

From laboratory to application: A multi-dimensional review of MOF-based heavy metal adsorption

Baocheng Zhou^{1,2,3,4}, Tu Hu^{1,2,3,4}, Guo Lin^{1,2,3,4*}, Shixing Wang^{1,2,3,4}, Hongying Xia^{1,2,3,4}, Zhao Ding^{5*}, Libo Zhang^{1,2,3,4*}, and Maziar Ashuri⁶

¹School of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093, PR China

²Yunnan Provincial Key Laboratory of Intensification Metallurgy, Kunming University of Science and Technology, Kunming, Yunnan 650093, PR China

³State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, Yunnan 650093, PR China

⁴The Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming, Yunnan 650093, PR China

⁵College of Materials Science and Engineering, National Engineering Research Center for Magnesium Alloys, National Innovation Center for Industry-Education Integration of Energy Storage Technology, Chongqing University, Chongqing, 400044, PR China

⁶Department of Mechanical, Materials and Aerospace Engineering, Illinois Institute of Technology, Chicago, IL 60616, USA

Abstract: Heavy metal contamination in water bodies poses a persistent threat to aquatic ecosystems and public health. Metal-organic frameworks (MOFs) have emerged as promising adsorbents due to their exceptional surface areas, tunable pore structures, and chemically versatile frameworks. However, despite extensive laboratory-scale success, the practical deployment of MOFs for heavy metal removal remains limited. This review argues that progress requires moving beyond isolated material optimization toward a system-level assessment. We evaluate MOF-based heavy metal adsorption through five interdependent dimensions that collectively determine real-world viability: water stability, selectivity in multi-ion matrices, regenerability over multiple cycles, scalability from gram to kilogram production, and real-water validation under authentic wastewater conditions. A critical observation is that while most studies report the number of cycles, very few investigate the root causes of performance decline during regeneration. We also highlight the gap between idealized laboratory conditions and complex real wastewater, where competing cations, natural organic matter, and suspended solids can severely compromise performance. Building on recent advances in adaptive MOFs, closed-loop resource recovery, and AI-driven material design, we propose an integrated framework uniting responsive materials, smart regeneration, and process engineering. This review offers a practical roadmap for transitioning MOF-based heavy metal remediation from laboratory promise to deployable technology, emphasizing that progress depends on system integration rather than incremental material refinement.

Key words: Metal-organic frameworks; Heavy metal adsorption; Water treatment; Scalable synthesis; Real-water validation

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1. Introduction

The contamination of aquatic systems with heavy metal ions has become a pressing global environmental and public health issue, intensified by rapid industrialization and urban expansion. Activities such as mining, smelting, and diverse industrial operations release substantial amounts of toxic heavy metal ions—including lead (Pb), mercury (Hg), chromium (Cr), cadmium (Cd), and arsenic (As)—into aquatic environments^[1,2]. Among these, Pb, Hg, Cd, and As are of particular concern owing to their pronounced toxicity, environmental persistence, and capacity for bioaccumulation^[3,4]. The reper-

cussions for human health are considerable. Mercury exposure is linked to neurological impairment, while cadmium can induce renal dysfunction and skeletal damage. Lead adversely affects the hematopoietic system, and arsenic exposure is correlated with an increased risk of skin and internal cancers. Moreover, the ionic form of these metals in aquatic systems resists biodegradation, enabling their progressive accumulation along the food chain. This persistence results in long-term hazards to ecosystem integrity and human health. According to a United Nations report, the global population is projected to reach 10 billion by 2050, with 30% of the current population already lacking access to clean drinking water^[5]. The interplay between water scarcity and water pollution has made the development of efficient, cost-effective, and sustainable water treatment technologies a central challenge in the field of environmental governance.

To tackle the challenge of heavy metal contamination in industrial wastewater, researchers have persistently explored and advanced novel removal technologies. Several tech-

Correspondence to: Lin G, guolin@kust.edu.cn; glin08@126.com; Ding Z, zhaoding@cqu.edu.cn; Zhang L B, zhanglibopaper@126.com

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niques have been employed to extract heavy metals from industrial wastewater, among which adsorption, chemical precipitation, ion exchange, and membrane separation are the most predominant^[6–9]. However, conventional methods such as chemical precipitation and ion exchange are often constrained by limitations including moderate removal efficiency and a significant potential for secondary pollution^[10,11]. Table 1 summarizes the principles and limitations of these mainstream technologies. As can be seen from Table 1, chemical precipitation, ion exchange, and membrane separation each face intrinsic operational or economic constraints that limit their applicability to complex, low-concentration heavy metal streams. Adsorption, by contrast, combines competitive removal efficiency with operational flexibility and the potential for adsorbent regeneration, positioning it as a particularly attractive strategy for decentralized and resource-sensitive treatment scenarios. Among the various water treatment strategies available, adsorption stands out as one of the most promising for practical deployment, due to its operational simplicity, high removal efficiency, and cost-effectiveness. Nonetheless, traditional adsorbents—such as activated carbon and ion exchange resins—suffer from inherent drawbacks, including restricted adsorption capacity, inadequate selectivity, and challenges in regeneration^[12]. As a result, the development of new, high-efficiency adsorbent materials has gained increasing attention as a key research direction in the field of environmental remediation.

As a class of highly designable crystalline materials, Metal–organic frameworks (MOFs) and related framework systems—including covalent triazine frameworks (CTFs) and Prussian blue analogs—have demonstrated exceptional versatility across a broad spectrum of applications, ranging from electrocatalytic energy conversion, supercapacitor energy storage, triboelectric nanogenerators, and photovoltaic devices to advanced battery systems and multifunctional sensing^[13–22]. Among these diverse applications, the use of MOFs as adsorbents for heavy metal removal from aqueous systems stands out as one of the most intensively investigated directions, owing to their precise control over pore size, pore environment, and surface chemical properties, which together offer an ideal platform for achieving efficient and selective adsorption of target species^[22–25]. Studies have demonstrated that such materials can achieve heavy metal ion adsorption efficiencies more than three times greater than those of conventional adsorbents^[26–28]. The significance and potential of this class of materials were underscored by the awarding of the 2025 Nobel Prize in Chemistry to three pioneers in the field of MOFs. The award recognized their groundbreaking work in developing a new generation of molecular materials character-

ized by well-defined internal structures featuring a high density of uniformly arranged nanoscale cavities. These cavities not only facilitate the unimpeded flow of molecules but also confer exceptional adsorption and separation capabilities.

Although laboratory-scale studies have confirmed the excellent adsorption performance of some MOFs for particular heavy-metal ions, many other factors still prevent their actual application^[29,30]. First of all, MOFs are generally not water-stable. Under extreme circumstances, such as high temperature and high humidity, or strong acid and base, the metal-ligand coordination bonds in MOFs can break, leading to damage of the framework and loss of function^[31–33]. For instance, in a high-humidity environment, some MOFs will take up water and change their structure, thus reducing the amount of pollutant adsorption^[34,35]. Water-stable MOFs are those that can maintain their structure in the presence of water, and are therefore required for actual applications. Secondly, the long-term stability of the synthesis route for the current MOFs is being verified. Traditional solvothermal synthesis generally uses a large amount of organic solvents, requires high-energy inputs and has extended reaction times, thus failing to meet the standards of green chemistry^[36,37]. For example, at high temperatures required for some catalytic reactions, some MOF structures are easily damaged and lose their catalytic function^[38–39]. Although alternative green synthesis routes (e.g., ultrasound-, microwave-, and mechanochemistry-assisted methods) have been explored, their feasibility and economic viability at large scales remain to be validated^[30]. Third, a fundamental mismatch exists between studies conducted in idealized single-metal systems and the complexity of real wastewater. Most research to date has focused on evaluating the adsorption performance of individual MOFs toward single heavy metal species in simple matrices. However, in natural aquatic environments, heavy metal ions rarely exist in isolation; they typically coexist with other heavy metals, common cations (Ca^{2+} , Mg^{2+} , Na^{+}), anionic ligands, and natural organic matter, forming complex multicomponent systems^[29]. Under such conditions, monofunctional MOFs often exhibit limited adsorption selectivity, susceptibility to competitive ions, and sensitivity to pH fluctuations^[40]. For instance, although ZIF-8 performs well in simultaneous removal of arsenic and antimony, the presence of Sb species still competitively hinders the adsorption of both As(III) and As(V)^[41].

The foregoing discussion reveals a central paradox in the field: the continuous optimization of material properties at the laboratory scale has not translated into commensurate progress in practical application. Static material parameters—such as maximum adsorption capacity and specific surface

Table 1. Comparison of technologies for heavy metal removal from wastewater

Technology	Principle	Advantages	Limitations
Chemical precipitation	Formation of insoluble metal hydroxides or sulfides	Mature technology, simple operation	Large sludge production, secondary pollution risk, poor removal at low concentrations
Ion exchange	Exchange between resin ions and heavy metal ions	High removal efficiency, metal recovery possible	High resin cost, complex regeneration, susceptibility to interference
Membrane separation	Pressure-driven selective permeation	High separation efficiency, small footprint	Membrane fouling, high energy consumption, high operating cost
Adsorption	Transfer of pollutants from liquid to solid adsorbent surface	Low cost, low energy consumption, high removal efficiency (up to 99.9%), operational simplicity, design flexibility, adsorbent regenerability	Performance depends on adsorbent properties

area—measured under idealized batch conditions have limited predictive value for dynamic column operation, competitive multi-ion environments, and long-term stability in real effluents. This situation calls for a paradigm shift: future breakthroughs will depend less on the discovery of yet another high-capacity MOF and more on a multi-dimensional systematic assessment that simultaneously considers five core dimensions: stability, selectivity, regenerability, scalability, and real-water validation. These dimensions are interdependent and often involve trade-offs; together, they determine the practical viability of MOF-based adsorbents. To establish the necessary foundation for this assessment, we first survey the principal MOF design strategies (Section 2) and the fundamental adsorption mechanisms (Section 3). The core of this review lies in Section 4, where we systematically evaluate MOF-based adsorbents across the five dimensions. Existing reviews have provided valuable surveys of specific MOF families^[42], individual heavy metals^[43], or fundamental adsorption mechanisms^[44], typically following a structure that introduces synthesis methods, adsorption mechanisms, and adsorption performance for a given category of materials or pollutants. However, these reviews generally treat stability, selectivity, and regenerability as independent properties, and rarely incorporate scalability or real-water validation as core evaluation criteria. This review differentiates itself in three respects. First, rather than cataloguing materials by structural family or target metal, we adopt a system-level perspective organized around five interdependent dimensions—water stability, selectivity, regenerability, scalability, and real-water validation—that collectively determine practical viability. Second, we explicitly examine the trade-offs among these dimensions (e.g., stability versus capacity, selectivity versus regenerability), which are often overlooked when each property is treated in isolation. Third, we place equal emphasis on the under-discussed engineering aspects of scale-up synthesis and real-water performance, bridging the gap between laboratory material design and field-deployable adsorption technology. By integrating these perspectives, this review provides not a catalogue of MOFs, but a practical roadmap for transitioning MOF-based heavy metal remediation from laboratory promise to environmental application.

2. Design strategies for MOF materials

To avoid ambiguity, the three types of MOFs-based adsorbents in this review are as follows. Monofunctional MOFs are

frameworks built with only one kind of metal node and organic linker, and they lack additional functional groups or other components; their adsorption properties originate solely from the inherent features of the parent framework. Multifunctional MOFs are those that have been specifically designed for functional groups (e.g., $-SH$, $-NH_2$, $-COOH$) in the pre-synthetic ligand or post-synthetic modification to provide target chemical reactivity towards heavy metal ions. Composite MOFs are hybrid materials that combine MOFs with one or more other distinct components, such as magnetic nanoparticles, carbon-based materials, polymers, or a secondary MOF phase, to achieve synergistic effects that neither component can achieve independently. The three categories are not always strictly separated; a multifunctional MOF can also be used as the matrix for a composite, but they provide a convenient organisational system for the following discussion. The Design strategies in this section provide the material basis for the five-dimensional assessment presented in Section 4. To understand how various functionalization approaches and composite architectures influence the material's properties, and subsequently assess their performance in terms of stability, selectivity, regenerability, scalability and real-water applicability, they need to be studied.

2.1. Monofunctional MOFs

Single-metal MOFs are the first type of materials in the MOF family that use a single kind of metal ion or cluster coordinated with organic ligands. The above materials have provided a basis for studying the structure-activity relationship and developing design rules for heavy-metal-adsorbent applications. The most widely studied families of single-metal MOFs include the University of Oslo (UiO) series^[45], Zeolitic Imidazolate Frameworks (ZIF) series^[46,47], Materials of Institute Lavoisier (MIL) series^[48], and Isorecticular Metal-Organic Frameworks (IRMOF) series^[44].

MIL-101(Fe), UiO-66 and its derivatives, and ZIF-8 are typical examples of monofunctional MOFs, as shown in Fig. 1^[27,28]. As shown in the figure, each framework has a distinct metal node and organic linker; these include Fe_3O clusters with terephthalate linkers in MIL-101(Fe), Zr_6 clusters in UiO-66, and Zn-imidazolate coordination in ZIF-8, and thus the metal-linker combination determines pore structure and possible adsorption sites. MIL frameworks are a large number of materials developed at the Institut Lavoisier, including aluminium, iron and chromium, etc. For example, MIL-101(Fe) is an iron-

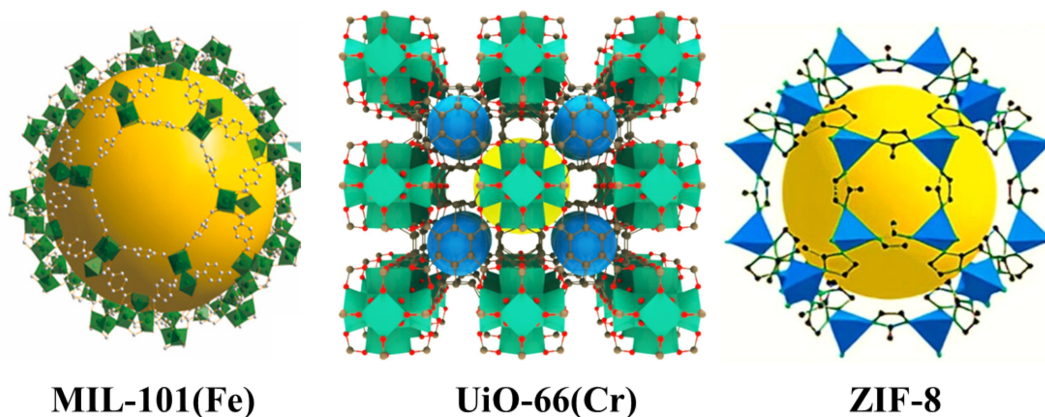


Fig. 1. Illustration of the structure of MIL-101(Fe), UiO-66(Zr) and ZIF-8.

based MOF with a large pore system and high specific surface area; it can adsorb pollutants such as antibiotics and heavy metals, as well as degrade them oxidatively. Its structure has many Fe^{3+} sites that can attract pollutants through electrostatic attraction and coordination bonding to adsorb them effectively^[29]. UiO series materials, such as UiO-66 and its derivatives, have received a lot of attention for their excellent chemical stability and high surface area. UiO-66 is a zirconium-based MOF that has good thermal and chemical stability due to its structure of Zr_6 clusters and terephthalate linkers. Zr–O bonds are relatively strong and thus more stable in a high-temperature aqueous environment. UiO-66 has a pore size of about 0.8 nm and is therefore more suitable for the adsorption of small-molecule pollutants, such as heavy metal ions and low-molecular-weight organic compounds^[30]. The ZIF series are based on zinc or cobalt ions coordinated with imidazolate ligands, and have good chemical and thermal stability as well as high porosity. ZIF materials have shown good results in the adsorption of radionuclides and heavy-metal-ion; they are zeolite-like in structure and exhibit size-selective adsorption. ZIF-8 is a zeolitic imidazolate framework consisting of zinc ions and 2-methylimidazole ligands; it has a high specific surface area and porosity, and is thus widely applied in gas adsorption, separation and catalysis. ZIF-8 has a high surface area and numerous imidazole groups in its original form, and can rapidly and stably adsorb copper ions in a wide pH range^[31]. To improve the adsorption effect, control the particle size and modify the pore structure by changing the synthesis conditions; thus, enhance the speed of adsorption. Tailored ZIF-8 variants with small particle sizes and modified pore structures have shown better removal performance for lead ions^[32].

Monofunctional MOFs are highly efficient for single-metal adsorption under ideal laboratory conditions but show a considerable drop in performance when exposed to real multi-ion matrices. Therefore, it can be seen that the "materials-first" method has a certain defect; structure optimisation alone is insufficient. The original structure is relatively simple and convenient for synthesis reproducibility; however, it may also be a problem in a system setting, as even if the pore tuning is optimized, it cannot compensate for a lack of operational adaptability in a complex aqueous environment. In the natural aquatic environment, heavy metal ions are rarely found alone; they generally occur in the presence of other heavy metal species and a large number of competing ions (e.g., Ca^{2+} , Mg^{2+} , PO_4^{3-}) to form complex multicomponent pollution systems. Under actual circumstances, the three above problems affect monofunctional MOFs in an interconnected way: competitive ion effects from coexisting cations (e.g. Ca^{2+} and Mg^{2+}) occupy non-selective binding sites; pH fluctuations alter both the surface charge and metal speciation; and interference from natural organic matter can block pore channels. Together, the above factors show why capacity indicators obtained from single-metal batch tests are unlikely to reflect actual performance in multi-ion environments^[33]. The amount of the competitive effect is relatively large. For example, pristine ZIF-8 has maximum adsorption capacities of 151.3 mg/g for As(III), 106.4 mg/g for As(V) and 104.7 mg/g for Sb(V) in a single-solute system. As(V) has a relatively strong inhibitory effect on the adsorption of Sb(V) in bi-solute systems, and pre-adsorbed species strongly suppress the uptake of subsequently added

ions^[49].

In addition to the above problems, there are other deficiencies of monofunctional MOFs that are not suitable for practical applications. First, they have relatively weak adsorption capabilities. MOFs have a high theoretical specific surface area, but in practice, many of the adsorption sites do not actively participate in the adsorption process^[35]. The reason for this inefficiency is that the pores are blocked, and the active sites have been occupied by previously adsorbed metal ions; as a result, the overall uptake capacity of heavy metal ions is reduced. More seriously, the capacity indicators obtained from a single-metal batch test have almost no predictive power for dynamic column operation with competitive ions. Second, the adsorption kinetics of monofunctional MOFs generally need to be improved. Some MOF structures have a relatively high equilibrium adsorption capacity but require a longer time to reach adsorption equilibrium. Such kinetics are not suitable for continuous-flow systems that generally have a residence time of <30 minutes. Finally, the cycling stability of monofunctional MOFs is also a problem. After a few adsorption-desorption cycles, the extent of the adsorption has generally decreased; this is mainly due to changes in the structure, a loss of active sites, or the accumulation of residual pollutants inside the framework. This decline will reduce the economy of scale by raising adsorbent-replacement costs.

2.2. Multifunctional MOFs and composite MOFs

Functionalized MOFs are the result of adding various chemical groups to the framework structure of MOFs to improve both their selectivity and adsorption capacity. This strategy can precisely control the interaction of the material with target heavy metal ions and address the defect in generic binding sites in pristine MOFs^[50]. Functionalization approaches can be broadly divided into three types: pre-synthetic ligand design^[51,52], post-synthetic modification (PSM)^[53–55], and defect engineering strategies^[56,57].

Amino functionalisation is now one of the better ways to improve the adsorption performance of heavy metals. The introduction of amino groups adds more coordination sites and increases the total surface charge; thus, it can be bound to metal ions strongly via electrostatic attraction and coordination^[58]. Recently, research on amino-enriched Zn-MOFs has focused on their self-reduction properties; now they can remove heavy metal ions from water without external energy and be electrochemically detected^[59]. Thiol functionalization is another high-performance type that can be used for mercury and other soft metal ion removal. Sulfur atoms have a strong affinity for soft metal ions and are thus highly selective and efficient adsorbents. Recent studies have reported that thiol-functionalised defective Zr-MOFs can achieve maximum adsorption capacities of 715.2 mg/g, 862.7 mg/g, and 450.5 mg/g for Pb(II), Hg(II) and Cd(II) respectively^[60]. Many oxygen vacancies and unsaturated adsorption sites exist in the defective structure, strong coordination interactions are formed, and thus the adsorption performance is improved. Carboxyl functionalization has shown good results for several heavy-metal ions, and the carboxylate group can coordinate in a monodentate, bidentate or bridging manner^[61]. Carboxyl groups have a pH-sensitive character and thus selectively adsorb in different environments; they generally show better performance in a pH range of 4–6. Carboxyl functionalisation has shown

good results in enhancing the heavy metal adsorption performance of MOFs. MIL-101(Fe) derivatives are taken as an example; after microwave-assisted synthesis with organic ligands containing multiple carboxyl groups (e.g., H₄BTEC), MIL-101-(COOH)₂ has been prepared, and its performance has been significantly improved over that of the pristine framework^[62]. In fact, the saturation adsorption capacity for Pb(II) reached 467.6 mg/g, far exceeding that of unfunctionalized MIL-101 (40.5 mg/g) and mono-carboxyl-functionalized MIL-101-COOH (90.3 mg/g).

Recently, the new directions for functionalisation have focused on creating multi-functional MOFs with synergistic effects. Several functional groups with different types of heteroatoms, such as thiol, oxime and thiourea groups containing sulfur and nitrogen, have shown excellent adsorption performance. Thiol-modified materials containing both nitrogen and sulfur elements had an adsorption capacity of 957.94 mg/g for Hg(II) and were approximately 1.99 times that of unmodified materials^[63]. Post-synthetic modification is suitable for functionalisation due to mild reaction conditions and the ability to selectively modify specific sites in the framework. However, this way also has problems, such as reduced accessibility of the internal area and possible structural damage during modification^[64]. Recently, defect engineering has provided new ways to add functional groups, and missing linker defects can be used to create coordination sites for further functionalization^[65].

Composite and hybrid MOFs represent a sophisticated approach to overcome the limitations of single-component materials by combining the advantages of different functional elements. These materials integrate MOFs with other functional materials, including polymers^[66,67], carbon-based materials^[68,69], magnetic nanoparticles^[70], and other inorganic compounds^[71], to create synergistic effects that enhance overall performance. Bimetallic and trimetallic MOFs represent another important class of composite materials, where multiple metal centers are incorporated into a single framework structure^[72]. These materials offer enhanced functionality through synergistic effects between different metal sites. Research findings indicate that the bimetallic ZIF-8, synthesized via a hydroxide double salt precursor, exhibits a maximum adsorption capacity for Cu²⁺ as high as 1196.82 mg/g, significantly surpassing that of monometallic ZIF-8, ZIF-67, and the ZIF-8/67 composite synthesized via the one-pot method^[73]. This enhancement is attributed to the synergistic effect induced by the introduction of dual metal centers (e.g., Zn²⁺ and Co²⁺), which not only increases the number of active sites on the material's surface but also potentially enhances the affinity and binding capacity for target heavy metal ions through modulation of the material's electronic structure and pore environment. The development of hierarchical porous structures through composite formation has addressed limitations associated with mass transfer in dense MOF structures. These materials combine large macropores for rapid transport with mesopores and micropores for high adsorption capacity, enabling enhanced kinetics and overall performance. Recent innovations in MOF composite design have focused on developing materials with tailored pore architectures and optimized surface chemistry for specific heavy metal removal applications.

If monofunctional MOFs fail due to singular functionality,

one might assume multifunctional/composite/hybrid MOFs—integrating electrostatic, coordination, and redox sites—would solve the problem^[36]. However, these advanced designs do not automatically resolve the fundamental system-level challenges. A quantitative illustration of this tension is evident in the regeneration performance of functionalized MOFs. UiO-66-EDA, an ethylenediamine-functionalized Zr-based framework, demonstrates effective initial adsorption of Pb(II), Cd(II), and Cu(II) from aqueous solution. However, after four adsorption-desorption cycles using 0.1 M HCl as the eluent, the removal efficiencies for all three metals decline measurably, with the most pronounced decrease observed for Cu(II)—attributed to the formation of exceptionally stable complexes between Cu(II) and the grafted amine groups that resist acid elution^[74]. Similarly, the thiol-decorated Zr-MOF Zr-DMSA retains approximately 63% of its initial Pb(II) adsorption capacity after ten consecutive cycles, with the performance loss traced to partial linker detachment and pore collapse during acid regeneration^[75]. These examples illustrate that while functionalization imparts high initial capacity, the same strong metal-binding interactions that enable effective adsorption can hinder complete desorption, creating an inherent trade-off between adsorption performance and long-term reusability that must be evaluated at the system level. While the integration of multiple functional sites can synergistically enhance adsorption capacity, several critical operational issues remain largely unaddressed, including: (i) achieving complete desorption without inducing progressive framework collapse; (ii) sustaining stable adsorption performance over extended cycling; and (iii) efficiently separating nanoscale adsorbent particles from treated effluents to prevent secondary contamination. The following examples illustrate a crucial insight: material-level synergy, though necessary, is not in itself sufficient to guarantee system-level viability. The core challenge lies not solely in achieving material synergy, but in bridging the gap between static adsorbent properties and the dynamic operational demands of practical systems.

The constrained adsorption capacity of pristine UiO-66 for heavy metals, owing to its scarcity of strong metal-coordinating functional groups, is a recognized limitation. To overcome this, surface functionalization has proven effective. The polyethyleneimine (PEI)-modified UiO-66-NH₂ demonstrates a marked enhancement in the adsorption of Pb²⁺ and Cd²⁺^[76]. As illustrated in Fig. 2a, the magnetic composite Ni_{0.6}Fe_{2.4}O₄-UiO-66-PEI removes Pb(II) and Cr(III) through chelation with grafted amine groups, while Cr(VI) is captured via electrostatic attraction to the positively charged surface. Yet, this enhancement comes at a system-level cost: PEI modification reduces mechanical stability and complicates regeneration, rendering such materials economically unviable for continuous-flow reactors—the very context where their selectivity is most needed. Consequently, functionalization that enhances selectivity at the material level may inadvertently complicate the engineering requirements for practical deployment^[77]. A comparative study of ZIF-8 and ZIF-67 for Pb²⁺ and Hg²⁺ removal reveals distinct mechanistic contributions (Fig. 2b)^[78]. In ZIF-8, adsorption proceeds through a combination of electrostatic interaction, π - π interaction, and surface interaction; in ZIF-67, only π - π interaction and surface interaction are operative, with electrostatic contributions absent. The figure highlights how the dif-

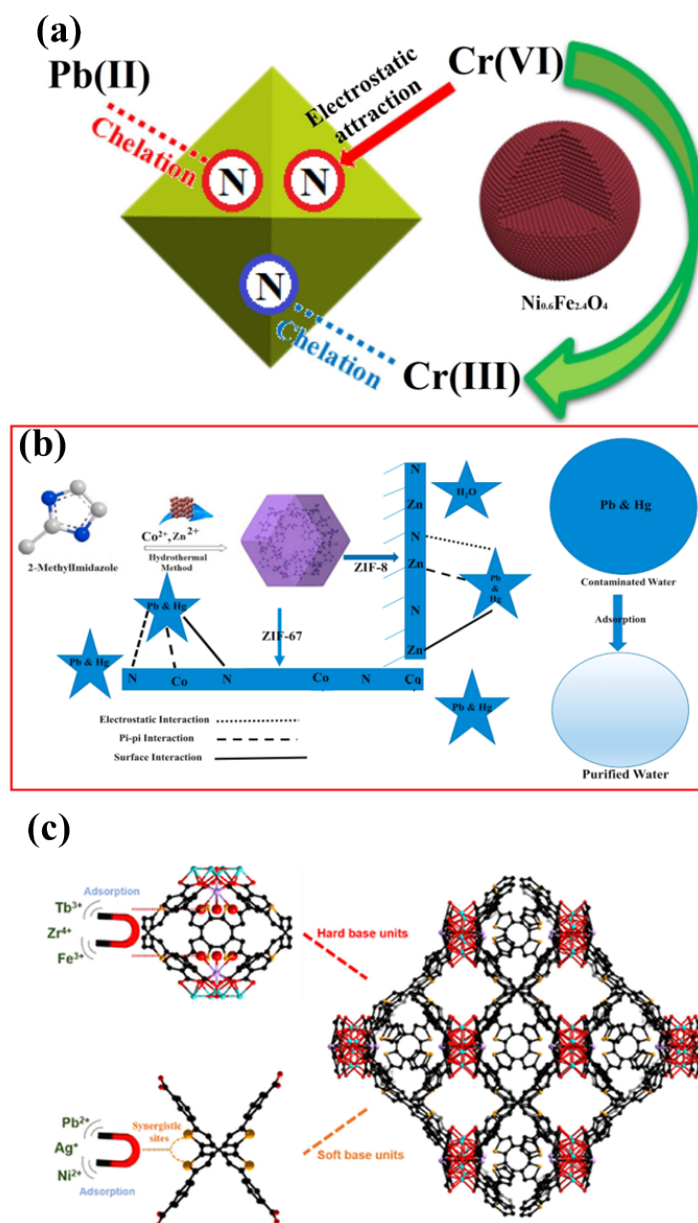


Fig. 2. Adsorption mechanism of $\text{Ni}_{0.6}\text{Fe}_{2.4}\text{O}_4\text{-UiO-66-PEI}$ (a), thiol-functionalized ZIF-8 (b), and CdK-m-COTTB (c) for the removal of heavy metals^[76,78,79].

ference in metal center (Zn^{2+} vs. Co^{2+}) alters the electronic environment and surface charge distribution, thereby modulating the dominant adsorption mechanism. Beyond monofunctional metal frameworks, bimetallic MOFs such as CdK-m-COTTB —constructed from sulfur-rich *m*-cyclooctatetrathio-phenylene tetracarboxylic acid (*m*- H_4COTTB) ligands and oxygen-rich bimetallic clusters—enable simultaneous capture of both soft and hard acid metal ions^[79]. Fig. 2c illustrates how the coexistence of S-rich ligands (soft base) and O-rich clusters (hard base) within a single framework creates dual binding environments that accommodate metal ions across the HSAB spectrum. This material achieves notable adsorption capacities of 636.94, 432.90, and 357.14 $\text{mg}\cdot\text{g}^{-1}$ for Pb^{2+} , Tb^{3+} , and Zr^{4+} , respectively, in single-component systems, while maintaining >99% removal efficiency across at least 12 metal ions in multi-component environments, alongside robust acid-base stability and recyclability. However, despite these impressive capacities, critical lifecycle data remain absent from current reports.

Key unknowns include the potential leaching of secondary metal ions from the bimetallic framework during regeneration and the structural integrity of the material after repeated acid-washing cycles. In the absence of such data, these bimetallic MOFs remain limited to the status of laboratory prototypes rather than viable system components.

2.3. Novel strategies and advances in material design

PSM, defect engineering and composite construction have increased the stability and function of MOFs, but these are still materials-centric improvements. True system integration of adsorption, desorption and resource recovery has yet to be realised; in particular, reactor configurations and dynamic operation protocols are still unknown. A typical approach is to modify UiO-66 by defect engineering in combination with the biodegradable chelator IDSA. The resulting adsorbent shows good binding ability for Pb^{2+} , Cu^{2+} , and Cd^{2+} , and maintains a high efficiency in the range of pH 4 to 7 (Fig. 3)^[80]. Defect engineering also has a repeated methodological

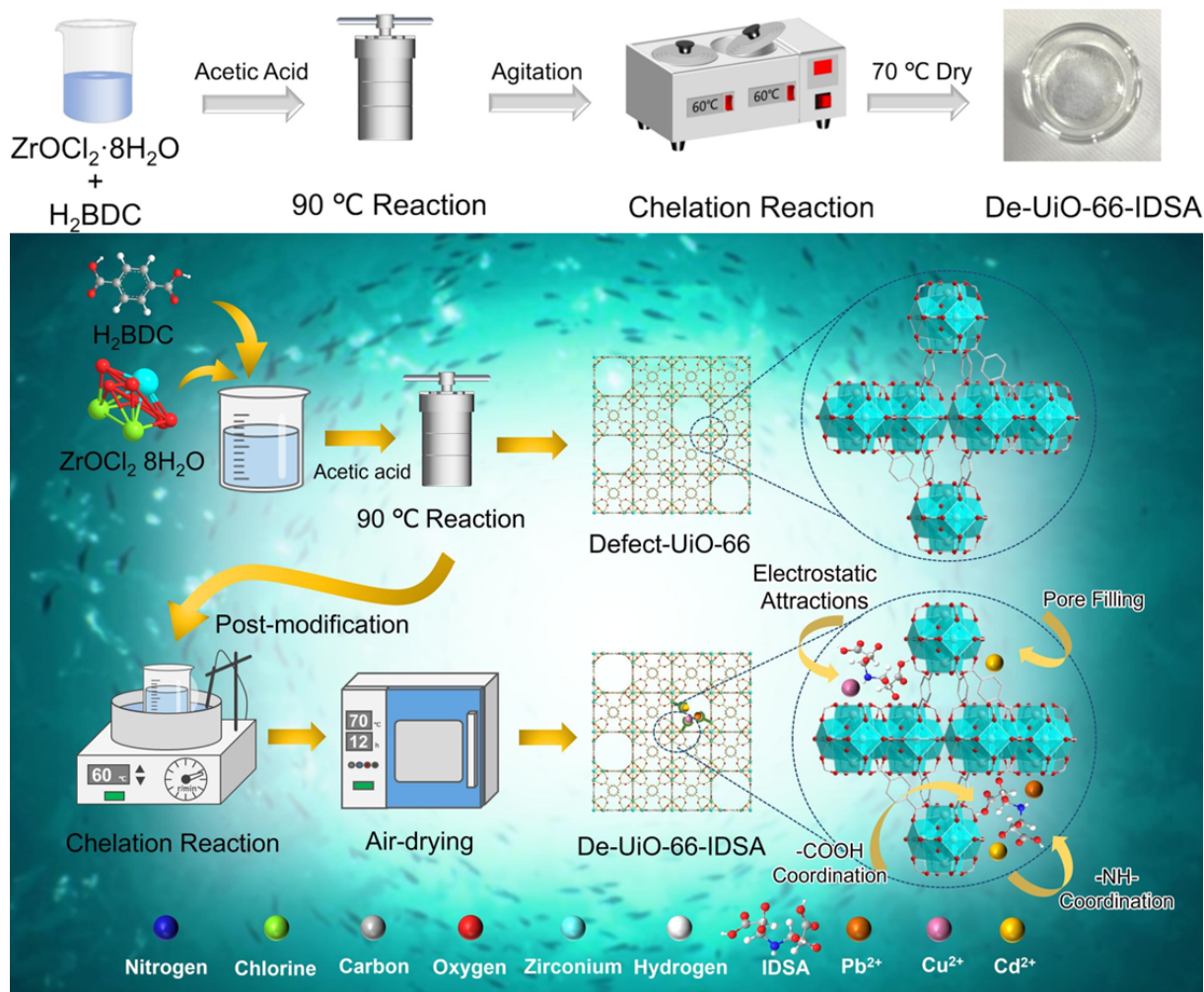


Fig. 3. Illustration of the preparation process and adsorption mechanism of De-UiO-66-IDSA^[80].

problem: the creation of new active sites may lead to an increased vulnerability to framework hydrolysis during regeneration. If a defective MOF degrades significantly faster than the pristine one, the increase in adsorption capacity will be offset by a shorter service life, and thus may not be economically feasible for the process.

A comprehensive evaluation of different MOF design strategies reveals significant variations in performance, cost, and practical applicability. The selection of appropriate design strategies depends on multiple factors including target metal ions, environmental conditions, cost constraints, and operational requirements. A systematic comparison of various strategies is essential for guiding material selection and future research directions. The selection of appropriate MOF design strategies requires a holistic approach that balances performance, cost, stability, and environmental impact considerations. While functionalized and composite MOFs offer superior performance in many cases, their increased complexity may limit practical applications. Future research should focus on developing simplified, cost-effective design strategies that maintain high performance while addressing practical implementation challenges.

Concurrently, contemporary material design philosophies are increasingly shifting from static architectures toward systems with dynamic responsiveness and integrated functionality^[81]. The convergence of machine learning and high-throughput computational screening offers a data-driven strategy for

the design of MOFs. This methodology allows for the rapid identification and optimization of superior performers, thereby advancing the development of solutions for heavy metal removal in aquatic remediation^[82]. A newly emerging design concept involves adaptive MOFs—materials whose pore structures or active sites can reconfigure in response to external stimuli such as pH, light, or specific molecules—thereby enabling intelligent and selective adsorption of different heavy metals^[83,84]. However, the controlled synthesis and in-depth mechanistic analysis of such responsive materials remain largely at the proof-of-concept stage. Wu et al. synthesized thiourea-modified UiO-66 (UiO-66-TU) for Au adsorption from electronic waste. After Au^{3+} uptake, in-situ reduction with NaBH_4 yielded Au nanoclusters embedded within the MOF matrix (Au NCs-UiO-66-TU), creating a functional composite material^[85].

At the same time, in the field of material preparation, green synthesis has gradually moved away from being an edge-case option and is now a major research direction. Among the many environmentally friendly paths, ultrasonic and microwave synthesis have gradually become relatively popular routes for the green synthesis of MOFs. Ultrasonic synthesis creates cavitation to generate a localised high-temperature and high-pressure environment, thus promoting the nucleation and growth of MOFs. For example, CoO/NiO@bio-char composites prepared by pyrolysis and ultrasonic treatment

have excellent adsorption performance for Zn(II) and Cd(II) ions, and the adsorption mechanism is mainly chemisorption supported by electrostatic interactions, surface complexation and intraparticle diffusion^[86]. Microwave synthesis can rapidly and uniformly heat at the molecular level via dipole rotation and ionic conduction to promote the homogeneous formation of crystal nuclei. As shown by microwave-synthesized UiO-66-GMA, this way can be used to prepare materials with a high specific surface area, excellent-developed porosity, good thermal stability and good reusability^[87]. This particular MOF has an adsorption capacity of 238.80 mg·g⁻¹ for Pb(II) and 208.45 mg·g⁻¹ for Cd(II), indicating that the microwave-assisted route is also suitable for preparing high-performance adsorbents. In addition to ultrasonic and microwave methods, the construction of nanoscale hierarchically porous MOFs has been proposed to improve mass transfer and active site accessibility, as recently reviewed by Duan et al^[88]. In particular, water-based synthesis under mild conditions has been used to prepare nanoscale hierarchical MOFs with enhanced adsorption and catalytic properties, as shown in the work of Yu et al.^[24]. However, green synthesis is still scale-limited; ultrasonic batch reactors face energy attenuation problems in large-scale operation, and microwave heating uniformity degrades in continuous-flow mode. A green-chemistry synthesis route at the gram-scale may not be economically viable for ton-scale production; this integration problem has not been systematically addressed.

3. Fundamental mechanisms of heavy metal adsorption by MOFs

A mechanistic understanding of how MOFs interact with heavy metal ions is a prerequisite for the multi-dimensional assessment in Section 4. The nature of adsorption sites and the forces governing metal binding directly determine how a material will perform with respect to stability, selectivity, and regenerability. A comprehensive understanding of the mechanisms by which MOFs adsorb heavy metal ions is essential for the systematic assessment of stability, selectivity, regenerability, scalability, and real-water validation that follows in subsequent chapters. Unlike conventional reviews that merely catalogue various MOF families, this section focuses on the nature of adsorption sites and the fundamental forces governing adsorption, providing a mechanistic foundation for the multi-dimensional analysis that constitutes the core contribution of this review.

3.1. Structural features of MOFs and types of adsorption sites

MOFs are constructed from metal nodes (metal ions or clusters) interconnected by organic linkers via coordination bonds, forming periodic network structures^[30]. This architectural design gives rise to three primary categories of adsorption sites: metal cluster sites^[89,90], organic linker sites^[91,92], pore confinement effects^[93,94].

3.1.1. Metal cluster sites

The metal clusters within MOFs serve as direct adsorption sites for heavy metal ions. Unsaturated coordination sites, commonly referred to as open metal sites (OMS), can act as Lewis acid centers that interact with heavy metal ions (acting as Lewis bases) through coordination bonds^[95]. For instance, the

Fe³⁺ sites in MIL-100(Fe) can capture heavy metal ions via electrostatic and coordination interactions^[96]. Furthermore, coordinatively unsaturated sites introduced through defect engineering can substantially increase the adsorption capacity of metal clusters. The enhanced affinity of De-UiO-66-IDSA toward Pb²⁺, Cu²⁺, and Cd²⁺ exemplifies this mechanism, where deliberately created defects provide additional binding sites^[80].

The accessibility of metal cluster sites is critically influenced by the framework's connectivity and the presence of terminating ligands. In frameworks with high connectivity (e.g., UiO-66 with 12-connected Zr₆ clusters), the metal nodes are fully coordinated by linkers, rendering them inaccessible without prior defect formation^[97,98]. This trade-off between structural stability and site accessibility represents a fundamental consideration in MOF design for adsorption applications. Incorporating metal doping into MOFs likewise enhances their adsorption performance and allows for the modulation of their structural and pore characteristics, thereby improving selectivity, activity, and stability^[99]. Following the partial substitution of Cu(II) sites in HKUST-1 with iron, Fe-HKUST-1 (5 mol% Fe) exhibits significantly improved water stability—retaining 86% of its crystallinity and 89% of its specific surface area after two hours of water exposure—along with excellent Pb(II) adsorption capacity (565 mg/g). However, excessive doping (>10%) can lead to structural collapse and reduced water stability, indicating that an optimal doping level must be determined to achieve favorable adsorption performance^[100].

3.1.2. Organic linker sites

Functional groups on organic linkers constitute the second major category of adsorption sites. Pristine linkers may contain carboxyl (–COOH), amino (–NH₂), hydroxyl (–OH), or other groups that can bind heavy metal ions through electrostatic interactions, hydrogen bonding, or coordination^[101]. More importantly, PSM offers a versatile route to introduce specific functional groups without disrupting the underlying framework architecture^[102]. This strategy enables the incorporation of soft base moieties such as thiol (–SH), which exhibits exceptionally high affinity for soft acid heavy metals like Hg²⁺, or amino groups that enhance capture of Pb²⁺ and Cu²⁺^[103–105]. Thiol functionalization fundamentally alters the adsorption mechanism through the introduction of sulfur-rich –SH groups. While conventional MOFs often rely on physical adsorption or weak electrostatic interactions, thiol-modified frameworks operate through specific chemical bonding—typically S–metal coordination—which simultaneously enhances both capacity and selectivity. The enhancements are primarily manifested in the following aspects. First, as soft bases, thiol groups exhibit exceptionally strong affinity for soft acid heavy metal ions such as Pb²⁺ and Cd²⁺, enabling chemisorption through the formation of stable thiolate–metal coordination bonds (e.g., S–Cd, S–Pb). This imparts the material with high adsorption capacities (e.g., up to 500 mg/g for Pb²⁺ and 370.4 mg/g for Cd²⁺) and rapid adsorption kinetics, far exceeding those of many conventional adsorbents^[106]. Second, the specificity of this soft acid–soft base interaction endows the MOF with remarkable selectivity, enabling it to preferentially and efficiently capture Pb²⁺ and Cd²⁺ even in complex aqueous solutions containing competing ions such as Cu²⁺, Zn²⁺, Fe³⁺, Co²⁺, and Mn²⁺. Additionally, through mixed-linker strategies (e.g., simultaneous use of mercaptosuccinic acid and thioglycolic

acid), thiol functionalization optimizes the pore structure and facilitates ion diffusion while ensuring the material's chemical stability in water. Moreover, this chemical bonding is reversible, allowing the material to be readily regenerated via acid washing and to retain high adsorption activity over multiple cycles, thereby achieving a dual enhancement of performance and sustainability.

The selectivity imparted by functional groups follows the principles of hard and soft acids and bases (HSAB) theory, which will be discussed in detail in Section 3.2. The thiol-functionalized defect-engineered MOF (Zr-MSA-DMSA) achieves heavy metal ion removal through the synergistic effects of coordination interactions via sulfur and oxygen atoms (forming M–S and M–O bonds), electrostatic attraction, and the abundance of defect sites within the material^[61]. Notably, the thiol groups, acting as soft Lewis bases, exhibit exceptionally strong specific affinity toward soft Lewis acids such as Hg(II). The maximum adsorption capacities for Pb(II), Hg(II), and Cd(II) reach 715.2 mg/g, 862.7 mg/g, and 450.5 mg/g, respectively, with rapid adsorption kinetics observed for Hg(II) and Pb(II) (within 5 min). In a mixed solution containing 11 coexisting ions, including Mg(II), Ca(II), Mn(II), Fe(III), Co(II), Ni(II), Zn(II), and Al(III), this functionalized MOF achieves removal efficiencies exceeding 95% for the target ions Pb(II), Hg(II), and Cd(II), while the removal rates for other competing cations remain below 5%, demonstrating exceptional anti-interference capability. Thiol functionalization exhibits significantly enhanced heavy metal uptake capacity, underscoring the powerful role of targeted functionalization based on the HSAB principle.

3.1.3. Pore confinement effects

The nanoporous architecture of MOFs contributes to adsorption not merely through high surface area but also through confinement effects that enhance adsorbate–adsorbent interactions^[107]. When the dimensions of heavy metal ions or their hydrated species match the pore apertures, size exclusion can confer selectivity^[108]. Moreover, confinement within nanopores can amplify binding energies through cooperative interactions with multiple functional groups lining the pore walls, a phenomenon distinct from bulk-phase adsorption^[109].

More specifically, the removal of heavy metals from contam-

inated water can be achieved through physical adsorption, whereby heavy metal ions diffuse into the pores of MOF adsorbents. Pore filling depends critically on the pore size and its compatibility with the metal ions. Optimal adsorption occurs when the size of the metal species closely matches the MOF pore aperture, thereby facilitating both chemical and physical interactions. This mechanism typically operates within microporous and mesoporous regimes, rendering pore size a key characteristic governing adsorption performance^[110]. Since most MOFs—particularly those that are modified or activated—possess well-developed porous structures, pore filling constitutes a dominant adsorption mechanism for heavy metal removal from aqueous solutions. The hierarchical pore structures present in some MOFs (micropores and mesopores) facilitate rapid diffusion while maintaining high adsorption capacity, addressing the kinetics limitations that plague many conventional adsorbents^[29]. The ZIF-8@GO-COOH composite exhibits a high specific surface area (1054.952 m²/g) and a hierarchical pore structure comprising both micropores and mesopores^[111]. During the adsorption process, heavy metal ions (e.g., Cu(II) and Pb(II)) are first rapidly captured by the abundant oxygen-containing functional groups (e.g., –COOH) on the surface, followed by diffusion and filling into the interior of the pores. This pore-filling mechanism not only significantly enhances the adsorption capacity, as the extensive internal surface area provides a vast number of potential adsorption sites, but also facilitates ion mass transfer through the well-defined pore channels, thereby improving the adsorption kinetics. The adsorption isotherms conform to the Langmuir model, confirming the dominance of monolayer chemisorption occurring on the internal pore surfaces. Consequently, the effective pore-filling process enables MOF-based materials to achieve efficient and rapid removal of heavy metal ions through the synergistic effects of physical confinement and chemical interactions.

3.2. Classification and identification of adsorption forces

Adsorption of heavy metals by MOFs rarely follows a single path; generally speaking, multiple forces work together to achieve this. Table 2 shows the main types of interaction, their origins, applicable objects and representative examples.

Table 2. Classification of adsorption forces in MOF-based heavy metal removal

Interaction type	Origin/Basis	Applicable targets	Representative examples	References
Coordination bonding	Formation of coordinate bonds between metal ions and donor atoms (N, O, S)	Transition metals, heavy metal ions (Pb ²⁺ , Hg ²⁺ , Cu ²⁺ , Cd ²⁺)	–SH functionalized MOFs for Hg ²⁺ ; –NH ₂ modified UiO-66 for Pb ²⁺ , Cd ²⁺	[112–114]
Electrostatic interactions	Coulombic forces between charged MOF framework and ionic heavy metal species	Cationic (Pb ²⁺ , Cd ²⁺) or anionic (Cr ₂ O ₇ ^{2–} , AsO ₄ ^{3–}) species	ZIF-8 at varying pH; MIL-100(Fe) for anionic pollutants	[95,115,116]
Hydrogen bonding	Interaction between hydrated metal ions and functional groups (–OH, –NH ₂ , –COOH)	Hydrated metal ions, oxyanions	Amino-functionalized MOFs; carboxyl-rich frameworks	[101,117–119]
π–π interactions	Stacking interactions between aromatic rings of linkers and aromatic moieties of pollutants	Heavy metal complexes with aromatic ligands; some oxyanions	MOFs with aromatic linkers (e.g., terephthalate-based frameworks)	[120]
Redox reactions	Reduction of high-valency heavy metals to lower valency or elemental states	Cr(VI) reduction to Cr(III);	Facile preparation of magnetic Zr-MOF for Pb(II) and Cr(VI)	[76]
Ion exchange	Exchange between charge-balancing counterions in MOF and heavy metal ions	Ionic MOFs with exchangeable anions/cations	Cationic MOFs for oxyanion removal; anionic MOFs for cation exchange	[121–123]

Among the six interaction types in Table 2, coordination bonding and electrostatic interactions are the two main modes of heavy metal adsorption by MOFs; the other four serve supporting or context-dependent functions. The following are the mechanisms that will be discussed, and coordination bonding will serve as the main source of adsorption selectivity. For example, ZIF and its modified composites mainly adsorb heavy metals by electrostatic interaction, coordination bonding and ion exchange (Fig. 4)^[46].

Among them, coordination bonding is the most pronounced and selective type of bonding, and its strength is determined by HSAB theory^[124–127]: hard acids (e.g., Fe^{3+} , Cr^{3+} , Zr^{4+}) prefer hard bases (e.g., $-\text{COOH}$, $-\text{OH}$, $-\text{PO}_3\text{H}_2$); soft acids (e.g., Hg^{2+} , Au^+ , Ag^+) have a strong affinity for soft bases (e.g., $-\text{SH}$, $-\text{SR}$, $-\text{SCH}_3$); and borderline acids (e.g., Pb^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+}) show both hard and soft base affinities and are thus less selective among competing ions. Based on the above classification, the specific functionalization route to achieve a particular target metal-ion-binding capability has been selected. Soft-base functionalisation (thiol, thioether) is recommended for mercury capture in industrial effluents; for lead and cadmium removal in the presence of competing calcium and magnesium, borderline bases combined with size exclusion may be more effective^[43].

3.3. Mechanistic case studies of representative MOF systems

To ground the foregoing mechanistic discussion in concrete examples, Table 3 summarizes the adsorption characteristics of three representative MOF families —MIL, UiO, and ZIF—which collectively illustrate the diversity of adsorption sites and mechanisms.

The MIL series, particularly MIL-100(Fe) and MIL-101(Fe), exemplifies metal-cluster-dominated adsorption. The Fe_3O clusters contain coordinatively unsaturated Fe^{3+} sites that function as Lewis acids, capable of binding Lewis basic heavy metal species through its oxygen atoms^[62,129]. Additionally, the overall positive charge of the framework under appropriate pH conditions enables electrostatic attraction of anionic heavy metal species. The adsorption mechanism of MIL-101 and Fe-MIL-101 for the heavy metal ion $\text{Pb}(\text{II})$ primarily involves interactions between surface functional groups and lead ions, with Fe-MIL-101 exhibiting enhanced adsorption capacity due to iron doping^[128]. For MIL-101, the carboxyl groups ($-\text{COOH}$) in its framework serve as the key sites for $\text{Pb}(\text{II})$ adsorption, binding through coordination interactions. Meanwhile, the surface charge state is influenced by the solution pH; when the pH exceeds the point of zero charge (pH_{pzc}

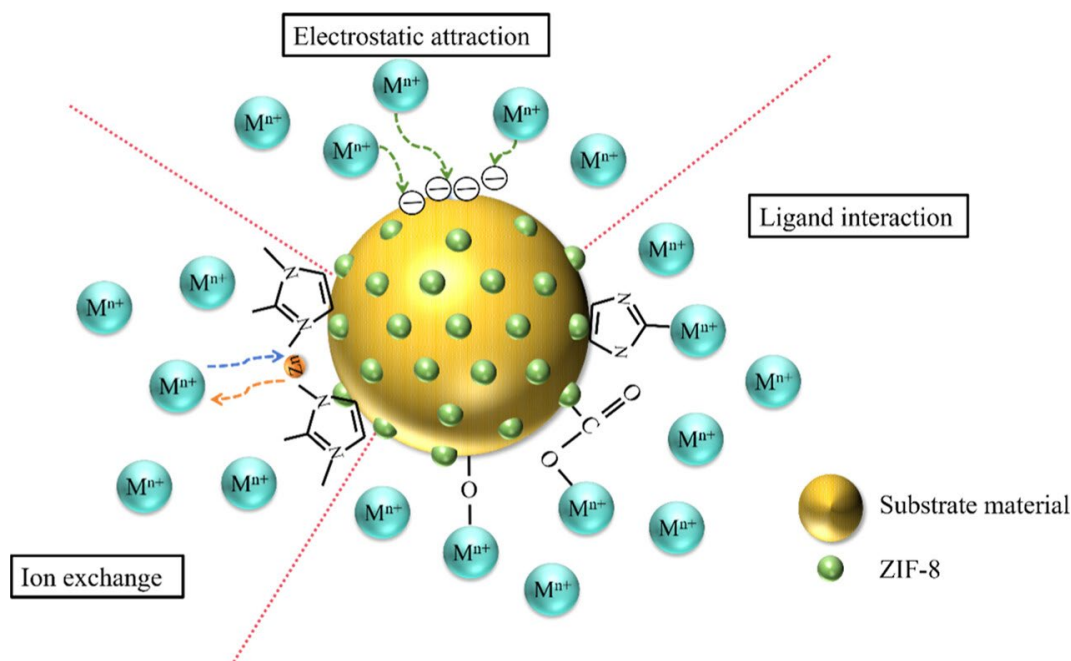


Fig. 4. The adsorption mechanism of ZIF-8 and its modified composites toward heavy metals^[46].

Table 3. Adsorption mechanisms of representative MOF systems

MOF system	Metal nodes	Organic linker	Primary adsorption sites	Dominant mechanisms	References
MIL-101(Fe)	Fe_3O clusters	Terephthalic acid	Fe^{3+} sites, carboxyl groups	Coordination, electrostatic, hydrogen bonding	[62,128]
MIL-100(Fe)	Fe_3O clusters	Trimesic acid	Fe^{3+} open metal sites	Coordination, electrostatic, ion exchange	[129]
UiO-66(Zr)	$\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters	Terephthalic acid	Defect sites, $-\text{COOH}$	Coordination, hydrogen bonding	[130–133]
UiO-66- NH_2	Zr_6 clusters	2-Aminoterephthalic acid	$-\text{NH}_2$, defect sites	Coordination, electrostatic, hydrogen bonding	[130,134]
ZIF-8	Zn^{2+}	2-Methylimidazole	Imidazole N, pore cavities	Coordination, electrostatic, ion exchange	[135]
CdK-m-COTTTB	Cd-K bimetallic	S-rich ligand	S atoms, bimetallic clusters	Coordination (hard–soft synergistic)	[79]

≈ 4.4), the surface becomes negatively charged, facilitating electrostatic attraction toward positively charged lead species such as Pb^{2+} and $\text{Pb}(\text{OH})^+$. In contrast, for Fe-MIL-101, the introduction of iron leads to the formation of iron oxyhydroxyl groups ($-\text{OH}$) on the material surface or within its pores. These hydroxyl groups engage in stronger surface coordination reactions with lead ions (e.g., $\text{Fe}-\text{OH} + \text{Pb}^{2+} \rightarrow \text{Fe}-\text{OPb} + \text{H}^+$), where the chemical interaction surpasses mere electrostatic attraction. Furthermore, iron doping increases the surface heterogeneity, providing additional active sites. As a result, Fe-MIL-101 efficiently adsorbs lead ions over a broader pH range (with optimal performance around $\text{pH} \approx 6$) through the synergistic mechanisms of electrostatic attraction and coordination complexation, thereby achieving higher adsorption capacity and faster adsorption kinetics compared to pristine MIL-101. The results confirmed that metal cluster sites play a dominant role, with adsorption energies correlating with the softness/hardness of the metal ions relative to the framework Lewis acidity.

The UiO series, exemplified by UiO-66, is renowned for exceptional stability derived from the strong $\text{Zr}-\text{O}$ bonds connecting Zr_6 clusters to dicarboxylate linkers^[136]. However, pristine UiO-66 lacks strong coordinating groups, limiting its intrinsic heavy metal adsorption capacity^[137]. This limitation has driven extensive research into defect engineering and functionalization strategies^[130–133]. Ahmadijokani et al.^[138] provided a comprehensive critical review of UiO-66 in water treatment, emphasizing that defect sites—missing linkers or missing clusters—create additional adsorption sites without compromising framework integrity. The amino-functionalized derivative, UiO-66- NH_2 , exhibits substantially enhanced adsorption for Pb^{2+} and Cd^{2+} through cooperative binding by amino groups and carboxylates^[130,134]. Zhai et al. demonstrated that functionalization exerts a dual impact on the performance of MOFs^[139]. On one hand, the introduction of functional groups (e.g., $-\text{NH}_2$, $-\text{OH}$) occupies pore space, leading to a decrease in specific surface area and pore volume, thereby impairing the removal capacity for ions that rely on physical adsorption (such as Ni^{2+} and Fe^{3+}). Consequently, pristine UiO-66, with the highest specific surface area ($1569.2 \text{ m}^2/\text{g}$), exhibits the optimal adsorption performance for these two ions. On the other hand, functionalization introduces specific chemical sites. For instance, the $-\text{OH}$ groups on the surface of UiO-66- $(\text{OH})_2$ undergo protonation under acidic conditions to form $-\text{OH}_2^+$, enabling efficient capture of negatively charged Cr^{6+} -containing oxyanions through strong electrostatic attraction. This chemisorption mechanism allows the material to achieve the highest adsorption capacity for Cr^{6+} (39.0 mg/g) and exceptional selectivity ($\text{Cr}^{6+}/\text{Ni}^{2+}$ selectivity up to 21.7), despite its relatively low specific surface area ($785.5 \text{ m}^2/\text{g}$). Therefore, functionalization not only modulates the physical structure of MOFs but also enables high-capacity, high-selectivity adsorption toward specific heavy metal ions through the introduction of targeted chemical interaction sites.

The ZIF series, particularly ZIF-8, combine the structural features of MOFs with the topology of zeolites^[140]. The imidazolate linkers provide nitrogen atoms capable of coordinating heavy metal ions, while the pore apertures (approximately 0.34 nm) can impose size selectivity^[135]. The application of ZIF-8 in adsorption primarily relies on coordination through imidazole nitrogen atoms, complemented by electrostatic interac-

tions that vary with the solution pH ^[141]. Liu et al.^[49] demonstrated excellent adsorption of $\text{As}(\text{III})$, $\text{As}(\text{V})$, and $\text{Sb}(\text{V})$ by ZIF-8 in aqueous solutions. In single-solute systems, the maximum adsorption capacities followed the order $\text{As}(\text{III})$ (151.3 mg/g) > $\text{As}(\text{V})$ (106.4 mg/g) > $\text{Sb}(\text{V})$ (104.7 mg/g). Furthermore, they elucidated that the adsorption mechanism primarily relies on the zinc hydroxyl groups ($\text{Zn}-\text{OH}$) on the ZIF-8 surface as the dominant active sites, which form surface complexes with the contaminants, thereby immobilizing them through chemical interactions. Nevertheless, competitive effects among arsenic species and with antimony ions remain significant: $\text{As}(\text{V})$ exhibits a stronger inhibitory effect on $\text{Sb}(\text{V})$ adsorption than does $\text{As}(\text{III})$, while $\text{Sb}(\text{V})$ shows relatively weaker suppression of arsenic adsorption. When arsenic and antimony are introduced sequentially, the pre-adsorbed species form stable complexes with ZIF-8, strongly inhibiting the adsorption of the subsequently introduced species, and this pre-adsorbed $\text{Sb}(\text{V})$ is more difficult to replace than pre-adsorbed arsenic. Moreover, at low pH (< 8.8), pre-adsorbed arsenic can be partially displaced by subsequently introduced $\text{Sb}(\text{V})$; however, this adverse effect is attenuated at high pH or high initial arsenic concentrations. This finding highlights the complexity of multi-component systems—a theme that will recur throughout this review. Mo et al.^[47] reviewed that pristine ZIF-8 powder suffers from issues such as easy agglomeration and difficulty in separation and recovery. In contrast, ZIF-8-based composite materials, formed by compositing with magnetic materials (e.g., Fe_3O_4), carbon materials (e.g., GO), or other functional materials, effectively improve dispersibility and recyclability, while exhibiting high adsorption capacity toward various heavy metals including $\text{Pb}(\text{II})$, $\text{Cr}(\text{VI})$, $\text{As}(\text{III})$, $\text{Cu}(\text{II})$, and $\text{Cd}(\text{II})$. They also pointed out that most current studies in this field remain limited to laboratory-scale single-pollutant systems, which are inconsistent with the complex composition of actual wastewater.

Recent advances have extended beyond unitary metal frameworks to bimetallic systems that exploit synergistic effects. Shen et al.^[79] reported CdK-m-COTTTB, a bimetallic MOF constructed from sulfur-rich ligands and oxygen-rich bimetallic clusters, which achieves remarkable adsorption capacities (636.94 mg/g for Pb^{2+} , 432.90 mg/g for Tb^{3+} , 357.14 mg/g for Zr^{4+}) in single-component systems. Critically, this material maintained >99% removal efficiency across at least 12 metal ions in multicomponent environments, demonstrating that bimetallic design can address selectivity limitations while retaining stability. The bimetallic Fe-Mg MOF exhibits adsorption capacities of 196 mg/g , 191 mg/g , and 175 mg/g for $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Cu}(\text{II})$, respectively, which are significantly higher than those of the corresponding monometallic Mg-MOF or Fe-MOF^[142]. The mechanism underlying this performance enhancement is primarily attributed to the bimetallic synergistic effect. First, the incorporation of Fe increases the specific surface area of the material, creating new micropores and additional adsorption sites. Second, the coexistence of Fe and Mg enhances the Lewis acidity of the material surface, providing more active sites that facilitate the adsorption of positively charged heavy metal ions via an ion exchange mechanism. Furthermore, under suitable pH conditions, the deprotonation of surface functional groups renders the material surface negatively charged, resulting in stronger electrostatic attraction toward heavy

metal cations in solution. Yu et al.^[143] synthesized a novel thiol-functionalized bimetallic Zn/Ni-MOF (ZNM-2), which exhibits a maximum adsorption capacity of 744.4 mg/g for Hg(II)—more than twice that of the monometallic Ni-MOF (NM, 328.8 mg/g). When applied to real water samples, ZNM-2 reduces the Hg(II) concentration to 0.3 µg/L, well below the national drinking water standard limit (1.0 µg/L). The bimetallic structure introduces a greater diversity of active metal sites, thereby providing more abundant adsorption sites and enhancing interactions with the target pollutant. Specifically, the bimetallic architecture of ZNM-2 enables Hg(II) to simultaneously coordinate with -SH groups, forming a bidentate coordination structure with higher adsorption energy (35.53 kJ/mol). In contrast, in the monometallic NM, the excessive distance between thiol groups allows only monodentate coordination (adsorption energy: 14.52 kJ/mol).

3.4. Mechanistic understanding as the foundation for multi-dimensional assessment

In summary, this chapter has established that MOF adsorption sites derive from three primary sources: metal clusters (open metal sites and defects), organic linkers (both intrinsic and post-synthetically introduced functional groups), and pore confinement effects. Adsorption proceeds through multiple mechanisms, with coordination bonding being the most selective and significant, governed by HSAB theory. Representative MOF families such as MIL, UiO, and ZIF illustrate different mechanistic regimes—metal-cluster-dominated, defect-site-dominated, and ligand-dominated adsorption, respectively. Furthermore, bimetallic and heterostructured MOFs demonstrate that synergistic design can overcome the limitations of unitary frameworks, particularly in multicomponent systems.

The strength of metal–ligand coordination bonds, for instance, determines a MOF's resistance to hydrolysis and framework collapse, and understanding which bonds are vulnerable under acidic, basic, or competitive conditions guides the design of water-stable MOFs. When turning to selectivity, the principles of hard and soft acids and bases (HSAB) together with functional group chemistry offer rational guidelines for designing MOFs that can discriminate among competing heavy metal ions and against common interfering cations such as Ca²⁺, Mg²⁺, and Na⁺. Regarding regenerability, the reversibility of the adsorption forces dictates the ease of desorption and the conditions required for regeneration; strong chemisorption may confer high capacity but complicates regeneration, whereas weaker physisorption facilitates cycling at the cost of selectivity. Mechanistic understanding also informs the choice of synthesis routes for scalability: frameworks that rely on defect sites may require precise synthetic control that challenges scale-up, while those depending on intrinsic linker functionality may prove more amenable to green, scalable methods. Finally, for real-water validation, the complexity of real wastewater matrices—including pH variations, competing ions, and natural organic matter—affects each adsorption mechanism differently, and predicting performance in real systems requires mechanistic models that account for these interferences. A mechanistic understanding is therefore not an end in itself but the essential prerequisite for addressing the five dimensions—stability, selectivity, regenerability, scalability, and real-water validation—that ultimately determine practi-

cal viability. The subsequent chapters will build upon this mechanistic foundation, systematically examining each dimension.

4. Toward application-ready MOFs

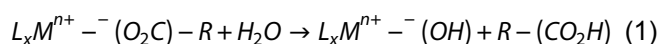
4.1. Water stability

The first demand for applying MOFs-based adsorbents to heavy-metal pollution is water stability. If it cannot withstand the damage caused by water, the other indicators are meaningless. Systematically explore the degradation mechanisms, design strategies and trade-offs between stability and adsorption capacity for MOFs in this section.

4.1.1. Degradation mechanisms of MOFs in aqueous environments

MOFs are prone to degradation in the presence of water because of the chemical nature of the coordination bonds in their framework. Water molecules can attack metal–ligand bonds in the following two ways: ligand displacement and hydrolysis^[144]. In ligand displacement, a water molecule coordinates at the vicinity of the metal–ligand bond without dissociation; thus, undissociated water is associated with the metal centre, and the linker becomes a dangling^[145]. Water dissociates in hydrolysis, breaking the metal–ligand bond and forming metal hydroxide and a protonated ligand^[146]. The latter is usually more damaging and irreversible.

Hydrolysis of MOFs can be classified into the two types shown in equations (1) and (2)^[147]. The first reaction adds a hydroxyl group to the metal centre and hydrogenates the organic linker; the second is direct water insertion with the release of the deprotonated organic ligand. Both ways result in framework degradation; however, the latter may be reversible deprotonation under certain conditions. Recently, atomistic studies based on reactive molecular dynamics and metadynamics have explored the energy landscape of hydrolysis in detail. Free-energy surfaces of Zn-based MOFs show that the stability of water is highly sensitive to linker size and chemical structure^[148]. ZIFs have a higher resistance to hydrolysis than IRMOFs because the Zn–N bonds are stronger than Zn–O bonds and the imidazolate linkers are hydrophobic. The activation barriers for hydrolysis are relatively large in all frameworks, generally ranging from 15–25 kcal/mol and varying with different metal–ligand combinations and coordination environments.



The Chemical stability of MOFs in the presence of strong acids or bases depends on the ease of dissociation of metal–ligand and coordination bonds. In an acidic environment, protons compete with metal ions for coordination to the linker, causing protonation of the carboxylate or other coordinating groups and thus framework dissolution^[149]. In a general sense, hydroxide ions can deprotonate coordinated water molecules or directly coordinate to the metal centre to form metal hydroxide or oxide precipitates on the framework surface^[150]. MOFs have different stability in the presence of acid and base according to the metal–node composition. Zirconium-based MOFs, such as

UiO-66, are very stable in the range of pH 1 to 11 because of strong Zr-O bonds and a high connectivity (12-coordinated) of Zr₆ clusters^[138,149]. Zinc-based MOFs, on the other hand, are unstable in the presence of weak acids and bases^[151–153]. A comparative study of Zr- and Ce-based UiO-66-NH₂ showed that although Ce-MOF had a higher adsorption capacity due to surface defects from partial Ce(IV) reduction, Zr-MOF retained better crystallinity after exposure to an aqueous environment^[154]. Schoenecker and his colleagues have systematically investigated the stability of seven MOF structures HKUST-1, Mg-MOF-74, UiO-66, UiO-66-NH₂, DMOF-1, UMCM-1 and UMCM-1-NH₂ in water adsorption at room temperature and relative humidity up to 90%^[155]. Based on the above results, MOFs containing copper paddlewheel clusters, magnesium and zirconium (HKUST-1, Mg-MOF-74, UiO-66, and its amino derivative) maintained good structural stability, whereas zinc carboxylate MOFs (DMOF-1 series, UMCM-1) completely lost crystallinity upon exposure to water. For DMOF-1 and UMCM-1, the diffraction peaks disappeared entirely; UMCM-1 showed characteristic peaks of Zn(OH)₂ and was fully hydrolyzed framework.

In addition to direct hydrolysis, MOF stability may be reduced by competing ligands in the real wastewater environment^[156]. Phosphates, carbonates and other anions that have a high affinity for metal centres can displace organic linkers and trigger framework degradation^[29,31]. Phosphate ions are relatively hazardous because they can strongly bind to hard Lewis acid metal centers, such as Zr⁴⁺, Fe³⁺, and Al³⁺^[12,29,157]. The coordinating mechanism among the above parties is suitable for the actual treatment of wastewater containing phosphates and carbonates.

4.1.2. Design strategies for enhancing MOFs stability

The rational design of water-stable MOFs has progressed significantly, guided by mechanistic understanding of degradation pathways. Several complementary strategies have emerged for enhancing aqueous stability.

High-valence metal nodes represent the most successful approach for achieving water-stable MOFs^[38,158]. The use of high-valence metal ions (Zr⁴⁺, Ti⁴⁺, Cr³⁺, Fe³⁺, Al³⁺) results in stronger metal–ligand bonds that resist hydrolysis due to their high charge density^[34,44]. The UiO-66 family, based on Zr₆ clusters, exemplifies this strategy, exhibiting remarkable stability in water, acidic solutions, and even boiling water^[138,159]. A comparative study of Ce- and Zr-based UiO-66-NH₂ revealed that while Ce-MOF exhibited higher adsorption capacity due to surface defects from partial Ce(IV) reduction, Zr-MOF demonstrated superior crystallinity retention after exposure to aqueous environments^[154].

Recent breakthroughs have extended beyond HSAB theory predictions. The HSAB theory has been widely considered a powerful tool for predicting MOF stability—hard high-valence metal ions paired with hard ligands tend to form stable coordination bonds^[160]. However, Gu and co-workers recently reported an ultrastable copper carboxylate MOF (Cu₂TBAPy) that defies conventional HSAB predictions^[161]. Using an innovative “envelope strategy” with H₄TBAPy (1,3,6,8-tetra(4-carboxyphenyl)pyrene) as a nano-coating layer, each copper cluster was covered by two hydrophobic pyrene cores, forming a sandwich-like hydrophobic center that effectively prevents water molecules from approaching

Cu–O coordination bonds. This material exhibits exceptional acid-base tolerance (pH 0–13), maintaining structural stability for 240 days in water at room temperature and 7 days in boiling water—far exceeding all previously reported copper carboxylate MOFs.

Rigid ligands and high connectivity also contribute significantly to stability. The Connectivity of the framework and the Number of Ligands Coordinated to Metal Clusters Affect Stability Directly. A high degree of connectivity reduces the number of open metal sites available for water adsorption and increases the energy required for ligand displacement^[162,163]. UiO-66 has a 12-connected Zr₆ cluster and is highly stable; MOFs with lower connectivity, such as MOF-5 with 4-connected Zn₄O clusters, are much less stable^[138,153]. Ligands are also relatively rigid; otherwise, if they were flexible, they would change shape and expose water molecules at the metal centre; rigid linkers, on the other hand, maintain the original structure. Recently, in the design of aliphatic ligands, bioisosteric substitution has been employed to rigidify flexible ligands through intramolecular non-covalent interactions, and stable, highly porous frameworks have been achieved^[164].

Hydrophobic modification and surface coatings can prevent water absorption of MOFs without changing the chemistry of the underlying framework^[23,36]. Post-synthetic modification with alkyl or fluoroalkyl groups introduces a hydrophobic surface that reduces water adsorption at the exterior of MOF crystals and delays the start of hydrolysis^[165]. He et al. integrated hydrophobic organotin-oxo clusters ([Sn₄O₂(carboxylate)₄]) and photosensitive copper-sulfur clusters ([Cu₈(thiolate)₈]) into a single heterocluster MOF named SnCu-*m*MBA-dia(9), used meta-mercaptopbenzoic acid (mMBA) as a bifunctional linker, and thus provided exceptional hydrolytic stability for the material^[166]. Stability is guaranteed by the high connectivity of the framework, the mechanical strength of a double-interpenetrating network, and, most importantly, a superhydrophobic surface (with a water contact angle of 164.2°) is created by hydrophobic butyl groups on the [Sn₄] clusters. These groups are hydrophobic and therefore do not adsorb or condense water molecules at the cluster surface. As a result, this MOF has maintained its structure after six months of exposure to air, one month in water, and even after 24 hours of boiling in water. On the other hand, a congener consisting only of copper-sulfur clusters is easily degraded in the presence of water.

MOF-composite protective strategies in hybrid structures have been proposed to improve stability and maintain the accessibility of active sites^[11,24]. Graphene oxide (GO) membranes intercalated with MOF@chitosan core-shell nanoparticles showed significantly improved structural stability compared to pure GO membranes and exhibited stable dye removal for over 120 hours^[167]. The MOF@CS nanoparticles are dual modifiers that optimise the interlayer spacing by intercalation and prevent swelling through covalent cross-linking of GO layers. Quasi-MOFs retain some long-range order and local coordination environments of the parent MOF but introduce controlled defects; thus, they are stable and multifunctional^[168]. The materials have been maintained in a crystalline state and, at the same time, show improved mass transport and active-site accessibility^[40,80].

A problem of the above stability research is that a high-stability material often has a lower adsorption capacity^[158]. Due

to the chemistry of basic materials, this trade-off must be made, and it will affect the Design of the application. The first reason is that there are no active sites for the trade-off. Sustainability of UiO-66 is a high-stability framework with fully coordinated metal nodes and few open metal sites. Although this structure has increased bond strength and hydrolysis resistance, the number of available adsorption sites has been reduced^[169]. On the other hand, MOFs with coordinatively unsaturated metal sites, such as MIL-100(Fe)^[96,170] or HKUST-1^[171,172], have abundant open metal sites for heavy metal coordination but are less stable. HKUST-1 shows good crystallinity after exposure to water, but its BET surface area is reduced by 26%, indicating damage at the active sites^[155]. Therefore, defect engineering has been introduced to add controlled defects and adsorption sites without severely altering the structure of the entire framework^[81]. The two effects of water on the stability of MOFs are both destabilizing and stabilizing; thus, they have been investigated computationally^[173].

Water stability of MOFs is the basic link in our system of assessment; without it, none of the other performance indicators are meaningful. The main contents of this chapter are that the causes of degradation are hydrolysis, acid/base decomposition, and competitive coordination; specifically, metal-ligand bond cleavage is the mechanism, and the precise path varies based on framework chemistry and the external environment. Design Strategies for Stability Include High-valence metal nodes, Rigid ligands with high connectivity, Hydrophobic modification, and Composite protection; each has its own strengths and weaknesses. Stability and adsorption capacity are in opposition; thus, coordination saturation cannot be achieved at the same time as the availability of active sites. Building on the above foundation, the next issue is selectivity; thus, it has been explored whether a water-stable MOF can perform well in a chemical environment under Section 4.2. The following chapters will use the stability foundation established above to explore how other attributes of selective, regenerative, scalable and real-water adsorption (MOFs-based adsorbents) are influenced by or related to aqueous stability.

4.2. Selectivity

As shown in the Introduction, due to the complexity of real wastewater matrices, high selectivity is required that single-metal capacity indicators cannot provide. This section explores how the above selectivity is realised by rational design^[29,44,174]. Problems caused by the complexity of real wastewater are presented in this section, design strategies to enhance selective adsorption are proposed, and the basic trade-off between selectivity and broad-spectrum adsorption capacity is explored.

4.2.1. Challenges of selective adsorption: The complexity of real wastewater

Real wastewater matrices are naturally complex systems that contain various chemical species which can affect the adsorption performance of MOFs to some extent. Unlike the ideal laboratory environment where only single heavy metal ions in deionized water are studied, real industrial wastewater, such as electroplating wastewater, mining drainage and other metallurgical process streams, contain multiple competing ions, natural organic matter, and fluctuations in pH; all of these factors affect the selectivity of MOFs-based

adsorbents^[12,30,76].

The first problem of selective heavy metal removal is that several kinds of heavy metals exist simultaneously and have similar chemical properties. Wastewater streams often contain a mixture of Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , etc., which have similar ionic radii and coordination preferences^[4,9]. Under such circumstances, the adsorption sites on MOFs are in competition for various metal ions to bind, and the presence of one metal can significantly inhibit the adsorption of others by site competition^[79,169]. Recently, some studies have shown that the competitive adsorption behaviour can be modelled by surface-site competition models. A new Chemoselective Surface Site Competition-Complexation Model (SSCCM) was constructed to investigate the selective adsorption of Pb^{2+} and Cr^{6-} from mixed solutions containing Co^{2+} , Ca^{2+} , As^{3+} , Mg^{2+} , Ni^{2+} , Zn^{2+} , Fe^{3+} , and Cu^{2+} at concentrations as high as 1000 ppm^[175]. The model shows that the interference of competing ions can be expressed as distribution coefficients, and thus selectivities under real conditions can be predicted. The synthesized 3-D Cd-MOF showed excellent selectivity for Pb^{2+} and Cr^{6-} in this study, and the interference strength of competing ions varied significantly; for adsorption of Cr^{6-} , Ca^{2+} had the strongest competitive effect at 107.77 mL/g, while Mg^{2+} had the weakest at 38.091 mL/g. The competitive mechanism generally forms stable complexes between the competing ions and functional groups to prevent access by the target metal. Carboxyl-functionalized MOFs are a typical example; in the presence of Ca^{2+} , Pb^{2+} adsorption is significantly reduced because Ca^{2+} strongly binds to the carboxylate groups, blocking the adsorption sites for the target metal^[40,96].

In addition to the above-mentioned heavy metals, non-toxic coexisting cations such as Ca^{2+} , Mg^{2+} and Na^{+} are also widely distributed in natural waters and industrial effluents. These ions are often present at concentrations several orders of magnitude higher than those of the target heavy metals, so they occupy adsorption sites and reduce the actual capacity for heavy metal removal significantly^[37,43]. In many real-world water systems, the concentration of Ca^{2+} and Mg^{2+} is in the range of tens to hundreds of milligrams per litre; at the same time, target heavy metals may only be at the parts-per-million or even parts-per-billion level, and thus non-target ions vastly outnumber the target species^[176–179]. The two types of interference are electrostatic and competitive coordination. Ca^{2+} and Mg^{2+} are hard Lewis acids that have a strong affinity for carboxylate groups and other hard-base functional groups often used in MOF design^[180,181]. Systematic research on carboxyl-functionalised MOFs (UiO-66-COOH and UiO-66-(COOH)_2) has found that, under single-ion conditions, both MOFs exhibited the highest adsorption capacity for Ca^{2+} , which is due to a smaller hydrated radius and favourable coordination with $-\text{COO}^-$ groups^[182]. Cu^{2+} had the strongest binding affinity and was more competitive in the multi-ion system containing Cu^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Ca^{2+} , Mg^{2+} and Na^{+} ; therefore, Cu^{2+} showed the highest uptake and thus achieved selectivity in the presence of many competing cations. Research on materials with high selectivity for these competing ions and stability under such conditions has also been carried out. Co(II)-PIIMs nanofibers developed via ion-imprinting technology showed very good selectivity factors for Ca^{2+} , K^{+} , and Mg^{2+} , such as 7.42, 55.98, and 72.30, respectively; thus, these common

cations did not significantly affect the material's strong preference for the target Co^{2+} ions^[183].

Another problem in the selectivity is the presence of anionic ligands in real wastewater. Phosphates, carbonates, sulphates and chlorides can form complexes with heavy metal ions to change their speciation and thus affect adsorption behaviour^[34,38]. These anionic species may also compete for the adsorption sites or cause structural damage to MOFs, especially those with coordinatively unsaturated metal sites^[27,32,44]. phosphate ions are relatively strong binders for hard Lewis acid sites such as Zr^{4+} , Fe^{3+} , and Al^{3+} ^[184–185]; therefore, they reduce the selectivity of heavy metal adsorption. Phosphates can either form complexes with the target heavy metals in the solution or compete for coordination sites on the MOF framework; thus, both the capacity and selectivity are reduced^[186]. Therefore, the Design of MOFs for selective heavy metal removal needs to consider the entire chemical matrix of the target wastewater, including the presence and concentration of such anionic species.

4.2.2. Design strategies for enhancing selectivity

Rational Design of Selective MOF Adsorbents is Based on the basic principles of coordination chemistry, pore engineering and molecular recognition^[187–189]. In recent years, many ways have been proposed to increase the selectivity of MOFs-based materials.

According to the HSAB classification in Section 3.2, the selectivity design for MOFs-based adsorbents is carried out by applying a hard/soft acid-base matching principle and a series of functionalisation strategies. The following subsections will introduce the three main types of thiol-, amino- and carboxyl-functionalisation strategies used so far, and for each method, the target heavy-metal-ion set and specific coordination chemistries will be specified. The Misono softness parameter is related to the stability of halogen complexes of metal ions, and thus it can be used to predict the reactivity and selectivity of metal ions in various adsorption systems^[190]. According to HSAB theory, some groups are suitable for certain metals; therefore, these are used in this study. Recently, the prediction methods for HSAB theory have been expanded to account for other factors such as coordination geometry, solvation effects and cooperative binding to improve selectivity in MOF design^[39,47,53].

The introduction of specific functional groups through either direct synthesis or post-synthetic modification is the most direct strategy for imparting selectivity to MOFs^[191–194]. The choice of functional group determines the binding affinity and selectivity profile of the resulting material. Thiol ($-\text{SH}$) functionalization exploits the strong affinity of soft sulfur donors for soft heavy metals such as Hg^{2+} ^[195]. Thiol-functionalized MOFs have demonstrated exceptional selectivity for mercury even in the presence of high concentrations of competing ions^[196,197]. Li et al.^[198] directly synthesized thiol-functionalized ZIFs (Zn-2-SH-Bim), which exhibited a distribution coefficient for Hg^{2+} as high as 190596 mL/g in solutions containing multiple competing ions, along with a $\text{Hg}^{2+}/\text{Ni}^{2+}$ separation factor of 23766. These results directly demonstrate the exceptional selectivity imparted by the thiol groups. Amino ($-\text{NH}_2$) functionalization provides binding sites for borderline metal ions including Cu^{2+} and Pb^{2+} ^[199]. The lone pair electrons on nitrogen atoms coordinate effectively with these metals, and

the basicity of amino groups can be tuned through pH control to modulate selectivity^[200]. Amine functionalization introduces $-\text{NH}_2$ rich in lone-pair electrons, providing strong coordination and chelation sites for metal ions. For instance, in the MIL-101(Fe)- NH_2 @ZIF-8 composite, the amine groups synergize with carboxylate groups to engage in strong coordination bonding and electrostatic interactions with soft Lewis acids such as Pb^{2+} , thereby significantly enhancing adsorption affinity^[201]. This specific binding endows the material with exceptionally high selectivity toward Pb^{2+} , with adsorption efficiency (94.9%) and capacity (297 mg/g) far exceeding those for other coexisting ions such as Cd^{2+} and Cu^{2+} . Therefore, amine functionalization not only directly increases the number of chemically active sites on the MOF surface but also drives the efficient recognition and capture of target heavy metal ions through modulation of interfacial charge and binding specificity, representing a core mechanism for achieving high-performance selective adsorption. Carboxyl ($-\text{COOH}$) functionalization offers binding sites for a broad range of metal ions, with selectivity governed by ionic radius and coordination geometry^[202,203]. Carboxyl-functionalized MOFs such as UiO-66- COOH and UiO-66- $(\text{COOH})_2$ exhibit pH-responsive adsorption behavior, with lower uptake under acidic conditions and enhanced adsorption under alkaline conditions due to deprotonation of the carboxyl groups^[182]. MIL-101- $(\text{COOH})_2$ exhibits broad-spectrum and efficient adsorption capability toward heavy metals of different Lewis acid types, including borderline acids such as $\text{Pb}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Ni}(\text{II})$; soft acids such as $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$; and hard acids such as $\text{Eu}(\text{III})$ and $\text{Cr}(\text{III})$. Moreover, it maintains high adsorption efficiency in coexisting ion systems, with residual efficiency below 1.54%^[62]. This exceptional selectivity is attributed to the strong coordination between the carboxyl functional groups and the target metal ions, which dominates the chemisorption process, thereby conferring significant advantages for the treatment of complex wastewater.

The precise pore size control achievable in MOFs enables selectivity based on molecular sieving effects^[204,205]. When the pore windows are smaller than the hydrated diameters of competing metal ions, size exclusion can confer selectivity even without specific chemical interactions^[206]. Subnanometer pore windows, such as the 6 Å apertures in UiO-66- COOH and UiO-66- $(\text{COOH})_2$, are narrower than the hydrated diameters of common divalent metal ions, which typically range from 4–8 Å^[182]. While this size regime does not completely exclude hydrated ions, it imposes kinetic constraints and enhances selectivity through preferential diffusion of smaller hydrated species. This pore confinement effect, combined with functional group chemistry, enables the pH-responsive selective adsorption observed in these materials. The concept of molecular sieving has been more fully realized in MOFs with pore apertures precisely tailored to exclude certain ions while allowing others to enter. For instance, MOFs with pore windows of approximately 3–4 Å can effectively exclude hydrated metal ions while allowing smaller water molecules and certain neutral species to pass, enabling applications in membrane-based separation^[207]. The combination of size exclusion with functional group chemistry provides a dual-mechanism approach to selectivity that can achieve extremely high separation factors^[84].

A fundamental consideration in MOF design for environ-

mental remediation is the inherent trade-off between selectivity and broad-spectrum adsorption capacity. Highly selective materials are optimized for specific target metals but may perform poorly when the contaminant profile changes, while broad-spectrum adsorbents can capture multiple pollutants but may lack the specificity required for metal recovery or for treating effluents where only certain metals exceed regulatory limits. Selectivity is the dimension that ultimately determines whether MOF-based adsorbents can function effectively in real wastewater environments. The complexity of actual water matrices—with their mixtures of competing heavy metals, abundant coexisting cations, and interfering anionic species—demands that selectivity be assessed not in idealized single-metal systems but under conditions that reflect real-world complexity. Without adequate selectivity, even the highest adsorption capacities reported in laboratory studies become irrelevant in real applications where competing ions occupy active sites and reduce effective capacity.

4.3. Regenerability

The regenerability of MOFs bridges the gap between laboratory-scale demonstrations and economically viable industrial applications^[29]. While high adsorption capacity and excellent selectivity are essential attributes, an adsorbent that cannot be efficiently regenerated and reused offers limited practical utility due to prohibitive material replacement costs and waste disposal burdens^[208,209]. This section examines the classification and mechanisms of regeneration methods, the causes and consequences of performance attenuation during cycling.

4.3.1. Classification and mechanisms of regeneration methods

The regenerability of MOFs adsorbents involves the desorption of captured heavy metal ions from the framework, thereby restoring the material's adsorption capacity for subsequent cycles^{[210],[211]}. The choice of regeneration method critically influences the structural integrity, long-term stability, and economic viability of MOF-based systems^[212]. Over the past two decades, a variety of regeneration techniques have been developed, each with distinct mechanisms, advantages, and limitations.

Acid washing is the most commonly employed regeneration method for heavy metal-loaded MOFs, operating on the principle of competitive desorption^[12,138]. Under acidic conditions, high concentrations of protons compete with the adsorbed heavy metal ions for coordination sites on the MOF backbone, displacing the metal ions into solution. This method is particularly suitable for MOFs that maintain structural integrity at low pH^[159]. However, acid washing is not without limitations. The corrosive nature of acidic solutions can gradually degrade the MOF structure, especially for those with labile metal–ligand coordination bonds^[76]. For MOFs containing metal ions that are prone to hydrolysis or ligand substitution under acidic conditions, repeated acid washing leads to progressive structural degradation, manifested as loss of crystallinity, reduced specific surface area, and diminished adsorption capacity^[12,34]. Alkaline washing is based on a similar competitive desorption principle but employs hydroxide ions to form metal hydroxide precipitates or soluble metal complexes^[213]. This method is suitable for heavy metals that form stable anionic complexes under alkaline conditions.

Chelating agent elution utilizes strong chelating agents capable of forming stable complexes with heavy metal ions, thereby extracting them from the MOFs adsorption sites. The most commonly used chelating agents include ethylenediaminetetraacetic acid (EDTA), thiourea, and various aminopolycarboxylic acids^[172,214,215]. The desorption mechanism relies on the formation of metal–ligand complexes with stability constants significantly higher than those of the metal–MOF coordination bonds, shifting the equilibrium toward desorption. Compared with acid washing, chelating agent elution offers milder conditions and is less prone to induce framework hydrolysis; however, it introduces secondary pollution issues associated with the handling of metal-loaded chelating agent solutions^[80]. The high cost of certain chelating agents, along with the need for additional processing steps to recover both the chelating agent and the metal values, further complicates their application at industrial scales.

Electrochemical regeneration has emerged as an alternative to chemical methods, offering the advantages of low chemical consumption, controllable regeneration conditions, and simultaneous metal recovery^[216,217]. This approach employs redox-active MOFs or MOF-based electrodes to achieve reversible capture and release of heavy metal ions through the modulation of electrochemical potential. For example, a copper-based MOF-74 has been used as a redox-active electrode material for the removal of cadmium ions^[216]. The electrochemical redox reaction of $\text{Cu}^{2+}/\text{Cu}^{+}$ within the MOF structure assists the reversible capture and release of Cd^{2+} , achieving excellent electrosorption (>100 mg/g) and regeneration efficiency ($>90\%$). By applying an appropriate overpotential, the oxidation state of redox-active metal nodes can be modulated, altering the coordination environment and binding affinity toward target metal ions^[217].

Thermal regeneration exploits the temperature sensitivity of adsorbate–adsorbent interactions to achieve desorption^[27,218]. When the adsorbed heavy metal species are volatile or thermally labile, heating can induce their release from the MOF framework. The PDEA-MOF-808 composite material achieves efficient regeneration after Hg adsorption by simply being treated in warm water at 55°C for 20 minutes, without the need for any chemical eluents^[219]. After ten cycles of use, the adsorption efficiency remains above 91.3%. The thermal regeneration mechanism is primarily attributed to the thermoresponsive polymer PDEAEAM loaded in the composite. Below its lower critical solution temperature (LCST, approximately 30°C), the polymer chains are hydrophilic and swollen, exposing abundant active sites such as tertiary amine groups, which strongly capture Hg(II) through coordination. When the temperature is raised to 55°C (above the LCST), the polymer chains undergo hydrophobic collapse. This conformational change not only weakens the coordination bonding with Hg(II) but also generates steric hindrance effects that expel the already adsorbed Hg(II), thereby enabling efficient desorption under mild conditions.

4.3.2. Performance attenuation during regeneration cycles

The regeneration of an adsorbent refers to the process of desorbing and releasing heavy metal ions from a saturated MOFs, thereby restoring its adsorption capacity^[220,221]. A critical observation from the literature is that while the vast major-

ity of studies on MOF-based heavy metal adsorption report regeneration experiments—typically presenting the number of cycles over which the material retains a certain percentage of its initial capacity—very few investigations delve into the underlying causes of performance decline during these cycles^[222,223]. Most studies limit themselves to stating that “the adsorption capacity decreased by X% after Y cycles” without characterizing the structural, chemical, or morphological changes responsible for this loss^[106,224,225]. This lack of mechanistic understanding hinders the rational design of more robust and recyclable MOF adsorbents. When performance attenuation does occur, it can arise from several degradation mechanisms that often operate synergistically.

One of the most direct causes of performance attenuation is the irreversible loss or deactivation of adsorption sites during regeneration. During repeated adsorption–desorption cycles of UiO-66-EDA, although the use of 0.1 M HCl as an acidic eluent effectively enables the desorption of metal ions and the regeneration of the material, the removal efficiencies for Pb(II), Cd(II), and Cu(II) all decrease after four cycles^[74]. Among these, the decline in removal efficiency for Cu(II) is the most pronounced, which may be attributed to the formation of exceptionally stable complexes between Cu(II) ions and the amine groups. Similarly, for carboxyl-functionalized MOFs used to capture Cu²⁺, Pb²⁺, and Ni²⁺, the inner-sphere coordination between –COOH groups and heavy metal ions can exhibit high binding energies (1.31 eV for Cu), which, while conferring high selectivity, may require carefully optimized regeneration conditions to avoid incomplete desorption and site occupation^[226]. The challenge of balancing high selectivity with easy regeneration is a recurring theme: selective adsorbents often require harsh regeneration conditions (high H⁺ concentrations) to achieve complete desorption, yet such conditions can themselves damage the framework. In some cases, the heavy metal ions may migrate into the MOFs lattice or form insoluble precipitates (e.g., metal hydroxides or oxides) within the pores, which cannot be removed by conventional regeneration methods, thereby permanently blocking active sites^[34,79]. X-ray photoelectron spectroscopy (XPS) or energy-dispersive X-ray spectroscopy (EDS) analysis after regeneration is rarely performed, but when it has been done—for instance, on a thiol-functionalized Zr-MOF used for Hg²⁺ adsorption—residual mercury signals were clearly detected after multiple regeneration cycles, confirming site occupation^[38].

Repeated exposure to regeneration conditions—particularly acidic or alkaline solutions—can induce gradual degradation of the MOF framework itself^[138,181]. The high concentrations of acids or bases typically used to regenerate MOF adsorbents can compromise their structural integrity and may generate additional environmental pollution, representing a significant challenge that limits their use in environmental applications^[227]. Zinc-based MOFs, such as ZIF-8 and MOF-5, are particularly susceptible to structural collapse under acidic regeneration conditions due to the lability of Zn–O or Zn–N coordination bonds^[157]. For ZIF-8 used in Cu²⁺ or Pb²⁺ adsorption, regeneration with dilute hydrochloric acid has been found to cause progressive amorphization, with a corresponding drop in adsorption capacity of up to 50% after four cycles^[228]. Even for highly stable MOFs such as UiO-66 (Zr-based), which can withstand a wide pH range in short-term exposures, cumulative

damage from multiple acid-washing cycles has been shown to cause loss of crystallinity and reduction in Brunauer–Emmett–Teller (BET) surface area^[155,159]. The Zr-DMSA material successfully underwent ten consecutive adsorption–desorption cycles, retaining approximately 63% of its initial adsorption capacity after ten cycles^[75]. The decline in performance is primarily attributed to partial structural degradation, manifested as partial pore collapse and loss of organic linkers during acid treatment. Thermogravimetric analysis indicated a loss of about 4.41% of the linkers in the first regeneration cycle alone. This is mainly because effective lead capture requires the partial detachment of linkers from the zirconium nodes to form so-called “pendant linkers,” an essential structural modification that compromises the integrity of the MOF, thereby leading to a gradual decrease in adsorption performance with increasing cycle number. A study on the regeneration of MIL-100(Fe) for Cr(VI) removal reported that after three regeneration cycles using alkaline solution, the BET surface area decreased by approximately 30%, accompanied by a loss of adsorption efficiency from 95% to 70%^[42]. Iron-based MOFs like MIL-100(Fe) and MIL-101(Fe), while possessing high adsorption capacities for heavy metals, are also prone to partial structural degradation during regeneration due to the formation of iron hydroxides or oxyhydroxides, particularly under alkaline conditions^[96]. The susceptibility to structural collapse varies significantly among MOF families, with frameworks constructed with high-valence metal nodes (Zr⁴⁺, Ti⁴⁺, Cr³⁺) generally exhibiting superior resistance to regeneration-induced degradation compared to those with low-valence metal nodes (Zn²⁺, Cu²⁺)^[159].

Incomplete desorption of heavy metal ions during regeneration leads to the accumulation of residual contaminants within the MOF framework. These retained species not only occupy active sites but also block pore channels, reducing the accessible surface area and hindering diffusion of target ions in subsequent cycles^[30,76]. The accumulation problem is exacerbated when treating real wastewater containing natural organic matter (NOM) or competing anions, which can co-adsorb onto the MOF surface and resist regeneration^[76,174]. Humic acids and other NOM components have been shown to bind strongly to the metal clusters of MOFs, forming surface coatings that impede heavy metal access^[174]. Over multiple cycles, this irreversible fouling leads to a steady decline in effective capacity and selectivity^[29]. Yet, the vast majority of regeneration studies are conducted in idealized single-metal systems using deionized water, thus failing to capture this realistic fouling mechanism.

Perhaps these three degradation mechanisms—active site loss, structural collapse, and contaminant accumulation—do not operate independently but rather reinforce one another. For instance, structural collapse exposes new, weaker binding sites that are more prone to deactivation; residual contaminants accelerate framework hydrolysis by creating local acidic or alkaline microenvironments; and the loss of active sites forces subsequent cycles to rely on less efficient sites, leading to a gradual decline in performance. Therefore, the assessment of regenerability must be conducted over a sufficiently large number of cycles (typically ten or more) under realistic regeneration conditions, using metrics such as cumulative adsorption capacity or capacity retention per cycle to fully

reflect the long-term viability of MOF adsorbents.

The above analysis shows that there is a serious deficiency in the current research: Although regeneration experiments are regularly conducted, the reasons for the decline in performance have rarely been systematically explored^[174,229]. Shah et al.^[229] have listed the problems of cost, toxicity and regenerability for MOFs in commercial application, and detailed research on the mechanism of regeneration-induced degradation is lacking. Most of the papers only report the percentage of capacity retained after a certain number of cycles and do not provide characterization data (e.g., PXRD, BET, XPS, ICP-MS of residual metals) to determine whether the loss is due to site blocking, framework collapse or pore blockage^[44,174]. Although factors that may influence the regeneration ability of MOFs have been identified in principle, their specific associations with a decrease in performance have not been systematically determined^[230]. Without such a mechanism, it is impossible to improve the design of MOFs for high recyclability rationally. As mentioned in recent studies, future research will focus on post-cycling characterisation and establish quantitative relationships among regeneration conditions, structural alterations and capacity retention to move beyond simply reporting the number of cycles and explore the underlying reasons for regeneration loss^[230,231].

Regenerability is the dimension that ultimately determines whether MOF-based adsorbents can transition from laboratory demonstrations to economically viable commercial applications. Without the ability to regenerate and reuse MOFs over many cycles, the high synthesis costs associated with these materials become prohibitive, and the environmental burden of spent adsorbent disposal undermines the sustainability claims of MOF-based treatment technologies.

4.4. Scalability

The transition from laboratory-scale synthesis to industrial-scale production is often referred to as the “last mile” of MOFs commercialisation. Although many MOFs with excellent properties have been synthesized on a gram scale in academic laboratories, producing these materials at the scale of kilograms or tonnes that maintain consistent heavy metal adsorption performance, structural stability and selectivity is still a significant problem^[232,233].

4.4.1. The gap between laboratory synthesis and industrial production

The world’s MOF market shows both the prospects and problems of MOF commercialisation. According to recent market research, The global MOF market was valued at USD 510 million in 2024 and is projected to reach USD 1.70 billion by 2030, growing at a compound annual growth rate of 22.1%^[234]. A large number of patent applications have been filed, with more than 13000 MOFs-related patents published so far; therefore, R&D and industrial cooperation have intensified^[234]. However, most MOFs are still prepared by a few types of methods, such as the stable solvothermal method; scaling up and achieving high-quality processing are thus difficult^[232,235]. There are many problems with the preparation of MOF faces at scale-up, such as strict synthesis conditions, extended reaction time, lower yield and higher cost^[236]. Traditional batch synthesis methods used in the laboratory for production often have problems such as low reproducibility, limited scalability and signifi-

cant batch-to-batch variation upon scale-up^[237]. The reasons are that the laboratory and the factory are not the same.

The first two are yield and productivity. Lab-scale synthesis generally prioritises purity and crystal structure over high-throughput production; therefore, it is not suitable for large-scale industrial production. Conventional solvothermal synthesis requires high-temperature heating for an extended period, so it is not suitable for large-scale production^[238]. A low-temperature and low-heat/mass-transfer environment in a large-scale reactor is thus created, extending the reaction time and reducing the space-time yield^[239].

Solvent consumption and environmental footprint present another major obstacle. Traditional MOF synthesis relies heavily on toxic organic solvents such as N,N-dimethylformamide (DMF), diethylformamide (DEF), and methanol, which are not only expensive but also pose significant environmental and health risks^[240,241]. A comparative life cycle assessment of ZIF-8 synthesis revealed that the choice of solvent dramatically influences environmental impact, and the substitution of DMF with glycerol carbonate —while seemingly greener— does not necessarily represent a more sustainable choice when considering the full production chain^[242]. The high solvent consumption (often tens to hundreds of milliliters per gram of product) generates substantial chemical waste, with E-factor values (mass of waste per mass of product) for MOF synthesis typically ranging from 50 to 500, far exceeding acceptable levels for green chemical processes^[243].

4.4.2. Scale-up approaches

New cost-effective and large-scale preparation methods for the industrial application of MOFs need to be developed. The main problem is how to scale up synthesis from the gram scale to the hundred-kilogram or even ton scale successfully and maintain the structure and performance^[244]. At present, the scale-up production of MOFs mainly follows two process routes: batch and continuous^[245].

Batch processes, such as bulk hydrothermal/solvothermal synthesis, increase the output by directly expanding the reactor volume. Seo and others prepared MIL-100(Fe) in a 10 L reactor, obtaining a space-time yield (STY) of 120–130 kg/m³ per day, and further scaled up to 200 L to increase the STY to 450 kg/m³ per day^[246]. Although the above results show that the solvothermal method can be scaled up to produce iron-based MOFs at a reasonable rate, a key problem for heavy-metal adsorption is whether the hierarchical porosity and density of Fe³⁺ open metal sites—both required for high adsorption capacity—are maintained under such a large-scale change. Given the different heat and mass transfer properties of large-vessel reactors, nucleation kinetics will change; therefore, the defect distribution may be affected and binding-site accessibility altered. The second kind of batch method is reflux synthesis; it is carried out at atmospheric pressure and is relatively simple and safe to operate. For example, Wen et al. prepared MOF-303 by refluxing in a 30 L glass reactor to obtain 103 kg/m³-day of STY^[247]; Wu et al. achieved kilogram-scale (~1.05 kg) production of an aluminum-based MOF (Al-PyDC) with an STY as high as 126 kg/m³/day^[248]. Reflux-based routes, operating under atmospheric pressure, offer simpler handling for scale-up. However, for heavy metal adsorbents such as water-stable Al-MOFs, it is essential to confirm that the lower synthesis temperature does not compromise crystallinity or produce frag-

mented particles that could reduce column permeability and metal uptake kinetics in flow-through systems. For zirconium/hafnium-based MOFs that are difficult to crystallize in aqueous media, the modulated hydrothermal method (MHT) incorporating modulators (e.g., acetic acid) has proven to be an effective green scale-up strategy, significantly improving product crystallinity for materials such as UiO-66 and MOF-808, with STYs in the range of 50–100 kg/m³/day^[249,250]. This is particularly relevant for UiO-66-type heavy metal adsorbents, where both the density of missing-linker defects (which create active sites) and the overall framework integrity (which determines hydrothermal stability) are sensitive to synthesis parameters. The successful translation of these materials to industrial-scale heavy metal removal will depend on demonstrating that MHT conditions can be tuned to maintain this delicate balance at production scale.

Compared to batch processes, continuous production is regarded as a more desirable industrial route due to its higher efficiency, better process control, and consistent product quality. Continuous stirred-tank reactors (CSTRs) are classic continuous reactors; McKinstry et al. used a CSTR to continuously produce MOF-5 under reflux conditions, achieving an STY of approximately 1000 kg/m³/day^[251]. Although MOF-5 itself is unsuitable for aqueous-phase heavy metal removal due to its well-known moisture sensitivity, this study laid the groundwork for the continuous production of other carboxylate-based MOFs. The translation of CSTR processes to water-stable frameworks such as UiO-66 or functionalized MIL-101 derivatives remains a logical but relatively unexplored step that would directly benefit the adsorption field. Microfluidic or millifluidic reactors (MFRs), with their extremely high surface-to-volume ratios and superior heat and mass transfer efficiencies, provide platforms for rapid screening of synthesis conditions and preparation of MOFs with specific morphologies (e.g., two-dimensional nanosheets). However, their inherently small reaction volumes limit single-batch output, posing challenges for large-scale powder production^[252]. Thus, while microfluidic platforms are powerful tools for discovering new synthesis conditions or optimizing the morphology of heavy metal adsorbents (e.g., generating high-aspect-ratio nanosheets with enhanced external surface area for rapid adsorption), they remain unsuitable for direct industrial production. Their primary value lies in accelerating the lab-scale discovery of scalable conditions for adsorption-optimized MOFs. Flow chemistry represents the current frontier in continuous scale-up synthesis of MOFs. In continuous flow hydrothermal/solvothermal synthesis (CFHS/CFSS), reactants are pumped through a heated, pressurized flow tube, where the reaction is completed within a very short residence time. For example, the synthesis of ZIF-8 can be completed in 1.8 min, achieving an STY as high as 3875 kg/m³/day^[253]. The very short residence time (1.8 min) is attractive for throughput, yet it must be verified that such rapidly crystallized ZIF-8 retains a high density of surface Zn–OH groups, which are the primary active sites for heavy metal coordination, and that the crystal size distribution remains favorable for both adsorption kinetics and downstream separation. The continuous version of mechanochemistry—twin-screw extrusion—has been developed by Nuada (formerly MOF Technologies). Using little or no solvent, it enables continuous production of various MOFs, including

HKUST-1 and ZIF-8, with an STY reaching 144000 kg/m³/day, demonstrating enormous scaling potential^[254]. However, from the perspective of heavy metal remediation, it remains to be validated whether the adsorption capacity, selectivity, and long-term reusability of these continuously extruded MOFs match those of their solvothermally-prepared counterparts. The intense mechanical forces inherent in extrusion may alter the defect density and surface chemistry—parameters that directly govern heavy metal binding—and rigorous post-synthesis characterization of the adsorption properties of extruded materials is still largely absent from the literature. Aerosol flow impact (AFI) synthesis is a solvent-free continuous gas–solid reaction method that uses high-speed gas jets to carry reactants to collide and react; it has been used to synthesize MOFs such as ZnBTEC, with a theoretical STY of 1.44×10⁶ kg/m³/day. However, its impact on product structural integrity requires further validation^[255]. Its impact on product structural integrity, and specifically on the defect populations that often serve as binding sites for heavy metal ions, requires further validation before such high-energy gas–solid routes can be considered for the production of adsorption-grade MOFs. For large-area preparation of MOFs membranes, the roll-to-roll (R2R) process is an established continuous technique. Ji et al. successfully achieved continuous roll-to-roll fabrication of ultrathin (~25 nm), large-area (0.33 m × 35 m) ZIF-8 hybrid membranes using a nanoreactor-confined crystallization strategy, providing a feasible solution for the industrial production of high-performance separation membranes^[256]. For heavy metal adsorption, this represents a significant step toward the scalable manufacture of MOF-based membranes for continuous-flow treatment. The key next challenge is to demonstrate that such R2R-fabricated membranes can achieve sustained heavy metal rejection and permeance over extended operation times in the presence of fouling species commonly found in industrial effluents. Furthermore, the combination of various technologies with flow chemistry has further expanded the boundaries of continuous synthesis. For example, coupling with high-speed gravity technology enables the preparation of ultrasmall MOF nanocrystals^[257]; integration with spray drying allows continuous production of MOFs microspheres and composites^[258]; aerosol-assisted flow synthesis yields highly crystalline MOFs^[259]; microwave-assisted flow synthesis dramatically shortens reaction times, achieving high-STY production of HKUST-1 (64800 kg/m³/day)^[260]; and high-pressure homogenization flow technology, which utilizes cavitation and shear forces generated under high pressure to promote reactions, offers a new route for the rapid continuous synthesis of materials such as HKUST-1 and ZIF-8^[261].

Although substantial progress has been made, the scale-up preparation of MOFs still faces practical problems such as large volumes of solvent use and recovery, high energy consumption, online quality control, and compliance with safety regulations. Future development will be based on the integration of multiple disciplines to combine high-performance reactor design, process intensification and green chemistry principles for the real-world industrialisation of MOFs^[262–265]. The development of scalable synthesis methods needs to be combined with shaping technology and post-synthetic modification to produce MOFs in applications-ready forms. If there is no large-scale production method, even excellent adsorption

performance in the laboratory cannot be applied to real-world problems of heavy metal pollution.

In short, considerable progress has been made in the scale-up of production for some representative MOFs, and continuous flow and mechanochemical routes have shown particular promise for high-throughput manufacturing. However, a scalable synthesis method for MOFs-based heavy metal adsorption is required, and the current one is not ideal for practical application. A relatively less studied issue is whether the scale-up process can maintain the same adsorption capacity, selectivity, structural integrity and regenerability as the adsorbents obtained in the laboratory. Scalable synthesis should be integrated with shaping technology (e.g., granulation, membrane fabrication or monolith formation) to produce adsorbents in forms suitable for packed-bed columns, stirred-tank contactors and continuous-flow membrane modules. Without such an integrated method of scaling up synthesis and applying shaping and performance tests, the MOF powder will not be effective in the field of real-world heavy metal pollution treatment based on its laboratory results.

4.5. Real-water validation

A realistic wastewater environment is a harsh test for MOFs-based adsorbents; if they perform well here, then they will be genuinely useful in practice. Although the previous chapters have studied the stability, selectivity, regenerability and scalability of each in isolation, their combined effect can only be revealed under complex, fluctuating and irregular conditions of actual wastewater.

The performance of NM-100-HBAP-1 shows that anionic and cationic heavy metals react differently in real water environments: In the control system (deionized water), the material removed Pb(II) and Cd(II) to about 95.61% and 91.55%, respectively, and Cr(VI) to about 94.61%; when exposed to Yan Lake water, which had a total nitrogen content of 1.64 mg/L, total phosphorus of 0.09 mg/L, and total organic carbon of 7.72 mg/L, the removal rates of Pb(II) and Cd(II) remained relatively unchanged at similar levels, but the removal of Cr(VI) dropped to 80.17%, an effect attributed to competition for the same positively charged surface sites of the adsorbent by chromate anions (HCrO_4^-) and abundant phosphate and nitrate anions (indicated by high TN and TP), as well as interference from dissolved organic matter; furthermore, at the slightly alkaline pH of the lake water (8.09), the surface of the material became more deprotonated and negatively charged, favoring the adsorption of cationic Pb(II) and Cd(II) while inhibiting the binding of anionic Cr(VI), thus resulting in a selective reduction in Cr(VI) removal efficiency but maintaining good performance for cationic metals^[266].

Fe-MOF-EDTA is directly compared with the laboratory results and field data^[77]. In the laboratory, when multiple metal ions (Zn^{2+} , Cr^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Cu^{2+}) were added to the simulated wastewater at the same or a similar initial concentration, the material had an average removal rate of about 93% after 12 hours of adsorption, as reported by the authors. However, the original study did not report the final removal rate for each individual metal ion in the lab experiments; only the overall average value and the kinetic profile of rapid initial uptake were provided. Therefore, the metal-specific comparison with real-world data cannot be conducted in the labora-

tory. In contrast, when applied to authentic industrial effluent from a stainless steel pipe manufacturing facility—where Cu^{2+} (0.593 mg/L), Cr^{2+} (50.491 mg/L), and Ni^{2+} (41.371 mg/L) were present at initial concentrations spanning two orders of magnitude—Fe-MOF-EDTA reduced these to 0.048 mg/L (92.0%), 1.821 mg/L (96.4%), and 1.274 mg/L (96.9%), respectively. These removal efficiencies in the real sample were comparable to the laboratory average, despite the far greater concentration heterogeneity. However, it should be noted that the Cu^{2+} concentration in the treated effluent (0.048 mg/L) remains near the detection limit, and whether this level can be maintained over multiple treatment cycles with the same real wastewater has not been reported.

In an aqueous solution containing only copper and nickel ions (30 ppm each), PVDF@MOF-303/PVDF@ZIF-67 (PMPZ) exhibits excellent adsorption performance, with an adsorption capacity of 495 ± 16 mg/g and an efficiency of $99.1 \pm 0.2\%$ ^[267]. When heavy metal ions were introduced into oil-in-water emulsion (dichloromethane/water, 1% oil) to simulate real industrial wastewater conditions, the adsorption capacity of PMPZ decreased to 413 ± 13 mg/g, with an adsorption efficiency of $82.7 \pm 0.5\%$. This discrepancy suggests that the presence of the oil phase in the emulsion may partially hinder the diffusion and contact of heavy metal ions toward the active sites on the membrane surface, leading to a reduction in adsorption performance compared to that in pure aqueous solution. Nevertheless, the membrane still maintains efficient simultaneous oil-water separation and heavy metal removal under simulated real wastewater conditions. However, although the researchers simulated real industrial wastewater, actual industrial effluents (e.g., from electroplating, machining, and other industries) typically have much more complex compositions, containing not only oil and heavy metals but also other interfering substances or fluctuating physicochemical conditions (e.g., salinity, pH).

Under ideal laboratory conditions (e.g., using deionized water as the matrix and treating a single pollutant), ZIF-67 exhibits rapid (within minutes) and highly efficient adsorption capacity toward the model polyphenol gallic acid (GA), achieving a removal efficiency exceeding 95% (up to 99% at low concentrations)^[268]. Meanwhile, the spent material ZIF@GA demonstrates an ultrahigh adsorption capacity (1020 mg/g) and near-complete removal of lead ions (Pb(II)) (99–100% removal within 15 min). However, under more complex conditions simulating real wastewater (e.g., synthetic tap water prepared according to French Norm NF P41–650, containing humic acid at 100 mg/L and GA at 100 mg/L, with or without Pb(II) spiked at 10 mg/L), ZIF-67 still achieved 97% GA removal in the presence of humic acid alone, and 92% GA removal along with 99% Pb(II) removal when Pb(II) was also present. In separate tests using deionized water containing organic dyes, the removal efficiency of GA decreased notably in the presence of cationic dyes (e.g., methylene blue, rhodamine B), attributed to electrostatic repulsion. Moreover, in single-metal solutions (10 mg/L, 15 min), ZIF@GA removed 58% of Cd(II) and 45% of Cr(VI), whereas Pb(II) was completely removed; in mixed-metal solutions (3 mg/L each), Pb(II) maintained the highest removal efficiency, confirming a strong selectivity order of $\text{Pb(II)} > \text{Cd(II)} > \text{Cr(VI)}$. To overcome the challenges of separation and recovery of powdered materials in practical applications, the

researchers immobilized ZIF-67 onto ordinary filter paper, achieving continuous flow removal of GA with over 95% removal efficiency and a stable flux of $983.86 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ —an approach that more closely resembles real water treatment scenarios. This validates the potential of the material for transitioning from laboratory research to practical applications.

Overall, the field has made meaningful progress in validating MOF performance under real-water conditions, with several studies demonstrating maintained efficiency, ultrafast kinetics, and excellent recyclability using authentic wastewater samples. However, the gap between laboratory validation and field deployment remains substantial. Future research should prioritize systematic evaluation across diverse real wastewater matrices, standardized testing protocols, long-term operational studies with comprehensive post-cycling characterization, and pilot-scale demonstration projects. Only when these gaps are addressed will MOF-based adsorbents transition from promising laboratory materials to proven environmental remediation technologies.

5. Conclusion and perspective

5.1. Conclusion

This review has systematically examined the development of metal–organic frameworks for heavy metal removal through a multi-dimensional lens that integrates five interdependent criteria: aqueous stability, selectivity, regenerability, scalability, and real-water validation. Rather than cataloguing materials by family or mechanism, our assessment has focused on identifying which classes of MOF-based adsorbents currently approach practical viability – and where critical gaps remain.

The first is that no single MOF class performs well in all five areas. Different materials are at various stages of practicality and application; thus, we need to choose according to what is feasible now. Zirconium(IV)-based MOFs (e.g., UiO-66) have set the benchmark for water stability, but their fully coordi-

nated nodes limit the intrinsic adsorption capacity; defect engineering has only partially alleviated this stability-capacity trade-off. Thiol-functionalized MOFs have excellent selectivity for Hg(II) due to soft-acid/soft-base interactions, but this strong binding also leads to difficulties in regeneration and raises concerns about irreversible site occupation. Research on regeneration generally only reports cycle numbers and does not explore the underlying reasons for performance decline, such as framework hydrolysis, pore blockage by residual contaminants or active site loss; thus, the actual recyclability of the material remains unknown.

Scalable synthesis has achieved some good results, and continuous-flow and mechanochemical routes have reached space-time yields of as high as $10^5 \text{ kg}/\text{m}^3/\text{day}$ for prototype MOFs such as ZIF-8 and HKUST-1. However, these methods have not been widely used to prepare functionalised MOFs for selective heavy metal adsorption. Real-water verification is the least developed front end. Research on MOFs using actual industrial wastewater has consistently shown lower performance compared to that in deionized water due to competitive cations (Ca^{2+} , Mg^{2+}), phosphate/carbonate anions, and natural organic matter. Crucially, very few studies have combined real-water tests with multi-cycle regeneration under the same actual conditions and thus have not provided extensive evidence for long-term operational feasibility.

In short, the actual progress of MOFs-based heavy metal remediation will not be made by discovering another high-capacity material, but by system-level integration that addresses the five dimensions and their inherent trade-offs simultaneously. The area will change from individual material optimisation to all-encompassing engineering, and adsorption, regeneration and real-world application will be jointly designed from the beginning.

5.2. Perspectives

Building on the above conclusions, we propose an integrated framework for future research, illustrated in Fig. 5. The

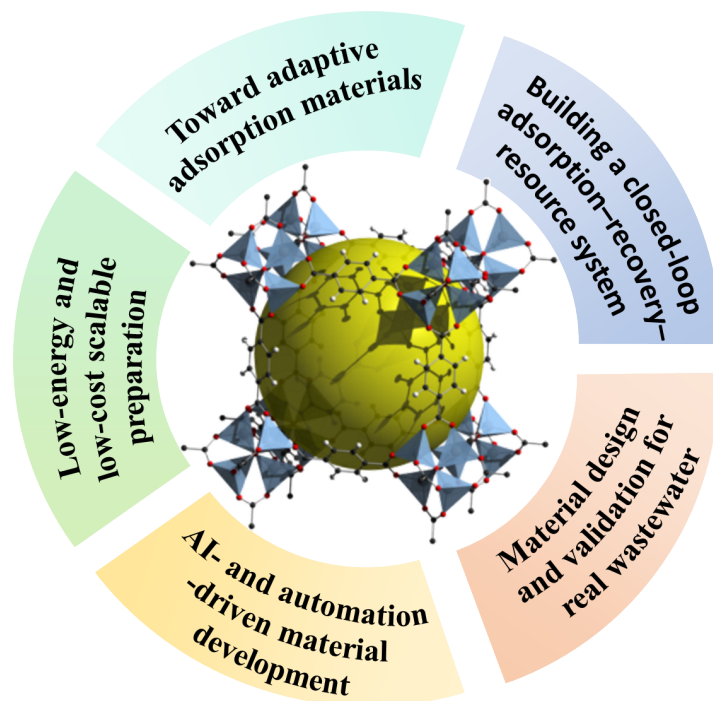


Fig. 5. Illustration of the future challenges and development directions.

following directions are not independent topics but interdependent components of a unified system architecture.

Toward adaptive adsorption materials. The adsorption behavior of most MOFs remains static (non-responsive). Future efforts should prioritize dynamically responsive MOFs – whose pore size, surface charge, or coordination sites can reversibly adapt to fluctuations in pH, competing ion concentrations, or specific target metals. This would enable intelligent recognition and capture under real-time wastewater variations.

Building a closed-loop adsorption–recovery–resource system. The vast majority of studies focus solely on adsorption performance, with post-adsorption treatment often limited to simple acid washing. A paradigm shift is needed: from conventional desorption-based regeneration to value-added material conversion. Instead of merely recovering the MOF or the heavy metal in its original form, we propose designing MOFs that, after heavy metal loading, can be directly transformed into functional materials (e.g., catalysts, battery electrodes) for secondary applications. This eliminates energy-intensive regeneration and creates a true circular economy model.

Material design and validation for real wastewater. Performance loss in real effluents reflects a fundamental design flaw, not an operational nuisance. There is an urgent need to establish structure–activity relationships under realistic hydrochemical conditions (including organic matter, suspended solids, and competing ions). Such insights should guide the rational design of MOFs with enhanced practical utility, and future studies must routinely include real-water matrix testing alongside multi-cycle regeneration assessments.

AI- and automation-driven material development. Although artificial intelligence is widely discussed, its integration with automated robotics for high-throughput synthesis, screening, and performance prediction of MOF adsorbents remains largely untapped. Dedicated databases that incorporate synthesis parameters, structural features, and adsorption performance – coupled with AI models – will dramatically accelerate R&D, shifting the paradigm from experience-guided to data-driven discovery.

Low-energy and low-cost scalable preparation. Scalable synthesis must be integrated with complementary technologies (e.g., membrane fabrication, granulation, or monolith formation) to produce adsorbents suitable for packed-bed columns or continuous-flow modules. Green synthesis routes (ultrasonic, microwave, mechanochemical) should be adapted to continuous-flow reactors, with concurrent life-cycle assessment of energy consumption and environmental impact. Coupling MOFs with other water treatment technologies will be crucial to developing integrated, efficient, and scalable remediation systems.

Finally, it should be acknowledged that the multi-dimensional assessment framework proposed in this review is a necessary precursor to, rather than a substitute for, the process-level engineering that will ultimately be required for industrial deployment. At present, MOF-based adsorbents have not yet achieved the simultaneous optimization needed to justify large-scale production; the high synthesis costs and performance trade-offs documented throughout this review underscore that the field remains at the material development stage. Our contribution is to provide a rational, multi-dimen-

sional screening framework that identifies which MOF systems are sufficiently advanced in all five dimensions to warrant the resource-intensive engineering investigations that constitute the next phase of translational research.

Declaration of competing interest

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.

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

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