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Precision remediation of water pollutants using metal-organic framework/biomass-derived carbon composites: A state-of-the-art review

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Abstract

Traditional water treatment technologies face limitations, including low efficiency, poor selectivity, and secondary pollution. Therefore, advanced multifunctional materials are needed. Metal-organic frameworks (MOFs) provide high surface area and tunable porosity, while biomass-derived carbons (BDCs) offer low cost and electrical conductivity. MOF/BDC composites combine these benefits, enabling synergistic adsorption and catalysis for precise water treatment. This review examines the design and synthesis of MOF/BDC composites. It focuses on structure-performance relationships, pollutant removal mechanisms, and applications in integrated treatment systems. To enhance material functionality, interface engineering helps integrate adsorption, catalysis, and separation. Therefore, these materials exhibit good target recognition, anti-interference stability, and recyclability in practical water treatment. Future directions include machine-learning-assisted material design, smart, responsive materials, modular system integration, and life-cycle assessment, to help move laboratory research toward large-scale applications for global water security and the circular economy.

Keywords: Metal-organic frameworks; Biomass-derived carbons; Adsorption

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1. Introduction

Water is essential for life. Its security and sustainability directly affect human health, ecosystem balance, and socio-economic stability. However, global industrialization, urbanization, and intensive agriculture are growing fast. A large number of pollutants from industrial wastewater, agricultural runoff, and domestic sewage flow into water bodies, creating a serious water security crisis.[1] Current water pollution is complex, persistent, and involves trace-level contaminants. Heavy metal ions such as lead, mercury, and cadmium pose a threat to aquatic life and human health because they are toxic, bioaccumulative, and non-biodegradable.[2–5] Persistent organic pollutants, dyes, and emerging contaminants, such as pharmaceuticals and personal care products, harm aquatic biodiversity and disrupt endocrine systems. They are resistant to natural degradation, so they remain in the environment and may cause secondary risks, such as antibiotic resistance.[6,7] Therefore, traditional wastewater treatment technologies, including chemical precipitation, conventional adsorption, flocculation, and non-

selective advanced oxidation processes, show clear limitations.[8] These methods have low efficiency, poor selectivity, high energy consumption, and often create secondary pollution[9,10] or toxic by-products when treating water pollutants. For example, non-selective oxidation can convert pollutants into more toxic intermediates. Conventional adsorbents lack specific binding sites[11], so they face severe competitive adsorption, limited capacity, and poor regenerability in complex water environments. In response, water pollution control is changing from "broad-spectrum removal" to "precision targeting." Therefore, advanced water treatment technologies must meet stringent, multidimensional requirements. Specifically, an ideal technical system should achieve high adsorption capacity and rapid degradation kinetics for target pollutants. In terms of selectivity, it should possess specific recognition and capture capabilities to resist interference from coexisting matrices. In terms of sustainability, it must meet the dual constraints of low-energy consumption and material recyclability. In terms of environmental safety, it should ensure that there is no secondary pollution from the material itself or the treatment process. To achieve precise treatment, researchers are developing new multifunctional materials. These materials require high performance, adjustable functionality, and good environmental compatibility, making them a research hotspot.

Among them, metal-organic frameworks (MOFs) and biomass-derived carbons (BDCs) have great potential due to their unique properties. However, both materials still face bottlenecks that must be urgently addressed. MOFs are crystalline porous materials self-assembled from inorganic metal nodes and organic linkers via coordination bonds.[12] Their core advantages lie in their designable ultra-high specific surface area and porosity, which provide abundant sites for pollutant interaction and accommodation.[12] MOFs have high design flexibility. Researchers can precisely control pore size, shape, and surface chemistry. This is achieved by choosing suitable metal nodes and organic linkers, and they can add functional groups such as amino ($–NH_2$), carboxyl (–COOH), and hydroxyl (–OH). Therefore, researchers can design materials specifically for adsorbing or catalyzing target pollutants. MOFs have various functions. They work as efficient adsorbents. They also perform well in advanced oxidation processes such as photocatalysis and Fenton-like catalysis. This is because they have semiconducting properties or metal active centers. However, the practical application of MOFs faces significant challenges. First, insufficient water stability: the metal-ligand bonds in many MOFs are prone to hydrolysis in aqueous media, especially at extreme pH values, leading to structural collapse and performance degradation.[12] Second, morphological defects hinder practical application: most MOFs exist as micro- or nano-sized powders that tend to agglomerate during water treatment, are difficult to separate and recover from treated water, and pose a potential risk of nanoparticle leakage.[13,14] Third, cost and scale-up remain bottlenecks: the synthesis often involves expensive raw materials and harsh conditions, so the economic viability and environmental friendliness of large-scale production need to be improved.

Biomass-derived carbons are carbon materials prepared from biomass waste precursors (e.g., rice husks, straw, nut shells, and algae) through pyrolysis, activation, and other processes.[11] The preparation of BDCs mainly employs pyrolysis and activation methods.[15] Pyrolysis includes one-step high-temperature pyrolysis (direct high-temperature carbonization) and two-step high-temperature pyrolysis (low-temperature pre-carbonization followed by high-temperature pyrolysis), and the latter enables more precise control of the pore structure. Activation methods are divided into physical activation and chemical activation, mainly using oxidizing gases such as carbon dioxide (CO_2) and water vapor, or activators such as potassium hydroxide (KOH) and phosphoric acid (H_3PO_4), thereby significantly increasing the specific surface area and porosity.[16,17] These preparation methods give BDCs special inherent features. They include hierarchical pore structures (micropores, mesopores, and macropores), which facilitate ion transport and mass diffusion. They also have abundant surface functional groups (e.g., oxygen [O]-containing and nitrogen [N]-containing groups) that can provide active sites[18], good electrical conductivity[17], and environmental friendliness.[16,17] As excellent carriers/supports, BDCs show great potential.[15,17] Their high specific surface area and hierarchical porous structure can effectively disperse and anchor active nanoparticles, preventing MOF agglomeration. Surface functional groups enhance interfacial interactions with active components and promote charge transfer.[15,17]

The construction of MOF/BDC composite materials originates from the in-depth deconstruction and functional recombination of the intrinsic properties of the two materials. As pyrolytic carbon materials, BDCs have high electrical conductivity[19], chemical stability, and tunable hierarchical pore structures; however, their surface active sites are limited, and their selectivity is insufficient. MOFs have atomically designable pores, ultra-high specific surface area, and abundant open metal sites; however, they have poor water stability, difficulties in powder separation, and high cost. The strategic combination of MOFs and BDCs aims to achieve triple "structure-function-electron" synergy through interface engineering. Structurally, the three-dimensional interconnected framework of BDC

provides mechanical support and a dispersion matrix for MOFs. It inhibits nanoparticle agglomeration and gives the material macroscopic formability. Functionally, the low cost and sustainability of BDC complement the high activity and designability of MOFs. Therefore, the composite has both a robust framework and targeted recognition ability. Electronically, the sp^2-conjugated structure of BDCs promotes interfacial charge transfer. It inhibits the recombination of photogenerated carriers in MOFs. Its confined pore channels regulate the reaction microenvironment. Thus, catalytic selectivity and efficiency are improved substantially. This design concept provides a scalable material platform for the synergistic adsorption-catalysis treatment of pollutants.

In this review, the term "precision remediation" is defined as the capability of a material or process to achieve targeted, efficient, and interference-resistant removal of specific pollutants in complex water matrices. From the perspective of materials science and water treatment engineering, precision is quantitatively characterized by four key indicators: (i) Selectivity: expressed as the distribution coefficient (K_d) or selectivity coefficient (α) toward a target pollutant in the presence of competing ions or coexisting organic matter; (ii) Recognition rate: the time required to reach a defined removal percentage (e.g., t_{80}) under realistic conditions; (iii) Anti-interference stability: the maintenance of removal efficiency (>80%) in real water matrices (e.g., river water, tap water, wastewater effluent) compared to ultrapure water; (iv) Regeneration precision: the ability to restore ≥80% of initial performance after multiple cycles without structural degradation. These indicators are not merely descriptive; they can also be optimized through rational MOF/BDC composite design. For instance, selectivity is enhanced by introducing specific functional groups (e.g., $–NH_2$ for hexavalent chromium [Cr(VI)] or thiol [–SH] group for mercury ion [Hg^{2+}]) or by tuning pore size via ligand selection; recognition rate is improved by the hierarchical pore structure of BDCs that facilitates mass transfer; anti-interference stability is achieved through the protective effect of the carbon matrix against hydrolysis and competing species; and regeneration precision is enabled by strong interfacial bonding (e.g., metal–O–carbon [M–O–C] bonds) that prevents active site loss. Throughout this review, these quantitative criteria will be used to evaluate and compare the precision remediation performance of various MOF/BDC composites.

While several recent reviews have summarized the synthesis and application of MOFs, BDCs, or their composites in water treatment, the present manuscript distinguishes itself by introducing and consistently applying the quantitative framework of "precision remediation" defined above. Unlike previous works that primarily report maximum adsorption capacity or degradation efficiency under idealized laboratory conditions, this review critically evaluates material performance in complex real-water matrices (e.g., river water, tap water, wastewater effluent), systematically compares the influence of MOF type, BDC precursor, and composite strategy through a dedicated summary table, and discusses emerging paradigms such as machine-learning-assisted design, smart responsive systems, and life-cycle assessment. By shifting the focus from "broad-spectrum removal" to "targeted, interference-resistant, and regenerable remediation," this review provides a forward-looking roadmap for developing MOF/BDC composites that are not only highly efficient but also practically viable and environmentally sustainable.

This review was compiled through systematic searches in the Web of Science, Scopus, and Google Scholar databases, covering the period from January 2015 to December 2025. The search employed combinations of keywords including "metal-organic framework" OR "MOF" AND "biomass-derived carbon" OR "biochar" OR "activated carbon" AND "composite" OR "hybrid" AND "water treatment" OR "adsorption" OR "degradation" OR "remediation." Additional relevant references were identified by cross-checking the bibliographies of retrieved articles. Only peer-reviewed research articles, reviews, and book chapters written in English were considered. Studies were included if they reported quantitative performance data (e.g., adsorption capacity, degradation efficiency, selectivity, or regenerability) for MOF/BDC composites in aqueous systems. Conference abstracts, preprints, and studies lacking sufficient experimental detail were excluded.

2. Design and synthesis strategies for metal-organic framework/biomass-derived carbon composites

2.1. Selection and pretreatment of precursors for biomass-derived carbon

In this composite system, BDCs serve as the support or matrix for MOFs. Their structure directly determines the performance of the final materials. The source of biomass plays a critical role. Different biomass types have unique chemical compositions and physical structures. Upon carbonization, these original differences result in obvious changes in pore structure, surface chemistry, and graphitization degree.[15] Therefore, these changes influence the loading and integration of MOFs into the matrix. Cellulose-based biomass, such as wood and straw, has a layered pore structure and abundant –OH groups[17,20], so it is easy to modify. During carbonization, it can be converted

into highly porous and mostly amorphous carbon materials. These materials have numerous O-containing groups on their surfaces. Heteroatoms such as N and sulfur (S) can be introduced through chemical modification. This step improves the interfacial binding between BDCs and MOFs.[21] However, lignin-based biomass contains many aromatic structures. After carbonization, it forms carbon materials with initial graphitic microdomains.[16,20] This structure offers good electrical conductivity. Therefore, these materials show excellent performance in electrochemical systems. Chitin- and chitosan-based biomass have high N content. After carbonization, they form N-doped carbon.[16,20] These N-doped carbons exhibit stronger surface basicity, enabling them to adsorb acidic pollutants more effectively. Algae and waste-derived biomass have two main advantages: they are easily available and low-cost. Carbon materials derived from these biomass sources typically exhibit well-developed mesopores and macropores. These pores accelerate the movement of pollutant molecules. Pretreatment is important for controlling the structure of BDCs. Common methods include hydrothermal carbonization, chemical activation, and physical activation. Hydrothermal carbonization converts biomass into carbon microspheres or porous carbons at mild temperatures, typically 180–250 °C. This method keeps numerous surface functional groups in the final products. Therefore, these materials can serve as soft templates for MOF growth. Chemical activation uses agents such as KOH, zinc chloride, or H_3PO_4. At high temperatures, these agents etch the carbon skeleton, forming numerous micropores and mesopores. This process greatly increases the specific surface area of carbon materials. Physical activation uses oxidizing gases such as CO_2 or steam at high temperatures to create pores. This method primarily produces mesopores, making it suitable for adsorbing large pollutant molecules. The choice of precursor clearly affects composite performance. For example, lignin-based BDCs show better electrochemical performance. Therefore, selecting a suitable precursor according to the target application is highly important.

2.2. Core composite strategies

2.2.1. In situ growth and immobilization of metal-organic framework onto biomass-derived carbons

This method uses BDCs as substrates. MOF crystals grow directly on BDC surfaces or inside BDC pores. This method achieves uniform MOF loading and stable anchoring[22,23] while avoiding a common problem in traditional MOF synthesis, in which polymers often block pores and reduce surface area.[24] Two main methods are widely used for *in situ* growth. The first one is the hydrothermal or solvothermal method.[25] In this method, researchers disperse BDCs in a solution with metal salts and organic ligands, then heat it using an autoclave. Therefore, MOF crystals nucleate and grow directly on the BDC surface. The surface functional groups of BDCs, such as –COOH, –OH, and N-containing groups, work as extra nucleation sites. They help MOFs grow uniformly and prevent random precipitation in the solution. Therefore, smaller MOF particles with a more even distribution are obtained. The second method is microwave-assisted synthesis.[25] It provides fast, even heating, thereby greatly reducing the growth time of MOFs on BDCs. This method usually produces smaller MOF crystals with more exposed active sites. Therefore, it is suitable for large-scale preparation.[25]

2.2.2. Encapsulation/confinement synthesis of biomass-derived carbons within metal-organic frameworks

This strategy takes the regular pore channels of MOFs as templates. First, carbon precursors are added to MOFs. Then, carbon nanoparticles or carbon layers can be obtained via carbonization.[26,27] The templating method works by filling MOF pore channels with biomass-derived or carbon-based precursors, such as glucose or pitch. After impregnation, heating is applied. This step creates either MOF@BDC core-shell structures or systems in which carbon nanotubes/layers are confined. Confined carbonization refers to the carbonization of biomass precursors under the protection of the MOF matrix. This method keeps the crystalline structure of MOFs. It also generates a highly dispersed carbon phase, thereby improving the electrical conductivity and stability of the composite.

2.2.3. Post-synthetic modification and functionalization

Functional components can be added to pre-synthesized MOF/BDC composites using chemical or physical methods, enabling the composites to better recognize and remove specific pollutants.[28,29] Heteroatom doping, which can introduce elements such as N, S, and phosphorus (P) via vapor- or liquid-phase methods[30], is effective in modifying these composites. Through doping, the composite's surface charge and chemical properties are changed, enabling selective adsorption of heavy metals and organic pollutants.[30] Functional group modification is another way to improve selectivity for specific ions. For example, –SH or $–NH_2$ groups can be attached through graft polymerization. Once modified, these groups bind more strongly with ions, particularly Hg^{2+} and Cr(VI). Nanometal loading can fix iron (Fe), copper (Co), silver (Ag), or other metal nanoparticles on the composite surface. This method imparts the material with catalytic

or antibacterial functions[30], thereby forming an integrated system with adsorption, catalysis, and disinfection.

2.2.4. Direct thermal conversion method

In the direct thermal conversion method, MOFs and biomass precursors are mixed together. Then, one-step pyrolysis is performed under an inert atmosphere at high temperature.[29] Two reactions occur simultaneously during this process. MOFs decompose into metal oxides or carbides, and biomass decomposes into porous carbon. The final product is a well-mixed and integrated MOF-derived porous carbon/metal oxide composite. This method is simple and efficient, so it is suitable for large-scale production. The pyrolysis temperature and holding time can be controlled properly. Therefore, part of the original MOF's regular pore structure can be preserved. At the same time, numerous defect sites are created. These sites enhance the catalytic activity of the composite.[29]

2.3. Structural and morphological control

Synthesis parameters strongly affect the morphology, pore structure, and interface properties of composites. These factors determine the materials' mass transfer, adsorption, and catalytic performance.

2.3.1. Morphological control

The growth kinetics of MOFs on BDC surfaces can be precisely controlled. This enables the construction of core-shell structures, such as MOF@BDCs or MOF@Carbon. This special structure protects the inner core material and creates unique interfacial effects. When BDCs are two-dimensional materials such as graphene sheets or BDC nanosheets, MOF nanoparticles grow uniformly on their surfaces. This process forms "sandwich-like" or interlayer insertion structures. Therefore, these structures stop carbon sheets from stacking and prevent MOF agglomeration.[26] When BDCs are three-dimensional porous aerogels or foams, MOFs can grow evenly inside and on the framework. Interpenetrating double-network structures can thus be obtained. These structures have high porosity, good mass transfer performance, and strong structural stability. Therefore, they are suitable for dynamic flow or membrane separation systems.[28,31]

2.3.2. Pore architecture engineering

An ideal composite should have a hierarchical pore system. The mesopores and macropores of BDCs are like "transport highways." They help pollutants reach active sites quickly. The micropores or mesopores of MOFs are "precision capture chambers" or "microreactors." They can enrich or transform pollutants selectively through size exclusion and specific interactions.

The pore size distribution of BDCs can be adjusted by varying the pyrolysis/activation temperature, precursor ratio, and other parameters.[32,33] In this way, the microenvironment of the composite can be adjusted.[34] In a study by Wang *et al.*[34], the isotherm of the Al-MOF/biochar (BC) composite was Type IV with an H3 hysteresis loop. It shows that the mesoporous structure is significantly enhanced. This structure is favorable for the diffusion of large molecule pollutants.

2.3.3. Interfacial property modulation

Synthesis temperature and time have a substantial influence on the bonding strength and the chemical state of the interface between MOFs and BDCs. In some cases, proper heat treatment can help form chemical bonds between BDCs and MOFs, such as M–O–C bonds. These bonds enhance electronic coupling, thereby improving the catalytic activity and stability of the composite and increasing the number of active sites. However, if the conditions are too strict, the MOF structure may collapse, or the interface may separate.

2.4. Key characterization techniques

2.4.1. Crystal structure and morphology

X-ray diffraction (XRD) can show the crystalline phases of MOFs. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can directly display the overall morphology of composites. These two methods are used to monitor MOF loading state, particle size distribution, and the interface integration between MOFs and BDCs.[27]

2.4.2. Pore structure analysis

Nitrogen adsorption–desorption isotherms can be combined with the Brunauer–Emmett–Teller models to measure the specific surface area of materials. The pore size distribution can be accurately calculated using non-local density functional theory or Barrett–Joyner–Halenda models to quantitatively analyze the volume and proportions of micropores and mesopores. These data are highly important for studying adsorption and mass transfer processes.[27]

2.4.3. Surface chemistry and elemental states

X-ray photoelectron spectroscopy (XPS) can provide quantitative data on surface element composition, chemical states, and relative content. These data are necessary to analyze heteroatom doping, metal valence states, and interface charge transfer. Fourier-transform infrared spectroscopy is used to identify characteristic functional groups of materials. Raman spectroscopy is used to characterize the degree of graphitization (G-band) and the defect density (D-band) of carbon materials.

2.4.4. Interfacial and electronic properties

In addition to structural characterization, Raman spectroscopy and XPS can indirectly reflect interface interactions. Ultraviolet (UV)–visible light (Vis) diffuse reflectance spectroscopy (UV-Vis DRS) is used to test the light absorption range and band gap of materials. Electron paramagnetic resonance can detect unpaired electrons or radical species in materials. Therefore, it is often used to study catalytic mechanisms.

2.4.5. Stability evaluation

Thermogravimetric analysis is used to evaluate the thermal stability of materials. To test chemical stability, materials are immersed in simulated water environments. Then XRD, SEM, and inductively coupled plasma mass spectrometry are utilized to analyze the structural integrity and metal leaching concentrations of the materials.

3. Targeted removal mechanism and performance of pollutants

3.1. Accurate capture of heavy metal ions

3.1.1. Adsorption mechanism

Biomass-derived carbons have abundant microporous and mesoporous structures.[34] These structures can physically adsorb and concentrate heavy metal ions. In addition, the surface of BDCs is rich in O-containing functional groups such as –COOH, –OH, and carbonyl groups (C=O).[19] Under appropriate pH conditions, these groups can be deprotonated to carry negative charges[35], forming coordination complexes with heavy metal cations and enabling ion exchange[36] and electrostatic attraction.[37] The metal nodes and functionalized ligands of MOFs provide high-density, precisely designable coordination sites. In amino-functionalized UiO-66-NH_2, the lone pair electrons of the –NH_2 groups can form coordination bonds with heavy metal ions[38], while the –OH groups within the zirconium oxide clusters can also participate in ion exchange.[39] This atomic-level coordination effect endows the MOF with high selectivity[40,41] for specific ions. For variable valence heavy metals, such as Cr(VI), the MOF/BDC composite exhibits unique redox conversion capability. The conductive carbon skeleton of BDCs can serve as an electron transfer channel[33,42], which rapidly transfers photo-generated electrons or external circuit electrons to the metal active center of the MOF, promoting the reduction of Cr(VI) to less toxic trivalent chromium (Cr) ion.[24] To summarize, the adsorption mechanisms of MOF/BDC materials are shown in Figure 1.

3.1.2. Adsorption performance

Adsorption capacity is the maximum mass or amount of adsorbate that a unit mass of adsorbent can adsorb under specific conditions. It represents the limit of the adsorbent's adsorption ability. Constructing MOF/BDC composites can significantly improve the adsorption capacity for various heavy metal ions, mainly due to increased specific surface area and active site density after composite formation. In different research systems, the composite material exhibits excellent adsorption capacity for specific heavy metal ions. Ghaedi *et al.*[43] demonstrated that the UiO-67/hardwood BC composite (MBC) was prepared via an *in situ* solvothermal method (Table 1). This material achieved maximum adsorption capacities of 121.1 mg/g for lead (Pb) ion and 59.7 mg/g for cadmium (Cd) ion in a singleion system. Polyakov *et al.*[44] reported similar results. They used MIL-100(Fe) combined with wheat straw BC. The adsorption capacities for Cu^{2+} and Pb^{2+} were 142 mmol/kg and 156 mmol/kg, respectively, which were about twice those of pure BC.

In complex systems with multiple heavy metal ions, adsorption selectivity is critical for the practical value of the adsorbent. Ghaedi *et al.*[43] fabricated the composite MBC. This material maintains high selectivity for Pb(II) and Cd(II) even in the presence of interfering ions such as zinc (Zn) and magnesium (Mg). It also maintains removal efficiencies of 90.8% and 89.5%. Its adsorption sites and mechanism can selectively bind target ions. In another case, Mhalshekar *et al.*[45] prepared the BC@Co-MOF 6H composite. In a mixed system with malachite green dye and Cr(VI), it achieved a Cr(VI) degradation rate of 81.65% under sunlight irradiation (Table 1). UV-DRS spectra and corresponding Tauc plots of cobalt (Co)-MOF and BC@Co-MOF composites are shown in Figure 2. The band gap energies were calculated using the Kubelka–Munk function. The values are 3.29 eV for pristine Co-MOF, 3.26 eV for BC@Co-MOF 1H, 3.14 eV for BC@Co-MOF 6H, and 3.20 eV for BC@Co-MOF 12H. Pure Co-MOF has strong absorption mainly in the UV region. However, BC@Co-MOF 1H shows a small redshift. This means the material has improved light-harvesting because MOF and BC exhibit better dispersion and stronger interfacial contact. Among all samples, BC@Co-MOF 6H has the smallest band gap. These results show the best synergistic effect between Co-MOF and the BC matrix. The improvement comes from defect states at the interface. These states help absorb visible light more effectively and separate charge carriers better. For BC@Co-MOF 12H, the band gap increases marginally. This is probably because of excessive MOF agglomeration or surface saturation. Overall, BC@Co-MOF 6H exhibits the best optical properties and is highly suitable for visible-light-driven photocatalytic applications.

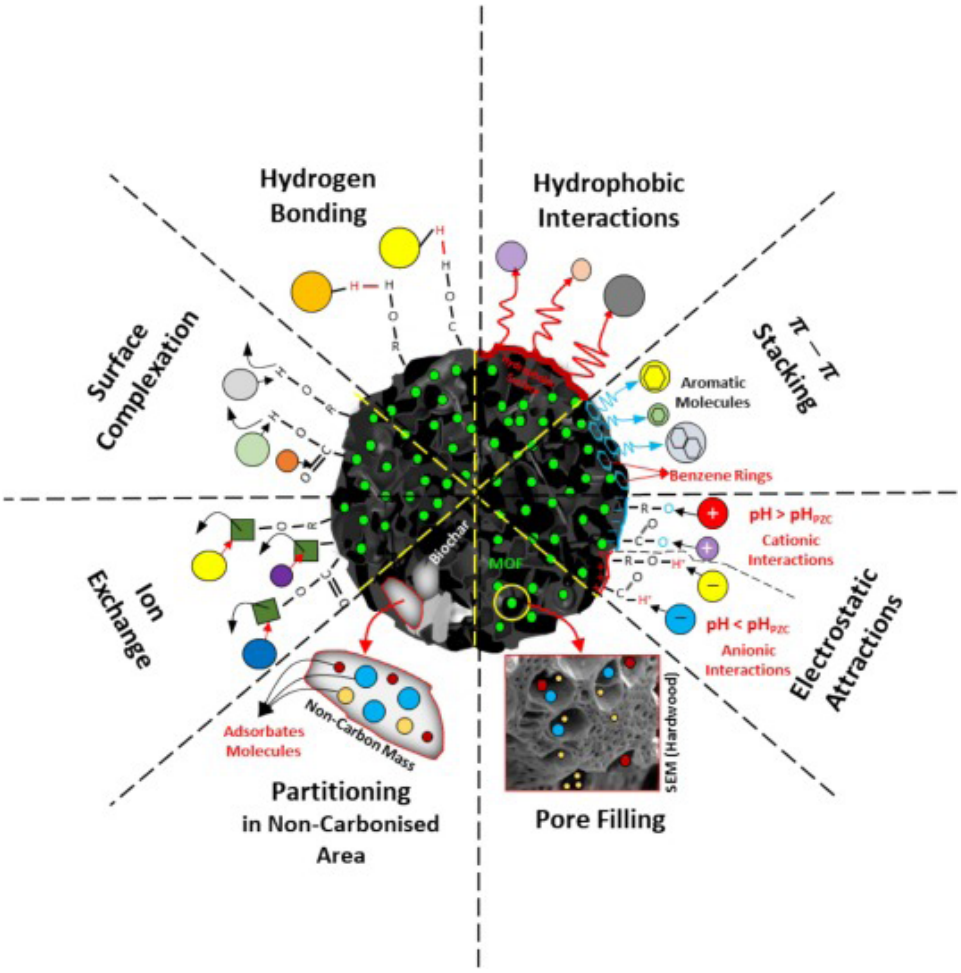


Figure 1. Schematic illustration of possible adsorption mechanisms in metal-organic framework-biochar composites[25]
Abbreviations: MOF: Metal-organic framework; SEM: Scanning electron microscopy.

Solution pH greatly influences heavy metal removal efficiency. This adaptability links closely to heavy metal speciation, material surface charge, and active site accessibility. For cationic heavy metal adsorption systems, such as Pb^{2+}, Cd^{2+}, and Cu^{2+}, composite materials generally show a wide pH adaptation range. Polyakov *et al.*[44] prepared the MIL-100(Fe)/wheat straw BC composite. This composite can effectively immobilize Cu^{2+} and Pb^{2+} in complex soil environments through surface complexation and cation-exchange mechanisms. In contrast, the removal of anionic heavy metals such as Cr(VI) is more sensitive to pH. Cr(VI) speciation changes with pH and material surface charge. The BC@Co-MOF 6H composite fabricated by Mhalshekar *et al.*[45] showed clear pH dependence in the photocatalytic reduction of Cr(VI). In particular, acidic conditions are most favorable. In contrast, alkaline conditions (pH > 10) are least favorable, and the degradation rate drops to 75%.

Regenerability is a key indicator for evaluating the economic feasibility of composite materials. Material regeneration capacity is affected by MOF/BDC binding strength, active-site stability, and operation configuration. Ghaedi *et al.*[43] prepared the MBC. After four cycles of use, MBC maintains about 87% removal efficiency for Pb(II) and Cd(II) (Table 1). XRD analysis further verifies this stability. It confirms that the MOF crystal structure shows no obvious collapse, indicating that UiO-67 is firmly bound to the BC substrate.

3.2. Selective removal and catalytic degradation of organic pollutants

3.2.1. Adsorption mechanism

Metal-organic framework/BDC composites combine

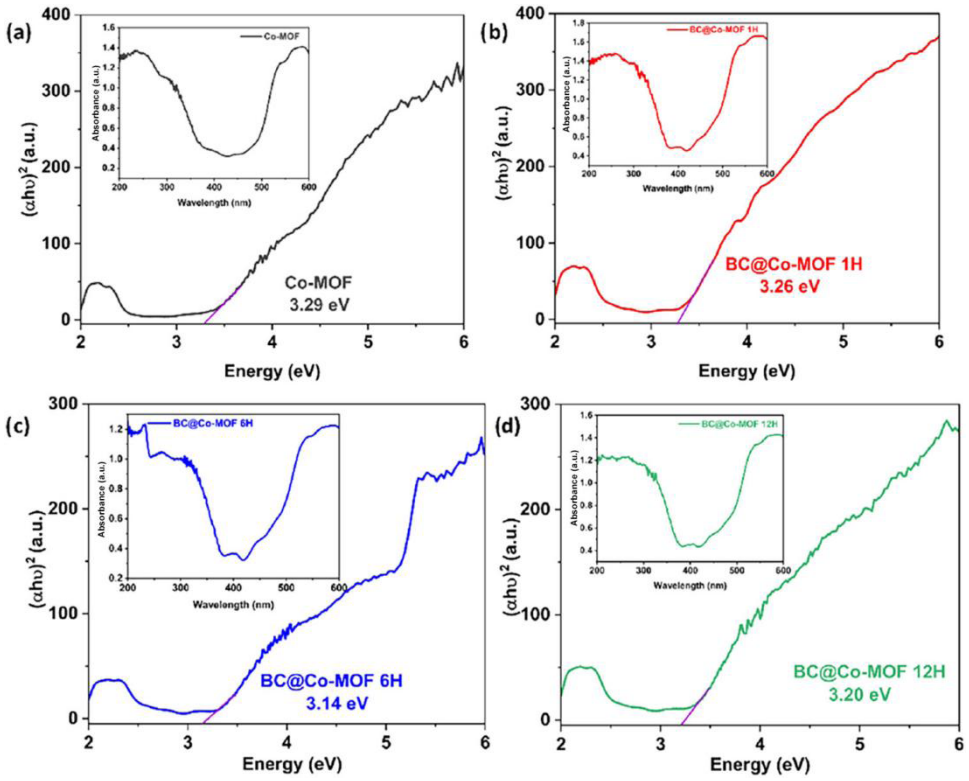


Figure 2. Ultraviolet-diffuse reflectance spectroscopy spectra and Tauc plot of (A) Co-MOF, (B) BC@Co-MOF 1H, (C) BC@Co-MOF 6H, and (D) BC@Co-MOF 12H[45]
Abbreviations: BC: Biochar; MOF: Metal-organic framework.

the uniform micropores of MOFs with the hierarchical pore structure of BDCs (micropores, mesopores, and macropores), forming a multi-level pore system. The well-defined pore size of MOFs can, in principle, act as a molecular sieve, potentially favoring the adsorption of pollutants with matching dimensions. For instance, the cage-like pores of MIL-101(Cr) have been reported to selectively adsorb antibiotic molecules of appropriate size while excluding larger background matrices, such as humic acid.[25] However, such size-exclusion behavior is highly dependent on the specific MOF–pollutant pair and should not be generalized as "precise recognition" without direct evidence. The presence of mesopores/macropores in BDCs can accelerate pollutant mass transfer and shorten diffusion pathways. The abundant π electrons in the aromatic ligands of MOFs within MOF/BDC can interact with the π electrons[25] of surrounding molecules through stacking interactions. BDC also contains various aromatic rings that participate in π-π interactions.[46,47] The combination of van der Waals forces and electron delocalization can form a strong bond between the MOF/BDC host and target molecules. This mechanism works well for the adsorption of nonpolar or weakly polar organic pollutants. These pollutants are rich in π-electron structures, such as tetracycline or dyes.[25,48] In advanced oxidation processes, variable-valence metals in MOFs catalyze the decomposition[27] of hydrogen peroxide (H_2O_2) or activate persulfate/peroxymonosulfate through redox cycles[49], generating highly oxidizing hydroxyl radicals (•OH) or sulfate radicals (SO_4•$^-$).[27,48,50] In addition, photo-generated electrons can further accelerate the regeneration of the metal cycle. They can also synergistically activate the oxidant and achieve coupled enhancement of photocatalysis and Fenton/persulfate oxidation. This can greatly improve reactive O species yield and pollutant degradation efficiency.[51] BC, with abundant surface functional groups, such as –OH, –COOH, $–NH_2$, and persistent free radicals, activates persulfate to generate reactive O species, such as SO_4•$^-$, •OH, and O_2•$^-$, which attack specific functional groups of drug molecules (Figure 3).[52] Concurrently, synergistic degradation involving both radical and non-radical mechanisms is achieved through the construction of an electron transfer pathway among the pollutant, BC, and oxidant, with the graphitized carbon framework

serving as an electron conductor[42,53,54], and through singlet O ($^1O_2$) mediated electrophilic addition.[55] When MOFs grow *in situ* inside BDC channels or on BDC surfaces, the confined space forms a "microreactor" environment. This environment can increase local pollutant concentrations, a phenomenon called the concentration effect, and stabilize active sites. Such confined spaces may accelerate reaction kinetics by concentrating pollutants near active sites. However, it remains difficult to directly measure these local concentration increases. The conductive BDC substrate and the MOF are in close contact, facilitating interfacial charge transfer. In several reported systems, this contact forms Schottky junctions or p–n heterojunctions. These structures improve the separation of photo-generated electron–hole pairs and reduce their recombination.[42,53,55] However, there is still little direct experimental proof for such junctions in MOF/BDC composites. Therefore, these ideas are possible mechanisms, not confirmed results. The carbon substrate anchors MOF nanoparticles. This process stabilizes active sites and reduces metal leaching.[33,41]

3.2.2. Degradation performance

Degradation efficiency is defined as the conversion rate of a target compound into harmless or low-toxicity products when catalyzed. The NiCo@BC-MOF synthesized by Arshad *et al.*[42] exhibited a degradation efficiency of 90.1% for amoxicillin under optimized conditions. A weakly acidic environment and elevated temperature were found to enhance the reaction rate. Roy *et al.*[27] found that the BC@MOF quantum dots (PBC-HK) composite material achieved degradation rates of 95.23% for pantoprazole and 96.31% for Victoria blue. These rates were significantly higher than those of the individual components, indicating a clear synergistic effect and a 30–40% reduction. Ling *et al.*[33] developed a BC@CoFe-activated peroxydisulfate system, achieving 97.7% degradation rate for tetracycline within 2 hours, with a reaction rate constant 1.66 times higher than that of single CoFe-d. The system still kept efficiency over 80% in actual water bodies.

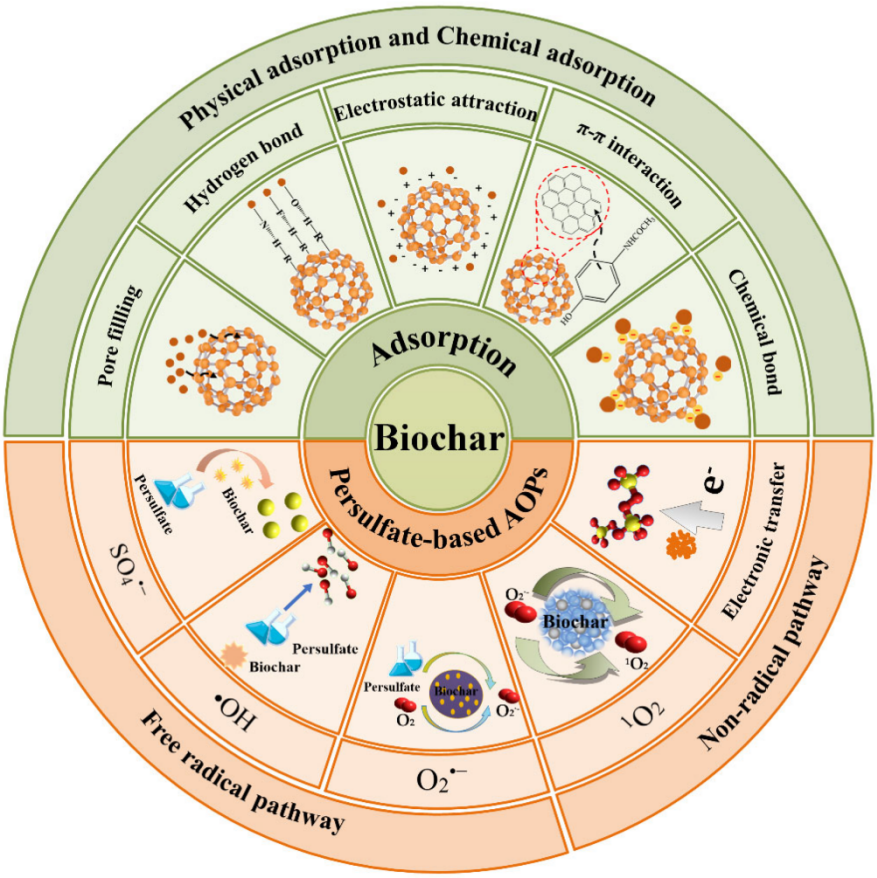


Figure 3. Removal mechanisms and main interactions of pharmaceutical pollutants by biochar[52]

Mineralization rate is the degree to which organic pollutants are completely oxidized and decomposed into small inorganic molecular products. The products include CO_2, H_2O, and inorganic ions. It reflects the catalytic system's deep oxidation capacity. Roy *et al.*[27] synthesized the PBC-HK composite material that showed total organic carbon (TOC) removal rates of 82.48% and 84.73% in degrading pantoprazole and Victoria Blue. Chemical O demand removal exceeded 90%, indicating substantial organic matter degradation and suggesting a high degree of mineralization.

Background matrix interference resistance refers to the ability of adsorption/catalytic materials to maintain efficient removal of target pollutants despite competition or inhibition from coexisting substances (e.g., ions, organic matter, and suspended solids) in complex real environments. PBC-HK maintained removal efficiency above 80% for target pollutants, even in complex aqueous solutions.[27] The solutions contained Cl^- (0.01 M), Al^{3+} (0.01 M), and humic acid (6 mg/L). However, high concentrations of Cl^- and Al^{3+} resulted in significant inhibition, with the removal efficiency dropping to 33–38%.[27] Ling *et al.*[33] developed the BC@CoFe/peroxydisulfate (PDS) system. It degraded efficiently even in the presence of sulfate (SO_4^{2-}), nitrate (NO_3^-), dihydrogen phosphate (H_2PO^{4-}), and 10 mg/L of humic acid. However, carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) greatly inhibited the reaction. The reason is that they generate weakly active carbonate radicals. In addition, the degradation efficiency was over 80% in actual water matrices, such as tap water and river water. Li *et al.*[48] proved that Fe-MOF@stalk BC kept stable performance in a wide pH range (3.0–8.0). Specifically, its degradation efficiency for sulfamethoxazole, norfloxacin, and erythromycin was stable in the pH range of 4.0–7.0. The material's point of zero charge (pHpzc) was 6.48. When pH was higher than this value (pH > pHpzc), the surface became negatively charged. It may restrain the adsorption of anionic pollutants.

The cycle stability of a catalyst refers to the durability of an adsorption or catalytic material in maintaining its original structural characteristics and adsorption or catalytic activity, as well as the degree of performance decay during repeated uses. The PBC-HK developed by Roy *et al.*[27] maintained an activity of > 80% after four cycles, with a Cu leaching level of < 0.041 mg/L, well below the WHO standard. Its crystal structure and surface functional groups remained stable, demonstrating good cycle stability and economic viability.[27] Ling *et al.*[33] developed BC@CoFe. It kept 73.23% degradation efficiency after 12 hours of continuous operation. Fe and Co leaching was reduced by 6.5–8.0 times compared to carrier-free CoFe-d. XRD and XPS analyses confirmed its structural stability. It shows that the BC support effectively eases aggregation and metal loss. Sun *et al.*[56] prepared MOF/corncob-derived porous carbon-5. After five cycles, the degradation rates of Rhodamine B and tetracycline decreased from 99.0% and 98% to 88.2% and 89.1%, respectively, demonstrating an activity loss of less than 15%. Thermogravimetric analysis–derivative thermogravimetry analysis showed that its thermal stability was better than that of pure MOF. Photocurrent response tests also proved its excellent photostability. Peighambardoust *et al.* conducted a similar study and reported that after seven adsorption–desorption cycles, PSB/CoFe2O4/MOF-808(Zr) exhibited a decrease in methylene blue removal rate from 98.86% to 81.76%. This was attributed to active site damage, pore blockage, and irreversible adsorption. However, the composite material still performed better than its individual components.[57]

3.3. Synergistic treatment of emerging micropollutants

3.3.1. Investigation of mechanism and performance

The synergistic treatment mechanisms of MOF/BDC composites for emerging micropollutants mainly include adsorption-catalysis and enhanced photoelectrocatalysis. In the adsorption stage, microplastics usually have negative surface charges. MOFs can carry positive charges through metal nodes or protonated ligands. The composite material can efficiently enrich microplastics, pharmaceutical residues and endocrine disruptors. It uses multiple synergistic mechanisms, such as electrostatic interactions, π-π stacking, hydrophobic interactions and hydrogen bonding.

Chen *et al.*[58] constructed the UiO-66-X@MF composite material. UiO-66-OH has the highest positive ζ-potential because of its defects and hydroxyl groups. It mainly captures microplastics via electrostatic interactions, with hydrogen bonding and van der Waals forces also playing a synergistic role. The poly(vinylidene fluoride) (PVD0F removal rate by UiO-66-OH@MF-3 is 90.1%. When three units are connected in series, the removal rate rises to 95.5%. The removal rates of poly(methyl methacrylate) and polystyrene are 88.2% and 85.7%, respectively. After 10 cycles, the material still keeps 90.7% efficiency. It can treat 1 L of water with 85.2% efficiency, and retains 94.2% efficiency in seawater. Therefore, it shows excellent cycling stability and practical applicability. Wan *et al.*[59] examined the adsorption of polystyrene microplastics using zeolitic imidazolate framework (ZIF)-67. They found that electrostatic interactions are the main driving force. At pH 6–10, positively charged ZIF-67 attracts negatively charged polystyrene. As shown in Figure 4, ZIF-67 adsorbs

polystyrene microplastics (PSMPs). The hydroxyl vibration peak at 3,300–3,700 cm^{-1} shows hydrogen bonding. This bonding forms between Co–OH or –NH groups and the –OH groups of PSMP. The imidazole ring in ZIF-67 and the aromatic structure in PSMP can also interact via π-π stacking. Hydrogen bonding and π-π stacking also work together to capture microplastics. Therefore, these two forces together promote adsorption. The Freundlich model fits the data best, indicating multilayer heterogeneous adsorption. Under optimal conditions, the adsorption rate of ZIF-67 for polystyrene microplastics reaches 92.1%, and the adsorption capacity is 11.6 mg/g. The adsorption equilibrium is achieved in 20 min, and the rate constant is 0.171 min^{-1}. The material maintains a removal rate above 82% over a wide pH range (3–10) and concentration range (5–50 mg/L). However, its structural stability after regeneration needs improvement. Haris *et al.*[60] developed a two-dimensional MOF@C@FeO nanocolumn composite material. The stacking of nanosheets was effectively inhibited by intercalating olive waste-derived C@FeO nanocolumns between two-dimensional MOF layers. The composite material possesses Fe–O–C bonds. These bonds work with chemical adsorption of O-containing groups on microplastic surfaces, π-π interactions, and electrostatic effects. Therefore, they together improve microplastic capture. The material shows strong adsorption of 1 μm polystyrene microplastics. It reaches a removal rate of nearly 100% within 60 minutes and maintains a 90% removal rate after six cycles (Table 1). Microplastic adsorption does not appear to occupy the active sites of the MOF. In addition, soluble pollutants are concentrated through hydrophobic interactions, and the material can be rapidly recovered by magnetic separation. In the catalytic stage, Zanaty *et al.*[61] constructed a hydrogenated titanate nanopipe (HTNT)@ZIF-67 composite. Using H_2O_2, this material exhibits a significant catalytic oxidation effect on microplastics. The Co^{2+} active site of ZIF-67 catalyzes the decomposition of H_2O_2 to produce reactive O species. HTNT provides a high specific surface area and diffusion channels. The synergistic electronic effect of Co–N and Ti–O–Ti bonds improves the catalytic performance. TOC analysis shows that organic carbon decreases significantly. FT–IR confirms the breakage of C–H bonds and the oxidation of aromatic rings. Optical microscopy shows that the particle size decreases from 300 μm to below 100 μm. The material maintains 78% efficiency after six cycles, indicating exceptional stability. The dissolved Co concentration is < 4 ppm, indicating a low risk of metal leaching.

Although current research on MOF/biomass carbon composites for microplastic removal remains limited, the examples above have demonstrated significant advantages

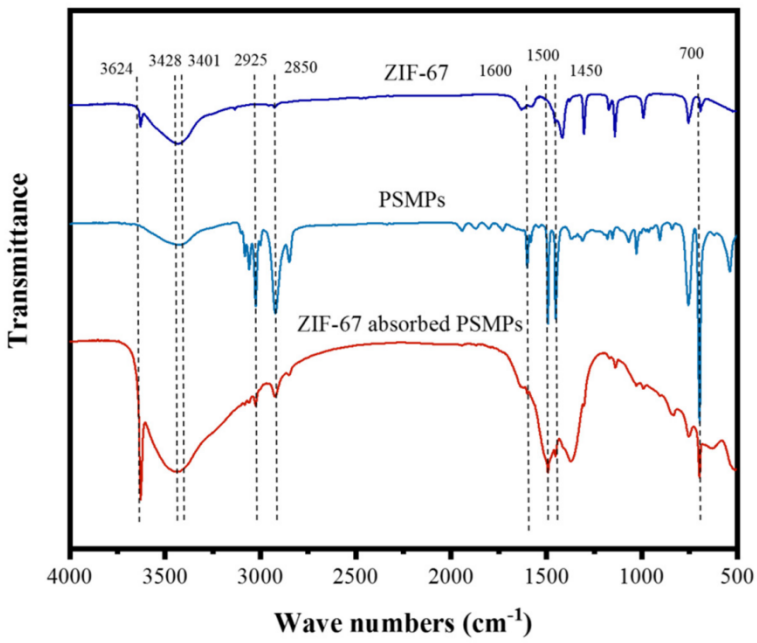


Figure 4. Fourier-transform infrared spectroscopy spectra for PSMPs and ZIF-67 during the adsorption process[59]
Abbreviations: PSMPs: Polystyrene microplastics; ZIF: Zeolitic imidazolate framework.

in adsorption capacity, cycle stability, and adsorption-catalytic synergy, providing an important direction for subsequent research.

4. Application systems and engineering explorations

4.1. Static batch mode

Static batch processing is the basic method for studying precise interaction mechanisms between materials and pollutants. Adsorption kinetics and isotherm studies can be used to measure the recognition rate and enrichment capacity of materials. We can achieve selective adsorption by precisely controlling the micropore size of BDCs (e.g., narrow pores of 0.4–0.7 nm can capture CO2 selectively)[62] or the surface functional groups of MOFs (e.g., amine groups are used to target Cr(VI)).[63] For instance, the mercury adsorption capacity of MOF composite materials can achieve 1,634 mg/g.[64] However, performance differences across studies often stem from inconsistent test conditions. In some cases, high adsorption capacity will reduce selectivity or increase costs, so a comprehensive balance must be considered. The recyclability of materials depends on the regeneration strategies used. Mild physical regeneration is suitable for weak bond adsorption. Strong chemical bonding may need acid washing and other methods, but these methods may damage the material's structure. Therefore, developing efficient and mild regeneration technologies is a key challenge.

4.2. Dynamic flow mode and fixed bed/column adsorption

Dynamic mode tests material performance under continuous flow conditions. These conditions are close to real-world applications, so this test is crucial for engineering applications. The core step is to process powder materials into fixed-bed fillers. For example, UiO-66-NH_2 can be loaded on silica gel beads to continuously remove Cr(VI).[65] The dynamic performance of these fillers can then be evaluated. Breakthrough curves can directly show the bed's actual treatment capacity and the adsorbent's precise retention efficiency. System pressure drop and processing flux are related to operational energy consumption and economic benefits. In actual complex water samples, coexisting impurities will compete for active sites. This competition leads to premature breakthroughs and reduces effective capacity. It is a severe test for the selectivity of materials. In addition, the mechanical and chemical stability of materials is a bottleneck for engineering applications. Materials need to withstand long-term hydraulic shear and harsh chemical environments. Therefore, enhancing the stability of MOFs through composites is crucial. Multi-cycle adsorption-regeneration cycle tests are the final standard. These tests determine whether materials can meet the long-term, precise treatment requirements.

4.3. Membrane separation and catalytic membranes

The MOF composites integrated into membrane matrices have changed from simple separation to an integrated mode with "adsorption-separation-catalysis" functions. They provide innovative solutions for the precise, continuous removal of pollutants from water. These membrane materials can combine the high selectivity of MOFs with the high throughput of membrane processes. They can achieve targeted recognition and transformation of target pollutants through a well-designed structure.

4.3.1. Classification and preparation strategies of metal-organic framework-based membranes

Based on the combination methods of MOFs and membrane matrices, they can mainly be classified into three categories. The first is nanofiber composite membranes, constructed by loading MOFs onto electrospun nanofiber networks, such as growing zirconium-based MOF-808 on polyacrylonitrile nanofibers, which significantly enhances the adsorption capacity for Cd^{2+} and Zn^{2+}.[66] The second type is mixed matrix membranes. In these membranes, MOFs act as functional fillers and disperse in a continuous polymer phase, such as polyethersulfone (PES), cellulose acetate, and PVDF. Studies show that adding MOF-5 can greatly improve membrane hydrophilicity and ion permeability, thereby facilitating the removal of Cu^{2+} and Co^{2+}.[67] The third is thin-layer nanocomposite membranes or biomimetic structure membranes, which achieve precise separation by constructing an extremely thin MOF active layer on a support layer. A "pearl necklace" structure, formed by growing ZIF-67 on cellulose acetate nanofibers, prevents MOF aggregation and exposes more active sites.[68]

4.3.2. Integrated adsorption-separation for precision remediation

The core advantage of MOF composite membranes is their tunable structure and function for precise pollutant remediation. First, the regular pores of MOFs enable precise molecular sieving based on molecular size. Second, MOF organic linkers or metal nodes can be functionalized (e.g., by introducing $–NH_2$, –COOH). This step enhances the membrane's selective binding capacity for specific heavy metal ions (e.g., $Hg2^+$, $Pb2^+$) and oxyanions (e.g., Cr(VI), phosphate) at the membrane surface. Third, MOFs with intrinsic photocatalytic or catalytic activity (such as amino-functionalized UiO-66-NH_2) can be integrated into membranes. In this way, membranes can simultaneously

adsorb and degrade pollutants. Adsorbed Cr(VI) can be reduced to less toxic Cr(III) *in situ*. This is a typical integrated design of "treatment-transformation".[68]

4.3.3. Performance advantages and key challenges

The MOF composite membrane technology has many significant advantages. Adding MOFs improves selectivity and adsorption capacity without reducing membrane flux. The polymer matrix improves the mechanical and chemical stability of membranes. In addition, these membranes are easy to integrate into continuous-flow systems for large-scale treatment. However, some key challenges remain. Poor dispersion and interface defects between MOF fillers and polymers may lead to non-selective channels. Therefore, the separation efficiency may decrease.[69] Membrane fouling will lead to flux decline, so it is necessary to develop antifouling surfaces. The long-term chemical stability of MOFs in harsh water environments, as well as the potential for leaching of active components, remains a concern. Moreover, the relatively high manufacturing cost of high-performance MOFs and their composite membranes limits large-scale commercial applications at present. In the future, researchers must focus on optimizing interfaces and developing low-cost, high-stability MOFs. Finally, in-depth evaluations of long-term performance in complex real water matrices should also be conducted.

4.4. Photoelectric/electrochemical coupled systems

These systems use external electric or light fields as precise control tools. They upgrade the treatment process from "adsorptive enrichment" to "directed transformation." We leverage the synergies between BDCs and MOFs in these systems. BDCs have good conductivity and stable structure, while MOFs have high selectivity and catalytic activity. Together, they provide an alternative approach for efficiently and controllably removing pollutants.

4.4.1. Electro-assisted adsorption systems

The core principle of electro-assisted adsorption systems is to use an electric field to drive target ions to migrate in a specific direction. These ions can be enriched onto the electrode material's electric double layer or active sites. BDCs have high conductivity and a large specific surface area. Thus, they serve as ideal electrode substrates. When BDCs are combined with MOFs, the electrode surface gains highly selective recognition sites. These sites include specific organic ligands (such as those with N and O groups) and metal nodes.

This design makes the material achieve targeted electro-adsorption of specific ions (such as heavy metals). It goes beyond simple physical retention. Studies show that combining ZIF-8 with BC can greatly improve CO_2 adsorption capacity and selectivity. This principle can also be used in electro-assisted adsorption systems.[9] In these systems, electric field parameters are the key to precise control. A suitable voltage can be applied to accurately control the electrode's surface charge. Thus, one can switch the electrostatic attraction for target ions on or off. By switching or removing the voltage, ions can desorb quickly, and the material can regenerate *in situ*. Therefore, this process is efficient and reversible.[9] Adding highly conductive carbon materials (such as graphene or carbon nanotubes) can create a fast electron-transport network within the composite. It addresses the poor conductivity problem in most pure MOFs. Therefore, it improves the speed of electro-adsorption and the stability during repeated use.[62]

4.4.2. Electrocatalytic degradation systems

Electrocatalytic degradation breaks down pollutant molecules directly via electrochemical reactions, thereby achieving complete removal. This process needs catalytic materials with high selectivity, activity, and stability. Therefore, it depends on effective synergy between the conductive scaffold and catalytic centers. In this context, BDCs can serve as a three-dimensional conductive network to facilitate electron transfer from the external circuit, while MOFs provide well-defined catalytic active sites for pollutant activation and transformation.[62] A typical use is the precise reduction of toxic Cr(VI). Some MOF composites with $-NH_2$ and other functional groups can reduce adsorbed Cr(VI) to less toxic Cr(III). In an electrocatalytic system, a precisely controlled cathodic potential should be applied. This potential drives the reduction process more efficiently and selectively, thereby avoiding the production of by-products. For hard-to-degrade organic pollutants, anodic oxidation systems based on MOF/BDC composites can be designed. These systems can produce strong oxidants such as hydroxyl radicals (•OH). Therefore, they can mineralize pollutants deeply.[9] Research on CNT-reinforced MOF composites for electrocatalysis provides important insights into the design of such anode materials.[70]

4.5. Case studies: Performance in real water/ complex matrices

4.5.1. Typical cases and precision remediation performance

FeCo-MOF/BC composite (BC@CoFe) was applied to tetracycline (TC) degradation in river and tap water. It achieved ~2-h degradation efficiency comparable to that in ultrapure water, with rate constants of 0.79, 1.06, and 1.22 $mM^{-1}{\cdot}min^{-1}$ for river water, tap water, and ultrapure

Table 1. Comparative summary of removal performance for heavy metals and organic pollutants by representative MOF/BDC composites

MOF type	BDC precursor	Composite strategy	Target pollutant	Removal performance	Key observations/trends	Ref.
UiO-67	Hardwood biochar	*In situ* solvothermal	Pb^{2+}, Cd^{2+}	121.1 mg/g (Pb^{2+}), 59.7 mg/g (Cd^{2+}); >89% after 4 cycles	High selectivity against Zn^{2+}/Mg^{2+}; good structural stability	43
MIL-100(Fe)	Wheat straw biochar	*In situ* growth	Cu^{2+}, Pb^{2+}	142–156 mmol/kg (~2 × pure biochar)	Surface complexation + cation exchange; wide pH adaptability	44
Co-MOF (ZIF-67 type)	Bacterial cellulose	*In situ* growth (6 h)	Cr(VI), malachite green dye	81.65% Cr(VI) degradation (sunlight)	Optimal band gap (3.14 eV) at 6 h composite; acid pH favorable	45
Cu-MOF@Co-MOF	– (bimetallic MOF, no BDC)	–	TC, DOX	434.78 mg/g (TC), 476.19 mg/g (DOX); >80% in 5–15 min	Synergy of H-bonding, π-π, coordination, electrostatic, pore filling	71
NiCo@BC-MOF	Biochar (unspecified)	Pyrolysis derivative	Amoxicillin	90.1% degradation	Weakly acidic and elevated T enhances the rate	42
BC@CoFe	Biochar (from biomass)	MOF derivative + PDS	Tetracycline	97.7% in 2 h; 73.23% after 12 h continuous	Tolerant to SO_4^{2-}/NO_3^-/HA; inhibited by CO_3^{2-}/HCO_3^-	33
MOF/gelatin aerogel (BC@MIL-88B(Fe))	Gelatin + biochar	Aerogel composite	TC, OTC	820 mg/g (TC), 930 mg/g (OTC); > 90% removal in real water	Tolerant to Na^+/SO_4^{2-}/HA; inhibited by Ca^{2+}/PO_4^{3-}; 35–40% loss after 8 cycles	41
Two-dimensional MOF@C@FeO	Olive waste-derived C@FeO	Intercalation	1 μm PS microplastics	~100% in 60 min; 90% after 6 cycles	Fe–O–C bonds + π-π + electrostatic; magnetic separation	60

Abbreviations: BDC: Biomass-derived carbon; DOX: Doxycycline; HA: Hyaluronic acid; MOF: Metal-organic framework; OTC: Oxytetracycline; PS: Polystyrene; T: Temperature; TC: Tetracycline.

water, respectively. The degradation was tolerant to SO_4^{2-}, NO_3^-, and humic acid (HA), but inhibited by CO_3^{2-}/HCO_3^-. In a fixed-bed membrane reactor, the composite maintained 73.23% degradation over 12 hours with low metal leaching.[33]

The MOF/gelatin aerogel (BCM/GA_{200}) was used for TC and oxytetracycline (OTC) removal in lake water and wastewater effluent. It exhibited high maximum adsorption capacities (820 mg/g for TC on BC@MIL-88B(Fe) and 930 mg/g for OTC), vastly exceeding those of traditional adsorbents. Removal rates exceeded 90% for TC and 80% for OTC in real waters. The process tolerated Na^+, SO_4^{2-}, and HA, but was inhibited by Ca^{2+} and PO_4^{3-}. Dynamic adsorption experiments treated 1,500–2,400 mL of water with > 93% removal at flow rates of 2.5–5 mL/min; removal efficiency dropped by 35–40% after eight cycles. The treatment also reduced the ecotoxicity of antibiotics.[41]

The Cu–Co bimetallic MOF (Cu-MOF@Co-MOF) was effective for low-concentration TC and doxycycline (DOX) in lake and tap water, achieving > 80% adsorption within 5–15 minutes and high capacities of 434.78 mg/g (TC) and 476.19 mg/g (DOX). It performed well over a wide pH range (2.0–11.0), retaining ≥420 mg/g capacity even at pH 2.0 and 11.0. High salinity (10 mol/L NaCl or KCl) reduced the capacity by 20.0–48.9%.[71] The adsorption mechanism is shown in Figure 5. The multiple phenolic hydroxyl, carbonyl, and amino groups and abundant conjugated benzene rings of TCs, together with the unique properties of MOFs, promoted a synergistic effect of hydrogen bonding, π–π interaction, coordination, electrostatic interaction, and pore filling, thereby enhancing the adsorption between TCs and Cu-MOF@Co-MOF.

Co@BC-500 was applied to industrial and domestic wastewater containing pathogens and organic pollutants. It enabled simultaneous pollutant degradation and disinfection via persulfate activation, with low metal leaching, showcasing an integrated "degradation-disinfection" precision remediation strategy in complex matrices.[72]

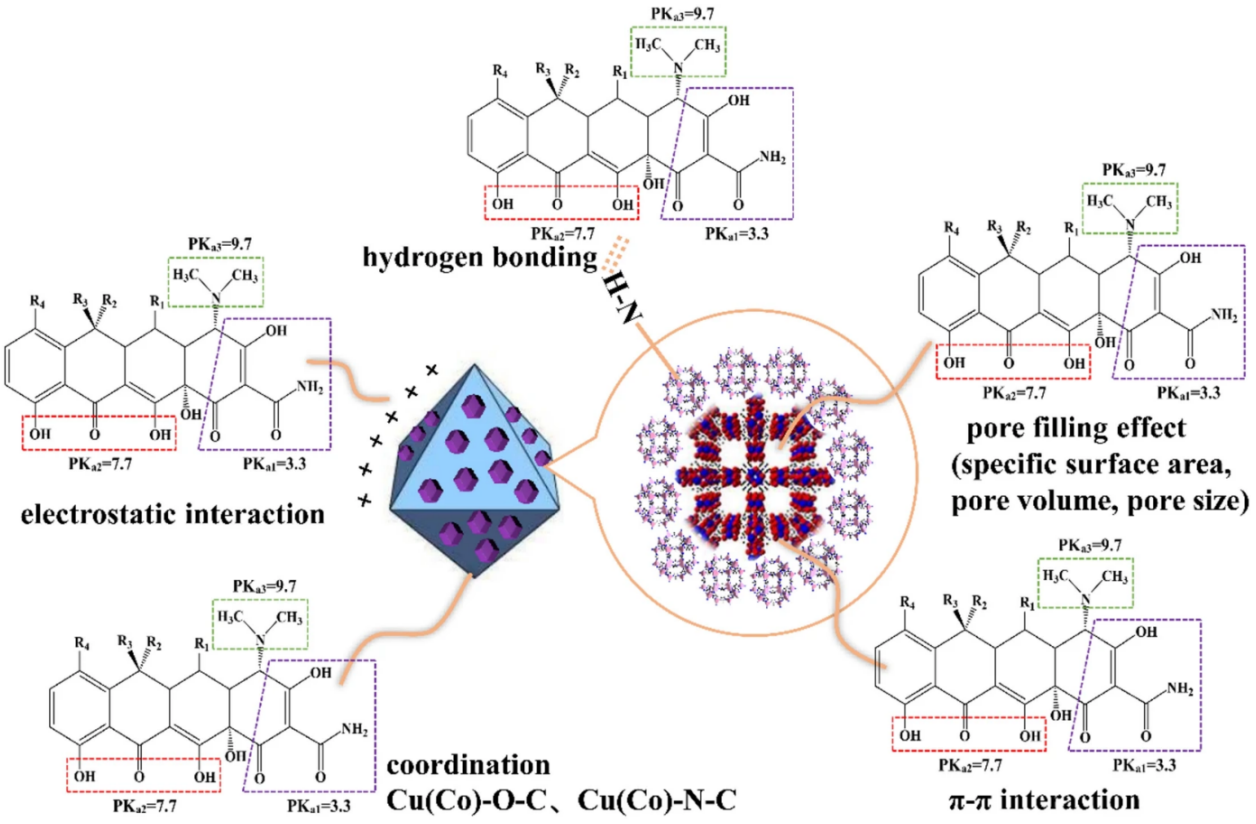


Figure 5. The adsorption mechanism of tetracyclines on Cu-MOF@Co-MOF[71]
Abbreviation: MOF: Metal-organic framework.

4.5.2. Common advantages and core limitations

The MOF composites demonstrate significant precision remediation advantages in real waters. For instance, incorporating supports such as BC or gelatin aerogels enhances tolerance to humic acid (HA) and low-valency ions (e.g., BC@CoFe tolerates SO_4^{2-}/NO_3^-/HA; BCM/GA_{200} tolerates Na^+/SO_4^{2-}/HA), enabling precise pollutant targeting.[33,41] Several materials integrate adsorption, catalysis, and separation (e.g., BC@CoFe, Co@BC) for "multi-pollutant synergistic removal".[33,65] Supports also reduce the risk of metal leaching and environmental impact (e.g., BC@CoFe, BCM/GA_{200}).[33,41] Core limitations include significant interference from specific ions (e.g., CO_3^{2-}/HCO_3^- inhibiting degradation; Ca^{2+}/PO_4^{3-} inhibiting adsorption), limiting application in high-hardness/alkalinity waters.[33,41] Regeneration and long-term stability remain concerns (e.g., BCM/GA_{200} loses 35–40% capacity after eight cycles).[41] Furthermore, inconsistent experimental conditions (initial pollutant conc.: 10–450 mg/L; material dose: 0.5–100 mg/L; time: 5 min–12 h) hinder direct performance comparisons across studies.[33,71]

5. Challenges, limitations, and future prospects

5.1. Current challenges

5.1.1. Challenges at the material level

The large-scale application of MOF/BDC composites faces dual constraints of green synthesis and cost control. The commonly used synthetic methods at present, such as the solvothermal method and *in situ* growth method, usually require high-purity metal salts, organic ligands, and a large amount of organic solvents, and the reaction conditions are rather harsh, such as high temperature and high pressure[73], which leads to high production costs and makes it difficult to meet the demands of industrial mass production. Composite materials still have significant

deficiencies in structural stability and batch consistency. The MOF component is prone to hydrolysis, metal leaching, or collapse of its crystal structure in actual water bodies with acidic, high-salt, or complex matrices.[73] However, due to differences in precursor sources and pretreatment processes, the pore structure and surface functional group distribution of BDCs are often non-uniform, which, in turn, affects the reproducibility of key properties, such as adsorption capacity and selectivity, of composite materials. The interfacial bonding strength between MOF and carbon carriers is usually insufficient[72], and peeling is prone to occur under dynamic water flow or during regeneration cycles, thereby shortening the material's service life.

5.1.2. Challenges at the mechanism level

In the complex environment of real water bodies, the precise mechanism by which composite materials remove target pollutants remains unclear. When multiple pollutants, such as heavy metals, inorganic anions, and natural organic substances, coexist, they compete for the adsorption sites of the material[74,75] and may exhibit synergistic or antagonistic effects, thereby reducing the selectivity of the composite material for specific targets. Most existing studies are based on a single-pollutant system and lack *in situ* dynamic characterization and theoretical analysis of the competition mechanism among multiple pollutants. The interfacial synergies between MOFs and BDCs at the microscopic level—such as interfacial electron transfer and confined catalysis—remain poorly understood. Current research mostly focuses on macroscopic property characterization. It does not sufficiently reveal microscopic processes. These processes include interfacial charge distribution, bonding modes, and the evolution of reaction intermediates. Therefore, it limits the directional design and optimization of material properties. In practical applications, the operating systems are complex, such as dynamic flow systems and photoelectric coupling systems. The mass transfer of pollutants and surface reactions are coupled. This makes the removal mechanism more complicated. The influence of mass transfer resistance on the total removal efficiency still needs systematic research to clarify and quantify. This is especially true for reaction kinetic bottlenecks that form under different operating conditions.[76]

5.1.3. Challenges at the application level

The recyclability of materials and their long-term operational stability are key challenges that limit the engineering-scale application of these materials. Some composite materials can be recycled by acid washing, thermal regeneration, and other methods. However, after multiple regeneration cycles, the materials often exhibit problems such as loss of active sites[71] and pore blockage. Therefore, their adsorption capacity will decrease significantly.[9] The regeneration process itself may consume large amounts of energy or chemical reagents, thus posing the risk of secondary pollution. Most existing research only remains at the laboratory-scale static batch experiment stage. It lacks long-term performance data from continuous operation in actual water bodies.[75,77] Optimization research on key engineering parameters is also insufficient, including system pressure drop, treatment flux, and operational energy consumption. The environmental safety assessment system for waste composite materials is incomplete. Systematic risk assessment and research on harmless treatment technologies are still needed. These aspects include the potential leaching risk of metal ions from MOFs, the biodegradability of carbon-based materials, and their long-term ecological impacts.[72]

5.1.4. Environmental safety assessment and end-of-life management of spent composites

Beyond green synthesis considerations, a systematic evaluation of the long-term environmental safety of MOF/BDC composites is urgently needed, encompassing three interconnected aspects: metal ion leaching, the biodegradability of the BDC carrier, and disposal strategies for spent materials.

Metal ion leaching and ecotoxicity. Although several studies have reported low metal leaching under optimized conditions (e.g., Cu leaching < 0.041 mg/L after four cycles[27]; Fe and Co leaching reduced by 6.5–8.0 times compared to unsupported MOFs[33]; Co dissolution < 4 ppm[61]), these data are mostly obtained from short-term batch experiments in idealized water matrices. Under real-world conditions—especially prolonged operation, extreme pH (e.g., pH < 3 or >11), or high salinity—the coordination bonds in MOFs may hydrolyze, releasing metal ions (e.g., Co^{2+}, Cu^{2+}, Fe^{3+}, Zr^{4+}) into treated water. The ecotoxicity of these leached metals, particularly their synergistic effects with residual organic pollutants, remains largely uncharacterized. Current risk assessments rarely consider chronic exposure or transformations in metal species (e.g., oxidation states, complexation with natural organic matter). Standardized leaching protocols (e.g., Environmental Protection Agency Method 1311 [Toxicity Characteristic Leaching Procedure]) and bioassays (e.g., Vibrio fischeri luminescence inhibition, Daphnia magna acute toxicity) should be incorporated into routine material evaluation.

Environmental fate of the BDC carrier. BDCs are usually viewed as harmless and biodegradable. However, we do not know much about their real persistence in natural waters.

Graphitized domains form during high-temperature pyrolysis, especially above 700 °C. These domains are chemically stable and can resist microbial degradation for a long time, so they may build up in sediments. Moreover, surface functional groups on BDCs can interact with metal ions or organic contaminants. Therefore, they may change the mobility and bioavailability of these substances. Long-term incubation studies under simulated environmental conditions (e.g., river water, groundwater, and seawater) are needed. These studies can measure the degradation half-life of different BDC types and identify any toxic by-products produced during oxidative aging, such as polycyclic aromatic hydrocarbons and quinones.

Treatment and cost-effectiveness of spent composites. After their service life, exhausted MOF/BDC composites must be safely disposed of or regenerated. Current regeneration methods (acid washing, thermal treatment, solvent rinsing) often suffer from performance decline (e.g., 35–40% capacity loss after eight cycles[41]) and the generation of secondary waste. Landfilling of spent composites risks long-term metal leaching, while incineration may release toxic metal fumes. Promising strategies include: (i) recycling of metal ions via acid digestion followed by re-synthesis of fresh MOFs; (ii) conversion into value-added products (e.g., using spent composites as precursors for magnetic carbon catalysts or electrode materials); (iii) bioremediation-assisted disposal where the BDC fraction is composted after metal recovery. However, the economic feasibility of these approaches has not been systematically evaluated. Life cycle assessment (LCA) should be applied to compare the environmental and economic trade-offs among different end-of-life scenarios. Without such assessments, the "green" label of MOF/BDC composites remains incomplete.

5.1.5. Engineering bottlenecks in practical application

Beyond material-level challenges, several engineering obstacles hinder the scale-up and real-world deployment of MOF/BDC composites:

For scaling up synthesis methods, most reported syntheses (solvothermal, *in situ* growth, microwave-assisted) are performed at gram-to-milligram scales. Key obstacles include: (i) high cost of raw materials—high-purity metal salts (e.g., $ZrCl_4$, $Co(NO_3)_2$) and organic ligands (e.g., terephthalic acid, imidazoles) account for >70% of production cost; (ii) low space–time yield—batch autoclave reactors have limited throughput and long crystallization times (hours to days); (iii) solvent and waste management—large volumes of organic solvents (N, N-dimethylformamide, N, N-diethylformamide) and post-synthesis activation steps generate hazardous waste, increasing environmental burden and cost. Potential solutions include continuous flow synthesis (e.g., microreactors), mechanochemical methods (solvent-free), and the use of cheaper, biomass-derived ligands, but these remain at early stages for MOF/BDC composites.

In powder handling in dynamic flow systems, most MOF/BDC composites are obtained as fine powders (nanometer- to micrometer-sized). When packed into fixed-bed columns or used in stirred reactors, they cause: (i) high pressure drop due to small particle size and irregular morphology, leading to excessive pumping energy; (ii) clogging and channeling—particle aggregation or swelling blocks flow paths, reducing effective contact; (iii) poor mechanical strength—weak interparticle bonding and fragility of MOF crystals cause attrition and fines generation under hydraulic shear; (iv) instability under long-term hydraulic shear—continuous flow erodes the composite surface, detaching MOF nanoparticles from the BDC support and leading to metal leaching and performance decay. To address these issues, strategies include:

- Granulation/shaping: Forming the composite into millimeter-sized beads, extrudates, or pellets using binders (e.g., alginate, chitosan, silica sol) without compromising porosity. For example, loading MOF/BDC into polymeric or ceramic foams has been shown to reduce pressure drop while maintaining accessibility.
- Aerogel or monolith fabrication: Preparing self-standing porous monoliths (e.g., MOF/BDC aerogels) that combine high permeability with structural integrity.
- Deposition on structured supports: Coating the composite onto honeycomb ceramics, metal meshes, or foam substrates, which provides low resistance to flow and easy replacement.
- Magnetic separation: Embedding magnetic nanoparticles (Fe_3O_4) allows recovery from slurry reactors without filtration, avoiding column packing issues.

Last but not least, membrane system issues also hinder the scale-up and real-world deployment of MOF/BDC composites, including: (i) Interfacial defects and fouling. In mixed-matrix membranes (MMMs), poor adhesion between MOF fillers and polymer matrices creates non-selective voids (interfacial defects), which reduce rejection efficiency. Mitigation strategies include:

- Surface functionalization of MOFs: Grafting $–NH_2$, –COOH, or –SH groups that can covalently bond with polymer chains (e.g., polyimide, PES) or hydrogen-bond with matrix.

- Using compatible polymers: e.g., Matrimid® or Polymer of Intrinsic Microporosity-1 that have similar polarity to the MOF.
- *In situ* crosslinking: Adding crosslinkers (e.g., diamines) that react with both MOF and polymer.
- Thin-film nanocomposite membranes: Depositing a thin selective layer of MOF/polymer on a porous support, minimizing defect probability.

(ii) Membrane fouling—caused by adsorption of organic matter (humic acid, proteins), inorganic scale, or biofilms—leads to flux decline and frequent cleaning. Strategies for fouling mitigation:

- Hydrophilization: Incorporating hydrophilic MOFs (e.g., UiO-66-NH_2, MIL-101(Cr)-SO_3H) or blending with PEG/PVP to reduce hydrophobic fouling.
- Antifouling coating: Grafting zwitterionic polymers or using photocatalytic MOFs (e.g., NH_2-MIL-125(Ti)) that degrade foulants under light.
- Surface patterning: Creating micro/nano-ripple structures to reduce foulant adhesion.
- Operational strategies: Backwashing, air scouring, and cross-flow velocity optimization.

Addressing these engineering bottlenecks requires close collaboration between materials chemists and process engineers. Future studies should report not only adsorption/degradation performance but also pressure drop, mechanical strength (e.g., crush test), and long-term stability under realistic hydraulic conditions (e.g., >100 h continuous operation).

5.2. Future prospects

5.2.1. Directional development of fusion calculation and experiment

Machine learning (ML) is reshaping material discovery from trialanderror to datadriven design. For MOF/BDC composites, ML offers three nearterm opportunities. First, performance prediction and highthroughput screening. Using existing MOF databases (e.g., CoREMOFs), ML models can rapidly predict adsorption capacity or degradation efficiency, screening thousands of candidates in silico. For example, gradient boosting regression has been successfully applied to predict the adsorption capacity of organic pollutants (e.g., tetracycline) on BC based on biomass composition and pyrolysis conditions.[78] Second, inverse design and synthesis optimization. Generative ML can directly propose composite structures with target removal rates, while random forest models can optimize pyrolysis conditions (temperature, precursor ratio) to maximize yield and surface area. Third, interpretable ML for mechanistic insight. Shapley additive explanation analysis reveals how features such as pH or pore size govern performance, providing design rules rather than blackbox predictions. Future work should build an openaccess database for MOF/BDC composites and integrate ML with automated "selfdriving labs" to accelerate the development of precision remediation materials.

5.2.2. Intelligent response and multifunctional integration

Smart MOF/BDC composites with stimulus-responsive units enable on-demand adsorption/desorption, remote regulation of activity, and facile separation. For example, pH-responsive designs use protonatable groups (–COOH, –NH_2) or pH-labile MOFs (e.g., ZIF-8) to trigger capture/release by pH swings, enabling metal recovery without harsh eluents; Photo-responsive composites incorporate azobenzene or spiropyran; UV/Vis light switches pore polarity or binding affinity, allowing light-triggered desorption or "on/off" catalysis; Temperature-responsive systems often employ poly(N-isopropylacrylamide) coatings: above its lower critical solution temperature (~32 °C), the polymer collapses, blocking pores; heating alone can regenerate the adsorbent; Magnetic-responsive composites contain Fe_3O_4 or $CoFe_2O_4$ nanoparticles, they enable rapid magnetic separation within 1–2 min and produce localized heating under an alternating magnetic field. This heating speeds up reactions and avoids bulk heating. Combining multiple responses (e.g., pH + magnetic) allows orthogonal control. Future work should focus on stability in real water matrices, response kinetics, and scalable synthesis. Such smart materials have the potential to transform MOF/BDC composites from passive sorbents into "sense-and-act" remediation systems, although most of these concepts are still at a proof-of-concept stage and require validation under realistic operating conditions.

5.2.3. Modular integration and resource recycling

To promote the transformation of technology into practical application, it is necessary to strengthen research on engineering system integration. Modular units, including a fixed-bed reactor based on a composite material, a mixed-matrix membrane module, and a mobile electrocatalytic device, are designed, and operating parameters, such as flow rate and residence time, are optimized to achieve continuous processing with high efficiency and low energy consumption. Attention should be paid to the construction of a closed-loop system for "treatment and resource utilization." For instance, composite materials can selectively adsorb noble metals from wastewater for recovery. Similarly, organic pollutants can be catalytically converted into valuable small-molecule chemicals. Therefore, this method improves the economic and environmental benefits of the entire treatment process.

5.2.4. Sustainable development

From the perspective of the entire life cycle, from raw material acquisition to waste disposal, the green transformation of technology should be promoted. In selecting raw materials, agricultural straw, food processing waste, and other renewable biomass are preferred to reduce the carbon footprint. In the synthesis process, green preparation methods such as room temperature synthesis, mechanochemical synthesis, and aqueous phase synthesis are developed to reduce the use of organic solvents and energy consumption. During the use phase, the cyclic stability of the material is improved through structural optimization and interface strengthening, thereby prolonging its service life. In the waste stage, establishing a systematic LCA framework for MOF/BDC materials would provide a quantitative basis and decision support for their sustainable design and application.

6. Conclusion

As a highly promising multifunctional platform, MOF/BDC composites have successfully integrated the atomic-level designable pores and high-density active sites of MOFs with the three-dimensional conductive framework, mechanical stability, and environmental friendliness of BDCs through ingenious structural design and interface engineering. This material system has achieved a technological leap from "passive adsorption" to "active identification—directional transformation," efficiently identifying, directionally transforming, and deeply mineralizing heavy metal ions, organic pollutants, and emerging micro-pollutants in water bodies, providing an innovative solution for water pollution control. It is necessary to deeply integrate many disciplines to advance this field. For example, materials science provides methods for structural regulation. Environmental engineering guides practical applications. Computational chemistry supports predictive design. Our goal is to overcome key bottlenecks. These bottlenecks include large-scale preparation, long-term stability, and complex mechanism analysis. Water shortage and pollution are becoming more serious worldwide. This technology has important strategic value. It can protect global water security and help achieve the Sustainable Development Goals. The material follows the idea of "treating pollution with waste." Therefore, it aligns with the principles of the circular economy. Its integrated design also lowers energy use in the treatment process. Intelligent responses and ML-assisted design are advancing rapidly. This platform can perform better in precise water governance, resource recycling, and ecological restoration, and provide key support for building a sustainable water environment in the future.

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Conflict of interest

The authors declare they have no competing interests.

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