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Review Paper

Research Progress on Adsorption of Heavy Metal Ions in Water by Metal-Organic Framework Materials

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Abstract. Metal-organic frameworks (MOFs) are a class of newly developed lattice compounds that spontaneously organize from organic linkers and metal nodes. Their exceptionally high porosity and vast internal surface make them attractive candidates for tasks such as gas storage, molecular separation, and as supports for catalytically active species. This overview consolidates representative water-compatible metal-organic frameworks and charts recent strategies for tailoring their affinity toward dissolved heavy-metal contaminants. Emphasis is placed on how post-synthetic ligand functionalization and the integration of MOFs into hybrid matrices decisively amplify uptake efficiency. The preparation and modification of MOF materials for the removal of heavy metal ions in water are promising. Nevertheless, before MOFs can be widely deployed as practical sorbents for water purification, two critical bottlenecks—elevated synthesis costs and limited long-term structural robustness under aqueous conditions—must still be overcome. There is still a long way to go for the engineering application of MOF materials.

Keywords: *Metal-organic framework; adsorbent; heavy metal ions; modification*

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1 Introduction

Metal-organic frameworks crystallize when metal nodes or clusters coordinate with O- or N-donor bi- (or multi-)dentate linkers in a self-assembly process, yielding architectures that combine exceptionally low framework densities with vast internal surfaces and expansive void fractions (Figure 1). This emergent family of porous solids is further distinguished by an extraordinarily broad structural repertoire. The variety of metal ions and organic ligands, as well as differences in coordination numbers, contribute to the structural diversity of MOFs. Owing to their distinctive characteristics, MOFs are emerging as attractive candidates across a spectrum of disciplines, notably heterogeneous catalysis, gas sorption, and molecular sieving [1].

The rapid development of Chinese society has been accompanied by increasingly severe water pollution problems. Heavy-metal contamination of aquatic systems has become one of the most pressing environmental threats. Among the available countermeasures—membrane filtration, biosorption, and adsorption—are the most frequently cited options for stripping dissolved toxic metals from water [2–5]. This article focuses on the adsorption method. Adsorption offers advantages such as low cost and convenient operation. Conventional porous sorbents—activated carbons, graphene derivatives, and bulk metal oxides—have been scrutinized extensively for sequestering aqueous heavy-metal ions, yet their practical uptake capacities remain modest.

Recently, metal-organic frameworks (MOFs) have emerged as a novel class of adsorbents, drawing considerable research interest for their potential in heavy-metal remediation [6,7]. Compared to traditional heavy metal adsorbents, MOF materials possess characteristics such as a large specific surface area and the ability to customize specific functional groups for targeted heavy metals, thus demonstrating excellent adsorption capabilities. This paper can provide reference and guidance for the design of MOF materials for the efficient removal of heavy metal ions [8].

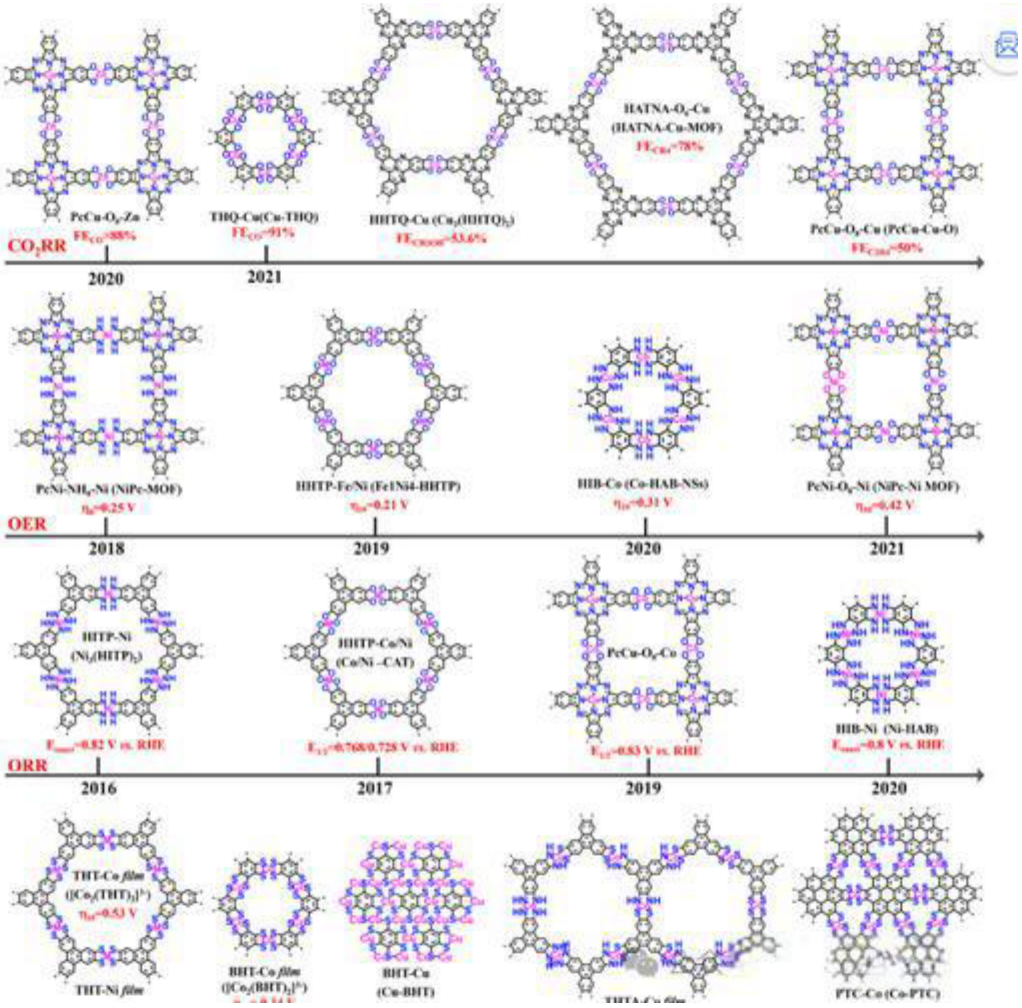

Figure 1 Schematic diagram of metal organic framework MOFs structure

2 Introduction to Metal-Organic Framework (MOF) Materials

MOF materials have the following advantages:

Diversity: MOFs are built from metal clusters stitched together by organic linkers; because the library of available linkers is vast, the resulting crystalline networks exhibit extraordinary compositional and structural diversity [9].

Highly Tunable Surface Chemistry: Targeted functional groups can be anchored onto the MOF backbone, allowing selective recognition and capture of particular metal ions from aqueous media [10].

Large Specific Surface Area: The specific surface area of traditional resin-based porous materials is usually less than 100 m^2/g, whereas most MOF materials can achieve a specific surface area exceeding 1000 m^2/g, providing a significant advantage as adsorbents for heavy metal ions in water [11,12].

Considering the water treatment process, MOF materials used as adsorbents should exhibit excellent water stability. In addition, heavy-metal uptake by MOFs is generally governed by the Hard-Soft Acid-Base principle: hard acid cations prefer hard basic sites within the framework, whereas soft acids partition to soft donor centers.Next, MOF materials will be categorized and introduced based on the valence state of the metal ions in the metal clusters [13].

2.1 Tetravalent Metal-Based MOF Materials

The most common tetravalent MOF materials are Zr-based MOFs [14-16], represented by UiO-66 and MOF-808.

Research by Jrad et al. has shown that UiO-66 possesses high chemical and thermal stability. Additionally, UiO-66 has nanostructural defects. Defect engineering offers a handle for tailoring the physicochemical profile of UiO-66 while leaving its principal building blocks untouched.The metal ions in the metal clusters of UiO-66 are not prone to leakage in water, and it has a large specific surface area, making it suitable for modification to improve its adsorption of heavy metal ions in water. For instance, Agnieszka's team appended thiomalic acid (MAA) to UiO-66, pushing its Hg^{2+} uptake to 332 mg g^{-1} in aqueous media, whereas Zhang et al. exploited UiO-66 and its mono- or dicarboxylated analogues (UiO-66-COOH and UiO-66-$(COOH)_2$) to sequester Th^{4+} from nuclear wastewater, attaining capacities as high as 250 mg g^{-1}.

MOF-808 was first prepared and reported by Yaghi and co-workers in 2014 .It is formed by connecting trimesic acid with Zr-based metal units. Two micropore sizes (1 nm and 1.8 nm) are observed in MOF-808. Furthermore, MOF-808 features a large specific surface area and easily functionalizable groups. Based on this, Peng Yaguang et al. designed and synthesized MOF-808-TGA and MOF-808-AA-EDT.

Other tetravalent MOF materials also exist, such as Ti-based MOFs represented by MIL-125. MIL-125 was first synthesized by the Ferey group in 2009.

2.2 Trivalent Metal-Based MOF Materials

MIL-53(Al), first synthesized by Loiseau and his team in 2004, exhibits a significant breathing effect. The internal structure of MIL-53(Al) can expand or contract under external stimuli, and it can return to its initial state once these stimuli are removed [17-20]. For example, when MIL-53(Al) contains water molecules, hydrogen bonding can cause its core structure to transition from a larger pore size to a microporous form.

Current research shows that most MOF materials possess a microporous structure. The framework's aperture acts as a molecular gate, sterically excluding bulky species and thereby limiting their competitive blocking of active sites during heavy-metal capture. Exploiting this size-exclusion feature to maximize uptake is now a vibrant research frontier. MIL-53(Al) exemplifies this strategy: its wide channels welcome hydrated metal cations, whereas the narrower micropores filter out larger organic contaminants, suppressing background interference.Furthermore, MIL-53(Al) exhibits excellent thermal stability, allowing the material to maintain its original crystal structure under high-temperature conditions. NH_2-MIL-53(Al) is also a unique flexible MOF whose pore structure can expand or contract with changes in pressure or temperature, known as the "gate-opening" effect.

Besides Al^{3+}-based trivalent MOFs, Cr^{3+}-based trivalent MOFs have been widely studied in recent years. Studies reveal that MIL-100(Cr) and MIL-101(Cr) both possess extra-large apertures, with diameters spanning 2.5–3.4 nm—dimensions that readily accommodate hydrated heavy-metal ions and their coordination shells. MIL-100(Cr) possesses high water stability and can serve as an efficient adsorbent for removing pollutants from water. MIL-101 can also stably exist in aqueous solutions. Moreover, the terminal ends of the secondary structure units in MIL-101(Cr) contain two water molecules, which are easily replaceable by other ligands. This characteristic makes it an excellent candidate for modification.

2.3 Divalent Metal-Based MOF Materials

In 1999, Yaghi et al. synthesized MOF-5 using $Zn(NO_3)_2 \cdot 4H_2O$ and terephthalic acid (H_2BDC). This material has a very high specific surface area, but its framework collapses when exposed to humid air. Subsequently, guided by the theory of reticular synthesis, the research team selected the $[Zn_4O(CO_2)_6]$ cluster with an octahedral structure as the basic building unit. By adjusting the R-group types in the ligands, they successfully synthesized a series of MOF compounds with similar topological structures, named IRMOF-n (n=1–16). The pore size of the IRMOF series compounds can be increased to 2.88 nm, and the porosity can be increased from 55.8% to 91.1%, far exceeding traditional materials like zeolites. The metal centers of divalent MOF materials are usually Zn and Cu. The internal structure of these materials is typically rigid and not easily altered by external stimuli. The adsorption of heavy metal ions is related to the specific structure of the synthesized MOF material [21].

Among Zn^{2+}-based divalent MOF materials, the ZIF series materials researched and synthesized by Yaghi et al. are the most classic. ZIF-8, discovered in 2006, is the most representative MOF material in the ZIF series. This MOF is synthesized from $Zn(NO_3)_2·4H_2O$ and 2-methylimidazole. The synthesis conditions can be at room temperature or under hydrothermal conditions. Synthesis at room temperature usually takes from a few minutes to several hours, while the hydrothermal method typically requires several hours to days. The particle size of the ZIF-8 product ranges from tens of nanometers to several hundred nanometers depending on the preparation conditions. It exhibits excellent thermal stability, hydrothermal stability, and solvothermal stability.

Besides Zn^{2+}-based divalent MOFs, researchers have also developed Cu^{2+}-based divalent MOF materials. Cu-BTC (also known as HKUST-1), synthesized by Williams and his team, has received widespread attention. The framework is synthesized under solvothermal conditions (180 °C, 12 h) by combining trimesic acid with copper(II) nitrate in an ethylene glycol–water solvent mixture. This MOF has a "pore-cage-pore channel" structure, presenting a three-dimensional interpenetrating square shape with a pore size of approximately 0.95 nm × 0.95 nm and a specific surface area as high as 692.2 m^2/g. Thermogravimetric analysis and high-temperature single-crystal diffraction experiments show that Cu-BTC remains stable up to 240°C. However, Cu-BTC has poor stability in aqueous environments.

Wang et al. used 1,2-ethanedithiol to post-modify $Cu_3(BTC)_2$ to improve its adsorption capacity. First, thiol groups were introduced into the unsaturated metal sites of the material. Then, H_2O_2 was used to oxidize the -SH groups to $-SO_3H$ active groups, ultimately obtaining the modified $Cu_3(BTC)_2-SO_3H$ material, which can effectively capture Cd^{2+} from water.

3 Preparation and modification of MOF Materials

MOF synthesis is being relentlessly refined: metal-oxo clusters are paired with purposely engineered, functionally decorated linkers, enabling precise control over both surface area and architecture. Synthetic toolkits now span solvothermal/hydrothermal, ultrasound-promoted, electrospinning, and microwave-assisted protocols (Figure 2). Among them, hydrothermal or solvothermal routes still dominate [54–56]; their elevated temperature–pressure regimes accelerate kinetics and open access to frameworks that are unattainable under ambient conditions. However, MOFs have drawbacks such as inherent instability, microporous structures, and collapsible spatial frameworks, necessitating further exploration of their preparation methods [22-25].

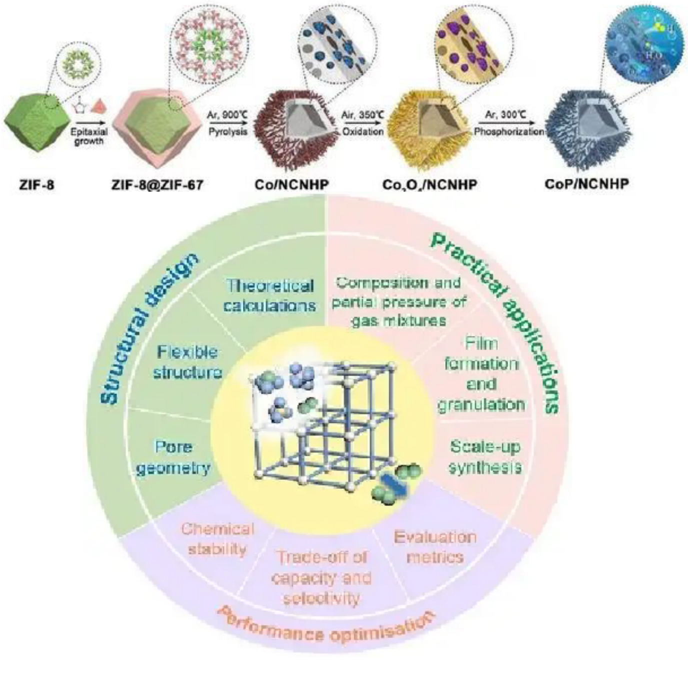

Figure 2 Preparation and utilization of MOFs

3.1 Post-treatment Methods

Post-synthetic maneuvers—chemical etching, sulfurization, or controlled calcination—transform parent MOFs into porous carbons, metal oxides, or metal sulfides while preserving the precursor's morphology [26]. Each post-treatment route bestows a unique set of attributes. Carbonizing the linker network boosts electronic conductivity and seeds extra-active sites, while the retained pore geometry and particle shape shorten diffusion paths, enlarge the interfacial area, and reinforce mechanical robustness.

3.2 Direct Mixing Methods

Although MOFs exhibit ultra-high surface areas, open porosity, and a versatile ligand palette that make them attractive sorbents [27,28], their practical use is hampered by intrinsic mechanical fragility, a powder-like morphology, poor shaping ability, and limited chemical stability. Despite their record internal areas, accessible pores, and tunable linker chemistry—assets that position MOFs as promising adsorbents [27,28]—these crystals remain intrinsically brittle, difficult to shape, and vulnerable to both mechanical and chemical breakdown, factors that severely restrict large-scale deployment.

3.3 In-situ Growth Methods

In-situ nucleation anchors MOFs directly onto supports, yielding films or particles that are uniformly dispersed, tightly bonded, and mechanically reinforced relative to their unsupported counterparts [29]. MOFs are mounted on supports via solvothermal deposition, vacuum seeding, or simple impregnation, yet these layers often delaminate because interfacial adhesion is weak or mass transport is restricted. Pre-anchoring metal precursors across both the exterior and interior of the support creates well-dispersed nucleation points; subsequent exposure to linker solution then drives heterogeneous MOF crystallization exactly at these grafted sites, locking the framework to the substrate.

3.4 Electrochemical Growth Method

The electrochemical growth method is not only capable of large-scale production of MOF powders but also serves as an effective technique for preparing thin films and coatings.Although solvothermal, vacuum, or impregnation routes are commonly used to coat supports with MOFs, the resulting films frequently peel off because the interface is poorly bonded and mass-transfer limitations starve the growing crystals. By first tethering metal ions throughout the external and internal surfaces of the host, discrete nucleation centers are created; subsequent contact with a linker solution triggers site-specific crystallization, mechanically stitching the MOF layer to the substrate. Electrochemical routes fall into three variants—anodic electrodeposition (AED), cathodic electrodeposition (CED), and electrophoretic deposition (EPD). AED and CED grow MOFs directly on the conductive substrate, whereas EPD assembles pre-formed MOF crystals into a film.

3.4.1 Anodic Electrodeposition (AED)

During AED, the anodic dissolution of a sacrificial metal plate releases metal ions that react with the dissolved linker at the electrode–electrolyte interface, precipitating a MOF layer. Yao et al. [14] exploited this principle by immersing a GO@AAO membrane in a linker–electrolyte bath and applying an anodic bias, thereby growing the framework directly on the conductive surface. At 50 °C and 2 V, HKUST-1 crystals nucleated on the GO-coated AAO; after ethanol-assisted delamination and 12 h vacuum drying at 60 °C, a free-standing HKUST-1@GO membrane was harvested. Experimental tests indicated that this membrane exhibited significant improvements in elastic modulus, hardness, and CO_2 selectivity compared to the original MOF material.

3.4.2 Cathodic Electrodeposition (CED)

CED forms MOF crystals on a substrate by deprotonating the linker through electrochemically generated hydroxide anions (in the presence of metal ions in the electrolyte). CED has garnered widespread attention from researchers due to its ease of operation and mild synthesis conditions [15]. However, MOF membranes prepared by CED often face issues of co-precipitated impurities. To address this, Xie et al. [16] investigated the application of hydrogen peroxide-assisted cathodic electrodeposition for preparing MOF membranes. Using a hydrogen peroxide-assisted method at an applied voltage of 1.6 V, they deposited a Cu-BET film onto an ITO substrate. A Cu-BET film was obtained after 10 minutes of deposition, and the purity of the film prepared by this method was significantly improved.

3.4.3 Electrophoretic Deposition (EPD)

Electrophoretic deposition (EPD) exploits the migration of charged, pre-synthesized MOF crystallites toward an oppositely biased electrode, where they accumulate and coalesce into a uniform film; this approach is especially popular for fabricating ZIF-8 coatings. Cationic ZIF-8 nanograins migrate to and anchor on the cathode, and further nucleation/crystal growth is spatially restricted to this interfacial zone, enabling defect-thin ZIF-8 skins [17]. Ji et al. leveraged this effect, fabricating a 300 nm ZIF-8 membrane on a bare, non-conductive support in a single step (0.65 mA cm^{-2}, 60 min). Moreover, both defect density and film thickness can be tuned on demand by simply varying the bath composition, deposition duration, or the polarity/duty cycle of the EPD waveform.

3.5 Green Synthesis/Scalable Preparation

Green-MOF research targets synthetic protocols that are benign by design: non-toxic building blocks, eco-friendly solvents, ambient or low-energy conditions, and negligible waste generation. Whenever possible, pair non-toxic metal hydroxides/oxides with protonated linkers in water; this route eliminates corrosive by-products like HCl or HNO_3 and leaves only water as the waste stream, maximizing atom economy. Because oxides and hydroxides are sparingly soluble, while acetate or other benign salts supply metal ions sluggishly, mechanochemistry—solvent-free or minimal-liquid ball-milling—has become the method of choice. Even so, the organic linker ultimately dictates framework topology and function, so its green credentials and structure-directing power remain the pivotal design variables.

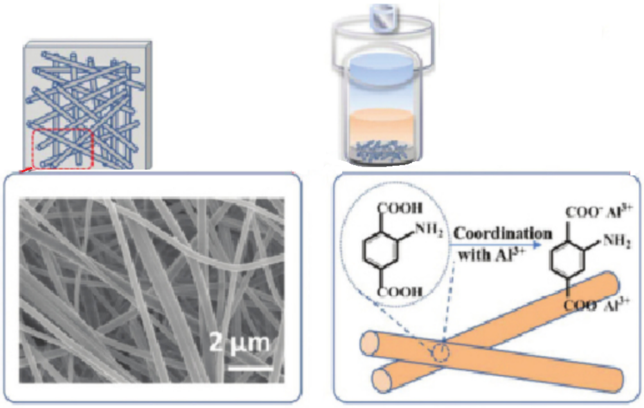

Figure 3 Modification of MOFs for the application in heavy metal ions adsorption

3.6 Grafting Functional Groups

Grafting functional groups is a common modification method (Figure 3). This can be achieved by coordinating functional groups to replace ligands in the MOF material. Peng Yaguang et al. immersed solid MOF-808 samples in sulfuric acid solution to obtain MOF-808-SO_4. The modified MOF material had a saturated adsorption capacity for Ba^{2+} of 131.1 mg/g at 298 K and exhibited excellent water stability [30].

From the perspective of post-modifying the metal clusters, functional groups can also be grafted onto the unsaturated sites of the metal clusters. Based on the coordinative exchange property of formate on the Zr metal clusters in MOF-808, Peng Yaguang et al. introduced 2-aminoethanethiol into MOF-808, designing and synthesizing MOF-808-AA-EDT. Based on the HSAB theory, it was found that functional groups containing S have a significant chelating effect with Hg^{2+}. The MOF-808-AA-EDT material achieved a remarkably high saturated adsorption capacity for Hg^{2+}, reaching 1077 mg/g [28].

3.7 MOF-Based Composites

MOFs are typically nanoscale or micron-scale powder materials. Employing MOF powders directly in large-scale sorption processes leads to severe aggregation, cumbersome solid/liquid separation, and the risk of particle breakthrough [31]. Fu et al. locked thiol-functionalized Zr-MOF crystallites inside an elastic, macroporous sponge scaffold, yielding a monolithic sorbent that removes Hg^{2+} while eliminating both fines loss and the need for downstream filtration. To overcome the handling limitations of MOF powders, Fu et al. embedded thiol-grafted Zr-MOF particles within an elastic, macro-porous sponge matrix. The resulting monolith captures Hg^{2+} quantitatively while preventing particle breakthrough and eliminating any solid–liquid separation step. The MOF-based sponge material achieved a saturated adsorption capacity for Hg^{2+} in water of 954.7 mg/g, whereas the -SH containing Zr-MOF powder had an adsorption capacity of only 589.1 mg/g for Hg^{2+} in water.

The above research indicates that MOF materials can serve as efficient adsorbents for heavy metals. However, shortcomings such as the easy agglomeration and difficult separation of MOF particles hinder their application. Moreover, the aggressive acidic or alkaline media often used to desorb captured metals can hydrolyze the framework, causing permanent loss of crystallinity and a sharp drop in cycling performance [19].

4 Adsorption of Heavy Metal Ions by MOF Materials

The uptake performance, kinetics, selectivity, thermodynamics, lifetime, and chemical robustness of MOFs are governed in concert by their hydrophilicity, framework regularity, surface functionality, specific area, pore hierarchy, and particle dimensions [32].

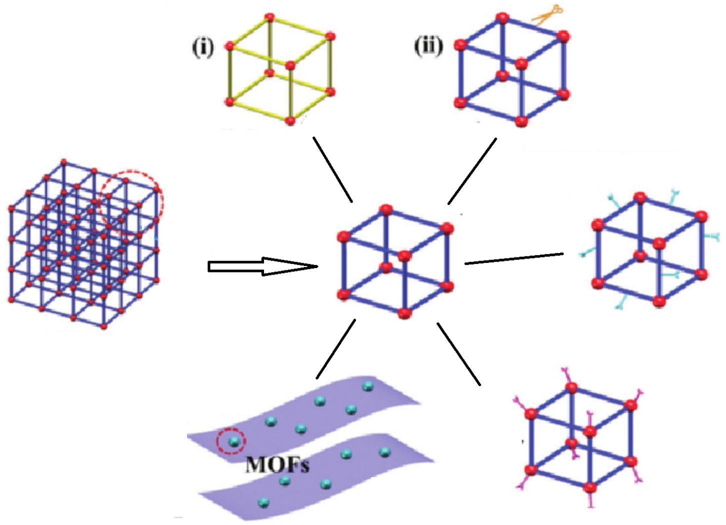

Figure 4 The adsorption capability of MOFs towards heavy metal ions

Five complementary levers (Figure 4) can boost MOF uptake:(i) **Extended bio-based linkers** – Frameworks such as UiO-68, UiO-67 or NU-1000 assembled from long, naturally derived struts generate wider channels that accelerate metal-ion diffusion and raise ligand density for binding. The drawback is high cost and limited commercial supply of these bespoke linkers.(ii) Defect engineering – Adding monocarboxylic modulators during synthesis creates missing-cluster or missing-linker defects that enlarge pores, expose internal functional groups and boost hydrophilicity, all at a fraction of the cost of elongated linkers (e.g., defect-laden UiO-66).(iii) Linker functionalization with natural analogues – Substituting part of the original linker with a bio-sourced variant bearing –SH, –OH or $–NH_2$ side chains introduces selective chelating sites without altering standard synthesis conditions, enhancing both capacity and selectivity.(iv) Metal-node modification – Employing metal precursors pre-grafted with target molecules incorporates functionality directly at the node, offering an orthogonal handle for metal-ion recognition.Liang et al., for example, anchored the soft donor $Co(NCS)_4^{2-}$ at open metal sites; the exposed sulfur atom binds Hg(II) with high affinity [185]. Post-synthetic ligand exchange or cluster modification is therefore the method of choice when bulky functional groups cannot be incorporated during initial synthesis—

the lower steric congestion around the node makes metal-bound reactants far more labile than linker-tethered ones. (v) **MOF–guest hybrids** – Embedding the framework within magnetic beads, carbon mats, or polymer fibers merges its intrinsic porosity with external functionality (e.g., effortless magnetic recovery). Kim et al. demonstrated this concept by pelletizing Cu-MOF-74 with γ-Fe_2O_3 nanoparticles; the resulting composite selectively scavenges Cd^{2+} from wastewater and is collected in seconds with a simple magnet [186]. MOF-74 is widely used in various applications, including gas storage, owing to its high surface area and honeycomb-like structure. Copper, a transition metal capable of existing in zero-, mono-, or divalent states, allows Cu-MOF-74 to serve as a stable redox-active material following redox reactions. The use of MOF crystals is advantageous because copper primarily exists in the divalent form (Cu^{2+}), which can readily undergo conversion to Cu^+ during cathodic processes, enabling stable adsorption and desorption of cadmium cations.

With the rapid development of industry, water pollution issues have gradually attracted people's attention. Thanks to their straightforward handling and almost limitless tunability, MOFs have moved to the forefront of sorbents for aqueous heavy-metal cleanup (Table 1). In a representative study, Zhang et al. compared UiO-66 with its dicarboxylated analogue UiO-66-$(COOH)_2$ and found that the grafted carboxylates boost Th^{4+} uptake capacity, highlighting how simple linker functionalization can translate directly into superior remediation performance. UiO-66-$(COOH)_2$ delivered a saturation loading of 360 mg Th^{4+} g^{-1}—among the highest values ever reported for solid sorbents—whereas the parent UiO-66 was essentially inert toward thorium, underscoring the decisive role of surface carboxyl groups.FTIR and XPS analyses revealed that Th^{4+} binding on UiO-66-$(COOH)_2$ proceeds via bidentate chelation between the pendant –COOH units and the actinide cation. Likewise, Ren et al. installed $–NH_2$ groups on MIL-125 to give MIL-125-NH_2; the aminated framework sequesters Ag^+ up to 139.8 mg g^{-1} through a dual mechanism—electrostatic attraction to protonated amines and lone-pair coordination to the metal center. Tang et al. first condensed 4-amino-3-hydroxybenzoic acid with terephthalaldehyde to yield the Schiff-base linker AHPP, which was then coordinated with $ZrCl_4$ to furnish AHPP-MOF. The resulting framework is water-stable and highly selective, delivering a Pd(II) capacity of 283.5 mg g^{-1}. XPS and zeta-potential measurements indicate that uptake proceeds through (i) electrostatic attraction between the protonated amine and the chloropalladate anion, followed by (ii) inner-sphere chelation of Pd(II) to the adjacent N and O donors. In oxic surface waters arsenic occurs almost exclusively as As(V), i.e. $HAsO_4^{2-}$ and $H_2AsO_4^-$. Li et al. showed that ZIF-8 scavenges trace As(V) up to 106.7 mg g^{-1}. The outstanding performance stems from (i) in-situ hydrolysis of Zn nodes and imidazolate linkers to generate Zn–OH and N–OH sites that form strong inner-sphere arsenate complexes, and (ii) the exceptionally high BET area (1 388 m^2 g^{-1}) that shortens diffusion paths and maximizes contact probability.

Table 1 Properties and advantages of metal organic framework MOFs

Name	Specific Surface Area (m^2/g)	Target Ion	Adsorption Capacity (mg/g)	Stability
UiO-66	990	Cu(II)	745.1	Strong water stability
MOF-808-TGA	1150	Hg(II)	758	Strong water stability
MIL-125-NH_2	1297	Ag(I)	139.8	Strong water stability
$Cu_3(BTC)_2$-SO_3H	445	Cd(II)	88.7	Strong water stability
UiO-66-MAA	1438	Hg(II)	332	Strong water stability
UiO-66-$(COOH)_2$	(~)	Th(IV)	350	Strong water stability
MOF-808-AA-EDT	704	Hg(II)	1077	Strong water stability
ZIF-8	1388	As(V)	106.7	Strong water stability
MIL-53(Al)	824	Ni(II)	58.22	Strong water stability
MIL-101(Cr)	3415	Rb(I)	72.66	Strong water stability

5 Potential of MOFs in Environmental Protection Applications

Metal-organic frameworks stand out among state-of-the-art porous solids, offering exceptional promise for tackling diverse environmental challenges. This review systematically examines the unique properties of MOFs that make them suitable for various environmental protection purposes, particularly focusing on their hydrophobic characteristics, stability, and porous structures that enable efficient pollutant removal and resource recovery [25, 28, 33].

5.1. Hydrophobic MOFs and Their Environmental Applications

Out of the tens of thousands of MOFs reported in the last twenty years, only a few hundred combine permanent porosity with appreciable hydrophobicity. Hydrophobic MOFs—though scarce—display rich structural variety, high crystallinity, narrowly distributed micropores, and robust water resistance, positioning them as premium sorbents for CO_2 capture, alcohol/water separation, and airborne or aqueous contaminant removal. Their water-repellent character is engineered through four main tactics: (i) pre-synthetic ligand design, (ii) post-synthetic linker functionalization, (iii) surface grafting of macromolecules, and (iv) controlled carbonization of the outer framework.

Xie et al. assembled two Zr-MOFs—$[Zr_6O_4(OH)_4(2,7\text{-ndb})_6]$ (BUT-67) and $[Zr_6O_4(OH)_4(1,3\text{-bdb})_6]$ (BUT-66)—from bent hornedicarboxylic acids 2,7-H_2ndb and 1,3-H_2bdb. At 25 °C and 0.95 P/P_0 their water uptakes plateau at only 103 mg g^{-1} (5.7 mmol g^{-1}) and 124 mg g^{-1} (6.9 mmol g^{-1}), far below the theoretical pore-fill values of ~420 and ~380 mg g^{-1}, confirming the channels are moderately hydrophobic.

Their unusual water-repellent character originates from two-fold interpenetration: one framework presents a hydrophobic carpet of phenyl rings, whereas the other retains hydrophilic –OH and $–COO^-$ motifs, so the internal pore walls are only moderately hydrophobic. In contrast, the external facets are overwhelmingly aromatic; water-contact angles > 120° and the crystals' ability to float—even though their skeletal densities exceed 1 g cm^{-3}—demonstrate that the outer surfaces are highly hydrophobic.

Chen et al. constructed the Cu-paddle-wheel MOF $[Cu_4(TDHB)]$ (BUT-155) from an octatopic ligand whose tetrahedral core is locked by six peripheral methyl groups. The rigid, highly connected net delivers 0.82 cm^3 g^{-1} pore volume and 2 070 m^2 g^{-1} BET area, yet survives repeated water exposure across a wide temperature window. Contrary to the prevailing view that Cu_2-paddle-wheel clusters are moisture-labile, BUT-155 remains intact thanks to (i) its elevated 8-connected geometry, (ii) conformational restriction imposed by the methyl substituents, and (iii) the hydrophobic methyl cloak that shields the pore surface from hydrolytic attack.

5.2. Modification and Functionalization Strategies

Grafting primary alkylamines of increasing chain length onto the open Cr sites of MIL-101(Cr) provides deterministic control over surface energy: longer alkyl tails raise the water contact angle, shift the adsorption step to higher relative pressures, and lower the ultimate uptake—demonstrating that post-synthetic ligand exchange can tune hydrophilic–hydrophobic balance at will.

Independently, Si et al. introduced a general route to core–shell HPLC media by enveloping silica microspheres with a nanometre-thin MOF–polymer skin, marrying the mechanical strength of silica with the adjustable chemistry of the framework. The incorporation of MOF particles and polyvinylpyrrolidone effectively suppresses silanol activity on silica surfaces, enhances composite resistance, and improves water compatibility. The resulting stationary phase demonstrates exceptional hydrophobic/hydrophilic properties for separating seven alkaloids, six sulfonamides, and five antibiotics, with remarkable durability (RSD: 0.4-0.7%).

5.3. Advanced Applications of Modified MOFs

A template-directed route yields hierarchical hydrophobic HZIF-8 in which polystyrene spheres imprint interconnected macropores while their hydrophobic surfaces simultaneously coat the intrinsic ZIF-8 crystallites. The resulting trimodal micro-/meso-/macroporous solid absorbs oils readily yet imbibes negligible water, affording exceptional oil–water separation efficiency.

MOF nanosheets only a few unit-cells thick retain the parent framework's crystallinity yet expose far more edge sites and withstand mechanical deformation better. When assembled into a composite electrode they deliver a Tafel slope of 48.1 mV dec^{-1}, drive urea oxidation at only 170 mV overpotential (10 mA cm^{-2}), lose < 7 % activity after 15 000 s continuous operation, and enable overall urea electrolysis at a cell voltage of just 1.42 V.

Tahmasebi et al. demonstrated that an azine-functionalized tri-zinc(II) MOF remains intact in water while extracting Cd(II), Cu(II), Pb(II), Cr(III) and Co(II) with high selectivity. Separately, a photoresponsive 2D trisilyl-MOF (TSi-MOF) bearing hexamethyltrisilyl aryl-silane units switches from superhydrophobic to hydrophilic under ambient UV light, simultaneously generating intense fluorescence. This writable wettability/fluorescence dual response permits micron-scale patterning of QR codes, text and logos for optical tagging and anti-counterfeiting applications.

5.4. Emerging Applications and Industrial Potential

MOFs are moving from bench to market in gas separations: several analogues are now manufactured at multi-ton scale for CO_2/CH_4 or O_2/N_2 splitting, and binder-free MOF films are commercially laminated inside produce crates, where their gradual release of 1-methylcyclopropene—an ethylene-receptor antagonist—extends shelf life by slowing fruit ripening.

Nanoscale MOF-based drug carriers fine-tune release kinetics, boosting bioavailability while minimizing peak-related side effects and systemic toxicity. Multifunctional nanoscale MOFs have shown substantial advances in drug delivery applications.

Vancomycin-tethered PCN-224 merges the antibiotic's cell-wall-binding specificity with the porphyrin-MOF's photonic efficiency, producing a nanoplatform that achieves potent, light-triggered killing of *Staphylococcus aureus* while maintaining dark biocompatibility—an attractive candidate for precision antimicrobial phototherapy.

Using tannic acid as a benign surface protectant, selective wet-etching of NH_2-MIL-125(Ti) generates TiO_2@MOF heterojunctions in which anatase nanodots are spatially pinned to the intact framework, yielding a robust photocatalyst with enhanced charge separation and visible-light activity. The tightly packed heterostructure ensures sustained photogenerated carrier migration while preventing electron-hole recombination, achieving remarkable hydrogen production efficacy (44 μmol) without noble metals [35].

Dai's team grew $ZnIn_2S_4$ nanosheets inside NH_2-MIL-53 pores using $Co(NO_3)_2·6H_2O$ as a growth modulator; the Co^{2+} ions halve the MOF crystal size (4.7 → 2 μm), constrict the band-gap, and expose additional reactive facets, driving photocatalytic H_2 production to 161.7 mmol g^{-1}.

One-step synthesized $CdLa_2S_4$/MIL-88A(Fe) Z-type heterojunction photocatalysts and NH_2-UiO-66/$ZnIn_2S_4$ composites prepared via silver-catalyzed decarboxylation demonstrate improved specific surface area, pore size, and light absorption, achieving maximum hydrogen production rates of 7.373 mmol h^{-1} g^{-1} under visible light irradiation.

Lei and colleagues developed MOFs@cellulose aerogel composites through room-temperature in situ growth on flexible cellulose aerogels. These composites effectively adsorb Cu^{2+} and Pb^{2+} from water with equilibrium adsorption capacities of 89.40 mg g^{-1} for Pb^{2+}, maintaining performance through five reuse cycles while increasing optimal decomposition temperature by 62.1°C.

Beyond catalysis, MOFs are now integral components of next-generation energy-conversion and storage hardware: their hierarchically porous scaffolds host O_2/CO_2 redox mediators in metal–air cells and act as solid-state electrolyte reservoirs in regenerative fuel cells, pushing round-trip efficiencies and cycle life to new highs (Figure 5). The MOF-derived Co_3O_4@Co/NCNT nanocomposite serves as an exceptionally efficient and robust trifunctional electrocatalyst, showing great promise for contributing to the widespread commercialization and utilization of renewable fuel cells. Both MOFs and metal-organic gels (MOGs) can be employed as excellent electrocatalysts for sustainable energy production, including metal-air batteries, hydrogen oxidation reactors, and fuel cells. Rational design of MOF or MOG precursors—tuning both the intrinsic activity of each node/linker and the spatial density of accessible active sites—delivers step-change improvements in oxygen-electrocatalysis kinetics, round-trip energy efficiency, and storage capacity.

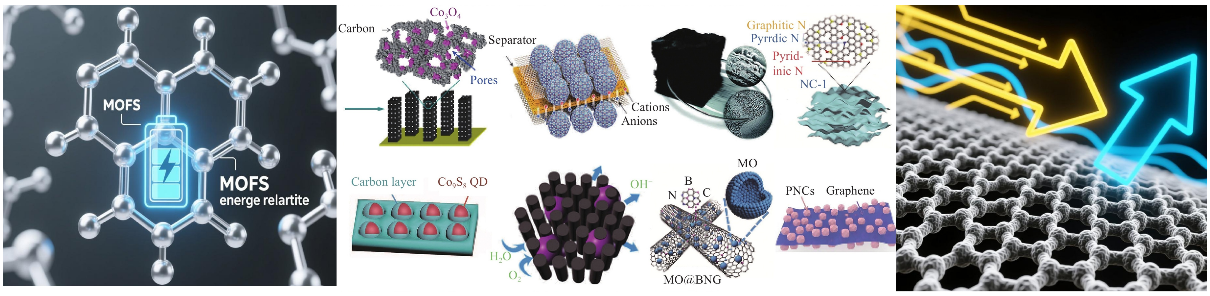

Figure 5 Schematic diagram of metal organic framework MOFs in energy storage

5.5. Stability and Practical Applications

Constructed from interchangeable metal nodes and organic linkers, MOFs deliver ultrahigh surface areas, adjustable pore sizes, and notable chemical/thermal stability, making them versatile tools across scientific disciplines. Their porous architecture and strong adsorption capability are increasingly harnessed for real-world environmental monitoring: Salarian et al. employed a Pb^{2+}-selective MOF-packed micro-column coupled with flame-AAS to detect trace lead in natural waters, achieving enrichment factors exceeding 50×. An in-situ solvothermal method was used to immobilize MOF-5/ionic-liquid-functionalized graphene onto etched stainless-steel wires, creating solid-phase microextraction fibers that achieved 85–102 % recovery of antibiotics from complex matrices such as honey, milk, serum, and urine. ZIF-8 microbeads have been applied as effective µ-SPE sorbents for extracting six priority polycyclic aromatic hydrocarbons from aqueous samples. Additionally, IRMOF-3 modified with ionic liquids and encapsulated in polydimethylsiloxane (IRMOF-3@ILs/PDMS) forms a robust, rough, and highly porous coating on stainless-steel wires, enabling efficient extraction of polycyclic aromatic hydrocarbons from water with a service life of over 100 cycles.

MOFs demonstrate tremendous potential in environmental protection applications through their tunable hydrophobic/hydrophilic properties, exceptional stability, and versatile functionalization capabilities. The continued development of MOF-based materials promises significant advances in pollutant removal, resource recovery, and sustainable technology development. Future research should focus on scaling up production, improving cost-effectiveness, and exploring novel applications in environmental remediation and resource management.

6 Conclusion

In short, MOFs offer a vast library of crystalline solids that unite high porosity, enormous surface area, low density, and tailorable pore metrics, positioning them as next-generation sorbents. For aqueous heavy-metal cleanup the benchmarks are clear: the framework must survive long-term water contact and offer densely accessible binding sites. Postsynthetic ligand grafting or node modification steadily boosts both selectivity and capacity, while encapsulating the crystals in magnetic or polymeric composites prevents aggregation and permits effortless magnetic or filtration recovery. Looking forward, research will most profitably focus on:

To meet the demand for selective removal of specific heavy metal ions, it is still necessary to develop MOF materials with relevant characteristic structures through post-synthetic modification methods.

Considering the inconvenience of recycling powdered MOF materials, there is a need to develop efficient MOF-based composites to enhance the application prospects of MOF materials.

Considering that the regeneration of MOF adsorbents under acidic or alkaline conditions may lead to structural collapse, affecting their recyclability, there is a need to further develop milder regeneration conditions for MOFs.

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