

Recent progress in environmental applications of metal-organic frameworks

Jianming Liu, Meichen Chen and Haohui Cui

ABSTRACT

Nanomaterials have aroused the interest of many researchers and become a research hotspot in recent years and metal-organic frameworks (MOFs) included in that are a class of new organic-inorganic hybrid porous materials formed through the self-assembly of organic ligands and inorganic metal ions. MOFs have been attracting increasing attention due to their structural diversification, large specific surface area, high porosity, inerratic pore space framework. These characteristics play their advantages in different fields and make some excellent achievements. This article summarizes the research progress of metal-organic framework in the field of environment especially the remarkable achievements in adsorption and provides a clear help for understanding the research progress and prospects for future research.

Key words | adsorption, environment, metal-organic frameworks, nanomaterials

Jianming Liu (corresponding author)

Meichen Chen

Haohui Cui

Tianjin Key Laboratory of Aquatic Science and Technology, School of Environmental and Municipal Engineering,

Tianjin Chengjian University,

Tianjin, 300384,

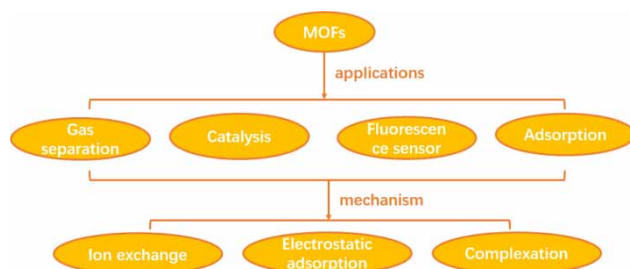
China

E-mail: ljs410rg@163.com

HIGHLIGHTS

- The application of metal-organic frameworks in various aspects is introduced.
- The application of metal-organic frameworks in adsorption is mainly introduced.
- Some suggestions on the improvement direction of metal-organic frameworks are provided.

GRAPHICAL ABSTRACT



INTRODUCTION

Nanomaterials have gradually become an important research field at the forefront of the national strategy since the 1970s. Highly ordered nano-porous materials such as various new zeolite (Fanta *et al.* 2019; Hui *et al.*

2019; Mahdi & Muraza 2019), carbon nanotube (Md Ariful *et al.* 2019; Wenyang *et al.* 2019), titanium dioxide nanotube (Jedi-Soltanabadi *et al.* 2018; Halit Levent Hosgun *et al.* 2019; Lopez *et al.* 2019), zinc oxide nanotube

(Elkady *et al.* 2017; Shuo *et al.* 2018), metal-organic framework (Ni *et al.* 2007; Xian *et al.* 2010; Sophie *et al.* 2012; Hoang *et al.* 2016; Mengyuan *et al.* 2018; Wang & Tang 2019), covalent organic framework (Jian-Xin *et al.* 2019; Meng *et al.* 2019), porous organic polymer (Tingting *et al.* 2018; Xiaokang *et al.* 2020; Xiaowei *et al.* 2020; Yadav *et al.* 2020) have been discovered one after another. The metal-organic frameworks (MOFs) became a hotspot for many scholars after the Yaghi research group first reported the MOF-5 with stable and high porosity in 1999. From then on, thousands of MOFs have been synthesized by researchers around the world. Their excellent performance has made great progress in gas separation, chemical catalytic sensors and adsorption, and has always attracted the attention of scholars. MOFs are a polymorphic topological structure formed by the self-assembly of metal ions/metal clusters and inorganic/organic ligands through coordination bonds. Compared to pure inorganic molecular sieves and porous carbon materials, MOFs have the following characteristics such as high porosity specific surface area and diverse structure, pure organic or organic-inorganic hybrid pore surface with more colorful surface physicochemical properties and some organic ligands with a certain flexibility over their long or single bonds. Moreover, MOFs can be modified to improve the porosity, thermal stability and catalytic properties by changing their metal ion centers or organic ligands or adding different groups. The adjustability of MOFs has more flexibility in adapting to different needs. In this paper, the environment applications of MOFs are introduced in detail, and a summary is given about the characteristics of each field. Finally, the existing problems and perspectives are discussed.

APPLICATIONS OF MOFS IN VARIOUS FIELDS

MOFs in gas separation

Methane, ethane, ethylene, acetylene and other light hydrocarbons play an important role in petrochemical industry. Ethylene, acetylene and propylene are widely used in the manufacture of ethanol, acetic acid and other important chemical products, as well as resin, rubber, and fiber synthesis. These light hydrocarbons are frequently obtained as mixtures, and their separation has been studied by many scholars. Belmabkhout and colleagues (Belmabkhout *et al.* 2018) introduced open metal sites in MOFs to obtain a very rare structural modification of ultrafine porous fluorinated MOFs. The main difference between the two structures (Figure 1) is the presence of uncoordinated Al^{3+} sites in AIFFIVE-1-Ni. AIFFIVE-1-Ni showed higher pore volume because of the presence of $[\text{AlF}_5]^{2-}$ inorganic pillar (after activation). It had higher capture potential for hydrocarbons than NbOFFIVE-1-Ni and also conduce to C_2H_2 interaction, resulting in selective enhancement of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ at low C_2H_2 concentration. Houxiao *et al.* (Houxiao *et al.* 2019) synthesized an In-soc-MOF-1 with good water stability and cycling performance to efficiently separate C_2H_6 molecules from the $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ mixture. The adsorption capacities of C_2H_6 and C_2H_4 were 4.04 and 3.72 mmol g^{-1} respectively at 298 K and 100 kPa. And note that the adsorption selectivity of $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ binary mixture gas (1:15, v/v) was 1.4. Therefore, In-soc-mof-1 could be considered as a selective adsorbent for $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ mixture in practical applications. XiuYuan *et al.* (XiuYuan *et al.* 2017) designed a Sr-MOF of an oxalic acid-containing ligand,

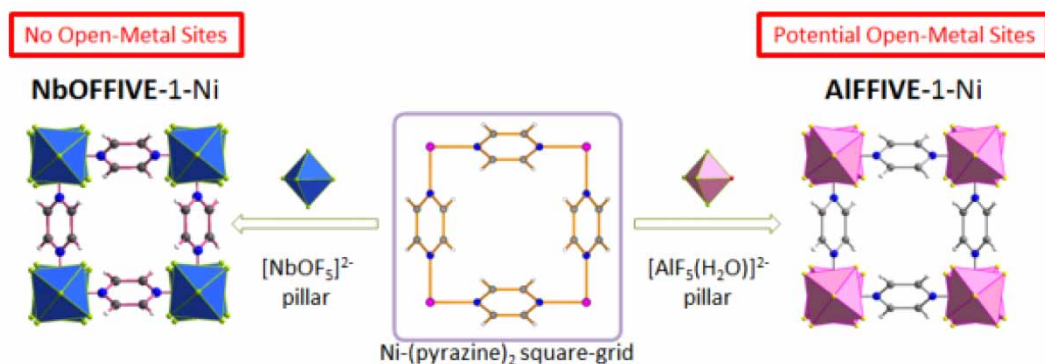


Figure 1 | Schematic showing the subtle difference in the crystal structures of NbOFFIVE-1-Ni and AIFFIVE-1-Ni-1 (Houxiao *et al.* 2019).

N,N'-bis(isophthalic acid)-oxalamide (H_4BDPO) with a structure of $\{[Sr(BDPO)_{0.5}(H_2O)].2H_2O\}_n$. A large number of Lewis acid metal sites and oxalamide groups are present in the Sr-MOF to modify the polar tubular channels. This material showed significant selectivity for both C_2H_6 , CH_4 and CO_2 , as well as CH_4 and CO . As is shown in Figure 2, the high Q_{st} value of CO_2 indicated that Sr-MOF had a strong affinity for CO_2 . The CO_2/CH_4 adsorption selectivity was 12.5 (Figure 2(b)) for the same molar mixture under 298 K and 1 atm. Similarly, the CO_2/CO and C_2H_6/CH_4 selectivity was 24.9 (Figure 2(c)) and 22.5 (Figure 2(d)), respectively. This high selectivity provided the possibility for the separation of light hydrocarbons in the future. Table 1 is a summary of some other MOF materials for light hydrocarbon separation. Although MOFs have obvious results in light hydrocarbon separation, many MOFs have poor structural stability, high cost and insufficient environmental protection, which become a huge obstacle to their further development.

MOFs in catalysis

Photocatalysis

Countries around the world are vigorously developing new energy sources such as solar, wind and nuclear energy to replace old energy sources and to cope with a series of huge challenges of energy shortages and environmental pollution caused by the rapid economic development. As an efficient and safe environmentally friendly purification technology, photocatalysis has an important application prospect in the fields of energy and environment by using solar energy to convert it into the energy needed for chemical reactions. In recent years, various catalysts with different structures have been developed to further improve photocatalytic activity. MOFs possess the superiority of diverse structure, functionalization and high porosity, showing great application potential in catalysis because of the excitation and transfer of photoelectrons by ultraviolet and visible light. Liangcheng *et al.* (Liangcheng *et al.* 2019) constructed Ag_3PO_4 and

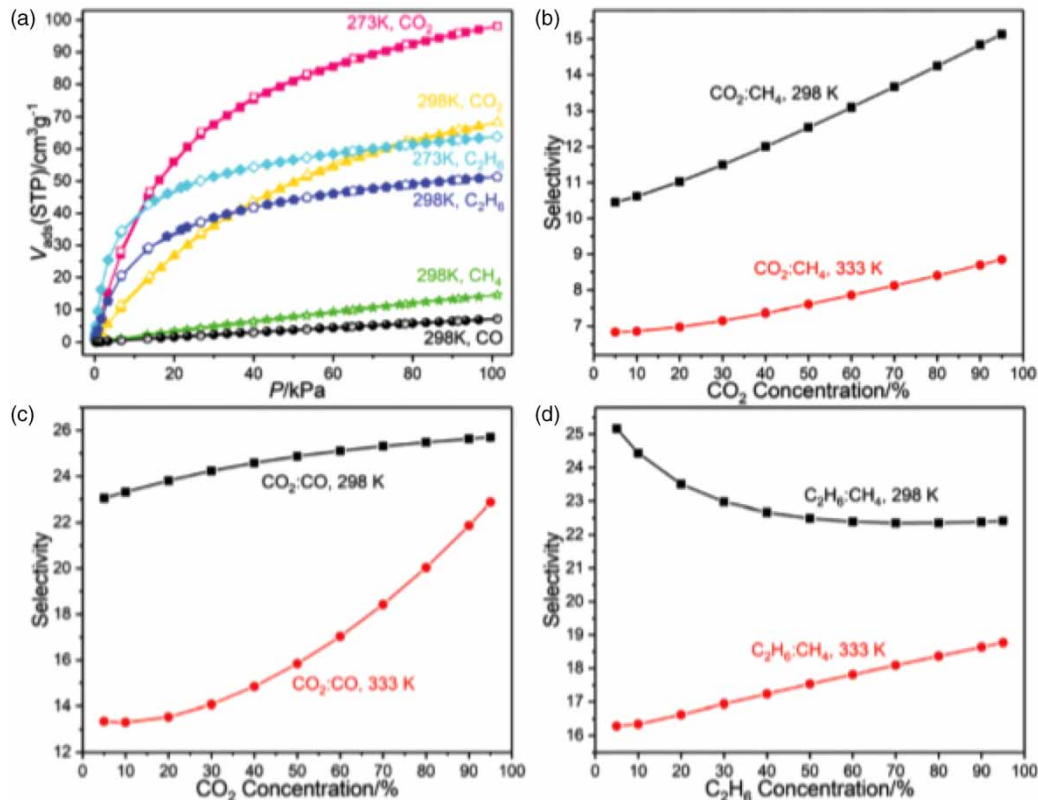


Figure 2 | Gas sorption isotherms of 1a for CO_2 , C_2H_6 , CH_4 and CO at 298 K and CO_2 and C_2H_6 at 273 K (a) and IAST adsorption selectivity of $CO_2:CH_4$ (b), $CO_2:CO$ (c) and $C_2H_6:CH_4$ (d) in 1a at 298 and 333 K with a diverse molar mixture (Zhenzhen *et al.* 2020).

Table 1 | The separation effect of other materials on gas mixture

MOF	Mixture	Selectivity value	Reference
ZJNU-15	C ₂ H ₂ /CO ₂	4.4	Zhenzhen <i>et al.</i> (2020)
	CO ₂ /CH ₄	5.0	
[Co ₃ (L)(OH) ₂ (H ₂ O) ₄] _n ·NMP·3H ₂ O	CO ₂ /CH ₄	5.0	Yunlong <i>et al.</i> (2019)
	C ₂ H ₆ /CH ₄	7.5	
Ni-MA-BPY	CH ₄ /N ₂	7.4	Xiaowei <i>et al.</i> (2019)
ZJNU-10	C ₂ H ₂ /CH ₄	29.9	Xiaoxia <i>et al.</i> (2019)
	CO ₂ /CH ₄	7.6	
[Zn(btzip)(H ₂ O) _{0.5}] _n ·H ₂ O	CO ₂ /CH ₄	7.0	Wen-Juan <i>et al.</i> (2020)
ZnZSM-5-pIM	CH ₄ /N ₂	8.44	Yaqi <i>et al.</i> (2019)
DMOF	C ₂ H ₂ /C ₂ H ₄	8.56	Yan (2016)
{[Zn(tztp)]·DMA} _n	C ₂ H ₆ /CH ₄	16.9	XiuYuan <i>et al.</i> (2018)
[Ni _{1.5} (4,4'-bipy) _{1.5} H ₃ L(H ₂ O) ₃](H ₂ O) ₇	H ₂ /CH ₄	2.25	Pal <i>et al.</i> (2017)
{[Co ₂ (SDB) ₂ (L)]·(H ₂ O) ₄ ·(DMF)} _n	CO ₂ /CH ₄	36	Qipeng <i>et al.</i> (2017)
	CO ₂ /N ₂	51.3	

MIL-53 (Fe) composite materials by in situ precipitation method and based on what to constructed z-scheme heterostructure. The construction of heterogeneous avoided the serious photocorrosion of Ag₃PO₄, and the charge transfer inside what could improve the separation efficiency of carriers. The composite material APM-3 with the optimal mass ratio of Ag₃PO₄ to MIL-53 (Fe) of 1:3 reached the best photocatalytic activity, the removal rates of antibiotics were 93.72% (TC), 90.12% (OTC), 85.54% (CTC) and 91.74% (DCL), respectively. Gomez-Aviles and his group (Gomez-Aviles *et al.* 2019) synthesized a Ti-Zr MOF by replacing part of Ti in NH₂-MIL-125 (Ti) crystal structure with Zr atoms. The lower the proportion of Zr, the clearer the crystal structure and the higher the photoactivity. The Ti-Zr MOF had a faster catalytic performance than any other catalysts they had tested, which could photocatalyze the degradation of acetaminophen (ACE) in 90 min. The results showed that O₂ was the main promoter of ACE photodegradation, although hydroxyl radicals and electrons generated by light play a catalytic role. As can be seen above, MOFs can be modified according to different requirements, such as introducing groups, changing metal centers and so on to improve the photoactivity of materials, so as to achieve high catalytic efficiency, which confirms its flexibility and has a broad application prospect in photocatalysis.

Electro-catalysis

Electrocatalysis is a catalytic action to accelerate the charge transfer reaction between electrode and electrolyte

interface. Selecting suitable electrode materials to accelerate the electrode reaction is the key factor to improve the overall performance of the battery. The selected electrode material acts as a catalyst in the electrical process, thus changing the reaction rate or electrode direction without qualitative change in itself. Therefore, it is a hot issue to research electrode materials in energy and environment. In electrocatalysis, MOFs can be used in hydrogen and oxygen production, oxygen reduction, carbon dioxide reduction and other directions. Songlin *et al.* (Songlin *et al.* 2019) synthesized Co-Fe alloy/N-doped carbon hollow spheres by dual-MOF-assisted pyrolysis approach. Co-Fe alloy nanoparticle composite had good catalytic activity to oxygen reduction reaction for its uniform distribution in porous N-doped carbon nanotubes. Figure 3 shows that the half-wave potential of Co-Fe alloy/NC-700 was 0.766v, and its Tafel slope was similar to that of Pt/C catalyst, which displayed the significant electrocatalytic activity of Co-Fe alloy/NC-700 sample. That might be attributed to the optimization of binding energy of O species via alloying Fe and Co in N-doped carbon matrix. Micheroni *et al.* (2018) reported the synthesis of Hf₁₂CoDBP/CNT for electrocatalytic proton reduction. The covalent bond between MOF and CNT improved the electrocatalytic activity by increasing the ratio of electrode surface area and active sites. In perchloric acid solution with pH = 1, Hf₁₂CoDBP/CNT had good electrocatalytic activity at an overpotential of 650 mV while the slope of Tafel was 178 mV dec⁻¹. They also added proton conduction Nafion into Hf₁₂CoDBP/CNT suspension.

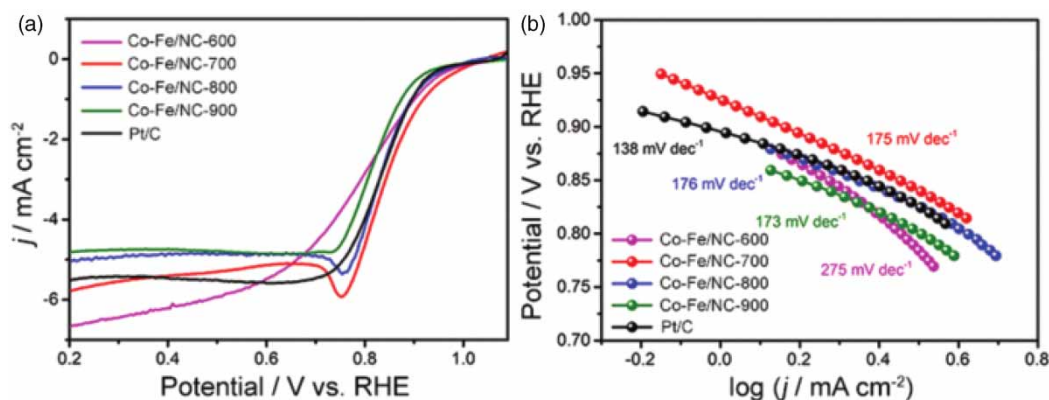


Figure 3 | Electrochemical performance evaluation of Co-Fe/NC composites prepared at different annealing temperatures of 600, 700, 800, and 900 °C. (a) Linear sweep voltammetry (LSV) curves in O₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹ at the rotating speed of 1,600 rpm. (b) Tafel slope curves (Songlin *et al.* 2019).

Experimental results showed that Hf₁₂CoDBP/CNT/Nafion not only had good electrocatalytic activity, but also had significant stability.

As can be seen from above, MOFs have more active sites and larger surface area, which makes them widely used in electrocatalysis. The recombination with other materials can improve its stability and thus enhance its electrocatalytic activity, which provides a direction for the development of electrocatalysis.

The excellent catalytic performance of catalysts could ease the environmental burden for saving raw materials and by-products generated in the production process. MOFs have a huge application prospect in organic synthesis catalysis owing to their highly tunable structure, high porosity and uniform distribution of catalytic activity sites. Du *et al.* (Miao *et al.* 2019) designed an MOF, having excellent physico-chemical stability and good catalytic performance. It could be employed for cyclic carbonate by perform cycloaddition reaction of epoxy compound and CO₂ without using cocatalyst at 100 °C and 1 atm. This method provided a new idea for solving carbon capture and designing MOFs with targeted functional sites for its advantages of low-cost and environmentally friendly. Hua *et al.* (Hua *et al.* 2019) prepared MnO_x-CeO₂-MOF via in situ pyrolysis of MOF-74 precursor. As soon as Ce was added, the surface area of the material was improved and the oxygen vacancy and oxygen storage capacity were enriched. The surface of Mn⁴⁺ was also a great contribution to the improvement of the catalytic activity of toluene oxidation. The T₅₀, T₉₀ values of MnO_x-CeO₂-MOF catalyst were 210 and 220 °C, respectively, and the apparent activation energy (E_a) was 82.9 kJ mol⁻¹, which was lower than other catalysts.

MOFs in fluorescence sensor

MOFs have attracted the attention of many scholars in chemical sensors with their unique photoelectric performance in recent years. MOFs have the following characteristics compared with other chemical sensors. They are reusable and can be selected by adjusting channel size. Specific groups can be introduced to achieve the detection of specific substances. MOFs based sensors typically exhibit solvent discoloration or vaporization, which relies on guest molecules to generate light signals providing a more direct and simple way to detect specific chemicals. This section mainly discusses MOFs' application in ion recognition, volatile organic compounds and gas detection, antibiotics and antibiotics, and phenolic compounds.

Ion recognition

With the rapid development of industry, wastewater containing iodide ions, heavy metal ions and other components is discharged into the environmental water bodies directly or indirectly. It is particularly important to detection of these ions for the harmful and unmanageable wastewater causing serious pollution to the environmental water body. Shi *et al.* (Erbin *et al.* 2019) impregnated MIL-101(Cr) with Bi and dropped it on the conductive carbon cloth electrode (CCE). Afterwards, bismuth was generated by electrochemical reduction of the Bi(III)/MIL-101(Cr) supported on CCE (Bi/MIL-101(Cr)/CCE). Trace amounts of Cd(II) and Pb(II) were detected by differential pulse anodic stripping voltammetry (DPASV) with detection limits of 60 and 70 ng L⁻¹, respectively. Bi/MIL-101 (Cr)/CCE had a broad application prospect due

to its wide linear range, low detection limit, good anti-interference and reproducibility. Zhiying *et al.* (Zhiying *et al.* 2019) synthesized a luminescent Eu-MOF using 4-(pyridin-3-yloxy)-phthalic acid (H₂ppda) and naphthalene-1, 4-dicarboxylic acid (H₂npdc) as ligands. The Eu-MOF had good fluorescence stability in aqueous solution with a pH of 2–13. It was a highly selective and sensitive luminescence sensor that could detect not only Fe³⁺, Al³⁺, Cr³⁺, but also PO₄³⁻ in various anions. MOFs, as sensors to identify ions, showing a wide linear range and strong selectivity, are worth exploring the luminescent sensor.

Volatile organic compounds and gas detection

Volatile organic compounds (VOCs) mainly come from coal chemical industry, petrochemical industry, fuel coating manufacturing, solvent manufacturing and other processes. As an important precursor of secondary pollutants such as fine particulate matter (PM_{2.5}) and ozone (O₃), they lead to urban haze and photochemical smog. Moreover, most VOCs are toxic, irritating, teratogenic and carcinogenic, with unpleasant odors. Especially benzene, toluene and formaldehyde will cause great harm to human health. Therefore, VOCs detection is a vital part of VOCs prevention and control project. Hromadka *et al.* (2018) used in situ crystallization technology to synthesize a VOC sensor based on long period fiber grating (LPG) by deposition of ZIF-8 thin film with controllable thickness on the surface of fiber LPG. The sensor worked accurately at phase-matching turning point (PMTP) by adjusting the grating period which greatly improved the sensitivity to analytes. The optimized sensor showed a sensitivity of 0.015 ± 0.001 and 0.018 ± 0.0015 nm/ppm and the limit of detection (LOD) were 6.67 and 5.56 ppm for acetone and ethanol, respectively. Yamagiwa *et al.* (2014) grew two MOF films from a COOH-terminated self-assembled monolayer onto the gold electrodes of sensor platforms, discussing the high sensitivity and selectivity detection of VOCs by the integration of MOF film and weight sensor platform. The VOCs detection method was proved by directly monitoring the adsorption kinetics of VOCs in MOFs by measuring the frequency change of the weight sensor modified by the porous MOF layer. In addition, the sensitivity and selectivity of MOF to VOCs sensing were enhanced by the large surface area and the regulated nanospace of the MOF layer.

MOFs not only achieve remarkable results in VOCs detection, but also have strong sensitivity to other gases. As one of the main pollutants in the atmosphere, SO₂ is the most common and irritating sulfur oxide, easily

dissolved in water to form sulfurous acid. In the presence of PM_{2.5}, sulfurous acid is oxidized to sulfuric acid, forming acid rain, and then causing serious pollution to the environment. Wang *et al.* (Meng *et al.* 2018) modified MOF-5 with amino functional groups to generate MOF-5-NH₂ and then detected SO₂ and its derivatives by luminescent paper in real time. The detection limit was about 0.168 ppm showing good selectivity and sensitivity. Electrons were transferred to the coordination metal ion (LMCT) by the amino group during the synthesis of MOF-5-NH₂. The LMCT effect was blocked a complex formed by the interaction of SO₂/SO₃²⁻ with amino groups and then the luminescence opening effect was caused. The higher the concentration of SO₂, the higher the luminescence degree of the luminescence test paper with 0.05 PPM of LOD luminescence concentration. H₂S, an acute highly toxic substance, is widely found in chemical production, such as mining and non-ferrous metal smelting. It is vital to detect for which has a strong stimulation effect on human central nervous system. Wu *et al.* (Xiaonan *et al.* 2019) fabricated ZIF-8 particle loaded ZnO (ZIF-8/ZnO) nanorod sensor capable of detecting H₂S at a level down to 50 ppb. The significant increase in the sensitivity of the sensor to H₂S was due to the increase in specific surface area and adsorption sites by ZnO surface-loaded ZIF-8 porous particles. Therefore, the ZIF-8/ZnO nanorod sensor had better gas adsorption and transduction functions. MOFs have high sensitivity and selectivity in gas detection, especially for some toxic gases such as VOCs and H₂S, which provides support for protecting people's health and is of great significance.

Antibiotics and phenolic compounds detection

On October 18, 2011, China's Ministry of Health said that the use rate of antibiotics in Chinese patients reached 70%, twice as much as in European countries, but less than 20% of the antibiotics were really needed. A large number of antibiotics that cannot be absorbed by people or animals were discharged into the environment as metabolites or even raw state, causing serious pollution to the environment. Liu *et al.* (Qiao *et al.* 2019) reported a nanoscale MOF(In-sbdc) with indium as the center and trans-4,4'-stilbenedicarboxylate (sbdc²⁻) as the ligand, which had specific response and effective spectral overlap to tetracycline (TC) type antibiotics. With the masking agent Na₂S₂O₄, the MOF could achieve selective sensing across a range of other types of antibiotics with detection limits of 0.28–0.30 μM. Yu *et al.* (2019) synthesized Zn-BTEC

and further explored the sensing performance of the Zn-BTEC as the probe to detect chlortetracycline (CTC) for sensitive detection. The results showed that Zn-BTEC could detect CTC selectively with a detection limit of about 28 nM. This was the first application of zinc-based metal-organic framework had been applied to fluorescence turn-on antibiotics detection based on aggregation-induced emission mechanism. The MOF showed no fluorescence itself while bright fluorescence upon the addition of traces of CTC which was thought to be the aggregation-induced emission of CTC when they defused and assembled in the MOF. More importantly, the MOF could distinguish CTC from other tetracyclines (TCs) antibiotics by showing special fluorescence emission wavelength and degradation characteristics and well applied in CTC detection including fish and urine.

Phenolic compounds can also cause great harm to the human body and the environment, even at very low concentrations. They remain in the environment for a long time due to the presence of aromatic rings in their structures, which are difficult to be degraded. Therefore, it is very important to develop a simple and effective detection technology. Jinson and his colleagues (Jinson *et al.* 2018) synthesized two multifunctional luminescent materials under different solvent thermal conditions, namely $\{[\text{Cd}_3(\text{BPDPE})(\text{BDC})_3 \cdot (\text{DMF})_2]_2 \cdot \text{DMF} \cdot 2\text{H}_2\text{O}\}_n$ (1) and $\{[\text{Cd}(\text{BPDPE})(\text{NDC}) \cdot (\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})\}_n$ (2) (BPDPE = 4,4'-bis(pyridyl)diphenyl ether, H₂BDC = 1,4-benzenedicarboxylate, H₂NDC = 2,6-naphthalenedicarboxylic acid). Complex 1 had stronger emission peaks. However, the absorbance of 2,4,6-trinitrophenol (TNP) was wide, and the range of the absorption spectrum was 300 ~ 500 nm when excited, which was consistent with the emission spectrum of complex 1. Therefore, fluorescence detection of TNP could be highly sensitive through luminescence quenching effect. MOFs show high selectivity in the detection of antibiotics and phenolic compounds, even in real samples such as fish, which can be used to detect the harmful substances in the environment.

MOFs in adsorption

Adsorption method has been widely used to deal with environmental problems. But the adsorption efficiency and range of use are determined by the selection of adsorbent. There are many problems about the traditional adsorbents such as low adsorption capacity, poor selectivity and difficulty in regeneration, so finding an adsorbent with high

efficiency and low energy consumption is the key to environmental protection.

Gas adsorption

H₂ and CH₄ storage. With the rapid development of industrialization and urbanization, energy demand is also rising steadily. Although coal is widely used, it inevitably produces more pollutants and causes serious environmental pollution problems. According to the 2018 China Ecological Environment Bulletin (Ministry of Ecological Environment of China 2018), coal consumption dropped 1.4% from 2017; consumption of clean energy, such as natural gas, rose 1.3% from 2017. In general, clean energy such as H₂ and CH₄ has been a powerful replacement for traditional fossil fuels. Hydrogen energy has the characteristics of abundant sources, good combustion performance, clean pollution and renewable energy. It is likely to be a significant energy source on the world energy stage in the 21st century. Methane as the main component of natural gas and is a clean and environmentally-friendly high-quality energy, which not only reduces the use of coal and oil, greatly improving the environmental quality, but also can be used safely at home and greatly improves the home environment. People are still faced with the transportation and storage of H₂ and CH₄ at normal temperature and pressure. Lestari *et al.* (Lestari *et al.* 2019) successfully synthesized Mg²⁺/HKUST-1 by in situ modification of HKUST-1 with Mg²⁺, leaving HKUST-1 structure unchanged. It was interesting to note that its surface area increased significantly from 713.283 m³g⁻¹ to 1,200.211 m³g⁻¹. Since the modified HKUST-1 had more binding sites and larger surface area, its hydrogen adsorption capacity increased to 0.292 wt% at 30 °C (1.2 bar) and 0.48 wt% at 80 °C (1.4 bar). Congcong *et al.* (2017) synthesized a series of new Zn₄O(-COO)₆-based mesoporous MOFs, which were named ST-1, ST-2, ST-3, and ST-4 respectively due to their similar structures but different topologies. It was found that the highest methane absorption rate of ST-2 was 324 cm³_{STP}/cm³, and the maximum transport capacity was 289 cm³_{STP}/cm³ under the conditions of 298 k and 250 bar. All previous records of porous materials had been surpassed. The ultra-high surface area and porosity of MOFs can enable them to absorb gas, but by design or structural modification. They can optimize the pore properties and functional sites, thereby improving the capacity of gas storage, and further promoting MOFs application in this respect, worthy of exploration.

CO₂ capture. Any gas in the earth's atmosphere that absorbs and releases infrared radiation and exists in the atmosphere is called greenhouse gas, mainly carbon dioxide, methane, ozone, nitrous oxide and so on. The increase of greenhouse gas concentration will lead to a series of serious natural environmental problems such as global warming, sea level rise and desertification. Although the greenhouse effect of carbon dioxide is relatively weak among all greenhouse gases, carbon dioxide is the most in the atmosphere, and its greenhouse effect accounts for about 60% of all greenhouse gases. In recent years, carbon dioxide capture and storage technology have attracted much attention of the international community. Adsorption method is considered as one of the effective methods to capture carbon dioxide owing to its low cost, low energy consumption and wide application range.

Yuanyuan and co-workers (Yuanyuan *et al.* 2019) fabricated three composites of Cu-BTC and porous carbon (OMC-Cu-BTC, AC-Cu-BTC and NC-Cu-BTC) exhibiting a synergetic effect. As an aside, the specific surface area and micropore volume of the composites were significantly higher than that of Cu-BTC and porous carbon matrix materials. This was because additional micropores were formed in the interfacial region between heterogeneous phases during synthesis of these composites, greatly improving the specific surface area and porosity. However, the CO₂ capacity of NC-Cu-BTC was the largest at 1 bar and 25 °C, which was 8.24 mmol g⁻¹ and 4.51 mmol g⁻¹, respectively. Mosca *et al.* (2018) prepared a novel material MOF M(BPZNO₂) (M = Co, Cu, Zn) (H₂BPZNO₂ = 3-nitro-4,4'-bipyrazole). The adsorption capacity of Zn(BPZNO₂) on CO₂ at 298 K and 1.2 bar was 4.95 mmol g⁻¹ due to the strong interaction between nitro group and C=O bond of CO₂, as well, the electrostatic interaction might involve the dipole moment of -NO₂ and the quadrupole moment of CO₂, so that the CO₂ adsorption rate was higher.

Wastewater adsorption

Organic wastewater. Pharmaceutical wastewater contains a variety of organic pollutants and complex components and its harm is deserved to be concerned. Since the introduction of penicillin in 1940, the abuse of antibiotic drugs has become a serious concern. Abazari *et al.* (2019) synthesized MOF samples, namely microchip, nanosheet and nanofilm by different chemical methods with the molecular formula of [Zn₆(IDC)₄(OH)₂(Hprz)₂]_n. Ampicillin, amoxicillin and cloxacillin antibiotics were adsorbed by the MOF nanometer tablets and nanometer flocculant. The removal rate

of antimicrobial molecules in amoxicillin, ampicillin and cloxacillin solutions with mass concentration of 60 ppm were 92.5, 88 and 89%, respectively, showing the highest adsorption capacity. Yu *et al.* (2020) synthesized MOF-525 and MOF-545 to remove sulfamethoxazole (SMX) from water. Both MOFs showed efficient adsorption capacities of 585 and 690 mg g⁻¹ for MOF-525 and MOF-545, respectively. The latter value exceeded the other adsorbents previously reported. The notable achievement provided the research direction for the future research of SMX removal.

Printing and dyeing wastewater is a kind of industrial wastewater with large water volume, high organic pollutant content, large alkalinity and great change of water quality. Jie *et al.* (Jie *et al.* 2018) synthesized a Zn-MOF with carbonyl group based on fluorenone-2,7-dicarboxylate ligand with high specific surface area and open channels. The MOF exhibited high selective adsorption for cationic dyes such as methylene blue (MB), rhodamine B(RhB), especially the maximum adsorption capacity of MB could reach 326 mg g⁻¹. This might be due to the remarkable adsorption capacity of mesoporous materials with appropriate pore size. Haichao *et al.* (Haichao *et al.* 2017) placed the synthetic PCN-222 in a single or mixed dye solution to do the adsorption experiment. In the single dye solution, the maximum adsorption capacity of anionic methylene blue (MB) was 906 mg g⁻¹, and that of cationic methyl orange (MO) was 589 mg g⁻¹. However, in the mixed dye solution of MB and MO, the adsorption capacity of the material increased by 36.8% (1,239 mg g⁻¹) to MB and 73.5% (1,022 mg g⁻¹) to MO. Hence, a push-pull mechanism was proposed to explain the enhancement of adsorption performance in the mixed dye solution. It was that MO could push MB dimerized, and MB dimer could pull MO together to adsorb on PCN-222, and vice versa. Additionally, the larger mesoporous size of PCN-222 provided a condition for the push-pull mechanism.

Phenolic wastewater, an important source of environmental water pollution, is one of the most harmful industrial wastewaters in the world. Phenols are found in many industrial wastes, such as gas, petroleum, chemical, organic synthesis, industrial plastics, etc. Wastewater discharged directly without treatment or irrigated farmland can contaminate air water, soil and food. Lin and Hsieh (Lin & Hsieh 2015) adsorbed p-nitrophenol (PNP) with a stable HKUST-1, and then explored the competitive adsorption of PNP and phenol on HKUST-1. The results showed that HKUST-1 could selectively adsorb PNP with adsorption capacity of about 400 mg g⁻¹. It was believed that the excellent adsorption performance was due to the great

interaction between PNP and HKUST-1 and the affinity of NO_2 of PNP to HKUST-1 copper. Ahsan *et al.* (Ahsan *et al.* 2019) synthesized MOF/graphene oxide and MOF/CNT-based hybrid composite nanocomposites Cu-BDC-GrO and Cu-BDC-CNT by single pot, green solvent-thermal method to adsorb bisphenol A (BPA). The results showed that the removal rates of BPA by these two composite materials were 182.2 mg g^{-1} and 164.1 mg g^{-1} , respectively, which was several times Cu-BDC's removal rate. The π - π interaction and h-bonding mechanism between BPA and mixed nanomaterials were considered to be the main adsorption mechanism.

MOFs have been widely used in organic wastewater adsorption, and the adsorption effect is very remarkable, which is mainly due to its variety, large pore volume and abundant pore channels. MOFs have the corresponding adsorption mechanisms for different organic pollutants, among which π - π interaction, electrostatic adsorption, hydrogen bond interaction and covalent bond play great roles.

Inorganic wastewater. Excessive discharge of phosphate into the water will lead to eutrophication of the water, even destroy the aquatic ecological balance. Nehra *et al.* (2018) prepared MIL-100 (Fe) for phosphate adsorption in aqueous solution with high specific surface area, non-toxic and biodegradable properties. The maximum adsorption capacity was 93.55 mg g^{-1} at neutral pH. One of the main factors of phosphate adsorption by MOFs might be the electrostatic interaction between MIL-100 (Fe) positively charged metal sites and phosphate. Selenium is an essential micronutrient for the survival of animals and humans. Excessive levels of selenium in water can lead to selenium poisoning. Importantly, water-soluble selenium is more toxic than elemental selenium, especially selenite. Shuo *et al.* (Shuo *et al.* 2019) prepared MOFs of MOF-802, UIO-66 and MOF-808 with different structures and then studied the adsorption behavior of Pd(II) anion (PdCl_4^{2-}) in acidic solution. The results showed that MOF-808 had the fastest kinetic speed and the strongest adsorption capacity for Pd(II), which might be due to the most convenient diffusion of PdCl_4^{2-} through the maximum pore of MOF-808. In contrast, MOF-802 had the lowest absorption rate of Pd(II) in the solution with low concentration of Pd(II) for the result of high binding energy (E binding) between the proton amine groups of MOF-802 and PdCl_4^{2-} .

At present, the emission of heavy metals, such as lead, mercury, cadmium and cobalt cannot be ignored. What is

different from other organic pollutants is that heavy metals are abundant in the environment and difficult to degrade. Some heavy metals are even toxic or carcinogenic, posing a certain threat to people's lives and health. Therefore, removing heavy metals becomes a necessary measure to protect human and environmental safety. Yang *et al.* (Yang *et al.* 2015) introduced $-\text{SO}_3\text{H}$ functional group into the pore surface of $\text{Cu}_3(\text{BTC})_2$, and the adsorption capacity of the synthesized MOF, $\text{Cu}_3(\text{BTC})_2\text{-SO}_3\text{H}$ on cadmium ions in aqueous solution was 88.7 mg g^{-1} . It also showed high selectivity in the presence of other metal ions such as Na^+ , Mg^{2+} , Ca^{2+} , Pb^{2+} , Cu^{2+} , and Ni^{2+} . $\text{Cu}_3(\text{BTC})_2\text{-SO}_3\text{H}$ could be easily recycled and utilized, and the adsorption rate could still be more than 85% after six cycles. Leus *et al.* (Leus *et al.* 2017) synthesized UiO-66-(SH)₂ with 2,5-dimercapto terephthalic acid and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. The adsorption performance of this MOF was significantly improved with the maximum adsorption capacity of Hg(II) being 236.4 mg g^{-1} . The results showed that the adsorption of Hg(II) was not affected by pH and potential interfering ions. What's more, the test of domestic sewage containing mercury showed that the water samples could be adsorbed and removed without any pre-treatment. Table 2 is the adsorption of heavy metal ions by other MOFs.

MOFs' application in inorganic wastewater treatment is also relatively stable. On the basis of raw materials, ions and some functional groups are introduced to promote ion exchange, electrostatic adsorption and complexation, thus improving the adsorption efficiency of pollutant ions. These are worthy of further study.

CONCLUSION AND PROSPECTS

MOFs have a very broad prospect in gas adsorption, chemical catalytic sensor and adsorption for the advantages of ultra-high specific surface area, ultra-high porosity, adjustable pore structure and excellent adsorption rate. And MOFs play a vital role in adsorption, especially gases and wastewater. However, a series of contradictions, such as high production cost, poor stability, environmentally unfriendly synthesis process and blocked industrial production, are also worthy of attention. Although the above problems have been solved to a certain extent with the in-depth study of MOFs, they still cannot be completely eliminated. Therefore, overcoming the shortcomings makes MOFs an excellent multi-functional material to solve more problems in application fields for people.

Table 2 | The adsorption of heavy metal ions by other MOFs

Adsorbents	Pollutants	q_{\max} (mg g^{-1})	Mechanisms	References
UiO-66-NH ₂	Au(III)	650	electrostatic attraction/complexation	Ziyong <i>et al.</i> (2020)
MIL-101-triglycine	Co(II)	232.6	coordination effect	Guoyuan <i>et al.</i> (2019)
PCN-221	Hg(II)	233	coordination bonds.	Hasankola <i>et al.</i> (2020)
PAN/chitosan/UiO-66-NH ₂ nanofibers	Pb(II)	441.2	chelating/electrostatic attraction	Jamshidifard <i>et al.</i> (2019)
	Cd(II)	415.6		
	Cr(VI)	372.6		
MOF-74-Zn	Hg(II)	63	coordination effect	Yang <i>et al.</i> (2017)
BUC-21/TNTs	Cr(III)	62.5	electrostatic interactions	Xun <i>et al.</i> (2019)
UiO-66-Schiff	Co(II)	256	coordination effect	Guoyuan <i>et al.</i> (2017)
HKUST-1	Cr(III)	24.2	electron sharing and transfer static interaction	Yang <i>et al.</i> (2019)
[Ni(3-bpd) ₂ (NCS) ₂] _n	Hg(II)	713	ion interaction	Shibashis <i>et al.</i> (2017)
UiO-66-EDTA	Eu(III)	99	coordination effect	Jin <i>et al.</i> (2019)
	Hg(II)	161.2		
	Pb(II)	153.8		
PAN – MOF-808 membrane	Cd(II)	225.05	ion interaction	Efome <i>et al.</i> (2018)
	Zn(II)	287.06		
BUC-17	Cr(VI)	121	electrostatic interactions	Jie <i>et al.</i> (2019)

DECLARATIONS

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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