The applications of pristine MOFs as membrane filler or membrane raw materials and adsorbents in the separation of heavy metals, dyes and antibacterials from wastewater have been reviewed. The pristine MOFs demonstrate huge potential in sustainable wastewater treatment.
Review article

Application of Metal Organic Framework in Wastewater Treatment

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Abstract

Water pollution is an increasingly serious environmental problem because many pollutants have carcinogenic effects on humans and aquatic organisms. Metal organic framework (MOF) made up of metal ions and multifunctional organic ligands has been one of the most concerned materials because of its adjustable and regular pore structure. MOFs have always shown attractive advantages in membrane separation and adsorption technologies, among which water-stable MOFs are particularly prominent in wastewater treatment (WWT) applications. This review systematically summarizes the application of MOF membranes in membrane filtration, membrane pervaporation and membrane distillation. Also, the adsorption mechanisms of heavy metals, dyes and antibacterials in wastewater have been concluded. In order to tap the full application potential of pristine MOFs in sustainable wastewater treatment, current challenges are discussed in detail and future research directions are proposed.

Keywords: Metal-organic framework; Membranes; Adsorption; Wastewater treatment
Contents

1. Introduction ........................................................................................................................................... 1
2. MOF membrane in wastewater treatment ......................................................................................... 10
   2.1. Membrane filtration ......................................................................................................................... 11
       2.1.1. Nanofiltration and organic solvent nanofiltration ................................................................. 12
       2.1.2. Microfiltration .......................................................................................................................... 14
       2.1.3. Ultrafiltration .......................................................................................................................... 15
       2.1.4. Forward osmosis ...................................................................................................................... 17
       2.1.5. Reverse osmosis ...................................................................................................................... 19
   2.2. Membrane pervaporation .............................................................................................................. 21
   2.3. Membrane distillation .................................................................................................................. 23
3. MOFs as adsorbent in wastewater treatment ....................................................................................... 26
   3.1. Heavy metal ions ......................................................................................................................... 27
       3.1.1. Mercury ions ............................................................................................................................ 28
   3.2. Dyes ............................................................................................................................................... 39
       3.2.1. Methylene blue ....................................................................................................................... 39
       3.2.2. Methyl orange ......................................................................................................................... 41
       3.2.3. Others ..................................................................................................................................... 43
   3.3. Antibacterials ............................................................................................................................... 44
       3.3.1. Quinolones .............................................................................................................................. 45
       3.3.2. Nitroimidazoles ...................................................................................................................... 47
       3.3.3. Tetracyclines ......................................................................................................................... 50
       3.3.4. Others .................................................................................................................................... 52
4. Conclusion and outlook ....................................................................................................................... 56
References ................................................................................................................................................ 60
1. Introduction

Water is the source of all life activities [1]. Although in traditional concepts, water is often considered as the cheapest and most abundant resource, however, the directly available freshwater resources in the world are very limited. Especially now, climate change and water pollution have made water resources increasingly scarce [2]. What is more worrying is that long-term exposure to pollutants in wastewater, such as heavy metals, dyes, antibacterial agents, etc., can cause serious harm to humans and aquatic organisms even at low concentrations, and even cause cancer. Therefore, it is imperative to protect water resources and solve the problem of water pollution [3–8]. Many studies have confirmed that separation technology is effective in treating wastewater, especially membrane separation and adsorption technology.

In recent years, the emerging porous metal organic framework (MOF) has been widely used [9–21], especially in separation applications [22–24]. They are made up of inorganic metal ions or metal clusters and multifunctional organic linkers [25–30]. The unique pore structures, controllable pore sizes, abundant adsorption sites, high specific surface area and porosity [31,32], collectively make them the main candidate materials for the development of separation membranes and adsorbents [33–40]. At present, it is widely used to manipulate the structure of inorganic secondary structure units with different ligand lengths to modify the pore size, and to use longer ligands to reduce the density and expand the surface area of the material [41]. For example, as a longer ligand, the thioether side chain can be conveniently designed into various sizes and
configurations, and provides unique advantages for a highly stable and functional porous framework. Organic ligands with functional groups, such as sulfur-functionalized ligands and amino-functionalized ligands, promote various intermolecular interactions of ions or molecular guests, and possess potential for the separation and removal of pollutants [42,43]. There are many different types of MOFs used for wastewater treatment, such as defective MOF, hierarchical-pore MOF and MOF based composites. For example, a defective amino-modified metal organic framework (UiO-66-D-NH₂) can capture two typical organoarsenic forms roxarsone (ROX) and p-arsenic acid (p-ASA) [44]. The adsorption affinity of UiO-66-D-NH₂ is 3.0 and 3.8 times higher than that of defective UiO-66 without amino modification (UiO-66-D) and pristine UiO-66, respectively. A series of Ce (III)-terephthalic (BDC) metal organic frameworks (Ce-BDC) with linker deficiencies can efficiently adsorb phosphorus (278.8 mg g⁻¹) [45]. The phosphorus uptake rate of Ce-BDC-48 synthesized with Ce:BDC ratio of 1:1 for 48 hours was 35% higher than that of defect-free Ce-BDC-72. In addition, Li et al. systematically reviewed MOF-based composites for the removal of metal ion pollutants from wastewater, discussed the adsorption properties of various MOF-based materials, and emphasized the mechanism of metal ion interaction with MOF-based materials [46]. In addition, A novel the ferrocene-based MOF membrane (Zr-Fc MOF/SWCNT/gelatin, ZSG) (single wall carbon nanotubes, SWCNT) with outstanding photothermal performance and excellent Fenton catalytic activity is reasonably designed for the production of clean water from volatile organic compounds contaminated water [47]. Due to the hierarchical pore structure, sound
hydrophilicity and fabulous photothermal performance of the ZSG membrane, an amazing water evaporation rate of 1.53 kg m\(^{-2}\) h\(^{-1}\) is reached under 1 sunlight exposure. Moreover, the Zr-Fc MOF has been confirmed to be an effective Fenton catalyst to enhance the generation of hydroxyl radical for degradation of phenol and methylene blue. It is worth mentioning that the Chemical oxygen demand value of the purified water is lower than the drinking water standard. These works have laid an important foundation for MOFs to be candidates for efficient wastewater treatment. However, it cannot be ignored that the main condition for MOFs to be used in WWT is the excellent water stability [48,49]. Water-stable MOFs have been more widely used in wastewater treatment processes such as adsorption and filtration, far superior to those in the current market [50]. Most of the recent researches have been to design the structure of MOFs through pre- or post-modification to improve their functions, making them promising alternatives to improve the performance of wastewater treatment. Therefore, this review discusses MOFs that are steady in water, which means, no structural decomposition occurs when exposed to water [51–53]. Take the commonly used zirconium-based MOFs (Zr-MOFs) as an example [54–58], because they exhibit excellent chemical and thermal stability in moisture and acids, their thermostability can reach 500 °C and remain stable in a variety of organic solvents. Even under high mechanical pressure, it still exhibits high structural stability, enabling the material the potential to become a composite membrane material and a high-efficiency adsorbent [59–61]. Of course, MOFs have also received extensive attention in the field of photocatalysis as effective decontamination materials. And many outstanding reviews have summarized the
breakthrough of MOF based photocatalysis in visible light environmental remediation. It is worth mentioning that Wang et al. have designed a series of strategies to regulate and modify pristine MOFs for improved photocatalytic properties, such as mixed-metal/linker strategy, ligand functionalization, dye sensitization and metal ion/ligand immobilization [62]. The above modifications could result in expanded efficient generation, transfer of photogenerated charges, visible light absorption, as well as sound recyclability. In addition, in Sharma's review, they summarized recent examples of photocatalytic degradation of dyes, highlighting that MOFs can enhance the properties of advanced oxidation processes (AOPs) (Fenton reaction method, photocatalysis and sulfate radical-mediated oxidation) [5]. Moreover, Fe-based MOFs showed outstanding catalytic properties on the sulfate radical-mediated oxidation and Fenton-based of organic pollutants such as phenols, drugs and dyes. The obviously promoted generation of reactive substances such as hydroxyl radicals and/or sulfate radicals by both heterogeneous and homogeneous catalysis was considered as the probable mechanism for wastewater treatment. It is concluded that MOFs act as light absorbers and adsorbents, enabling the photocatalytic process with excellent performance. In this review, we mainly summarized the application of MOF in membrane separation and adsorbent in wastewater treatment.

Membrane filtration technology uses the permeability and selectivity of membrane pores to perform fine separation, allowing solvents, small molecules, inorganic ions, etc. to overgo the membrane while intercepting large molecules and particles. Although MOF membrane was first used for gas separation and storage, the application prospects
of membrane separation technology in the treatment of industrial wastewater are better than gas separation [63,64]. In recent years, the number and types of MOF membranes used for WWT have been increasing, and membrane separation technology has significant effects on WWT (Fig. 1) [65–82]. Facts have proved that in WWT, MOF has better compatibility than other inorganic porous materials, because MOF membrane can effectively improve the filtration efficiency of different filtration categories such as nanofiltration (NF), microfiltration (MF), ultrafiltration (UF), forward osmosis (FO) and reverse osmosis (RO). Introducing MOF as a filler in mixed matrix membranes (MMM) and thin film nanocomposite (TFN) membranes to customize the pore size and shape can obtain a new type of composite membrane with better selectivity and permeability [83–85]. For example, the TFN nanofiltration membrane prepared by interfacial polymerization of nano-scale UiO-66-NH$_2$ has higher hydrophobicity, zeta potential and roughness [86]. In addition, TFN film has excellent dispersion in organic phase. Owning to the introduction of MOF and the formation of MOF/polyamide interfacial passageways, the TFN membrane exhibits higher water permeability. The properties of membrane pervaporation and membrane distillation can be significantly improved by adding appropriate MOF filler to the membrane. Since suitable MOF nano-additives can improve the pervaporation performance of composite membranes by enhancing the selective adsorption and diffusion of water molecules [87]. Additionally, the addition of MOFs can improve the pore size, porosity, surface roughness and mechanical stability of the membrane, thereby enhancing the performance of membrane distillation [88]. In addition, MOF can also be used as a raw
material for film formation. Because the pore size of MOF can be precisely adjusted in a large range, they have good selectivity for many guest species of different sizes and shapes [89]. In addition, in some cases, MOFs can also be reused as a filler, still showing satisfactory results. Therefore, MOF membrane is a prospective candidate for wastewater treatment (WWT) because of its better selectivity, permeability and anti-fouling performance.

![Diagram of MOF membrane for wastewater treatment](image)

**Fig. 1.** MOF membrane for wastewater treatment.

Because the adsorption technology is easy-to-use and economical, and does not cause too much secondary pollution, it is considered to be one of the most effective and commonly used treatment methods to remove a variety of pollutants in wastewater. As a traditional adsorbent, activated carbon has been widely used in the adsorption treatment of wastewater. However, it is difficult to regenerate in practical application because of its weak interaction and low adsorption capacity [90,91]. Therefore, the
development of more efficient and reproducible adsorbents is a main research topic for researchers. In the search for more effective adsorbents, porous materials have received extensive attention [92–94]. Compared with traditional adsorbents, MOFs have unique structures and functions [95,96], such as structural diversity adjustable pore properties, and higher thermal and mechanical stability, making it an adsorbent with ideal adsorption characteristics [97–103]. Based on the unique qualities of MOF, functionalized MOFs have more applications in adsorption [104,105]. They combine the functions of MOF and other functionalized structures. For example, sulfur-functionalized and amino-functionalized MOFs are quite effective in the field of heavy metal removal. Like most adsorbents, the most common mechanism for MOFs to adsorb pollutants is electrostatic interaction. Of course, there are other adsorption mechanisms, such as hydrogen bond adsorption, π-π interaction, and acid-base interaction (Fig. 2). When MOF is dispersed in the water phase, its net surface charge will be adjusted according to the pH value of the solution to form an electric charge [106]. The net charge on the MOF can also be changed by protonation and deprotonation [107]. MOF with opposite charge and the adsorbate form a chemical bond through electrostatic interaction. Therefore, the net charge on the MOF and the different charge (cation or anion) of the adsorbate can effectively interact electrostatically. Recent studies have found that MOFs are more effective at removing anionic pollutants such as phosphate, arsenic and fluoride. For example, two stable amine-functionalized MIL-101 based on trivalent metal iron and aluminum synthesized by solvothermal method can strongly adsorb phosphate ions, and their adsorption
performance is better than that of most adsorbents, showing faster adsorption kinetics and better adsorption capacity [108]. The unbounded metal sites and amine groups in NH$_2$-MIL-101(Al/Fe) play important roles in the adsorption process. The main mechanisms are electrostatic attraction and exchange between the phosphate ions and the hydroxyl groups on the metal nodes. The research confirmed that trivalent metal-based NH$_2$-MIL-101 is a promising candidate for adsorption of phosphate from wastewater with high selectivity and efficiency. A series of hierarchical Ce-based composites were obtained by thermal treatment of Ce-MOF in N$_2$ atmosphere [109]. It was found that the partially decomposed samples showed extremely high phosphate absorption capacity, which was 2-4 times higher than that of ceria. Ce-based materials with different valences have significant effects on capturing phosphorus, among which Ce (III) species play a major role in binding to phosphate. It is worth mentioning that Ce-MOF-500 obtained by thermal decomposition at 500 °C showed excellent maximum adsorption capacity (189.4 mg g$^{-1}$), and had great selectivity for phosphate in a wide pH range. Especially under alkaline condition, Ce-MOF-500 possessed obvious stronger phosphate adsorption capacity, which was attributed to the fact that the hydrolyzed Ce (III) species brought more active sites in the form of hydroxyl groups, so as to facilitate the exchange of ligand and phosphate. Facts have proved that MOFs have outstanding detection capabilities for organic pollutants in liquid phase extraction, and show significant adsorption potential, which can quickly remove pollutants from wastewater [110–125].
Membrane fillers and adsorbents based on pure MOF have made great progress in the removal of pollutants from wastewater, but there are few comments, and this review aims to fill this gap. Compared with MOF derivatives, most pure MOFs not only possess simple preparation methods and low preparation costs, but also exhibit excellent properties. Actually, before 2014, numerous pure MOFs were developed to remove dyes from wastewater [126]. The diversity of metal groups and ligands of MOFs endows them with rich functions. For example, they are widely used as membrane fillers and adsorbents to purify wastewater, which makes pure MOF meet the most practical needs as much as possible. At that time, only a few MOF derivatives...
were used in decontamination research. Since then, researchers have become increasingly interested in the applicability of MOF derivatives in wastewater treatment. It is worth mentioning that several excellent review articles highlighting MOF derivatives for wastewater treatment have been reported in the recent past. Yang et al. reviewed the latest research achievements in the preparation of MOF derivatives for various applications including the removal of organic dyes, heavy metal ions and other harmful substances in wastewater, and emphasized the working mechanisms of adsorption, photocatalytic degradation and membrane separation technologies for the removal of pollutants from wastewater [127]. In He's review, they highlighted compositional manipulation, morphology control, pre-synthetic modulation and post-synthetic treatment to improve the properties of MOF derivatives, and systematically summarized the recent progress of MOF derivatives in environmental cleaning, especially for the wastewater treatment and air purification [128]. Herein, we systematically review the progress of pure MOFs as raw materials or fillers and adsorbents to remove common pollutants from wastewater. In short, this review can provide useful insights into the applications of pure MOFs in WWT. It will provide important insights for MOF research and promote the development of more advanced functional materials in various industries.

2. MOF membrane in wastewater treatment

In recent decades, membrane separation technology has great potential in energy
conservation and environmental protection. For example, membrane-based gas separation which is easy to maintain and operate has great potential in practical applications due to its low energy consumption and environmental friendliness. As a new type of inorganic and organic hybrid materials, MOF materials stand out in separation applications. However, the hydrothermal stability of MOF has always been a key issue in its application in aqueous separation [129]. Because the pore size of the MOF membranes can be adjusted, it has a good prospect in WWT [130]. MOF membranes are usually crystalline microporous membranes formed by self-assembly of MOF crystals on porous organic-inorganic supports. Due to their ever-changing pore sizes and chemical properties, they exhibit great separation capabilities. MOF microporous membrane has high design and adjustability in structure and function. It can be controlled rationally through the interaction of inorganic metal ions and organic ligands, or through various methods [131]. This chapter will emphasize the application of MOF membrane to WWT and regeneration in membrane filtration, membrane pervaporation and membrane distillation [132]. With the development of MOF in recent years, the application of MOF membranes in WWT has become more important. Table 1 generalizes some information about the water-stable MOFs to manufacture membranes for WWT.

2.1. Membrane filtration

Filter membrane has been extensively used to treat pollutants in wastewater.
According to the pore size of the top surface, filtration membrane can be classified as nanofiltration (NF), microfiltration (MF), ultrafiltration (UF), forward osmosis (FO) and reverse osmosis (RO).

2.1.1. Nanofiltration and organic solvent nanofiltration

Nanofiltration is used in many ecological fields because of its low equipment cost, high separation efficiency, low energy consumption and other excellent properties, especially for WWT [133]. Additionally, organic solvent nanofiltration (OSN) is a pressure driven separation methodology that has expanded the application range of membrane from WWT to the concentration and filtration of organic solutions.

Recently, thin film composite (TFC) polyamide (PA) membrane is considered as the most energy-efficient and successful NF membranes. TFN membranes incorporated into the TFC membrane are a new type of membranes that can effectively improve membrane properties. Moreover, MOFs are very attractive to the preparation of TFN membranes due to their unique structure and properties. In addition, the existence of organic ligands in MOF can improve their integrativeness with the PA layer matrix [134]. Based on that, the NF process has been extensively developed in the wastewater purification technology.

The combination of MOFs with NF membrane in different methods are researched to prepare NF composite membrane with higher selectivity and permeability, which is expected to have an important role on WWT. The novel pure ZIF-300 membrane (Fig. 3f) prepared on an underlying substance α-Al₂O₃ by the second-growth mean (Fig. 3a)
was used to remove heavy metal ions (Fig. 3b) from water environment [135]. As shown in Fig. 3c and g, the obtained ZIF-300 membrane had the excellent water stability and size discrimination performance, exhibiting high rejection rate (99.21%) for CuSO$_4$ and enhanced water permeability (39.2 L m$^{-2}$ h$^{-1}$ bar$^{-1}$). Therefore, the pure ZIF-300 membrane showed extraordinary potential in NF to remove heavy metal ions from wastewater. Additionally, UiO-66-NH$_2$ nanoparticles (NPs) were used as nanofillers to obtain a novel type of MOF membrane for NF, which was widely used to separate kinetic hydrate inhibitor (KHI) from wastewater [136]. Thanks to the loading of UiO-66-NH$_2$ nanoparticles, the surface hydrophilicity of the PA-MOF layer was enhanced 38%. As shown in Fig. 3d, e, h and i, when 0.05% UiO-66-NH$_2$ was added, the permeation flux of the composite membrane increased from 38 L m$^{-2}$ h$^{-1}$ to 59.9 L m$^{-2}$ h$^{-1}$ while the rejection rate of the membrane remained almost unchanged or even higher than 96%. Besides, studies have found that adding MIL-101(Cr) in TFN membrane could significantly enhance the performance of the novel membrane. For instance, when 0.05% MIL-101 was put into an organic solution, the water permeability of the membrane increased by 44% [137]; when the Langmuir-Schaefer technology was used to embed MIL-101(Cr) nanoparticles, the interception rate of sunset yellow and rose Bengal could be kept above 90% at the same time and the methanol permeability of the membrane was increased [138]. In addition, embedding 0.15% UiO-66 in TFN novel membrane could efficiently remove selenium and arsenic from wastewater [139].
2.1.2. Microfiltration

Microfiltration (MF) uses the pressure difference on both sides of the membrane as the driving force to separate through membrane screening. MF technology has been widely used in WWT, and it rejects particles between 0.1 and 1 μm. It can effectively remove particles, colloids and microorganisms while allowing inorganic salts and macromolecular organics to penetrate [140,141].

The MOF composite membranes are extensively used in membrane MF because
the combination of MOF and its polymeric matrix can further enhance a membrane adsorption performance, which has been widely used to remove micro-pollutants from wastewater [142,143].

The ZIF-8/PTEE composite membrane obtained by modifying the high-porosity double-layer polytetrafluoroethylene (PTFE) microfiltration membrane with zeolite imidazole metal organic framework (ZIF-8) particles was used for testing, namely, using progesterone (PGS) as a pollutant compound to investigate the property of ZIF-8/PTEE composite membrane for removing micro-pollutants from wastewater [144]. Findings showed that its water permeability almost doubled and the adsorption capacity increased by 40%. The improvement of composite membrane property can be attributed to (i) the incorporation of ZIF-8 provides a mutually reinforced influence on increasing membrane adsorption capacity and water permeability; (ii) the increase in the effective specific surface area and the formation of hydrogen bonds between the hormone (hydrogen acceptor) and ZIF-8 (hydrogen donor) enhance the adsorption capacity of the membrane and (iii) the hydrophobicity of MOF nanoparticles inhibits the attrition between the membrane surface and water and ZIF-8 nanoparticles form hydrogen bonds with water, thereby improving the penetration property of the novel composite membrane.

2.1.3. Ultrafiltration

Due to its unique properties such as excellent stability, low operating pressure, high separation efficiency, and low working temperature, ultrafiltration (UF) is often
used as one of the separation methods of WWT [145]. UF membrane has pore diameters ranging from 0.001 to 0.1 μm and needs bigger pressure as the driving force. UF can effectively separate high molecular compounds, organic particles and bacteria from wastewater [146].

Recently, the hydrophilic modification of UF membranes has proven to be an effective method to improve the membranes performance, especially anti-fouling ability and water permeability [147,148]. Moreover, the research point can be shifted to biodegradable novel MOF composite membranes with high permeability, high stability and anti-fouling performance, so as to be greener in application [132].

The author found that a new hydrophilic hollow zeolite imidazole ester framework-8/ultrafiltration polysulfone (hZIF-8/PSF) membrane functionalized with tannic acid and PSF prepared by a phase inversion method exhibited excellent performance [149]. Because of the well-tailored nanostructure and surface performance of hZIF-8, the hZIF-8/PSF UF membrane exhibited an enhanced water permeability, which was 2.8 times higher that of the pristine PSF membrane, while maintaining good interception and anti-fouling performance. Commendably, compared with ZIF-8, the obtained hZIF-8 not only produced a distinct hollow structure without damaging the inherent frame but also possessed a higher hydrophilic surface of the embedded tannic acid. More importantly, the addition of hZIF-8 enhanced the resistance of membranes to fouling. In addition, during the process of combining the UF ceramic membrane (Fig. 4a) with the MOFs adsorbent, the adsorbed heavy metal can be rejected by the membrane. For example, using amino-functionalized Zr-MOFs (UiO-66-NH₂) as
adsorbents directly combined with UF ceramic membranes could effectively adsorb Pb\textsuperscript{2+} ions (1795.3 mg g\textsuperscript{-1}) in wastewater [150]. It is worth mentioning that when the pH value was controlled at 4.5, the adsorbed Pb\textsuperscript{2+} could be effectually desorbed during 6 cycles (Fig. 4b). Therefore, the method of combining MOFs and UF ceramic membranes exhibits great advantages in WWT.

2.1.4. Forward osmosis

Forward osmosis (FO) is a membrane separation technology that naturally diffuses under an osmotic gradient. It is usually used to remove salt, dissolve organic matter and trace organic chemicals in wastewater. FO has low equipment cost and energy consumption during FO operation, which shows great attraction in the field of separation. So it may be a promising alternative to any process that needs to extract water from the stream [151].

In recent years, how to improve the high-efficiency filtration effect of the membrane has become the focus of researchers. They found that using MOF to reasonably improve FO membrane at the nanometer level to prepare nanocomposite membrane is a very potential method. Moreover, this method can also decrease internal concentration polarization and mass transfer obstruction of the membrane, achieving the effect of reducing energy consumption in practical applications.

Using UiO-66 nanoparticles as the hydrophilic filler of the TFN-FO membrane, a novel type of TFN membrane was fabricated [152]. Compared with unmodified pure polyamide TFC membrane, the intrinsic separation performance was improved because
of super-hydrophilic properties and the molecular sieving of UiO-66 nanoparticles. Under a load of 0.1% UiO-66, the water flux enhanced from 2.19 to 3.33 L m⁻² h⁻¹ bar⁻¹ (an increase of 52%) while the NaCl rejection (95%) remained almost unchanged. This study for the first time attempted to implement Zr-MOFs (UiO-66) onto the TFN-FO membrane. Besides, without affecting the selectivity of FO applications, MOF nanosheets (copper 1,4-benzenedicarboxylate nanosheets, CuBDC-NS) were successfully embedded into PA active layer as fillers to prepare a reconcilable TFN membrane (Fig. 4 e and f) with enhanced water permeability and anti-fouling performance [153]. Compared with the original membrane, TFN membrane exhibited higher water permeability and lower reverse solute flux ($J_s$). About 50% reduction in specific reverse solute flux ($J_s/J_w$) and 50% growth of FO water flux ($J_w$) were noticed for the 0.12 wt/v % CuBDC-NS TFN membrane compared with the pristine membrane, when using 1.0 M NaCl as the draw solution in the feed solution mode of the active layer (AL-FS) (Fig. 4 c and d). Moreover, the excellent performance of CuBDC-NS combined with TFN membrane is still reflected in the successive flow examination of actual wastewater. These researchers concluded that antifouling behavior of TFN membrane containing compatible CuBDC-NS is related to the improvement of hydrophilicity and biocidal ability. In addition, Lee et al. applied C300 (HKUST-1), A100 (MIL-68) and F300 (Fe-BTC), which are MOFs based on copper, aluminum and iron, respectively, as fillers to prepare membranes for FO application [154]. The result showed that the dissolution rate of C300 in water was the highest (96%). Therefore, the
membrane contained C300 vacancies exhibited higher hydrophilicity and porosity, as well as lower tortuosity, which resulted in an enhancement of water flux.

Fig. 4. (a) Diagrammatic sketch of ceramic ultrafiltration setup in recycle mode; (b) Desorption cycles of MOFs combined with ceramic UF membrane (CFV = 4.5 m·s⁻¹, TMP = 0.05 MPa, pH = 4.5 and T = 35 °C). Reproduced with permission. [150] Copyright 2016, Elsevier. Wastewater treatment and anti-fouling properties of the membrane: (c) Comparison between original TFC membrane and TFN membrane with 0.12 wt/v % CuBDC-NS; (d) With the passage of time the normalized water flux of the membranes decreased (1 M NaCl was used for the purpose of DS and wastewater was used for the purpose of FS, T = 25 °C, AL-FS); TEM images confirming the existence of CuBDC-NS in PA active-layer: (e) original TFC membrane; (f) TFN membrane with 0.12 wt/v % CuBDC-NS. Reproduced with permission. [153] Copyright 2018, Elsevier.

2.1.5. Reverse osmosis

Compared with forward osmosis, reverse osmosis (RO) is a more traditionary filtering method. In actual operation, by increasing the pressure higher than permeate pressure, the water seeps according to the osmotic gradient. The main application of RO is seawater desalination. In addition, it is often used to remove organic pollutants from wastewater.

The application of modified MOF in RO membranes is becoming more and more
popular. By reasonably adjusting the size of the MOF particles to improve RO membranes, the properties of the membranes and the filtration efficiency can be effectively improved [155]. In short, continuous research and reasonable improvement of RO membranes (for example, adding appropriate MOF particles to manufacture RO composite membranes) can efficiently improve the economic benefits and reduce energy consumption.

Cu$_3$(BCT)$_2$ (BTC = 1,3,5-benzenetricarboxylate, HKUST-1) MOF treated with sulfuric acid was used to prepare a novel reverse osmosis MOF composite membrane, which had good performance [156]. The research indicated that the water flux enhanced by 33% and the salt interception reaction enhanced to 96%. Because the modified RO membrane had better hydrophilicity and porous structure, the anti-fouling ability of the composite membrane was significantly improved. The study found that the new type of RO composite membrane obtained by embedding certain MOF nanoparticles as fillers into the TFN membrane had excellent performance. For example, the TFN membrane prepared by incorporating the hydrophobic and hydrothermally stable ZIF-8 into the selective PA layer of TFN had a remarkable ability in water desalination applications [157]. After embedding in 0.4% ZIF-8 (Fig. 5a), the TFN membrane was better than the original PA: (i) faster water transportation theoretically in the frameworks and (ii) the TFN surface was less crosslinked and more hydrophilic. Specifically, in: ZIF-8 with a nanometer size of 200nm enhanced water permeability to 3.35±0.08 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ under a load of 0.4% (w/v), which was 162% higher than original polyamide membranes (Fig. 5d); at the same time, high NaCl interception was retained (Fig. 5e).
Another study revealed that a TFN membrane composed of ZIF-8 with particles size of 50 nm possessed the best properties because of the highest dispersion in PA layer [158]. These two works confirmed that the application prospects of ZIF-8 particles in TFN RO membranes was promising. The performance study of the composite membrane obtained by embedding MIL-101(Cr) NPs into the TFN membrane showed that compared with the conventional membrane with a 2.2 L m⁻² h⁻¹ bar⁻¹ flux, the water flux is enhanced by 44%, while the rejection of sodium chloride maintained almost unchanged at 99% [159]. Because the water absorption capacity (1.67 g H₂O/g ads) and high surface area (3264 m² g⁻¹) of MIL-101(Cr) provide a potential short path for the passage of water molecules; using MIL-125 and UiO-66 as fillers in TFN membrane also prepared RO composite membranes with good performance [160]. These works pointed out the feasibility and importance of using MOF nanoparticles as fillers for TFN membranes in reverse osmosis operations. In addition, studies have found that the preparation of pure UiO-66-NH₂ membrane on the surface of alumina could greatly improve the selectivity of cations, and had the potential to become an efficient reverse osmosis membrane for desalination [161].

2.2. Membrane pervaporation

Pervaporation (PV) is a membrane separation operation that can separate liquid mixtures. The separation of substances is realized through the difference between diffusion and adsorption [87]. Pervaporation is mainly used in the recovery of organic
solvents in wastewater, which makes the hydrophobicity, selectivity, permeability and stability of the PV membrane especially significant.

Past studies have shown that the selective adsorption and selective diffusion of water molecules can be improved by adding appropriate fillers, and the pervaporation performance can be improved [162]. Among various porous materials, hydrophobic MOFs are usually selected to remove organic pollutants from wastewater by pervaporation. Because MOFs have great potential as fillers to manufacture MOF composite membranes, the pervaporation performance of membranes is improved [163,164].

Studies have found that the mixed matrix membrane (MMM) prepared by adding certain MOF nanoparticles to polydimethylsiloxane (PDMS) had better selectivity, permeability and stability for recycling some organic solvents in wastewater. For example, adding super-hydrophobic and high-porosity RHO-[Zn(eim)2] (MAF-6) to PDMS could prepare MMM for ethanol recovery [165]. Research data showed that when MAF-6 loading rate was 15 wt%, the hydrophobicity of the MMM membrane was the highest, showing the highest separation factor (14.9) and flux (1200 g m⁻² h⁻¹); Adding silane-modified ZIF-8 nanoparticles to PDMS could prepare MMM for recovery of n-butanol [166]. Research data showed that the separation factor and flux of n-butanol increased by 34% and 85%, respectively. In addition, some researchers have applied the MIL-53 membrane [167] to the pervaporation recovery of ethyl acetate and MIL-160 membrane [168] to xylene isomers, and the same good membrane performance was reflected on them. Adding MOF nanoparticles to a polyvinyl alcohol
(PVA) matrix could also prepare a novel type of MMM for pervaporation of organic solvents, especially ZIFs membranes and their composite membranes [169,170]. For example, adding hydrophilic ethylenediamine-modified ZIF-8 nanoparticles to a PVA matrix could prepare novel PVA/ZIF-8-NH$_2$ MMMs for the pervaporation of ethanol [171]. The experimental results showed that when the loading rate of ZIF-8-NH$_2$ is 7.5 wt%, the MMM membrane had the best performance for the pervaporation dehydration of ethanol at 40 °C.

2.3. Membrane distillation

Membrane distillation (MD) is a heat-driven approach in which two streams of cold and hot water flow with each other, and only the steam penetrates into the hydrophobic membrane [172]. It is this characteristic that can be driven completely by waste heat and only steam permeates to the cold side. Membrane distillation has a good application prospect in WWT [173,174].

The MD performance is determined by the membrane pore structure parameters [175]. Adding appropriate nano-additive MOF to the membrane can improve the pore size and porosity, the surface roughness and the mechanical stability of the membrane, thus enhancing the comprehensive properties of the membrane [170].

Coating certain MOF nanoparticles on hydrophobic polyvinylidene fluoride (PVDF) membranes could prepare new TFN membranes with good performance for MD. For example, coating 5 wt% Fe-BTC on PVDF membranes (Fig. 5 b and c) could
prepare superhydrophobic PVDF nanofiber membrane for seawater desalination [177].

Studies shown that when the composite membrane was used for direct contact membrane distillation (DCMD), the contact angle of water was increased to 138.06 ± 2.18°, the water vapor flux was enhanced, and an excellent NaCl rejection rate (99.9%) was obtained. Coating an ultra-thin ZIF-8/chitosan layer on a hydrophobic PVDF membrane could also prepare a novel TFN membrane for MD [178]. The outcomes exhibited that the NaCl interception rate remained at 99.5% while the water permeability enhanced by 350%. Moreover, the existence of the chitosan layer enhanced the antifouling performance. In addition, a novel type of MOF integrated membrane prepared by hybridizing and modifying the NH₂-MIL-53(Al) membrane on the surface-functionalized porous alumina support layer stands out in membrane distillation for seawater desalination [179]. In this work, due to the compatibility of the alumina carrier with MIL-53, it served as the active site for the growth of MIL-53. The feature solved the delamination problem of the MOF layer; in addition, because the amino group reacts with the perfluoroalkyl chloride, the surface energy was reduced, and the surface hydrophobicity was significantly increased. Furthermore, the roughness of the membrane can be predicted by controlling the MOF ratio. Therefore, the membrane synthesized by this method had the inherent advantages of high temperature and pressure resistance, high water permeability, and high hydrophobic surface. Compared with the PTFE (12.0 L m⁻² h⁻¹) discovered by Alsaadi et al. [180], the new membrane exhibited higher permeance (32.3 L m⁻² h⁻¹) and satisfactory desalination rate.
Fig. 5. (a) TFN membrane. Reproduced with permission.[157] Copyright 2014, Elsevier. SEM images of the surface of the membranes of (b) PVDF; (c) 5 wt % Fe-BTC. The small-scale bar shown on the bottom is 1 µm corresponds to single fiber and larger scale bar is 5 µm. Reproduced with permission.[177] Copyright 2018, American Chemical Society. Influences of ZIF-8 particles loadings on (d) NaCl and water permeance; (e) apparent and corrected NaCl rejection of the TFN membrane. Reproduced with permission.[157] Copyright 2014, Elsevier.
Table 1
Information about the water-stable MOFs to manufacture membranes for wastewater treatment.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Metal center</th>
<th>Ligands</th>
<th>Hydrophilic/hydrophobic property</th>
<th>Application in water treatment</th>
<th>Refs</th>
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<td>Microfiltration, Ultrafiltration, Reverse osmosis, Pervaporation, Membrane distillation</td>
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<tr>
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<td>Hydrophobic</td>
<td>Pervaporation</td>
<td>[171]</td>
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<td>Hydrophilic</td>
<td>Nanofiltration, Forward osmosis, Reverse osmosis</td>
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<td>Hydrophilic</td>
<td>Nanofiltration, Ultrafiltration, Reverse osmosis</td>
<td>[124,138,161]</td>
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<td>Forward osmosis</td>
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<td>[179]</td>
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<td>[177]</td>
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3. MOFs as adsorbent in wastewater treatment
Due to its low cost, convenient operation, simple design, and wide range of applications, the adsorption technology has been considered to be superior to other decontamination technologies. Among the many porous adsorbents, MOF stands out. Because MOF has various pore geometries, high surface area, easy functionalization and adjustable porosity, these unique properties make it irreplaceable in the adsorption and removal of various toxic components in wastewater [181]. The diversity of central metals and coordinated unsaturated metal sites in the MOF framework provide a new strategy for the adsorption of various harmful compounds. In addition, MOF materials can be endowed with more functions through simple modification or functionalization, so that these materials can be used more widely. Therefore, in future research, MOFs may be the most powerful adsorbent for wastewater purification [182].

3.1. Heavy metal ions

Heavy metal ions are non-biodegradable and highly toxic to creatures even at a low concentration. Therefore, the effective removal of the extremely harmful heavy metal in water quality is of great significance for protecting human life and health and maintaining green ecological environment [46,183]. MOF has been widely used as an adsorbent to remove a variety of heavy metal from wastewater. Table 2 summarizes some information about the adsorptive removal of heavy metal by MOFs.
3.1.1. Mercury ions

3.1.1.1. Sulfur-functionalized MOFs. Based on the intensive interaction coordination between sulfur atoms and various metal ions, highly active sulphur atoms and sulphur-containing functional groups can be incorporated into MOFs (MOFs are sulfurized) to realize the removal of heavy metal, especially the adsorption and removal of Hg [184–186]. The ligand can be vulcanized before the MOF material is synthesized so as to obtain a pre-sulfurized MOF material. This not only enhances the adsorption capacity of MOF for heavy metals, but also broadens the application of MOFs. To date, several thiolated MOF and thioetherified MOF have been studied to eliminate Hg$^{2+}$ in wastewater.

The sulfur content of the reported thiol-functionalized [Co(NCS)$_2$(pyz)$_2$]$_n$ (pyz = pyrazine) (2D-NCS) nanosheets is as high as 19.1%, which has excellent adsorption capacity (1698 mg g$^{-1}$) for mercury ions (Fig. 6a-c) [187]. The large number of active sites exposed in the 2D-NCS nanosheets make the adsorption kinetics very fast, and the concentration of mercury ions can be decreased from 10 ppm to 1 ppb within 15 minutes. What is more attractive is that even if the mercury ion strength is as high as 100 mM, 2D-NCS nanosheets can maintain excellent adsorption capacity and reusability in a wide pH range. Creatively introducing sulphhydryl groups at positions 2 and 5 of 1,4-terephthalic acid could obtain a Zr-based MOF (Zr-DMBD) that effectively adsorbed Hg$^{2+}$. The Zr-DMBD MOF formed by coordination with high-valent metal ions exhibits high stability. Moreover, Zr-DMBD has good water stability, and sulphur is close to the
Zr-O cluster, which gives Zr-DMBD MOF the premise of adsorbing Hg$^{2+}$. What is remarkable is that the Hg elimination rate of the prepared Zr-DMBD MOF is over 99.9%, and it can reduce mercury ion concentration in the wastewater to less than 0.01 ppm [188]. The adsorption mechanism of this material was deeply explored by Ding et al. They proved through experiments that Hg$^{2+}$ coordinated with sulphur by substituting the hydrogen in the sulfhydryl group, and the substituted hydrogen entered the solution to form hydrogen ions, which can adjust the solution pH [189]. And the influence of pH on the Hg$^{2+}$ adsorption was tested. The results showed that the best adsorption environment for mercury ions is weakly acidic. When the pH is 6, the highest adsorptive capacity of Hg$^{2+}$ is 171.5 mg g$^{-1}$. Unlike Zr-DMBD, which introduces aryl mercaptans into the MOF framework, Zr-MSA (HOOC-CHSH-CH$_2$-COOH, MSA) MOF first introduces alkyl mercaptans. Since alkyl mercaptans have a strong affinity for Hg$^{2+}$ and there are dense alkyl mercaptans in Zr-MSA, the adsorption capacity of Zr-MSA for mercury ions is as high as 734 mg g$^{-1}$. Compared with the above-mentioned Zr-DMBD, it shows a strong adsorption capacity. More importantly, the Zr-MSA synthesis process uses environmentally friendly solvent water instead of toxic organic solvents, which makes Zr-MSA materials more popular in mercury removal applications [190]. Another thiol-functionalized Zr-based MOF UiO-66-(SH)$_2$ also showed a strong capability to remove Hg$^{2+}$ [191]. Additionally, a sulfhydryl functionalized HKUST-1 MOF was discovered, which can also remove mercury efficiently [192]. After the coordination unsaturated central metal in HKUST-1 was modified with -SH group in dithioethanol, the sulfhydryl functionalized HKUST-1 showed a surprising adsorptive capacity.
(714.29 mg g\(^{-1}\)) for Hg\(^{2+}\) and high adsorptive affinity (\(K_d = 4.73 \times 10^5\) mL g\(^{-1}\)). In addition, the benzyl alcohol groups of Cr-MIL-101-A4 were converted into MOF (Cr-MIL-101-AS) with thiol function through the method of tandem postsynthetic modification, and it was found that the latter had a strong binding effect on heavy metal substances, thereby effectively removing mercury ions in water [193]. The sulfhydryl functionalized SH-MIL-68(In) also showed high adsorptive capacity for Hg\(^{2+}\) in water [194]. These studies open up an energy-saving way to remove heavy metals from wastewater by using modified functionalized MOF adsorbents after synthesis, effectively avoiding repeated exploration of complex synthesis conditions.

Based on the predominant adsorption capacity of thioetherified adsorbents for mercury ions, a type of Co-MOFs (NENU-400) with independent thioether groups was developed. Although NENU-400 has a strong adsorptive capacity for mercury ions in the aqueous solution, the NENU-400 frame has insufficient stability and is prone to collapse. In order to overcome this shortcoming, researchers installed H\(_2\)INT as the upholder into NENU-400, and obtained NENU-401 with good stability in aqueous circumstance (Fig. 6 d and e) [195]. As shown in Fig. 6f, NENU-401 can remove Hg\(^{2+}\) and Pb\(^{2+}\) efficiently, but can hardly adsorb the rest of the metal ions (Fe\(^{3+}\), Zn\(^{2+}\), Na\(^{+}\), K\(^{+}\) and Ca\(^{2+}\)). It is worth mentioning that NENU-401 could reduce the concentration of Hg\(^{2+}\) in the solution from 10 ppm to 0.02 ppb in a short period of time. Moreover, as depicted in Fig. 6g, the crystal of NENU-401 could still maintain 90% of mercury capture efficiency after 4 cycles, indicating excellent reusability. The high adsorption properties of NENU-401 are credited to a lot of -SH groups on the internal surface and
the clear pore size. Another thioether modified \(\{\text{Cu}^{II}\}_{4}[(S, S)\text{-methox}]_{2}\cdot5\text{H}_{2}\text{O}\) MOF has been studied because of its excellent adsorption properties and high selectivity for \(\text{HgCl}_{2}\) [196]. Although under the interference of different cations such as \(\text{MgCl}_{2}\), \(\text{NaCl}\), \(\text{AlCl}_{3}\), \(\text{CaCl}_{2}\), and \(\text{FeCl}_{3}\), \(\{\text{Cu}^{II}\}_{4}[(S, S)\text{-methox}]_{2}\cdot5\text{H}_{2}\text{O}\) could still selectively adsorb \(\text{HgCl}_{2}\) and the removal rate could be as high as 99.7% within 5 minutes, and reduced the concentration of \(\text{HgCl}_{2}\) to the allowable range of drinking water within 10 minutes. Because of the specific coordination between sulphur atoms and \(\text{HgCl}_{2}\), the obtained \(\text{HgCl}_{2}\text{S}_{2}\) adduct has a very stable tetrahedral conformation. Removal of Hg metal in mild conditions is more meaningful in practical applications. Therefore, the researchers captured some water-stable MOFs for adsorbing mercury ions at room temperature. The MOFs containing a series of thioether side chain ligands L1-L4 have attracted wide attention due to their unique structure and excellent performance. Taking \(\text{Zr-L4}\) as an instance, the introduction of thioether side chain not only have the effect of adsorbing mercury ions, but also can improve the stability of the MOF framework. The adsorptive removal rate of \(\text{Hg}^{2+}\) by \(\text{Zr-L4}\) is 96% and the partition coefficient is \(2.4\times10^{4}\ \text{mL}\cdot\text{g}^{-1}\). It is worth mentioning that even if the \(\text{Zr-L4}\) crystal is soaked in a solution of \(\text{pH} = 1\) for 24 h, it can still maintain a high degree of crystallinity [197]. Moreover, the thioether side chain counts not only in improving the stability of MOF materials exposed to the air, which gives MOFs the potential for the application in gas-solid interface, but also in electrochemical sensing of \(\text{Hg}^{2+}\) [198–204]. In addition, the adsorption capacity of \(\text{Zr-M1}\) (a pentaerythrityl side chain equipped with three-pronged thioether donors, M1) with rich sulfide groups for \(\text{Hg}^{2+}\) in aqueous solutions is 275 mg g\(^{-1}\) [205]. Moreover,
the formed Zr-MOF-HgCl₂ excellently heightens the structure order, so that the originally disordered MOF materials can be analyzed by single crystal X-ray diffraction (SCXRD). A recent research indicated that a novel tetrathiafulvalene-functionalized Zr (IV)-based metal organic framework (Zr-TTFTB) with the synergistic disulfide sites exhibits high affinity for Hg²⁺ and excellent chemical stability, showing superhigh Hg²⁺ adsorption capacity (962 mg g⁻¹) and distribution coefficient value (Kₐ = 1.15 × 10⁸ mL g⁻¹) [206]. This allowed it to rapidly reduce the Hg²⁺ concentration to below 0.88 ppb, well less than the standard for drinking water. More interestingly, Zr-TTFTB exhibited the outstanding renewable properties in adsorption-regeneration cycles. Therefore, the introduction of the ligand thioether has an apparent effect on the adsorption of Hg²⁺ and the stability of the MOF framework, which is of great significance in practical applications.

Fig. 6. (a) Diagrammatic sketch of the capture of HgCl₂ by using 2D-NCS, the followed formation of 2D-NCS@Hg and the regeneration of 2D-NCS; (b) Optical image of 2D-NCS@Hg; (c) SEM image of 2D-NCS@Hg. Reproduced with permission. [187] Copyright 2019, Elsevier. (d, e) Two types of cages in NENU-400 and NENU-401, respectively; (f) Capture efficiency in removing metal ions; (g) Cycle performance for Hg²⁺ removal. Reproduced with permission. [195] Copyright 2018, American Chemical Society.
3.1.1.2. Ammonia-functionalized MOFs. In addition to combining with sulfur, Hg$^{2+}$ also interacts mightily with nitrogen. Consequently, the ammonia-functionalized MOF is an important adsorbent for removing heavy metal. The TMU-40 MOF ligands synthesized in situ contain free amine groups, which can be used as Hg$^{2+}$ adsorption sites to remove Hg$^{2+}$ [207]. The study found that the highest adsorptive capacity of TMU-40 for Hg$^{2+}$ could reach 269 mg g$^{-1}$. It is worth mentioning that TMU-40 can reduce the 40 ppm wastewater to the acceptable limit of 2 ppb for drinking water in a short time. TMU-40 is widely used in practical applications due to its good adsorption performance. In addition, the ammoniated MOF formed by post-synthesis modification method also exhibits an excellent adsorptive capacity for Hg$^{2+}$. The MOF-808-EDTA has excellent adsorption capacity (592 mg g$^{-1}$) and interception rate (99%) for mercury ions, and can decrease the solution concentration from ppm to ppb. What's amazing is that MOF-808-EDTA can not only effectively adsorb soft acid ions such as mercury, but also capture 22 kinds of heavy metal including edge metal and hard metal [208]. More interestingly, the ammoniated MOF can not only adsorb Hg$^{2+}$, but also serve as a fluorescence sensor to detect Hg$^{2+}$. The bifunctional material Nin-NH-MIL-101 (Al) conformed by introducing ninhydrin into MOF through the covalent interaction between amino group and ninhydrin was used to adsorb Hg$^{2+}$ [209]. After testing, Nin-NH-MIL-101(Al) showed excellent sensitivity and selectivity to mercury ions with a concentration of only 1 ppb. The adsorptive capacity of Nin-NH-MIL-101(Al) for mercury ions is 124.8 mg g$^{-1}$, the removal rate is 92%, and the adsorption of Hg$^{2+}$ is reversible. The material is not only widely used in the treatment of industrial wastewater, but also has a
promising future in detecting and removing mercury ions in electronic waste. In addition, the new thymine-functionalized MIL-101 (MIL-101-Thymine) (Fig. 7 a and b) synthesized by post-synthesis approach exhibited excellent mercury removal performance [210]. The study found that the highest adsorptive capacity of mercury was 51.27 mg g⁻¹, and the selectivity coefficient was as high as 947.34. The excellent performance was attributed to the strongly selective interaction of T-Hg²⁺-T in MIL-101-Thymine and the coordination of Hg²⁺ with the N of thymine in MIL-101-Thymine. Furthermore, the adsorption of Hg²⁺ was in fine agreement with the Langmuir model, and the adsorption rate was in keeping with the pseudo-second-order kinetic model (Fig. 7d). It is important that even if MIL-101-Thymine is used to remove Hg²⁺ in actual wastewater, its efficient recovery rate can be obtained (Fig. 7c).
3.1.2. Others

At present, MOF-based adsorbents are used to eliminate different heavy metal ions. The maximum adsorptive capacity of ED-MIL-101 for Pb$^{2+}$ prepared based on the strong complexation of EDTA and Pb$^{2+}$ is 81.09 mg g$^{-1}$, which is 5 times of the adsorption capacity of the original MIL-101 [211]. Due to the strong complexation between EDTA and Pb$^{2+}$ and the fit of the metal radius to the pore structure of MIL-101, ED-MIL-101 shows relatively high selectivity to Pb$^{2+}$ in the actual water sample treatment, which is better than other divalent metal ions. In addition, NH$_2$-MIL-53 with a nitrogen-based functional group has a higher Pb$^{2+}$ ion adsorptive capacity (492.4 mg g$^{-1}$) [212]. The adsorption capacity can be adjusted by changing the concentration of the amino group in the material. Sulfuric acid functionalized HKUST-1 ($\text{Cu}_3(\text{BTC})_2\text{SO}_3\text{H}$) is commonly used to remove Cd$^{2+}$ in wastewater, even if it exhibits low adsorption capacity (88.7 mg g$^{-1}$) [213]. However, due to the chelation between the Cd$^{2+}$ ion and the -SO$_3$H group, it has excellent adsorption properties: (i) The adsorption of $\text{Cu}_3(\text{BTC})_2\text{SO}_3\text{H}$ on Cd$^{2+}$ is not interfered by other cations (such as Na$^+$, Mg$^{2+}$, Ca$^{2+}$, Pb$^{2+}$, $\text{Cu}^{2+}$ and Ni$^{2+}$) (ii) it can be reused for more than 6 cycles without significant loss of adsorptive capacity. In addition, FJI-H9 also shows high adsorptive capacity (225 mg g$^{-1}$) and excellent selectivity for Cd$^{2+}$ adsorption [214]. A stable Al-based metal organic framework (MOF-303) was used to efficiently and selectively separate Cu$^{2+}$
from Cu\textsuperscript{2+}/Co\textsuperscript{2+} and Cu\textsuperscript{2+}/Ni\textsuperscript{2+} (2662 and 6076 for Cu\textsuperscript{2+}/Co\textsuperscript{2+} and Cu\textsuperscript{2+}/Ni\textsuperscript{2+} respectively) binary systems [215]. Owning to the distinctive chelation effect of bispyrazole sites distributed parallel to the 1D channel direction, MOF-303 showed simultaneously a high adsorption capacity for Cu\textsuperscript{2+} (330 mg g\textsuperscript{-1}). Combined with experimental methods and theoretical calculation, the adsorption mechanism of Cu\textsuperscript{2+} based on the synergistic bispyrazole sites in MOF-303 was obtained. Moreover, the regeneration of MOF-303 and the recovery of Ni\textsuperscript{2+} were realized through the designed process. This work reveals the significance of the unique bispyrazole sites in MOFs, which can facilitate the separation and recovery of metal ions. ZIF-8, the first MOF used for Cu\textsuperscript{2+} adsorption, exhibits extremely high removal rate (95.4%) [216]. Studies found that ZIF-8 can effectively adsorb Cu\textsuperscript{2+} in the pH range of 3–6 even in a solution with high Cu\textsuperscript{2+} concentration. The adsorption mechanism at high and low Cu\textsuperscript{2+} concentration is that the nitrogen groups on 2-methylimidazole coordinate with the copper ions while ion exchange is carried out at low initial Cu\textsuperscript{2+} concentration at the same time. Some MOFs that can remove different heavy metals simultaneously have also attracted the researchers’ attention and promoted further explorations. Sulfur groups have high complexing capacity for soft metal cations. The maximum adsorption capacity of UiO-66-NHC(S)NHMe for Cr\textsuperscript{3+}, Cd\textsuperscript{2+}, Hg\textsuperscript{2+} and Pb\textsuperscript{2+} are 117, 49, 769 and 232 mg g\textsuperscript{-1}, respectively [217]. In addition, amino-functionalized Zr-MOFs (NH\textsubscript{2}-Zr-MOFs) are often used to simultaneously remove Pb\textsuperscript{2+} and Cd\textsuperscript{2+} [218]. When the initial concentration is 40mg·L\textsuperscript{-1}, it shows adsorption capacities of 177.35 and 166.74 mg g\textsuperscript{-1} for Cd\textsuperscript{2+} and Pb\textsuperscript{2+}, respectively. TMU-5 can adsorb Cd\textsuperscript{2+}, Co\textsuperscript{2+}, Cr\textsuperscript{3+}, Cu\textsuperscript{2+} and Pb\textsuperscript{2+} in
wastewater, showing good adsorption performance [219]. It has been reported that Zeolite Imidazolium Framework-67 (ZIF-67) can efficiently remove uranium (VI) from aqueous solutions [220]. The research results exhibited that ZIF-67 had an ultra-high adsorption capacity (1683.8 mg g$^{-1}$) for uranium in aqueous solution, and the removal rate of uranium could reach more than 99% at both ppb and ppm levels, which is quite remarkable. The possible mechanism is revealed that ZIF-67 generated large amounts of Co-OH and active sites after dispersing in water, and Co-OH was the key factor for ZIF-67 to achieve high affinity and adsorption capacity for uranium (VI). Additionally, a novel azo MOF of polycarbon 3D array with staggered 2D bilayers, namely Zn$_2$(DMF)(ADC)$_2$(L)$_0.5$ (H$_2$ADC=azobenzene-4,4'-dicarboxylic acid, L=N, N'-di(pyridin-4-yl) naphthalene-1,4-dicarboxamide, ECUT-100), exhibited high adsorption capacity for uranium (VI) (381 mg g$^{-1}$) [221]. It is worth mentioning that this value is much higher than that obtained in most of established adsorbents, and no pre-treatment of the synthesized ECUT-100 samples is required. This is attributed to the possible special interactions between the independent azo and amide groups from L and ADC$^{2-}$ ligands and the uranium (VI) ions. These research results lay the groundwork for the development of new MOFs which can remove different heavy metal ions from wastewater at the same time.

<table>
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<th>Heavy metal ion</th>
<th>MOF</th>
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<td>Zr-M1</td>
<td></td>
<td>three-pronged thioether donors</td>
<td>275</td>
<td>96.0</td>
<td>[205]</td>
<td></td>
</tr>
<tr>
<td>UiO-66-NHNC(S)NHMe</td>
<td>2-aminoterephthalic acid, N,N-dimethylformamide (DMF)</td>
<td>769</td>
<td>99.0</td>
<td>[217]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>Cu</td>
<td>1,3,5-benzenetricarboxylate (H₃BTC)</td>
<td>714.29</td>
<td>99.0</td>
<td>[192]</td>
<td></td>
</tr>
<tr>
<td>MIL-101-Thymine</td>
<td>thymine-1-acetic acid, 2-aminoterephthalic acid</td>
<td>51.27</td>
<td>99.9</td>
<td>[210]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SH-MIL-68</td>
<td>In</td>
<td>NH₂-H₂BDC (H₂BDC=1,4-benzene dicarboxyllic acid), benzoic acid, pyridine</td>
<td>450</td>
<td>99.0</td>
<td>[194]</td>
<td></td>
</tr>
<tr>
<td>NENU-401</td>
<td>Co</td>
<td>3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylic acid, isonicotinate, DMF, N,N-dimethylacetamide</td>
<td>600</td>
<td>99.7</td>
<td>[195]</td>
<td></td>
</tr>
<tr>
<td>TMU-40</td>
<td>Zn</td>
<td>5,6-di(pyridin-4-yl)-1,2,3,4-tetrahydropyrazine, TPA</td>
<td>257</td>
<td>99.9</td>
<td>[207]</td>
<td></td>
</tr>
<tr>
<td>Nin-NH-MIL-101</td>
<td>Al</td>
<td>2-amino terephthalic acid (H₃aBDC), DMF</td>
<td>124.8</td>
<td>92.0</td>
<td>[209]</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>ED-MIL-101</td>
<td>ethylenediamine (ED), benzenedicarboxylates</td>
<td>81.09</td>
<td>97.2</td>
<td>[211]</td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Cu(BTC)-2SO₄H</td>
<td>H₃BTC, dithioglycol, sulfonic acid</td>
<td>88.7</td>
<td>80.0</td>
<td>[213]</td>
<td></td>
</tr>
<tr>
<td>FJI-H9</td>
<td>Ca</td>
<td>2,5-thiophenedicarboxylate (H₂thb)</td>
<td>225</td>
<td>99.9</td>
<td>[214]</td>
<td></td>
</tr>
<tr>
<td>NH₂-Zr-MOF₃</td>
<td>Zr</td>
<td>4-benzenedicarboxylic acid, 2-NH₂-1</td>
<td>177.35</td>
<td>99.9</td>
<td>[218]</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>ZIF-8</td>
<td>2-Methylimidazole</td>
<td>95.4</td>
<td>95.4</td>
<td>[216]</td>
<td></td>
</tr>
<tr>
<td>MOF-303</td>
<td>Al</td>
<td>3,5-pyrazoledicarboxylic acid</td>
<td>330</td>
<td>99.0</td>
<td>[215]</td>
<td></td>
</tr>
<tr>
<td>U⁶⁺</td>
<td>ZIF-67</td>
<td>2-methylimidazole</td>
<td>1683.8</td>
<td>99.0</td>
<td>[220]</td>
<td></td>
</tr>
<tr>
<td>ECUT-100</td>
<td>Zn</td>
<td>azobenzen-4,4'-dicarboxylic acid, N, N'-di(pyridin-4-yl)naphthalene-1,4-dicarboxamide</td>
<td>381</td>
<td>99.0</td>
<td>[221]</td>
<td></td>
</tr>
</tbody>
</table>
3.2. Dyes

Residual dyes remaining in the water have carcinogenic effects on human bodies and aquatic organisms. Therefore, the pollution of water caused by synthetic dyes has become a problem that cannot be ignored. Adsorption technology has been widely used to remove dyes in wastewater. Compared with traditional adsorbents, MOFs have greater advantages in the removal of dyes in wastewater [126,222,223]. This section mainly summarizes the adsorption performance and mechanism of different MOFs when used to remove some typical dyes in wastewater. Table 3 summarizes some information about the adsorptive removal of dyes by using MOFs.

3.2.1. Methylene blue

Methylene blue (MB) is a typical toxic cationic dye that can cause varying degrees of harm (such as gastritis, vomiting and dyspnea) to the human body after exposure. Therefore, it is necessary to eliminate MB dye from the actual aqueous solution. A variety of MOFs adsorbents used to remove MB in wastewater have been reported, and they all show excellent adsorption performance. For example, a widely studied MOF, HKUST-1, was discovered at a relatively early time, which showed a series of characterizations. The characterizations and experimental data of HKUST-1 (such as Langmuir isotherm, Gibbs free energy function) confirmed its potential application
value in treating wastewater containing MB (Fig. 8a-c) [224]. The author found that the adsorption process of this material to MB is spontaneous, and the enthalpy change is the main driving force. Interestingly, after being washed with ethanol, HKUST-1 can be readily regenerated and retain the adsorptive capacity (Fig. 8d). Thus, HKUST-1 may be one of the most promising candidates for dye removal. Later, an aluminum-based MOF MIL-68 was developed [225]. The material was characterized by SEM, XRD, FTIR, and Brunauer–Emmett–Teller (BET) analysis. The author also studied its adsorption isotherm and adsorption kinetics in detail. The kinetic study results showed that the adsorption of MB and rhodamine B (RhB) on MIL-68(Al) conformed to the pseudo-second-order model. According to the Langmuir isotherm, the highest adsorptive capacities in single and binary solutions are 1666 and 1111 mg g\(^{-1}\) for MB, 227, and 29 mg g\(^{-1}\) for RhB. In addition, after being washed with methanol, the adsorbent can be readily reused in subsequent operations. It is worth mentioning even in actual samples of tap water, spring water, sea water and laundry wastewater mixed with specific amounts of two dyes, this material still maintains efficient removal ability.

Recently, Zn-MOF with carbonyl group based on fluorenone-2,7-dicarboxylate ligand \([\text{Zn}_5(\text{FODC})_2(\text{OCH}_2\text{CH}_2\text{O})_3(\text{H}_2\text{O})]\) (MOF 1) was directly synthesized to selectively absorb cationic dyes such as MB [226]. Due to the unique structure and excellent performance of MOF 1, its maximum adsorption for adsorbing MB can reach 326 mg g\(^{-1}\). Moreover, electrostatic interaction is the main driving force, which is the most common mechanism in adsorption. In addition, another new Zn-MOF, \([\text{(CH}_3)_2\text{NH}_2] [\text{Zn}_{1.5}(\mu_3-\text{O})_{0.5}(\text{F-tzba})_{1.25}(\text{bpy})_{0.25}(\mu_2-\text{F})_{0.5}] \cdot 2\text{DMF} \cdot 2\text{H}_2\text{O} \quad (\text{F-tzba} = 2\text{-F}-4-(1H-
tetrazol-5-yl) benzoic acid, bpy = 4,4’-bipyridine, DMF = N,N-Dimethylformamide) (MOF 2), also has a remarkable ability (328 mg g⁻¹) to adsorb MB [227].

3.2.2. Methyl orange

Methyl orange (MO) is an anionic dye from dye-containing wastewater, which is highly toxic and can cause great harm to human bodies and even cause cancer under long-term exposure. Therefore, it is imperative to carry out the adsorption and removal of MO in wastewater. For ten years, two types of MOFs, MIL-101 and MIL-53, have been widely used to remove MO by adsorption [107]. The study found that the adsorption kinetic constant and adsorptive capacity of MIL-101 are better than that of MIL-53. This study indicated the importance of pore size and porosity to the adsorptive process. Moreover, the adsorption capacity of MIL-101 decreases as the pH value of the solution increases. Inspired by this, we found that the electrostatic interaction is the main driving force for adsorption. Based on this research, cationic adsorbents with high porosity may be potential materials for removing anionic dyes. In recent years, a zirconium-based water-stable MOF UiO-66 has been synthesized to adsorb and remove MO and MB [228]. For UiO-66, the first challenge was to be soaked in an aqueous solution for up to 12 months. Analytical methods were used to study the adsorption behavior of UiO-66, as well as adsorption kinetics and adsorption thermodynamics. The results showed that the adsorptive kinetics of UiO-66 was depicted by pseudo-second-order (Fig. 8e) and Freundlich isotherm (Fig. 8f) models revealed excellent fit with adsorptive data. The adsorption of these two dyes by UiO-66 is spontaneous. The
difference is that the adsorption of MO is dominated by enthalpy effect, while that of MB is dominated by entropy effect. Experimental results showed that the adsorptive capacity of UiO-66 for MO is higher than that for MB, especially in acidic and neutral environments. This is due to the more powerful electrostatic interaction and π-π stacking between MO and UiO-66. What is attractive is that even after four continuous adsorption-desorption researches, UiO-66 can still maintain the initial structure and adsorption capacity, showing good reusability (Fig. 8g). In addition, MOF-235(Fe) also exhibited excellent adsorption performance for MO and MB [229], and was recommended as a potential adsorbent for removing harmful substances in the liquid phase.

Fig. 8. (a) SEM micrograph of HKUST-1 particles; (b) Test graph of second-order kinetic model for MB adsorption on HKUST-1; (c) Image of the MB adsorption by HKUST-1 with a contact time of 20 min; (d) Influence of recycle times of HKUST-1 on the MB adsorptive capacity. (MB solution, \(C_0 = 8 \mu\text{mol·L}^{-1}\); pH = 7; \(T = 298\) K; \(V = 10\) mL; \(m = 20\) mg) Reproduced with permission. [224] Copyright 2014, Elsevier. Model fits of the experimental data with (e) pseudo-second-order kinetics and (f) for the adsorption of MB and MO on UiO-66; (g) Influence of recycle times on the adsorptive capacities of MB and MO. Reproduced with permission. [228] Copyright 2018, Elsevier.
3.2.3. Others

Other common dyes, such as Congo red (CR) and reactive dyes can also cause damage to ecosystem and human bodies when exposed to aqueous solutions. Therefore, the corresponding MOFs adsorbents have been explored and studied. The rhombic dodecahedral shaped ZIF-67 and boat-shaped flaky Co-MOF were synthesized by green one-step precipitation and the one-step methods respectively, both of which exhibited significant removal efficiency for CR [230]. The authors studied a series of influencing factors, such as contact time, initial CR concentration, adsorbent dosage and pH values of the solution. The experimental data revealed that the adsorption of CR by ZIF-67 and Co-MOF was consistent with the pseudo-second-order kinetic model and Langmuir model. It is worth mentioning that the maximum adsorptive capacities of ZIF-67 and Co-MOF at 25 °C were 1044.58 and 1019.06 mg g⁻¹, respectively, and the equilibration time was less than 5 minutes, which was attributed to the powerful π-π stacking and electrostatic interactions of CR with ZIF-67 and Co-MOF. The synthesis methods of these two adsorbents are simple and green, and their removal efficiency is remarkable. Thus, they are materials with great potential for decontamination in the future [231]. MIL-101-Cr was proved to be a highly effective adsorbent, showing excellent adsorption effects on four toxic industrial reactive dyes, blue 2 (RDB 2), black 5 (RDBK 5), red 24 (RDR 24) and yellow 15 (RDY 15) [232]. The study found that the maximum adsorptive capacities of MIL-101-Cr for RDB 2, RDBK 5, RDR 24, and RDY 15 were 377, 386, 390, and 397 mg g⁻¹, respectively. The main driving force for adsorption is the powerful physical adsorption on the MOF surface. It is worth
mentioning that in the first 30 minutes, 87-94% of dyes can be removed by the MOF at the same time, and then the removal efficiency gradually increases to 99%. Interestingly, the MOF can achieve a good regeneration effect after being washed with DMF, and can maintain a satisfactory removal rate after 4 consecutive cycles of use.

Table 3

Information about the adsorptive removal of dyes by MOFs.

<table>
<thead>
<tr>
<th>Dye</th>
<th>MOF</th>
<th>Metal center</th>
<th>Ligands</th>
<th>Adsorption capacity (mg g⁻¹)</th>
<th>Removal efficiency (%)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene blue</td>
<td>MIL-68 Al</td>
<td>Terephthalic acid</td>
<td>1666</td>
<td>99.9</td>
<td>[225]</td>
<td></td>
</tr>
<tr>
<td>MOF 1 Zn</td>
<td>MIL-68 fluorenone-2,7-dicarboxylate (H₂FODC), glycolate dianions([OCH₂CH₂O]₂⁻)</td>
<td>326</td>
<td>99.0</td>
<td>[226]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOF 2</td>
<td>MIL-68 F-H₂tzba, bpy, DMF</td>
<td>328</td>
<td>98.9</td>
<td>[227]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>MIL-68 Al</td>
<td>Terephthalic acid</td>
<td>1111</td>
<td>98.5</td>
<td>[225]</td>
<td></td>
</tr>
<tr>
<td>Methyl orange</td>
<td>UiO-66 Zr</td>
<td>1,4-Benzenedicarboxylate</td>
<td>83.7</td>
<td>94.8</td>
<td>[228]</td>
<td></td>
</tr>
<tr>
<td>Congo red</td>
<td>Co-MOF Co</td>
<td>2-methylimidazole</td>
<td>1019.06</td>
<td>99.4</td>
<td>[230]</td>
<td></td>
</tr>
<tr>
<td>Reactive black 5</td>
<td>MIL-101 Cr</td>
<td>Terephthalic acid</td>
<td>386</td>
<td>99.9</td>
<td>[232]</td>
<td></td>
</tr>
<tr>
<td>Reactive blue 2</td>
<td></td>
<td></td>
<td>377</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive red 24</td>
<td></td>
<td></td>
<td>390</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive yellow 15</td>
<td></td>
<td></td>
<td>397</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3. Antibacterials
The use of antibacterials has a major contribution to the prevention and treatment of biological diseases [233,234]. Nevertheless, with the rapid development of pharmaceutical industry, some water bodies have been polluted by pharmaceutical wastewater. Under long-term exposure, some antibacterials can easily interact with trace elements (e. g. Fe, Ca, Zn, Mg) needed by human body, causing various adverse reactions. Therefore, proper treatment of antibacterials in wastewater is particularly important for human health and the ecological environment. Among a variety of adsorbents, MOF has been used as an excellent adsorption material due to its unique structure and function [235,236]. It is widely used to remove antibacterials in wastewater and exhibits excellent adsorption performance. This section summarizes the adsorption performance and mechanism of different MOFs when used to remove some common antibacterials in wastewater. Table 4 summarizes some information about the adsorptive removal of antibacterials by MOFs.

3.3.1. Quinolones

Quinolone antibacterials, including ciprofloxacin (CIP), ofloxacin (OFL), enoxacin (ENX) and norfloxacin (NOR), are extensively used in the treatment of biological bacterial infections. However, water pollution caused by the use of them has become a problem of increasing concern. To date, some MOFs used to adsorb these substances in pharmaceutical wastewater have been reported.

Studies have found that quinolones contain two pKa values. When the pH of the solution is lower than pKa1, the molecules mainly exist in the form of cations; when the
pH is in the scope of $pK_a_1 \sim pK_a_2$, zwitterionic molecules are the main existing form; when the pH is higher than $pK_a_2$, the molecules mainly exist as anions. Inspired by this, when the pH of the solution is lower than $pK_a_1$ or higher than $pK_a_2$, adsorption caused by electrostatic interaction may dominate. MIL-101-SO$_3$H(Cr) MOF has great water stability, large specific surface area and channels [237]. Investigations have shown that this MOF has a high adsorption capacity (greater than 400 mg g$^{-1}$) in removing OFL, ENX and NOR antibacterials from wastewater [238]; electrostatic interaction is the driving force for adsorption. Therefore, with the characteristics of charges and pores, MIL-101-SO$_3$H is a very attractive quinolone adsorbent. In addition, a similar adsorption mechanism also exists in the adsorption of ZIF-8 [216]. With its unique pore structure, ZIF-8 can effectively adsorb and remove NOR (66.8 mg g$^{-1}$).

Quinolones have multiple functional sites in their structure, including free carbonyl, piperazine, carboxyl and fluorine groups. Therefore, it is feasible to carry out the idea of using hydrogen bond interaction as the main driving force to adsorb such substances on MOF. PCN-124-stu(Cu) is a pzh-topology framework with large specific surface area and pore diameter. It can be seen from Fig. 9a that PCN-124-stu(Cu) still has excellent stability in an aqueous solution with such a wide pH range (pH = 2~12), which is impossible for many adsorbents. MOF has good water stability and can efficiently adsorb NOR, OFL and Enrofloxacin (ENR) in wastewater [239]. Configuration Bias Monte Carlo (CBMC) experiment indicated that the excellent adsorption performance of PCN-124-stu(Cu) is due to the strong hydrogen bond interaction between the carboxyl and amide. Moreover, as shown in Fig. 9b-d, PCN-
124-stu(Cu) can slowly free quinolone drugs in physiological saline and maintain its frame structure after 4 cycles of adsorption/desorption.

Flexible MOF materials such as MIL-88B(Fe) have attracted people's exploration because of their unique breathing effect. Under the external stimulations of temperature, pressure and guest molecules, the pores of the flexible MOF will expand. Therefore, by using the breathing effect of the flexible MOF, the adsorption performance of the material can be improved. With the inspiration from this, the adsorption properties of CIP molecules in flexible MIL-88B(Fe), flexible MIL-53(Al) and rigid UiO-66(Zr) have been studied [240]. Under the excitation of CIP molecules, the pores of flexible MIL-88B(Fe) and MIL-53(Al) both became larger, resulting in an increase in their adsorption capacities (226.9 mg g\(^{-1}\) and 155.2 mg g\(^{-1}\), respectively). The higher adsorptive capacity of MIL-88B(Fe) was attributed to the fact that Fe-O clusters of MIL-88B(Fe) are more likely to coordinate with free carboxyl groups of CIP than Al-O clusters of MIL-53(Al). In contrast, the rigid UiO-66 was limited by steric hindrance of the rigid frame and weak interaction between the host and the guest, resulting in the inability to capture CIP well. Therefore, this research proves the importance of the central metal and the breathing effect in MOF.

3.3.2. Nitroimidazoles

Nitroimidazole antibacterials include metronidazole (MNZ), tinidazole (TNZ), menidazole (MZ), dimetridazole (DMZ) and so on. These drugs are widely produced for anti-viral, anti-parasitic and anti-tuberculosis, but they may also cause water
pollution problems. Thanks to their small molecular sizes and low pKa values (<3.0), many microporous positively charged MOFs participate in the capture of these substances.

Previous reports have already reported the adsorptive behavior of DMZ molecules on microporous flexible MIL-53(Al), rigid Al-1, 4-NDC and MIL-68(Al) [241,242]. Similar to previous reports, powder XRD technology proved that flexible MIL-53(Al) had obvious breathing effect and two-stage adsorption; and the hydrogen bond coordination between μ-OH and -NO₂ of DMZ is the prime driving force. Surprisingly, the adsorptive capacity of MIL-53(Al) is 467.3 mg g⁻¹. In contrast, rigid Al-1,4-NDC and MIL-68(Al) showed lower adsorption capacity. More interestingly, due to the relatively weak hydrogen bond coordination, MIL-53(Al) has good reusability. In addition, CAU-1 can easily capture TNZ molecules and has high adsorptive capacity, which is superior to previously discovered general porous MOFs (Fig. 9g) [243]. Since CAU-1 is rich in -OH and -NH₂ groups and the surface of the framework has strong positive charges (Fig. 9 e and f), hydrogen bond and electrostatic interaction are the main adsorption mechanisms. Interestingly, under simulated physiological conditions, the controlled release of loaded TNZ molecules could be achieved by adjusting the pH of the solution, and the material has good reusability (Fig. 9h). This work confirms that this material has great potential in removing TNZ.
Fig. 9. (a) PXRD of PCN-124-stu(Cu) and PCN-124-stu(Cu) after immersion in different pH for 7 days; (b) The content of adsorbed quinolones at equilibrium for 4 adsorption/desorption cycles; Transfer kinetics of (c) NOR, (d) ENR from PCN-124-stu(Cu) in normal saline at 37 °C. (Two parallel tests for each FQs release, the red line represents the first run, the black line represents the second run) Reproduced with permission. [239] Copyright 2017, Wiley-VCH. (e) Framework structure of CAU-1; (f) SEM image of CAU-1; (g) TNZ adsorptive capacity of CAU-1 and other common MOFs (T = 298 K, C₀ = 100 mg L⁻¹, pH = 5.2); (h) Recycle times of TNZ adsorption on CAU-1 (T = 298 K). Reproduced with permission. [243] Copyright 2019, American Chemical Society.

A series of water-stable MOFs (UiO-66, UiO-66-NH₂, MIL-101 and MOF-808) have been developed to remove MNZ molecules from wastewater [244]. In this work, studies have found that even though these MOFs had similar host-guest interactions and charge properties, they exhibited different adsorption capacities. Among them, the capturing ability of large-pore MIL-101 and MOF-808 was much lower than that of UiO-66-NH₂ and UiO-66. Based on this, it can be inferred that the adsorption sites are closer to each other in the microporous MOF, which facilitates the capture of guest molecules. In addition, the presence of amino groups enhances intermolecular hydrogen bonds and electrostatic interactions, resulting in more obvious adsorption capacity of UiO-66-NH₂ (265.5 mg g⁻¹) than UiO-66 (200.2 mg g⁻¹). Similar results were found by
Jhung et al. Even though the adsorptive capacity of melamine- and urea-MIL-101 to DMZ was higher than that of MIL-101 [245], it was still far less than that of MIL-53(Al) [246]. Consequently, the possible decisive factor for MOF to adsorb nitroimidazole molecules is the proper pore structure for host-guest interactions rather than the larger pore size and specific surface area.

3.3.3. Tetracyclines

Tetracycline antibacterials include tetracycline (TC), oxytetracycline (OTC) and tetracycline hydrochloride (TH). They are a class of drugs composed of four hexatomic rings and abundant functional groups, carbonyl and hydroxyl groups in particular. Such drugs can be used to prevent and treat biological bacterial infections. However, due to the slow metabolism and low absorption efficiency of these drugs, a large amount of them are released into the environment. MOF-based adsorbents have been widely used in the elimination of tetracycline antibacterials.

Studies have found that tetracyclines have three pKa values. When the pH of the solution is lower than pKa₁ (3.3), the molecules exist in a cationic state; when the pH is in the range of pKa₁~pKa₂, the zwitterion is the prime form; when the pH is higher than pKa₂ (7.5), the molecules mainly exist in an anionic state with the valence state of -1 or -2. It can be inferred that in the weak neutral and acidic environment (pKa₁~pKa₂), the existence of electrostatic repulsion would weaken the electrostatic interaction between the host and the guest. The study found that in this pH range, the main adsorption mechanism of TC on MOF-5 was the π-π interaction [247]. Besides, in the
study of the adsorption of TC molecules by water-stable Zn-MOF \([(\text{ZnCl}_2)_3(L)_2\cdot\text{DMF})_n\] (L = 1,3,5-tris(pyridin-4-ylsulfanyl)methyl)benzene)] (MOF 3), it has been confirmed that the pyridine and benzene rings of the MOF could adsorb TC molecules through π-π interactions and hydrogen bonds [248]. Moreover, the adsorption isotherms matched the Langmuir adsorption model well, and the adsorptive kinetics best fit the pseudo-second-order model. It is noteworthy that after the adsorptive experiment, the structure of MOF 3 remains intact, and even in a strong alkaline environment, MOF 3 still has great stability and maintains high adsorption capacity, which is a rare example of MOF playing a role in an alkaline environment. In addition, the large-channel hierarchical porous ZIF-8 (HpZIF-8-10 (1.5)) is superior to the microporous ZIF-8 (mZIF-8-10) in terms of the adsorption performance of TH molecules [249].

Tetracycline antibacterials have a large molecular size. Therefore, MOFs with large pores may be more advantageous. Mesoporous MIL-101(Cr) and its modified substances have attracted more and more attention due to its high water stability and large pores [250]. Two types of MIL-101 with different properties prepared by using HF and HCl as mineralizers were used to remove OTC in wastewater [251]. The results showed that although both types of MIL-101 have acid-base and π-π interactions, MIL-101 (HCl) with a larger specific surface area still has higher adsorption capacity (115.3mg g\(^{-1}\)) than MIL-101 (HF) (91.6mg g\(^{-1}\)). Therefore, this study is aimed at proving the significance of the specific surface area. In addition, amino-functionalized NH\(_2\)-MIL-101 is also used to eliminate TC in wastewater [252], but it exhibited smaller adsorptive capacity (50.8 mg g\(^{-1}\)). Although there are hydrogen bonds and π-π
interactions between the materials and TC molecules, the presence of amino-group limits the pervasion of TC into the internal cages, resulting in lower adsorption capacity. It is worth mentioning that Deng et al. discovered a new type of water-stable MOF-818, which has very large adsorptive capacity (442.5 mg g⁻¹) [253,254]. Thanks to its window size (3.1 nm) and large pore diameter (3.8 nm), MOF-818 is an excellent material for loading large-size molecules. Moreover, the adsorption of TC·HCl proved its water-phase adsorption capacity. The adsorption process involved various driving forces, including hydrophobic effect, pore-filling effect, chemical coordination, van der Waals force and π-π interaction. The authors suggested that this is because the large channels of MOF promote the mass transfer process. However, these strong interactions also make it difficult for TC molecules to desorb from MOF.

3.3.4. Others

In addition to the above-mentioned three types of antibacterials, β-lactams, nitrofurans and chloramphenicol antibacterials are also often used in daily life. However, while used for preventing and curing diseases, they also caused some pollution problems, especially the pollution of wastewater from the pharmaceutical industry. MOFs have great potential in dealing with these pollutions.

Cefradine (RAD) is a kind of typical β-lactam antibacterial. Due to its prime zwitterionic form in the weak acidic environment, it has no strong electrostatic interaction. Therefore, other types of driving forces are needed to achieve purification. A Zr-based MOF (PCN-222) has been discovered to possess the best adsorption
properties for RAD when the pH of the solution is 5 [255]. This is because of the "push-pull" effect, that is, RAD\(^+\) is firstly adsorbed on the surface of PCN-222 by interacting with the anion unit of RAD\(^-\), and then anionic unit of another RAD\(^+\) coordinates with the untapped cationic unit. Interestingly, the porphyrin-based ligand of this MOF is relatively cheap, and it has good reproducibility and negligible secondary pollution.

The adsorption removal of typical nitrofuran drugs such as nitrofurantoin (NFT) and nitrofuran (NZF), has been extensively researched. Two isostructural Zr-based MOFs, BUT-12 and BUT-13, all exhibit excellent performance in removing NFT and NZF but are slightly different [256]. The specific surface area of NFT is 3387 m\(^2\) g\(^{-1}\) while that of NZF is 3948 m\(^2\) g\(^{-1}\). The methyl groups enhance the hydrophobicity of the MOF and dents the coordination of the water molecule frames. It is worth noting that because the pore size of BUT-13 is larger than that of BUT-12, BUT-13 can better promote the diffusion of guest molecules and adsorb NFT and NZF faster. Besides, the water-stable Tb-MOF that can be used to adsorb and remove NFT and NZF has been intensively studied [257]. Tb-MOF contains two different large one-dimensional channels, quadrilateral pores (12.22 Å×19.21 Å) and rectangular pores (11.12 Å×13.23 Å). Due to its excellent pore structure, the material has high efficiency in removing NFT and NZF. Moreover, the MOF also has good recyclability. This is a rare adsorption example in rare earth metal-based MOF materials. These two studies are aimed at revealing the importance of the hydrophobicity and pores.

Chloromycetins such as thiamphenicol (TA) and chloramphenicol (CAP) have single pKa values and relatively larger molecular sizes, indicating that the macroporous
MOFs with opposite charge performance can be used to adsorb and remove them. PCN-222, which has abundant μ-OH groups and large one-dimensional channel, can be used for the rapid adsorption of CAP [258]. Since the pHpzc (pHpzc is the pH value when the zeta potential is zero) of PCN-222 is higher than the pKa value of CAP, the host-guest electrostatic interaction is induced. In addition to the synergy of the channel, the hydrogen bond interaction and the adsorption of CAP are strengthened. Therefore, the MOF showed excellent adsorptive capacity (370.0 mg g\(^{-1}\)) and fairly fast adsorption equilibrium (less than 60 s). Moreover, MIL-68(Al) with these properties also manifested the same high adsorption capacity, while MIL-101, MIL-101-NH\(_2\) and MIL-53 without these properties manifested inefficient adsorptions [258]. Therefore, these researches highlight the synergy between μ-OH groups and large one-dimensional channels.
Table 4
Information about the adsorptive removal of antibacterials by MOFs.

<table>
<thead>
<tr>
<th>Antibacteria</th>
<th>MOF</th>
<th>Metal center</th>
<th>Ligands</th>
<th>Adsorption capacity (mg g(^{-1}))</th>
<th>Removal efficiency (%)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFL</td>
<td>MIL-101-SO(_3)H</td>
<td>Cr</td>
<td>Monosodium 2-sulfoterephthalic acid</td>
<td>450.4</td>
<td>99.9</td>
<td>[238]</td>
</tr>
<tr>
<td>ENX</td>
<td></td>
<td></td>
<td></td>
<td>425.5</td>
<td>99.9</td>
<td></td>
</tr>
<tr>
<td>NOR</td>
<td>ZIF-8</td>
<td>Zn</td>
<td>2-Methylimidazole</td>
<td>408.2</td>
<td>99.9</td>
<td>[216]</td>
</tr>
<tr>
<td>NTR</td>
<td>ZIF-8</td>
<td>Cu</td>
<td>5, 5’-(4, 4’-(pyridine-3, 5-dicarboxyl) bis (azanediyl) bis (benzoyl) bis (azanediyl) diisophthalic acid</td>
<td>354</td>
<td>99.8</td>
<td>[239]</td>
</tr>
<tr>
<td>OFL</td>
<td></td>
<td></td>
<td></td>
<td>292</td>
<td>99.8</td>
<td></td>
</tr>
<tr>
<td>ENR</td>
<td></td>
<td></td>
<td></td>
<td>198</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>DMZ</td>
<td>MIL-53</td>
<td>Al</td>
<td>Terephthalic acid</td>
<td>467.3</td>
<td>98.5</td>
<td>[246]</td>
</tr>
<tr>
<td>MNZ</td>
<td>UiO-66-NH(_2)</td>
<td>Zr</td>
<td>NH(_2):H-BDC</td>
<td>265.5</td>
<td>99.7</td>
<td>[244]</td>
</tr>
<tr>
<td></td>
<td>UiO-66</td>
<td></td>
<td>Terephthalic acid</td>
<td>200.2</td>
<td>99.4</td>
<td></td>
</tr>
<tr>
<td>TC</td>
<td>MOF-5</td>
<td>Zn</td>
<td>Terephthalic acid</td>
<td>233</td>
<td>96.3</td>
<td>[247]</td>
</tr>
<tr>
<td></td>
<td>(ZnCl(_2):(L):D</td>
<td>Zn</td>
<td>1,3,5-tris(pyridin-4-ylthio)methyl)benzene), DMF</td>
<td>29.78</td>
<td>99.2</td>
<td>[248]</td>
</tr>
<tr>
<td>TH</td>
<td>HpZIF-8-10(1.5)</td>
<td></td>
<td>Poly(diallyldimethylammonium chloride), 2-methylimidazole (2-MIH)</td>
<td>49.3</td>
<td>98.6</td>
<td>[249]</td>
</tr>
<tr>
<td>OTC</td>
<td>MIL-101 (HCl)</td>
<td>Cr</td>
<td>Terephthalic acid, HCl</td>
<td>115.3</td>
<td>99.4</td>
<td>[251]</td>
</tr>
<tr>
<td></td>
<td>MIL-101 (HF)</td>
<td></td>
<td>Terephthalic acid, HF</td>
<td>91.6</td>
<td>99.5</td>
<td></td>
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<tr>
<td>TC</td>
<td>NH(_2)-MIL-101</td>
<td></td>
<td>NH(_2):H-BDC</td>
<td>30.8</td>
<td>53.3</td>
<td>[252]</td>
</tr>
<tr>
<td></td>
<td>MOF-818</td>
<td>Zr</td>
<td>1H-pyrazole-4-carboxylic acid (H(_2)PyC), trifluoroacetic acid</td>
<td>442.5</td>
<td>96.2</td>
<td>[254]</td>
</tr>
<tr>
<td>RAD</td>
<td>PCN-222</td>
<td></td>
<td>tetrakis (4-carboxyphenyl) porphyrin (TCPP)</td>
<td>333.33</td>
<td>99.5</td>
<td>[255]</td>
</tr>
<tr>
<td>NFT</td>
<td>Tb-MOF</td>
<td>Tb</td>
<td>1,3,5-tris (4-carbonylphenyloxy) benzene (H(_2)TCPB)</td>
<td>536.6</td>
<td>81.3</td>
<td>[257]</td>
</tr>
<tr>
<td>NZF</td>
<td>Tb-MOF</td>
<td>Tb</td>
<td>1,3,5-tris (4-carbonylphenyloxy) benzene (H(_2)TCPB)</td>
<td>557.0</td>
<td>84.4</td>
<td>[257]</td>
</tr>
<tr>
<td>CAP</td>
<td>PCN-222</td>
<td>Zr</td>
<td>TCPP</td>
<td>370</td>
<td>99.0</td>
<td>[258]</td>
</tr>
</tbody>
</table>

55
4. Conclusion and outlook

MOF is a new type of porous material. Owing to its distinctive structure and characteristics, it has always been a topic of great concern. This review mainly summarizes the applications of MOF membranes and MOF adsorbents in the elimination of many harmful substances in wastewater and discusses their separation mechanism, demonstrating their potential in becoming the next generation of the most popular separation materials for precise molecular/ion separation in environmental and energy related fields.

In recent years, MOF membranes have become more and more widely used in membrane-based liquid phase separation, particularly in WWT due to its highly adjustable pore structure and good compatibility. MOF, when used as a membrane filler or raw material in the membrane separation technology, shows good compatibility with the membrane, increases the selectivity and permeability of the composite membrane, and thereby can efficiently separate solvents, inorganic ions, small molecules, etc. from the wastewater. This article summarized the application of MOF membranes in NF, MF, UF, FO, and RO according to their different particle sizes. The membrane pervaporation technology uses the discrepancy in vapor pressure between the penetrate vapor and feed solution as the driving force. The membrane distillation technology uses the vapor pressure discrepancy consisting in both sides of the porous hydrophobic membrane as the driving force. These two technologies, when combined with MOF with both permeability and selectivity, can enhance the selectivity, permeability, hydrophobicity
and stability of the membrane. The high selectivity of water-stabilized MOF for WWT enables researchers to explore the probable development orientations of MOF composite membranes. At present, common water-stable MOFs can be classified into three categories: MOFs with metal azolate frameworks, MOFs with metal carboxylate frameworks composed of high-valence metals, and MOFs with special functions. As seamless combinations of fillers and polymers, MOFs still need to be explored and improved, and we are looking forward to the possible future directions of MOF membranes, as shown in the following four points.

(1) New multifunctional nanomaterials formed by applying MOF and other nanostructured compounds have great application prospects, because the merits of these two materials can coexist.

(2) To design membranes for wastewater treatment without changing their surface characteristics appears to be a comparatively large vacancy in the field of MOF membranes, which is a recommended direction for future research.

(3) Water stability of the membranes is a crucial consideration. The next step of researches can be transferred into exploring how to maintain the lasting stability of MOF membranes in complex conditions, such as high temperature, acidic or alkaline environments.

(4) Characterization technology is constantly evolving. The future trend is to characterize the performance of materials at a smaller level, especially to study the formation mechanism of materials by using in-situ characterization techniques, so as to obtain some outstanding and controllable MOF membrane materials.
MOFs have become a new generation of adsorbents. Some MOFs are very effective for WWT owing to their high adsorption capacity, quick adsorption kinetics and high selectivity to toxic materials. When used as adsorbents, MOFs can efficiently separate heavy metals, dyes, antibacterials and other pollutants from wastewater. Electrostatic interaction is the main mechanism of adsorption. The net surface charge carried by the MOF dispersed in the water phase interacts with the opposite charge (cation or anion) on the adsorbate to form chemical bonds, thereby strongly removing pollutants from the wastewater. In addition, some functionalized MOFs, such as sulfur-functionalized and amino-functionalized MOFs, can interact strongly with certain heavy metals, thus enhancing the adsorption capacity of MOFs for heavy metals. We are looking forward to the possible future directions of MOF adsorbents, as shown in the following four points.

(1) Functionalized MOFs are important adsorbents for removing pollutants. Their significantly enhanced adsorption capacity stems from their extremely ordered porous structures and functional groups, which can be controlled to improve the adsorption efficiency.

(2) By appropriately selecting metal ions and organic linkers/functional groups, and applying known synthesis strategies to adjust the porosity of such materials, it is expected that the adsorption kinetics of MOF can be further optimized.

(3) The direct structural information of the adsorbed compounds was obtained by single crystal X-ray crystallography. It is of great significance for determining the
adsorption mechanism, which in turn helps to design and adjust the structure of MOF adsorbent for specific adsorption purposes.

(4) Post-synthesis chemistry can also be used as a means to improve the adsorptive capacity of multifarious highly porous MOFs. The production cost of MOFs for adsorption is often considered. By developing fast and green methods (for example, hydrothermal and mechanochemical synthesis), the production cost of MOF can be reduced.

Water-stable MOFs have been widely used in wastewater treatment processes such as membrane separation and adsorption. However, the problems of poor stability, high cost, poor regeneration, and possible toxicity caused by MOFs in wastewater treatment in practical applications also bring great challenges for future research. All the research findings are required to be expanded from laboratories to large-scale productions and applications and to be friendly to the environment and society. Therefore, designing MOF materials that are economical and environmentally friendly at the same time is a considerable challenge and opportunity for the current use of MOFs in WWT. In addition, strategies such as post-modifications or design of novel MOFs may mitigate the toxicity of MOFs, while fine shaping techniques could also prevent the release of toxic substances during use. In conclusion, a series of MOFs seem to meet the requirements for actual wastewater treatment, manifesting the promising prospects of playing a core role in decontamination applications.
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Conflict of Interest

The authors declare no conflict of interest.

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Profile:

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2. The application of MOF membranes in membrane filtration, membrane pervaporation and membrane distillation are summarized.

3. The application and mechanism of MOF-based adsorbents for the removal of heavy metals, dyes and antibacterials from wastewater are summarized.

4. The current challenges and future development of MOF in sustainable wastewater treatment are discussed.
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.