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REVIEW

Metal Organic Framework Based Membranes for Efficient Wastewater Purification: Syntheses and Applications

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Wastewater treatment utilizing metal organic framework (MOF) based membranes have gained significant attention in recent years owing to their versatile range of properties, ease of synthesis and tunable geometry of pores. During the last decade, innumerable attempts have been executed by global scientific communities in the development of novel MOF based membranes for eliminate several constituents, such as, heavy metals, oil and micro-pollutant, organic dyes, *etc*. This review aims to explore the synthetic methods for MOFs, as well as, MOF based membranes for efficient water purification and their applications in removing the causes of water pollution. This study also enlighten the applications of MOFs based membranes in the desalination of brackish and seawater. So, this review covers all the key synthetic strategies of MOFs-based membranes and their use in purifying and elimination of different hazardous material of wastewater.

Keywords: Metal organic frameworks, Membrane, Wastewater, Water treatment.

INTRODUCTION

The exponential surge in the population and concurrent industrial expansion has raised profound doubts about the viability and longevity of natural resource sustainability in the imminent future. Foremost among these concerns is the escalating scarcity of freshwater sources, with projections indicating that by 2030, half of the world's population will struggle with water stress [1]. Approximately, three-quarters of the Earth's crust is composed of water, primarily distributed across oceans, lakes, rivers, glaciers and groundwater. Nonetheless, the majority of this water, about 97%, is saline seawater, rendering it unsuitable for drinking or agricultural purposes. Of the remaining 3%, approximately 2.3% is locked in polar ice caps and glaciers. Merely 0.7% is suitable for human use, predominantly sourced from groundwater (about 0.66%), with a negligible fraction, less than 0.03%, available in lakes and rivers as freshwater [2]. Water is regarded as precious due to its limited availability and wastage is discouraged. Factors such as water pollution, unregulated usage and poor management of water resources contribute to an increasing water scarcity. Globally, the annual water demand increases by approximately 1%. This escalating need for freshwater is fueled by growing populations, globalization and industrialization, leading the world towards a water crisis. According to the United Nations, approximately 2.2 billion people lack access to freshwater and this number continues to rise with each passing day [3].

To resolve the water scarcity issue thus appears as the upmost priority for the worldwide scientific communities. Specifically, controlling water pollution is deemed one of the primary approaches to mitigate water shortages [4]. Separation technology has emerged as a crucial and remarkably effective tool in the water treatment sector. Membrane technologies offer efficient separations and have been extensively employed in water purification since the 1960s. Reverse osmosis (RO) has emerged as the premier choice for seawater and brackish water desalination, while nanofiltration (NF) membranes have demonstrated satisfactory performance both as a pretreatment for RO and as an autonomous filtration process in water treatment. This efficiency is rooted in the membrane's ability to selectively allow desired molecules to pass through its pores without undergoing phase changes along with devoid of addition of any external chemicals [5]. As a consequence, membrane based separation, recognized as a promising method in addressing energy and environmental challenges, has undergone substantial development in recent decades. Membranes enable the separation, purification and concentration of various components of a feed liquid through selective separation [6-10]. However, proper balancing between permeability and selectivity must be taken into consideration to have efficient purification [11].

Metal-organic frameworks (MOFs) represent a class of porous coordination polymers, formed by the combination of organic ligands and metal, resulting in highly crystalline structures [12]. These nanomaterials typically exhibit exceptional porosity and possess a high surface area. Further refinement of MOF structures can be achieved through additional functionalization or exchange of constituent materials [13]. Over the past decade, MOFs have undergone extensive research and have emerged as one of the most captivating classes of materials for scientists and engineers. This is due to their advantageous features such as regular and tunable pore structures, abundant adsorption sites and more. Moreover, their organic ligands enable MOFs to establish robust coordination interactions with polymeric membranes, thereby enhancing membrane stability. Leveraging these advantages, membrane materials functionalized with MOFs have been synthesized using various methods and are extensively explored for applications in water and wastewater treatment. Despite displaying promising performance for wastewater treatment, the application of MOFs is hindered by their instability in water [14]. Generally, MOF structures with outstanding stability often possess robust coordination bonds, ensuring thermodynamic stability or significant steric hindrance, providing kinetic stability [15]. These characteristics enable them to withstand damages to metal-ligand bonds during hydrolysis reactions. Water stable MOFs can be categorically divided into three classes [16] *viz.* (i) azolate based MOF formed by N-donating ligands; (ii) carboxylate based MOFs with the metal in high oxidation state; and (iii) MOFs with hydrophobic surface.

All these MOFs appear as significantly stable in aqueous medium and thus can be utilized in the development of potential MOF membranes by depositing over silica, alumina or even polymer supports. These MOFs exhibit stability in water and are suitable for constructing MOF membranes on support materials such as silica, alumina or polymers. Their high selectivity, permeability and uniformity, along with variable pore size and easily modifiable structures, make them ideal candidates. Additionally, some of these MOFs can be reused and recycled, further enhancing their appeal for various applications.

Metal organic framework (MOF) based membranes have displayed their potentiality in the wastewater purification and treatment. Several synthetic strategies have been found to be very much promising for fabricating MOF based membranes for efficient water treatment for years. These MOF based membranes offer several advantages and thus making themselves efficient for eliminating several environmental hazards, such as oil and micro-pollutant, heavy metals, organic dye and salty constituent of brackish water to make them usable. The present review comprehensively summarizes the potential synthetic procedures, as well as, the efficient applications of MOF based membranes in the wastewater purification and thus expected to be very much beneficial for the environmental chemists concerning the environmental hazards of wastewater. Fig. 1 displays the complete schematic diagram of the present review showing the potential synthetic procedures and efficient applications of MOF membrane in wastewater treatment.

State of the art: To have the complete scenario of the research involving metal organic frameworks for water treatment the bibliometric analysis was executed from the web of science (WoS) database as it reveals more related works on search. The search string for this particular analysis was TS = [(metal organic framework) OR (mof) AND ((wastewater) AND (treatment OR purification))]" and the period was limited to 01-01-2014 to 31-12-2023, *i.e.* the last decade. A total 92506 number of publications were found to be published, which includes articles, reviews, conference proceedings, *etc.* To have the complete idea of the research executed on the present theme, the year-wise growth of publications, most publishing countries, WoS categories and research areas were analyzed in the WoS window and plotted in Microsoft Excel.

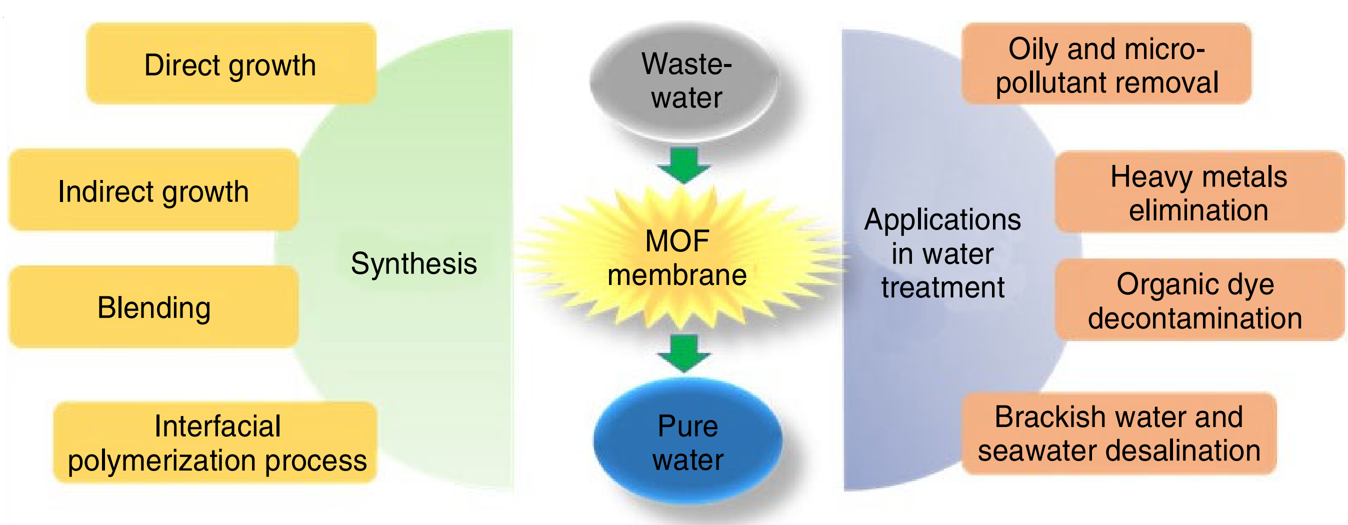

Fig. 1. Scheme summarizing synthetic procedures and applications of MOF based membranes in wastewater treatment

The year-wise growth, most publishing ten countries, ten most related WoS categories and five most associated research areas related to MOF based water treatment has been plotted in Fig. 2. As evident from Fig. 2a, the number of publications were increased in each year till 2022, a slight decrease in number of publications was found in 2023. Fig. 2b represents 10 countries publishing the highest number of articles on the present theme. As can be seen, P.R. China published huge number of articles on the present theme. USA, India, South Korea and Iran followed China in number of publications, although the numbers are significantly lower as compared to China. The 10 top WoS categories associated with MOF for water treatment has been depicted in Fig. 2c. As evident from the figure, 'Chemistry Multidisciplinary' and 'Materials Science Multidisciplinary' appears as the most associated WoS categories of MOF based water treatment. This was followed by 'Chemistry Physical', 'Chemistry Inorganic Nuclear', 'Nanoscience and Nanotechnology', *etc.* Fig. 2d represents the areas on which the articles on MOF in water treatment were published. As can be found, the highest numbers of articles were published from Chemistry, followed by Materials Science, Science Technology, Engineering and Physics. This result is very much obvious as the present field of investigation is much related to chemistry and its application in developing new technologies and thus materials science, science technology and engineering appeared in the priority list just after chemistry.

Synthetic methods of MOFs: MOFs are typically constructed by combining metal ions with organic linkers to create porous and crystalline materials. The utilization of MOFs in diversified applications has found to be propagated in the last decade. In this short span of time, numerous manufacturing methods for MOF materials have been developed. Furthermore, researchers have begun to recognize the potential of incorporating MOFs as fillers into polymeric membranes for water treatment applications. Following is a discussion of some significant synthetic processes for metal-organic frameworks (MOFs):

Microwave/ultrasound-assisted synthesis: The emergence of microwave and ultrasound-assisted synthesis methods in recent years is regarded as environmentally friendly and efficient. These methods significantly reduce crystallization and reaction times while ensuring high yields of MOF products, making them a subject of extensive research. By subjecting mixed raw materials containing metal ion sources and organic ligands to specific ultrasonic or microwave conditions, the desired MOF materials can be obtained. Microwave technology facilitates the formation of local super-hot spots and rapid heat transfer, resulting in a swift and consistent nucleation process. This ultimately leads to the production of MOF particles with more uniform size distributions. The utilization of modulators can control the nucleation process in the formation of crystallites, thereby allowing for adjustments in the size and crystallinity of MOF particles [17]. In a typical procedure, the substrate mixture, along with an appropriate solvent, is placed inside a Teflon vessel, which is then closed and sealed. The vessel is kept undisturbed into the microwave at a suitable temperature and time. Inside the microwave, electromagnetic energy is

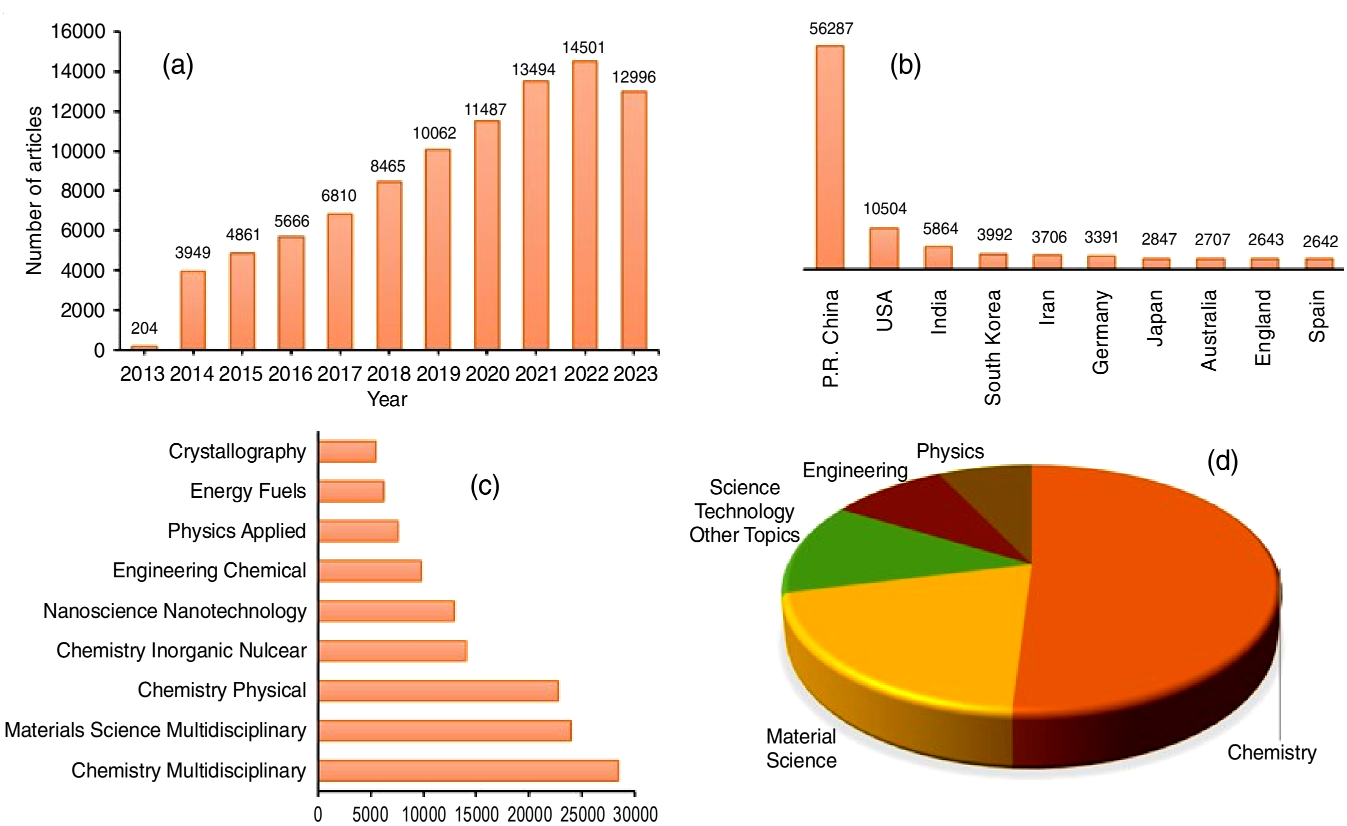

Fig. 2. (a) Year-wise growth in the number of publications, (b) Country-wise publication, (c) WoS categories and (d) Five most active research areas related to MOF water treatment research

converted into thermal energy. The microwave connects with the applied electric field, which has a constant or permanent dipole moment of the molecules present in the mixture. This interaction elevates the temperature of the mixture [18]. In an electromagnetic field with an oscillating nature, the polar molecules within the substrate mixture align themselves. This alignment leads to a permanent alteration in their orientation. The application of desired frequency leads to the collision between molecules, raising the kinetic energy and consequently temperature of the system. The system thus gets heated associated with the direct interaction between the electromagnetic radiation and the solution. Achieving uniform nanocrystals relies on critical factors such as selecting the right solvent and ensuring a specific energy input [19].

Solvo/hydrothermal synthetic method: The solvothermal method is widely recognized as one of the most efficient and commonly used approaches for preparing MOFs of various sizes [20]. In the solvothermal method, if water is selected as the solvent to dissolve the raw materials, the reaction is termed as hydrothermal. The solution, consisting of the starting materials and the solvent, is then placed in a hydrothermal pot and heated to a specific temperature, typically ranging from 100 to 200 ºC [21]. Reactions in the water phase within a non-equilibrium synthesis system often yield porous nanomaterials with exceptional properties. This method is widely employed for the synthesis of MOFs due to its effectiveness and versatility [22]. Despite its superiority over other synthesis methods, the solvothermal method requires precise control over temperature and reaction time. Even slight variations in temperature can alter the morphology of particles, while changes in reaction time may lead to the degradation of MOF particles [23,24].

Electrochemical method: In electrochemical synthesis, metal ions are not sourced from metal salts; instead, they are obtained through anodization. Utilizing anodization to derive metal ions reduces the likelihood of anion interference associated with introducing a metal source. *In situ*, ions produced near the surface of the support could help limit impurities, resulting in purer crystals [25,26]. Voltage and pulse signal are the controllable variables in electrochemical synthesis and this process can be conducted at standard temperature and pressure [25]. This method facilitates the attainment of crystals of desired size and quality by tuning controlling factors like, voltage, electrolyte and time. The membranes produced exhibit variable pore sizes and pore density, achieved through ion-track technology and regulation of electrodeposition time, resulting in parallel pore sequencing. This electro-analytical technique can be very much promising to reduce the cost of membrane fabrication by combining it with other synthetic methods.

Mechanochemical method: Mechanochemical syntheses are widely used in recent days for large scale synthesis of the MOFs owing to their eco-friendly green approach and ease of preparation. Mechanochemical synthesis, involving simple mechanical grinding of the constituent, is regarded as the most potential method of MOF fabrication. This method allows for the preparation of fine granular MOFs in a short duration (typically 10-60 min) with high yield and minimal reaction time. Importantly, mechanochemistry is a solvent-less green synthesis method, making it environmental friendly [27]. This solid-state thermo-mechanical method is preferred for producing various types of MOFs, especially for preparing them as microcrystalline powders [28]. Mechanochemistry involves the interaction between solids under mechanical energy. In the absence of a solvent, the combination of metal salt and organic ligand is ground in a ball mill or using a mortar and pestle. Subsequently, to remove water and other volatile compounds that may function as byproducts of the reaction, the mixture is heated [29].

Sonochemical method: In recent period, the sonochemical method has emerged as a rapid technique for the synthesis of MOFs by reducing the crystallization time through ultraradiation. MOFs are prepared using cyclic mechanical vibration ranging from 20 kHz to 10 MHz. The process involves introducing a combination of metal salt and organic linker into a Pyrex reactor in the shape of a horn, equipped with a sonicator bar and variable power output, without the need for external cooling [30]. Ultrasonication is the primary factor that induces cavitation in the liquid. Cavitation refers to the formation and subsequent collapse of bubbles in the solution following ultrasonic treatment.

Design strategies for MOF-based membranes: The *in situ* preparation techniques are primarily employed to fabricate bare MOF membranes consisting of a continuous and intergrown layer of MOF. To have uniform layer, distribution the continuous layer must be devoid of any imperfections. The MOF grains get distributed evenly forming interconnected structures through formation of internal chemical linkages. Typically, these membranes incorporate a porous support layer, such as porous alumina, integrated with a MOF layer instead of using nanoparticles. Conventionally, two methods are there for efficient growing of MOFs on porous supports (i) direct growth and (ii) secondary growth. Both the direct and secondary growth methods were initially adapted for the preparation of MOF membranes for effective gas separations. The inherent porosity of these MOFs facilitates optimum efficacy during separation of gas molecules. The same selectivity can be offered by the MOFs during wastewater treatment if the MOF structures remain stable in water medium retaining its structural integrity during membrane based separation.

Direct growth: In the direct growth method, the substrate is immersed into the growth solution, but no crystals attach to the surface initially. During the preparation stage, crystal nucleation, growth and co-growth on the substrate all occur simultaneously. However, this method often lacks control over the orientation and continuous growth of MOF crystals due to weak bonds between the MOF layer and the support layer. Therefore, many direct growth methods necessitate either a specific unmodified support surface or modification of the support surface to improve the interfacial bonding between the MOF and the support layers. For direct growth on modified supports, chemically modifying the supports is considered an effective strategy to address poor substrate bonding. This alteration improves the process of heterogeneous nucleation and directs the formation of the MOF membranes.

Secondary growth: While the direct growth method heavily relies on the characteristics of the support surface, secondary growth methods offer an alternative approach. These methods enable substrate-insensitive fabrication of dense and continuous MOF membranes through a seed-assisted process. Although secondary methods involve additional complexity in terms of synthesis steps compared to direct growth, they provide finer control over the final orientation and dense, continuous growth of the MOF crystals. MOF fabrication involves the formation of coordination linkages between organic and inorganic components in the solution. In the secondary growth method, similar to the direct growth method, the seeding step is carried out *in situ*, a process referred to as reactive seeding. Layer-by-layer (LBL) is indeed a potential alternative for developing MOF membranes. While the LBL method is well-known for fabricating MOF films rather than membranes, it is challenging to achieve a defect-free membrane using this approach.

Interfacial polymerization process: Interfacial polymerization is a process that involves a polycondensation reaction occurring at the interface between two solutions containing different monomers that do not mix. This reaction is initiated from the organic side of the interface. Interfacial polymerization is commonly used for fabricating thin-film composite membranes, which consist of both a polymer layer and a polymer support. Interfacial polymerization primarily focuses on polymerization at the liquid/liquid interface. It is a reliable and easy-to-use method, especially when using robust substrates like ceramics to construct a polyamide layer on the substrate. By integrating interfacial polymerization of MOFs with thin-film nanocomposite membranes, the performance of the membrane can be readily enhanced.

Blending: This method is widely applied method for constructing MOF-based mixed matrix membranes (MMMs) [31]. A mixed matrix membrane is a composite membrane obtained by combining inorganic or inorganic-organic hybrid materials, such as micro or nanoparticles, with a polymer matrix. While MOF-based MMMs are stable, they can be expensive and complex to construct. Blending is often the preferred approach for preparing MOF-based MMMs. Blending can be categorized into two types *viz.* (i) substrate-based blending and (ii) substrate free blending. The process of substrate blending occurs in three steps. Firstly, the MOF and polymer are combined into the substrate to create a MOF ink. Next, the mixture is applied onto the porous support using techniques such as spin-coating, dip-coating or flat membrane casting. Finally, the casting solvent is eliminated during desiccation or drying [32]. The substrate-free blending method is relatively more flexible because it does not require a substrate. This method allows for easier removal from non-porous supports. To ensure desirable mechanical strength and permeance, the thickness of the resulting membrane is typically kept between 18 and 30 μm.

MOF based membranes for efficient water treatment: The customizable configurations, regulated arrangements and outstanding separation capabilities of membranes incorporating MOFs position them as viable solutions for addressing water pollution challenges. These include tasks such as extracting oily and micro-pollutants, purging heavy metal ions, purifying organic dyes, as well as desalinating both brackish water and seawater.

Oily and micro-pollutant removal: The rise in population and global industrialization has exacerbated environmental concerns, particularly the issue of wastewater stemming from daily human activities and industrial discharge from industries such as textile, steel and petroleum as well as from frequent oil leaks during extraction or transportation. Modern water pollution primarily comprises soluble organic molecules like antibiotics and insoluble organic molecules, such as oils. Antibiotics are frequently utilized to combat bacterial infections in both humans and animals. However, these antibiotics can infiltrate water reservoirs, becoming a source of organic pollution. Consequently, this pollution can foster the emergence of drug-resistant bacteria, thereby heightening the incidence of infections in humans and illnesses in aquatic life [33]. As a result, the development of facile procedures and novel materials for the efficient elimination of antibiotics, such as ciprofloxacin, has garnered significant attention among researchers. Micropollutants pose significant risks to human health and are challenging to remove from water sources. Although the advanced oxidation process has been extensively researched for micropollutant removal, it is not widely utilized owing to their high cost and complexities associated with recovering nanoparticles [34]. MOF immobilized membranes, owing to their excellent sets of properties, have been widely investigated for the removal of oily wastewater. These MOF membranes exhibit varying affinities for the oil/water phases on their surfaces, enabling selective separation of oil-water mixtures. The super-hydrophobic and super-lipophilic characteristics of membranes towards oily wastewater can be further improved through the combined effects of super-wettability and abundant porosity. For instance, Gu *et al.* [35] developed a superhydrophobic/super-lipophilic ZIF-8@rGO@sponge membrane by embedding MOF nanomaterials within GO nanosheets followed by a high temperature reduction self-assembly process. The resulting ZIF-8@rGO @ sponge membrane exhibited remarkable sorption selectivity for oils, achieving ultrahigh separation efficiency (> 98%) attributed to synergistic effects. Additionally, the composite membrane maintained excellent oil removal efficiency even after 100 cycles, highlighting its outstanding recyclability. Considering its superior removal capacity, enhanced selectivity and excellent recyclability, the ZIF-8@rGO@sponge membrane not only offers promising materials for water-oil separation and wastewater treatment but also introduces a novel concept for the advancement of membranes containing MOFs. In another work, Dai *et al.* [36] integrated ZIF-8 nanoparticles into poly-(lactic acid) (PLA) to produce PLA/ZIF-8 composite electrospun membranes for oil/water separation applications. The contact angle test affirmed that as the ZIF-8 content rose, the diffusion time of saxoline droplets on the PLA/ZIF-8 composite membrane notably decreased, primarily due to the substantial enhancement of the membrane's oil wettability. Leveraging the membrane's roughness, wetting ability and the adsorptive capacity of polyporous ZIF-8 nanomaterials, the oil/water mixture poured onto the PLA/ZIF-8 membranes exhibited a rapid absorption of oil globules by the membranes, while water molecules permeated through the membranes. This conferred upon the membrane high separation efficiency for diesel/water separation.

In addition to oil contaminants, micro-contaminants such as pharmaceuticals, endocrine disruptors, personal care products, pesticides and polycyclic aromatic hydrocarbons contribute significantly to water pollution even at low concentrations. In recent years, there has been exploration into the incorporation of MOFs into polymeric substrates to create multifunctional membrane materials, offering a potential solution for the efficient removal of micropollutants. This approach capitalizes on the strong complexing ability of MOFs, which holds promise for tackling the challenge of micropollutant contamination in water systems. As an example, Ragab *et al.* [37] conducted research where they functionalized a polytetrafluoroethylene (PTFE) bilayer filter membrane with ZIF-8 and employed it for the removal of progesterone. Compared to the pure membrane material, the adsorption capacity of composite membrane containing MOF increased by approximately 40%. Furthermore, even after three regenerative cycles using hormone solutions with high concentrations, the removal efficiency of the composite membrane remained as high as 95%. Furthermore, Dai *et al.* [38] explored the integration of MIL-101(Cr) into a polyamide layer to produce a thin film composite (TFC) membrane with a 0.20 wt/v % MOF concentration. This membrane was designed for the removal of endocrine disrupting compounds (EDCs) including methylparaben, propylparaben, benzylparaben and bisphenol A. The incorporation of hydrophilic MOFs led to the formation of water/EDCs selective channels, thereby increasing the rejection of EDCs.

In summary, MOF membranes have demonstrated outstanding removal efficiency for micropollutants, primarily attributed to mechanisms such as hydrophobic interactions, hydrogen bonding and π-π interactions. However, the majority of research on the elimination of micropollutants by MOF membranes has been conducted at the laboratory scale. While the potential of these studies is significant, for commercial and practical applications, MOF membranes must be effectively deployed in real wastewater scenarios. Therefore, further investigations are necessary to design and develop MOF membranes that can be successfully utilized in sewage treatment plants for the effective removal of micropollutants.

Elimination of heavy metals: Industries are always in the process of evolving to meet the needs of a growing global population. However, the rapid industrialization has led to a significant issue like water pollution. Various heavy metals, including copper (Cu), silver (Ag), mercury (Hg), chromium (Cr), cadmium (Cd), nickel (Ni), cobalt (Co) and lead (Pb), have been identified as major pollutants originating from activities such as chemical production, coal mining, the application of chemical fertilizers, the deposition of solid waste in landfills and sewage discharge [39,40]. When the levels of contamination in water surpass acceptable thresholds, it can result in the accumulation of pollutants within organisms along the food chain, thereby posing significant risks to humans, animals and the overall ecosystem.

Due to the scarcity of water, disposing of water contaminated with heavy metals is not an acceptable approach. Therefore, it is necessary to decontaminate water polluted by heavy metals to make it suitable for drinking and irrigation purposes again. Various methods have been developed for the decontamination of water from heavy metals, including adsorption, coagulation, ion exchange, membrane filtration, electrochemical methods and chemical precipitation. Among these methods, adsorption stands out as highly effective and favourable due to its ease of operation, cost-effectiveness and efficiency. Adsorption for water decontamination can be achieved using various adsorbents such as graphene, carbon nanotubes, composite materials and MOF membranes. MOF membranes, in particular, are popular due to their exceptional selectivity, efficient rejection of metal ions and the availability of reactive functional groups. Zeolitic imidazolate framework (ZIF) membranes offer enhanced thermal and chemical stability compared to other materials. Yuan *et al.* [41] successfully fabricated a pure ZIF-300 membrane on an alumina (Al_2O_3) support using the secondary growth method. This membrane exhibited exceptional water stability and size discrimination properties. Notably, it demonstrated a remarkable rejection rate of 99.21% for Cu(II) ions and a water permeance of 39.2 L/m^2 h bar, which are highly desirable characteristics for membrane applications. On the other hand, Li *et al.* [42] developed a novel PAA/ZIF-8/PVDF hybrid membrane. This hybrid membrane combines poly(acrylic acid) (PAA), ZIF-8 (a specific type of ZIF) and polyvinylidene fluoride (PVDF). This membrane exhibited remarkable qualities, including an excellent capacity for decontaminating Ni(II) even in water systems with higher concentrations of salts. This demonstrates the potential of hybrid membrane systems in addressing challenges related to water purification, especially in environments with varying levels of contaminants. Liu *et al.* [43] demonstrated the fabrication of a variety of fibrous MOF membranes by incorporating different polymers such as polyurethane (PU) and polyacrylonitrile (PAN) with the UiO-66 series of MOFs. These fibrous MOF membranes were designed to possess certain desirable properties. Significantly, the as-fabricated MOF membranes exhibited equivalent uptake rates of Pd and Pt compared to the pristine MOFs. This suggests that the incorporation of polymers did not significantly compromise the uptake capabilities of the MOF membranes for these metals. Efome *et al.* [44] synthesized four types of MOF/polymer nanofiber composite membranes (NMOM) by incorporating mixed MOF 808 (Zr(IV) based MOFs) and F300 (Fe(III) based MOFs) into polyacrylonitrile and polyvinylidene fluoride (PVDF) matrices using the electrospinning technique. These composite membranes were then applied for the removal of Hg(II) and Pb(II) from aqueous solutions. Since, PAN is inherently more hydrophilic than PVDF, the NMOM(PA) composite membranes prepared with PAN exhibited better adsorption performance for both Pb(II) and Hg(II) compared to NMOM(PV) prepared with PVDF. The higher hydrophilicity of PAN likely facilitated better interactions with the metal ions in the aqueous solution, leading to enhanced adsorption performance.

MOF containing membranes have demonstrated rapid equilibrium times, excellent removal capacities and high selectivity for targeted heavy metal ions. They have shown the ability to maintain superior properties even under extreme environmental conditions. The reaction mechanisms underlying their effectiveness are primarily attributed to electrostatic interactions and pore filling actions. However, most current study focuses on the selective elimination of a single target ion, whereas real world water environments are complex and dynamic. Therefore, conducting more indepth investigations into the simultaneous removal of multiple contaminants by MOF-containing membranes is crucial for practical wastewater purification applications. By exploring the simultaneous disposal of multiple contaminants, researchers can better address the challenges posed by diverse and unpredictable water pollution scenarios. This could lead to the development of more versatile and efficient membrane systems capable of treating complex wastewater streams effectively. Additionally, understanding the interactions between different contaminants and the MOF-containing membranes could provide valuable insights for optimizing membrane design and operation in real-world applications.

Organic dye waste decontamination: Dye wastewater, originating primarily from textile, paint, rubber, leather, plastic and paper industries, presents a significant environmental challenge. Its discharge poses a serious threat to human health due to the presence of highly toxic compounds and potential carcinogens [45]. MOF-containing membranes can effectively decontaminate organic dye wastewater through the strategic selection of MOF types based on size exclusion principles. For instance, ZIF-8 particles, with pore sizes fitting between the dye molecules (such as rhodamine B and rose red) and water molecules, demonstrate efficient retention of organic dyes. Guo *et al.* [46] and Li *et al.* [47] successfully constructed ZIF-8 separation membranes, achieving high retention rates ranging from 90.3% to 97.5% for rhodamine B and 92.5% to 98.9% for rose red, respectively. Furthermore, researchers have recognized that factors such as the thickness of the MOF layer, the interlayer space of flaked-MOF membranes and the hydrophilicity/hydrophobicity of MOF particles significantly impact the removal capacity of these membranes. In response, various research endeavors have been dedicated to optimizing these factors. For example, Chen *et al.* [48] developed a PVDF/Cu-BTC composite membrane on a poly(vinyl difluoride) hollow fiber support. This membrane exhibited a water flux of 64.8 kg/m^2 h and exceptional Congo red (CR) rejection rates exceeding 99.5%, attributed to the presence of multiple Cu-BTC layers. Yang *et al.* [49] developed a range of Sm-MOF/GO nanocomposite membranes using graphene oxide (GO) nanosheets and samarium metal-organic frameworks (Sm-MOFs) *via* a vacuum filtration approach. Their findings demonstrated that the M-0.31 composite, with a mass ratio of 0.31 between the MOF material and the total mass of the Sm-MOF/GO nanocomposite, exhibited outstanding permeance at 26 L m^{-2} h^{-1} bar^{-1}, along with high rejection (> 91%) of rhodamine B dye. This performance enhancement was attributed to the increased interlamellar spacing facilitated by the higher Sm-MOF content. Li *et al.* [50] fabricated PDA/ZIF-67@PP composite membranes by constructing a biomimetic polydopamine (PDA) and ZIF-67 layer on a polypropylene (PP) substrate. The incorporation of hydrophilic functional groups (amino and hydroxyl) onto the PDA material enabled the resulting PDA/ZIF-67@PP composite membrane to achieve a retention rate of over 92.0% for both methylene blue and methyl orange dyes. Moreover, the water flux reached 216.8 kg/m^2 h, significantly surpassing that of the pure PP membrane (below 40.4%, 86.7 kg/m^2 h). This improvement was attributed to the efficient interception of contaminant molecules by the separation membrane through size screening, coupled with the surface functionalization of modified MOF particles, which increased their hydrophilicity and facilitated water molecule entry.

Numerous studies have demonstrated that membranes containing metal-organic frameworks (MOFs) exhibit superior dye elimination capacity compared to single substrates and materials. The elimination of most dyes occurs through electrostatic interactions with the MOF-containing membranes. Despite the advantages of using MOF-containing membranes for dye elimination, practical applications face significant challenges related to stability in wastewater and resilience to complex pollutants in the water environment. Furthermore, there is limited research on the effects of coexisting ions and operational modes on dye elimination from wastewater. Therefore, a thorough investigation of the factors influencing dye removal and reaction mechanisms is essential to enhance the ongoing use of MOF-containing membranes in dye decontamination processes. Such intensive studies can contribute to the development of more robust and effective membrane systems for addressing dye pollution challenges.

Brackish water and seawater desalination: With the increasing demand for freshwater, there is a growing need to scale up the desalination of ocean and brackish water on a global level to meet this water requirement [51]. Despite the vast reservoir of water present in the oceans, it is of little use if it cannot be consumed. Desalination, the process of removing salts from brackish and ocean water, offers a solution to address water scarcity by producing water suitable for drinking, industrial and domestic use. Scientists worldwide are actively researching and demonstrating the environmental effects of desalination, whether through thermal or reverse osmosis processes. Among these, reverse osmosis, particularly seawater reverse osmosis (SWRO), is gaining prominence due to its lower energy requirements and economic feasibility. SWRO has seen a significant increase in installed capacity in recent years, with the global capacity of installed seawater desalination plants reaching approximately 5000 million m^3/year in 2012. The Middle-East accounts for 45% of this capacity. In the near future, SWRO is expected to dominate new desalination facilities, comprising around 68% of the total capacity. While thermal desalination plants will still be in operation, many of them will adopt hybrid approaches, combining SWRO and thermal processes for improved efficiency and cost-effectiveness [52]. This trend underscores the importance of desalination in addressing the water scarcity issues and highlights the role of SWRO as a key technology in meeting the world's freshwater needs. Membrane filtration has garnered significant interest within the scientific community due to its porous structure and permeability, particularly in the desalination of brackish and ocean water. Widely regarded as a promising solution for water desalination, membrane filtration stands out for its ease of operation and high efficiency.

In recent years, numerous research institutes have directed their efforts towards developing thin-film composite (TFC) membranes with enhanced performance and efficiency by incorporating nanoparticles such as zeolite, SiO_2, graphene oxide (GO), covalent organic frameworks (COFs) and metal-organic frameworks (MOFs) into the polyamide layer to create thin-film nanocomposite (TFN) membranes. This integration of nanoparticles has led to improvements in rejection performance and permeation by altering surface morphology, membrane hydrophilicity and roughness. The selection of appropriate and effective membrane materials is crucial for the purification of water and desalination of brackish water and seawater. Among the aforementioned materials, MOFs have demonstrated significant potential in fabricating membranes for brackish and seawater desalination. This is attributed to their controllable pore size, high porosity and adaptable chemistry, making them an ideal choice for embedding within polymeric substrates. In 2011, Hu *et al*. [53] conducted a molecular simulation to explore the potential of ZIF-8 membranes for water purification. Their study demonstrated the selective filtration properties of a dense and precisely engineered ZIF-8 membrane, effectively blocking the passage of sodium and chloride ions during ocean water desalination. Gupta *et al.* [54] conducted the simulations on seawater desalination using a variety of ZIF membranes featuring different pore sizes and polarities. Their findings highlighted the significant impact of functional group polarity on the desalination efficiency of MOF-containing membranes. However, given the constraints of simulation studies, the feasibility of desalination processes would need to be verified through successful experimental preparation of water-stable MOF membranes. Wang *et al.* [55] developed a continuous and high-quality UiO-66-$(OH)_2$ membrane using a post-synthetic defect healing method, aiming to mitigate the disadvantages associated with ligand deficiencies in membranes. Their work emphasized that membrane selectivity was primarily influenced by the size of the target molecules or ions. Experimental data confirmed varying rejection rates for different salt ions (*e.g.* 26% for Na^+, 42.5% for Zn^{2+} and 54.7% for Fe^{3+}) based on a size exclusion mechanism. However, the relatively low water flux (*e.g.* 0.73 kg/m^2 h for Na^+, 0.45 kg/m^2 h for Zn^{2+} and 0.56 kg/m^2 h for Fe^{3+}) was attributed to the sluggish spread of hydrated ions, possibly due to single-file diffusion in microporous channels. While the research highlighted the promising potential of UiO-66 separation membranes for water desalination, challenges in constructing dense, defect-free MOF membranes led to some disparities between the experimental outcomes and the theoretical predictions. Hence, further research efforts are warranted to develop well-intergrown, continuous and dense membranes to enhance water flux and salt retention performance [55]. Apart from the aforementioned factors, the incorporation of MOFs also leads to modifications in membrane properties such as hydrophilicity, surface charge and overall porosity, thereby influencing desalination performance. For example, Kadhom *et al.* [56] embedded MIL-125 and UiO-66 into thin film nanocomposite (TFN) membranes and examined the impact of different MOFs as additives on membrane performance. Their findings revealed that adding 0.15 wt% of UiO-66 increased water flux from 62.5 to 74.9 L/m^2 h, while the addition of 0.3 wt.% of MIL-125 raised water flux to 85.0 L/m^2 h. This enhancement was primarily attributed to the hydrophilic nature and water transportation channels facilitated by the MOFs. Despite differences in the surface charge and pore size, both cases maintained a similar water flux-salt rejection trade-off ($\geq$ 98.5%). Similarly, Zirehpour *et al.* [57] successfully incorporated the hydrophilic MOF nanomaterial Cu-BTC into cellulose acetate/triacetate (CTA) membranes for water desalination. Compared to unmodified membranes, the addition of 3.0 wt.% Cu-BTC significantly increased water flux from 10.0 to 30.0 L/m^2 h. This improvement aligned with the selective water absorption capacity and water transportation channels provided by the highly porous structure and hydrophilic surface of Cu-BTC materials.

Conclusion

In summary, the metal organic framework (MOF) based membranes are found to be promising in the wastewater treatment owing to their robust nature, selectivity and efficacy in the separation of ions. The tunable structure, pore size and surface chemistry make themselves efficient in water purification as well as seawater desalination. MOF based membranes thus can play effective role in terminating global water scarcity and make innovative solution to the water purification era. Several synthetic strategies are there to obtain MOFs as well as MOF immobilized membranes. Procedures like microwave, solvothermal, sonochemical, mechanochemical are widely used by chemists for obtaining MOFs. From these, mechanochemical method appears as environment friendly green approach as it involves mechanical force devoid of any solvent. The MOF membranes can also be fabricated *in situ via* immobilization of the MOF over a support layer. Direct growth, indirect growth, blending and interfacial polymerization technique are found to be promising in designing innovative membranes for efficient water purification. Pollutants, such as pesticides, dyes, microplastics and heavy metals tends to contaminate the ground water *via* leaching from industrial effluents and human activity. MOF based membranes are found to be very much efficient in separating the pollutant molecules effectively make the water pure and usable. In addition, the desalination of salty water has remained as a tremendous challenge for global scientific community due to its huge abundance and urgent requirement to make it usable. Most surprisingly, UiO-66 and ZIF-8 MOF membranes displayed good potentiality and high selectivity in the desalination of seawater. This membrane technology can be efficient, scalable and commercially viable in the treatment of wastewater as well as salty water to make it usable for living being.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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