorporating iron 1,3,5-benzenetricarboxylate MOF into the PVDF membrane led to pore and porosity enlargement of the membrane, and subsequently improved the water flux. Incorporation of graphene oxide-modified MOF, namely HKUST-1@GO, into the membrane is reported to produce a hybrid membrane with a larger pore and smoother surface (compare to an acetate cellulose membrane); the HKUST-1@GO-blended membrane is proven to accelerate the solvent and non-solvent exchange in the PI process [66]. Other research groups also demonstrated that a MMM modified with ZIF-8 or TMU-5 MOF has a larger pore than the pristine membrane [47,49].

The MOF (or other similar NPs) acts as nucleation materials, which cause enlargement of membrane pores post-penetration, during the membrane modification process. Incorporation of MOF produces a thermodynamically unstable membrane which is more active to bind the guest molecules (i.e., salts, volatile compound, and charged ions); this behavior is leading to the improvement of solvent and non-solvent exchange rate during the PI process. One thing to note is that excessive MOF loading into the membrane will lead to a sudden kinetic hindrance, which demoted the efficiency of solvent exchange performance. This is because a higher MOF loading will cause particle aggregation and a decrease in crystallinity [47–49,67,68].

4. Concept of MOF-embedded membranes

4.1. Factors affecting desalination performance

It has been demonstrated that the hybridization of TFN or TFC membrane with MOF can produce layers that are better compatible with the polyamide matrix, faster water transport theoretically in the framework, and hydrothermally more stable. Also, the enormous porosity of the MOFs provides a waterway for the rapid passage of water molecules through TFN or TFC layers [30,33,34]. Based on several reports, the following factors have a profound influence on the desalination process: the amount of MOF, surface area, hydrophobicity, surface charge, and inlet temperature. The next paragraphs outline the evidence regarding these influential factors.

The incorporation of MOF particles in the proper amount provides an excellent contribution to improving desalination performance. Increasing the number of MOFs, however, may reduce desalination performance. The addition of 0.08 wt.% AgBTC to PA thin-film, in the preparation of TFN-0.08, produced TFN with a higher B/A permeability ratio (B = solute and A = water) compare to TFN-0.04 – which means the solute permeability in TFN-0.08 is higher than TFN-0.04. The proper addition of MOF can increase the hydrophilicity of the membrane, thus attracting the water molecules [36]. However, incorporation of an excess number of MOFs is resulting in lower salt rejection (higher B/A permeability ratio) as it will crack the TFN membrane [29,32].

The higher surface area is another increase resulting from the addition of MOF to the membrane. This is since the presence of MOF in the membrane matrix causes higher pore formation, thus allows faster water permeance. Furthermore, rapid water permeation can be achieved by changing the affinity of the membrane toward the water. The addition of hydrophobic MOF (not hydrophilic MOF) results in a membrane with rapid water permeation caused by the absence of friction. The addition of hydrophobic MOF facilitates water permeability by reducing the affinity between water molecules and the pore walls of the membrane [30,31].

Ma et al. [40] show a more intrinsic factor affecting the desalination performance, which is the surface charge of the membrane. A measurement on the surface charge of MMM, which was modified with mixed MOF NH_2-MIL-101(Al) and NH_2-MIL-101(Cr), shows positive charges. The positive charge of the membrane arouses the repulsion force to reject denser positive ions rather than the lower charged ions. Contrariwise, the divalent anions are less rejected than monovalent anions since the negative divalent ions experience stronger interaction with the membrane. These combined effects make the salt rejection order to be $MgCl_2$ > $CaCl_2$ > NaCl > Na_2SO_4. Moreover, such a phenomenon can be explained by looking into the characteristics of the membrane and molecule. The larger radii of Mg^{2+} and Ca^{2+} make them held back by the membrane, while smaller Na^+ ion is easier to pass through [40].

The inlet temperature (hot or cold) cause a significant difference in the desalination result. The desalination process was carried out in two beds of the adsorption system. The effect of inlet temperature is clearly explained by Elsayed et al. [43] in their study. A CPO-27(Ni) (also known as MOF-74) and aluminum fumarate-MOF were used as the membrane modifier. Aluminum fumarate works by adsorbing water in the inner pores of the materials without the existence of unsaturated metal sites. Meanwhile, the unsaturated metal sites and the hydrophilic organic linker of CPO-27(Ni) will provide

additional binding sites for water. CPO-27(Ni), aluminum fumarate, and MIL-101(Cr) exhibited a maximum adsorption capacity of 0.47 g H_2O/g_{ads}, 0.53 g H_2O/g_{ads}, and 1.47 g H_2O/g_{ads}, respectively [69]. By operating in the optimum condition, the CPO-27(Ni) produced freshwater 4.6 m^3·1/(ton d) at an evaporation temperature of 5°C and a regeneration temperature of 110°C. In comparison, aluminum fumarate produced 6.3 m^3·(ton d)$^{-1}$ at an evaporation temperature of 20°C and a regeneration temperature of 70°C. This study showed that CPO-27(Ni) has a better performance than aluminum fumarate at high regeneration (desorption) temperature and low evaporation temperature. In comparison, aluminum fumarate has a better performance at a higher evaporation temperature [43]. The effect of inlet temperature to the desalination also has been stated by Youssef et al. [70] using the same CPO-27(Ni) MOF in a 1-bed adsorption cycle. The use of CPO-21(Ni) allows maximum water output of 22.8 m^3/(ton d), with the inlet temperature of 40°C for the evaporator and 5°C for the condenser.

4.2. Mechanism of desalination improvement

The presence of MOF particles in the membrane causes the membrane to crack and form pores around it. The more pores that form around MOF particles will provide a significant increase in surface area, thereby increasing desalination performance [71,72]. Without the presence of MOF, the pores formed by the polymer are uneven – even sometimes, there are areas on the membrane that have very small (or absent) pores that do not allow water permeance (Fig. 8a). By adjusting the number of embedded MOF, the pores formed will be adequate and facilitate water permeance (Fig. 8b). Logically speaking, increasing the number of MOFs should provide a very significant increase in the number of pores. But unfortunately, this is not the case; embedding excessive amounts of MOF can cause unwanted membrane damage (Fig. 8c). Embedding MOF beyond the capacity of the membrane will create a large membrane crack, and thus, large pores are formed, and the water (also ions) can pass freely [29,39,71–73].

Membrane pores that are too small induce a higher affinity between water molecules and pore walls; this causes high surface tension of water molecules (Fig. 9a) [74]. In this case, higher pressure is needed to enable a proper desalination process, but this is often not feasible because excessive force will cause damage to the membrane. The existence of MOF can disturb the affinity of water. MOF can help break down water molecules so that the surface tension of the water is lowered. Previous reports have shown that the use of MOF with different water-philicity provides different desalination mechanisms. Hydrophilic MOF breaks surface tension by attracting water molecules toward it (Fig. 9b), while hydrophilic MOF breaks surface tension by applying repulsive forces to water molecules (Fig. 9c). A new approach to surface-philicity design is the omniphobic membrane surface, which has excellent wetting resistance against low surface tension solutions. The utilization of such a membrane has been introduced in the MD process [75–78]. However, many trials and errors are still needed to improve omniphobic membranes; especially in overcoming their weakness, which is easily damaged by the condensation process.

Insight into the MOF performance in desalination led to the idea that adsorption capability drove the MOF performance. MOF adsorption capability is innate from the unsaturated metal sites that actively bind the guest molecules, and therefore improved the desalination efficiency. Also, MOF loading into the membrane led to porosity enlargement. The simple illustration of the desalination process using the MOF-modified and unmodified membrane is shown in Fig. 10. In most cases, the improvement effect (in desalination) of MOF can be further escalated by forming composites (i.e., MOF@GO). Later on, it believed that there would be more particular requirements in desalination membranes that can be met by the MOF-composites, such as specific or selective membrane against individual guest molecules, and thermal/magnetic/electric membranes. It can be concluded that, although the exploration of composite materials has just barely begun, the prospects of MOF-composite-incorporated membranes are vast and will keep on increasing [79]. The primary purpose of every sustainable development is the feasibility of its application in the industry. The engineers have agreed that a desalination membrane must possess specific properties to fulfill this purpose: stable (no performance declining) over a long term

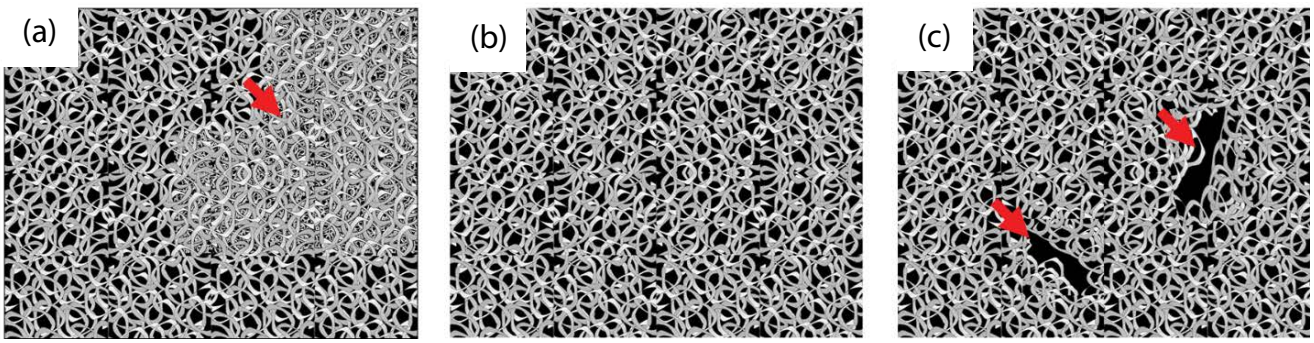

Fig. 8. Illustration of pores properties of the desalination membrane. (a) Membrane with absence of MOF particles, the arrow shows the area with tiny (absent of) pores, (b) membrane with MOF particles embedded, and (c) membrane with excess MOF particles embedded, the arrows show the area with large membrane crack.

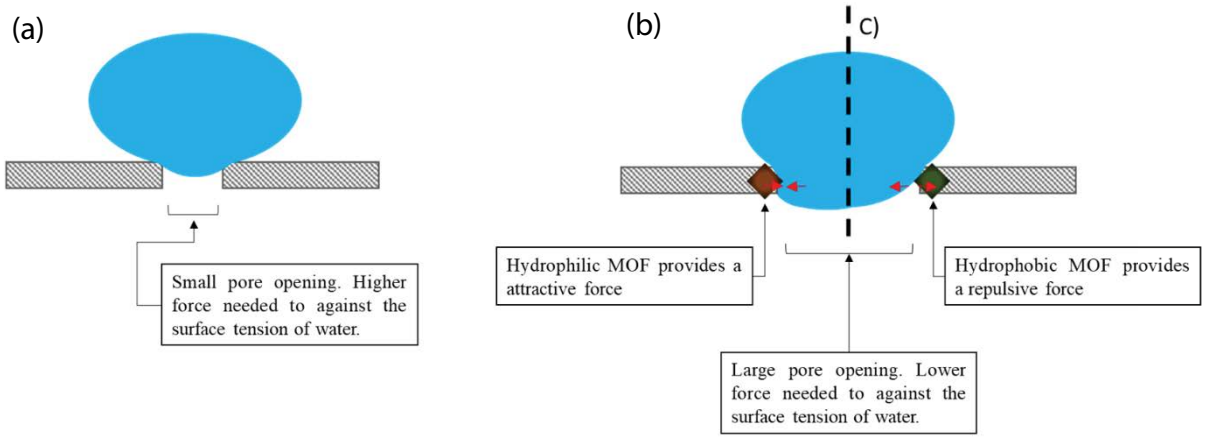

Fig. 9. Affinity of water molecules and membrane pore walls. (a) Membrane without MOFs, (b) membrane with hydrophilic MOFs, and (c) membrane with hydrophobic MOFs.

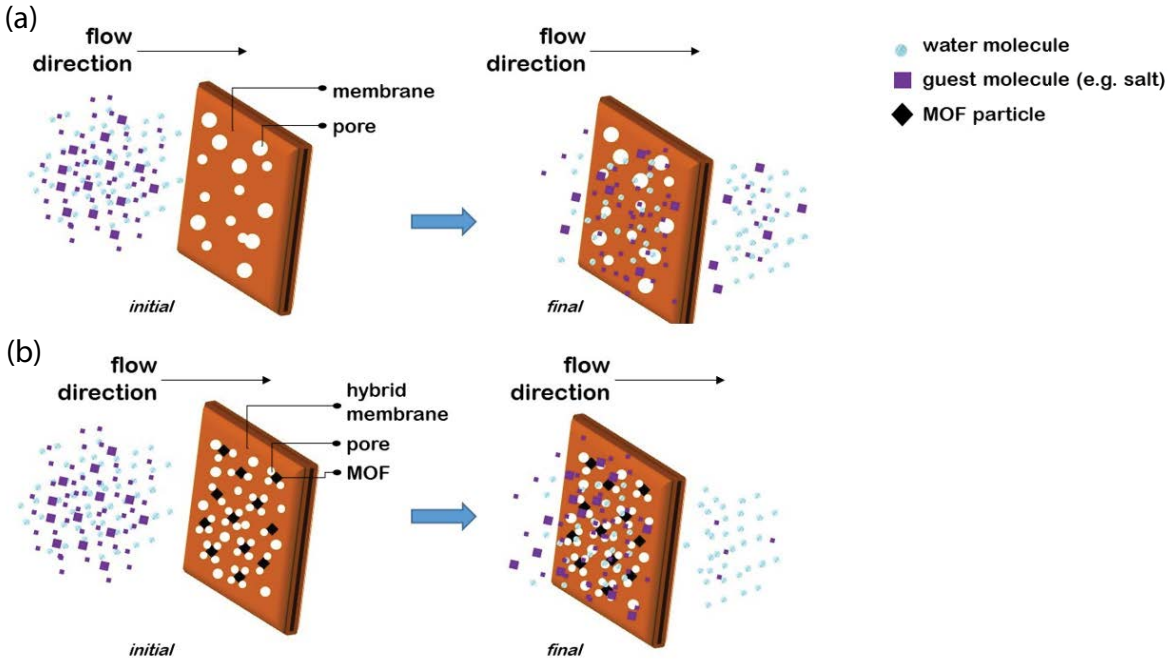

Fig. 10. Illustration of the desalination process. (a) Desalination by using an unmodified membrane; the pores structure is limited and (b) desalination by using MOF-modified membrane; the structural pore is enlarging thus the surface area is higher. More pores with smaller size created due to the incorporation of MOF NPs, the smaller pores give higher solute rejection.

process, reusable, high efficiency, environmentally friendly, and low cost.

4.3. Prospect and challenges

For the past decade, RO has been the most widely used method for saline water desalination. However, the growing development of MOF nanotechnology has proven to be able to produce high-properties membranes for desalination, such as MOF-based TFN membranes, MOF-based electrodes, MOF-based adsorbents, etc. The MOF-hybridized membranes are proven to improve desalination performance—thanks to their superior cycling stability and durable structure. The fact that MOFs apply to every possible method for desalination makes it attractive for sustainable development in this field.

Nevertheless, the persistent challenges in membrane fabrication with MOFs are the achievement of superior desalination capability, high durability, minimum degradation, and proper safety for humans and the environment. So far, current studies only focused on comparing the MOF embedded membrane to the plain membrane, or characteristic of the membrane, and improving the salt rejection and water flux in a lab-scale process. In which some of

them are not feasible to implement for industrial purposes. Industrial-scale processes are required a distinctive investigation and design, with their separated trials and errors. The industrialized amount of feed water, as well as salt concentration, is needed in applicative researches as real natural seawater is the targeted application. Furthermore, more research needs to be done, considering the economic and environmental sustainability of incorporating MOF in the water desalination process.

5. Conclusions

Fresh and clean water scarcity has become an issue in many parts of the world. To overcome this global issue, extensive researches have been developed to establish an advanced novel technology of water desalination, with lower cost, lower energy consumption, and environmentally friendly. Nanomaterials such as MOFs have been used in various nanotechnology to enhance the desalination process, including forward osmosis, reverse osmosis, adsorption, capacitive deionization, and membrane distillation. MOFs are endowed with excellent properties such as high surface area, high porosity, high chemical stability, and feasible combination of inorganic and organic matters. The exceptionally promising efficiency improvement of desalination performance by MOF has been demonstrated throughout this review. The factors that are inducing the improvement are porosity enlargement of the membrane; additional adsorption sites provide by MOF, improved selectivity, and unique properties (e.g., magnetic). The combination of the desalination membrane with MOF offers a remarkable improvement in desalination performance, which can be a promising solution for overcoming water scarcity in the future. Still, there are some challenges in the future application of seawater desalination, that is: (1) the high energy requirements – especially for practical applications, (2) the possibility of environmental damage during the construction of desalination equipment and piping systems, and (3) the disposal of concentrated salt water (reject-salt) which can be critical environmental disturbances. Efforts in the sustainable development of the desalination process are apparent, for instance, the employment of robotic-automation technology, the use of renewable energy (e.g., solar cell) to operate the system, the development of reject-salt disposal systems (e.g., deep well injection), and the emerging of environmental regulation regarding the seawater desalination. At last, research and design on desalination systems should focus not only on developing eco-friendly and high-performance membrane materials but also on increasing cost and energy efficiency.

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