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Metal–Organic Frameworks and Coordination Polymers for Environmental Remediation: Design Strategies, Functionalization, and Industrial Applications

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Abstract

Rapid industrialization, urbanization, and population growth have significantly increased environmental pollution, leading to severe contamination of water, soil, and air by heavy metals, organic dyes, pharmaceuticals, pesticides, endocrine-disrupting compounds, volatile organic compounds (VOCs), and greenhouse gases. Conventional remediation technologies often suffer from limited efficiency, poor selectivity, high operational costs, and secondary waste generation. Metal–organic frameworks (MOFs) and coordination polymers (CPs) have emerged as highly promising porous materials owing to their exceptionally high surface area, tunable pore structures, controllable functionality, structural diversity, and excellent catalytic properties. Their modular architecture allows precise selection of metal nodes and organic linkers, enabling rational design for targeted pollutant adsorption, catalytic degradation, gas separation, sensing, and resource recovery. Recent advances in post-synthetic modification, nanocomposite fabrication, hybrid materials, and green synthesis have further expanded their environmental applications. This review summarizes the fundamental chemistry, design strategies, functionalization approaches, pollutant removal mechanisms, industrial applications, recent technological advances, current limitations, and future prospects of MOFs and coordination polymers in sustainable environmental remediation.

Keywords: *Metal–organic frameworks, Coordination polymers, Environmental remediation, Water purification, Wastewater treatment, Adsorption, Photocatalysis, Heavy metals, Green chemistry, Industrial applications.*

1. Introduction

Environmental pollution has become one of the most significant global challenges due to rapid industrial development, urban expansion, agricultural intensification, and increasing consumption of synthetic chemicals. Industrial wastewater, municipal effluents, mining activities, textile manufacturing, pharmaceutical production, petrochemical industries, and agricultural runoff continuously release hazardous pollutants into natural ecosystems. These contaminants include toxic heavy metals, synthetic dyes, antibiotics, pesticides, endocrine-disrupting chemicals, phenolic compounds, microplastics, persistent organic pollutants, and greenhouse gases that threaten ecosystem stability and human health through bioaccumulation and long-term environmental persistence. Conventional remediation technologies such as chemical precipitation, coagulation, activated carbon adsorption, membrane filtration, biological treatment, and ion exchange have contributed substantially to pollution control. However, these methods often exhibit limitations including low adsorption capacity, limited selectivity, membrane fouling, sludge generation, incomplete degradation of emerging contaminants, high energy requirements, and significant operational costs. Consequently, there is an urgent need for advanced materials capable of achieving efficient, selective, sustainable, and economically viable environmental remediation.

Metal–organic frameworks (MOFs) and coordination polymers (CPs) have emerged as revolutionary porous coordination materials that combine the advantages of inorganic chemistry, coordination chemistry, materials science, and nanotechnology. These crystalline materials consist of metal ions or metal clusters interconnected by multifunctional organic ligands, producing highly ordered three-dimensional networks with exceptionally high surface areas, tunable pore dimensions, adjustable functionality, and remarkable structural diversity. Their modular design enables precise control of pore size, hydrophilicity, catalytic activity, and chemical stability according to specific environmental applications.

Recent advances in coordination chemistry have facilitated the synthesis of numerous MOFs and CPs capable of removing heavy metals, degrading organic pollutants, capturing greenhouse gases, detecting environmental contaminants, catalyzing advanced oxidation processes, and recovering valuable resources from wastewater.

Furthermore, integration with nanotechnology, polymer science, magnetic materials, biochar, graphene oxide, and renewable biopolymers has substantially improved their mechanical strength, regeneration capability, and industrial applicability.

This review discusses the design principles, functionalization strategies, pollutant removal mechanisms, environmental applications, industrial implementation, recent technological developments, challenges, and future perspectives of MOFs and coordination polymers for sustainable environmental remediation.

2. Fundamentals of Metal–Organic Frameworks and Coordination Polymers

Metal–organic frameworks and coordination polymers belong to an important class of crystalline porous coordination materials synthesized through self-assembly between metal-containing building units and multidentate organic ligands. Although both materials are constructed through coordination bonds, MOFs generally possess highly ordered three-dimensional porous architectures with permanent porosity, whereas coordination polymers may exhibit one-dimensional, two-dimensional, or three-dimensional network structures depending on the coordination geometry and ligand connectivity.

The structural versatility of MOFs originates from the almost limitless combinations of metal ions and organic linkers. Transition metals such as zinc, copper, iron, cobalt, nickel, chromium, manganese, zirconium, titanium, cerium, and aluminum are commonly employed because of their variable oxidation states, coordination numbers, and chemical stability.

These metal centers serve as nodes that connect organic ligands through coordination bonds to generate extended porous networks. Organic ligands including terephthalic acid, trimesic acid, imidazole derivatives, bipyridine, porphyrins, Schiff bases, amino acids, and naturally derived polyphenols provide structural rigidity while introducing functional groups capable of interacting with environmental pollutants.

The exceptionally large surface areas of many MOFs, frequently exceeding 5,000–7,000 $m^2\ g^{-1}$, provide abundant adsorption sites for contaminant capture. Their highly ordered pore systems facilitate rapid diffusion of molecules, while adjustable pore dimensions allow selective adsorption based on molecular size, polarity, or chemical affinity. In addition, unsaturated metal coordination sites, functionalized organic linkers, and tunable electronic structures contribute to catalytic activity, ion exchange, redox reactions, and photocatalytic degradation of pollutants.

Coordination polymers generally exhibit lower porosity than MOFs but offer greater structural flexibility and synthetic simplicity. Depending on the metal-ligand combination, coordination polymers can function as efficient adsorbents, photocatalysts, sensors, ion exchangers, or antimicrobial materials. Their mechanical stability and ease of fabrication make them attractive for large-scale environmental applications.

The remarkable diversity of MOFs and CPs enables precise molecular engineering to address specific environmental challenges. Structural modification through ligand substitution, mixed-metal synthesis, defect engineering, pore functionalization, and composite formation has significantly expanded their performance in environmental remediation.

Table 1: Comparison Between Metal–Organic Frameworks and Coordination Polymers

Property	Metal–Organic Frameworks (MOFs)	Coordination Polymers (CPs)
Structural dimensionality	Primarily 3D	1D, 2D, or 3D
Surface area	Very high (>1000–7000 $m^2\ g^{-1}$)	Moderate
Permanent porosity	High	Variable
Crystallinity	Highly crystalline	Moderate to high
Catalytic activity	Excellent	Good
Adsorption capacity	Very high	Moderate to high
Industrial applicability	Rapidly expanding	Well established

3. Design Strategies for Environmental Remediation

The outstanding performance of MOFs and coordination polymers largely depends on rational design strategies that optimize structural properties for specific environmental applications. Modern coordination chemistry enables systematic manipulation of metal nodes, organic ligands, pore architecture, surface functionality, defect density, and composite formation to achieve highly selective and efficient pollutant removal.

Selection of appropriate metal ions represents the first critical design consideration. Zirconium-based MOFs exhibit exceptional hydrolytic stability suitable for aqueous environments, whereas iron- and titanium-based frameworks demonstrate excellent photocatalytic activity because of their favorable redox properties. Copper- and cobalt-based materials are particularly effective catalysts for advanced oxidation processes, while zinc-based frameworks provide excellent adsorption performance with relatively low toxicity.

Organic linker design provides another powerful strategy for controlling framework properties. Functional groups such as amino ($-NH_2$), hydroxyl (-OH), thiol (-SH), sulfonic acid ($-SO_3H$), phosphonate ($-PO_3H_2$), and carboxyl (-COOH) significantly enhance interactions with heavy metals, dyes, pharmaceuticals, and other environmental contaminants. Mixed-ligand strategies further expand structural diversity by introducing multiple functional groups within a single framework. Pore engineering enables optimization of adsorption selectivity through precise control of pore size, pore volume, and channel architecture. Microporous frameworks efficiently capture small gas molecules such as carbon dioxide and methane, whereas mesoporous materials accommodate larger pollutants including pharmaceutical molecules, synthetic dyes, proteins, and microplastics.

Hierarchical pore systems combining micro-, meso-, and macropores improve mass transfer and accelerate pollutant diffusion during remediation processes. Defect engineering has recently emerged as an important strategy for enhancing catalytic activity. Controlled introduction of missing linkers or missing metal clusters generates unsaturated coordination sites that improve adsorption capacity, catalytic efficiency, electron transfer, and photocatalytic performance. Simultaneously, hybridization with graphene oxide, carbon nanotubes, activated carbon, magnetic nanoparticles, cellulose, biochar, and biodegradable polymers significantly enhances mechanical strength, electrical conductivity, chemical stability, and recyclability. Green synthesis strategies further improve sustainability by employing aqueous solvents, renewable ligands, plant-derived compounds, amino acids, and environmentally benign reaction conditions. These approaches reduce hazardous waste generation while maintaining excellent structural and functional properties suitable for large-scale environmental applications.

Table 2: Major Design Strategies for MOFs and Coordination Polymers

Design Strategy	Purpose	Environmental Benefit
Metal selection	Catalytic optimization	Improved degradation efficiency
Ligand functionalization	Enhanced selectivity	Better pollutant adsorption
Pore engineering	Size-selective adsorption	Higher removal capacity
Defect engineering	Increased active sites	Enhanced catalysis
Nanocomposite formation	Improved stability	Better recyclability
Green synthesis	Sustainable production	Reduced environmental impact

4. Functionalization Strategies for Enhanced Environmental Performance

Functionalization has become one of the most effective approaches for improving the environmental performance of metal–organic frameworks (MOFs) and coordination polymers (CPs). Although many pristine frameworks exhibit excellent adsorption capacity and catalytic activity, their practical application is often limited by insufficient selectivity, poor hydrolytic stability, restricted visible-light absorption, and limited regeneration capability. Surface modification and structural functionalization overcome these limitations by introducing active chemical groups, secondary metal centers, nanoparticles, polymers, or carbon-based materials that enhance pollutant interactions and improve long-term operational stability.

Pre-synthetic functionalization involves incorporating functional organic ligands during framework synthesis. Ligands containing amino (-NH_2), hydroxyl (-OH), thiol (-SH), sulfonic acid (-SO_3H), phosphonate (-PO_3H_2), and carboxyl (-COOH) groups provide additional adsorption sites for heavy metals and organic pollutants. Amino-functionalized MOFs exhibit enhanced affinity toward carbon dioxide and acidic pollutants through hydrogen bonding and electrostatic interactions, while thiol-functionalized frameworks demonstrate exceptional selectivity for mercury, lead, cadmium, and arsenic owing to the strong affinity of sulfur atoms for soft metal ions.

Post-synthetic modification (PSM) has emerged as a versatile technique for introducing new functional groups into preformed frameworks without disrupting their crystal structure. Covalent attachment of organic molecules, metal ions, catalytic nanoparticles, enzymes, or photosensitizers significantly expands the range of environmental applications. Post-synthetic modification enables optimization of adsorption behavior, catalytic efficiency, hydrophilicity, pore accessibility, and chemical stability according to specific remediation requirements.

Hybrid composite formation represents another important functionalization strategy. MOFs and coordination polymers are increasingly combined with graphene oxide, reduced graphene oxide, carbon nanotubes, activated carbon, biochar, cellulose nanofibers, chitosan, silica nanoparticles, titanium dioxide, zinc oxide, magnetic iron oxide nanoparticles, and biodegradable polymers. These composites improve mechanical strength, thermal stability, electrical conductivity, photocatalytic efficiency, and ease of recovery after treatment. Magnetic composites are particularly advantageous because they can be rapidly separated from treated water using external magnetic fields, facilitating repeated reuse. Metal doping and mixed-metal framework synthesis further enhance catalytic activity by modifying electronic structures and introducing additional active sites. Bimetallic and trimetallic frameworks often exhibit superior photocatalytic degradation, redox activity, and adsorption performance compared with single-metal systems due to synergistic interactions between different metal centers. Recent advances in defect engineering have demonstrated that controlled creation of missing ligands or missing metal clusters generates coordinatively unsaturated active sites that substantially increase adsorption capacity, catalytic activity, and pollutant diffusion. These defect-rich frameworks have become promising candidates for advanced environmental remediation technologies.

Table 3: Functionalization Strategies for MOFs and Coordination Polymers

Functionalization Strategy	Modification	Improved Property	Environmental Application
Amino functionalization	–NH_2 groups	CO_2 adsorption	Carbon capture
Thiol functionalization	–SH groups	Heavy metal selectivity	Hg^{2+}, Pb^{2+} removal
Carboxyl functionalization	–COOH groups	Enhanced adsorption	Dye removal
Graphene oxide composite	Carbon hybrid	Electrical conductivity	Photocatalysis
Magnetic nanoparticle incorporation	Fe_3O_4	Easy recovery	Wastewater treatment
TiO_2 hybridization	Semiconductor coupling	Visible-light photocatalysis	Organic pollutant degradation
Defect engineering	Missing linkers	Increased active sites	Catalysis and adsorption

5. Applications in Water Purification and Wastewater Treatment

Water purification remains the most extensively investigated application of MOFs and coordination polymers because of their exceptional adsorption capacity, tunable porosity, and catalytic versatility. Industrial wastewater contains a complex mixture of heavy metals, dyes, pharmaceuticals, pesticides, phenolic compounds, endocrine-disrupting chemicals, personal care products, radionuclides, and pathogenic microorganisms that require advanced treatment technologies beyond conventional methods. Heavy metal removal represents one of the most successful applications of MOFs. Toxic metals including lead, cadmium, mercury, arsenic, chromium, uranium, copper, and nickel are effectively captured through coordination, ion exchange, electrostatic attraction, and surface complexation. Functional groups such as amino, thiol, phosphonate, and carboxyl moieties provide highly selective binding sites, enabling efficient removal even at trace concentrations. Zirconium-, iron-, and zinc-based MOFs have demonstrated particularly high adsorption capacities for multiple heavy metals owing to their excellent hydrolytic stability and abundant active sites. Synthetic dyes released from textile, leather, printing, cosmetic, and paper industries constitute another major environmental concern. MOFs remove dyes through a combination of adsorption, photocatalysis, and catalytic oxidation. Under visible or ultraviolet irradiation, semiconductor-modified frameworks generate electron-hole pairs that produce hydroxyl radicals and superoxide radicals capable of mineralizing dye molecules into carbon dioxide, water, and other environmentally benign products. Emerging contaminants such as pharmaceuticals, antibiotics, hormones, pesticides, and endocrine-disrupting compounds have become increasingly important because conventional wastewater treatment plants incompletely remove these persistent pollutants. Functionalized MOFs containing catalytic metal centers effectively degrade these compounds through photocatalysis, Fenton-like oxidation, persulfate activation, and electrochemical oxidation. Simultaneously, porous frameworks adsorb pharmaceutical molecules through hydrogen bonding, π–π interactions, and hydrophobic effects. Coordination polymers also contribute significantly to wastewater treatment owing to their structural flexibility, lower production costs, and facile synthesis. Many coordination polymers function as efficient adsorbents for heavy metals and dyes while exhibiting remarkable chemical stability under acidic and alkaline conditions. Incorporation into membrane systems further enhances pollutant rejection, reduces membrane fouling, and improves long-term operational performance. Integration with magnetic nanoparticles enables rapid separation and regeneration of spent adsorbents, while hybrid nanocomposites containing graphene oxide, activated carbon, or biochar exhibit synergistically improved adsorption capacity and photocatalytic efficiency. Consequently, MOFs and coordination polymers represent versatile multifunctional materials capable of simultaneously removing multiple pollutant classes from complex wastewater streams.

Table 4: Environmental Applications of MOFs and Coordination Polymers

Environmental Problem	Representative Material	Target Pollutants	Removal Mechanism
Heavy metal contamination	UiO-66, MIL-101	Pb^{2+}, Hg^{2+}, Cd^{2+}	Adsorption, coordination
Textile wastewater	ZIF-8, MIL-53	Organic dyes	Photocatalysis, adsorption
Pharmaceutical wastewater	NH_2-MIL-125	Antibiotics	Advanced oxidation
Agricultural runoff	Fe-MOFs	Pesticides	Catalytic degradation
Radioactive wastewater	Functionalized MOFs	U(VI), Cs^{+}	Selective adsorption
Municipal wastewater	Coordination polymers	Mixed pollutants	Adsorption and catalysis

6. Industrial Applications of MOFs and Coordination Polymers

The exceptional physicochemical properties of MOFs and coordination polymers have accelerated their transition from laboratory research to industrial applications. Water treatment industries are increasingly investigating MOF-based adsorption columns, catalytic reactors, membrane systems, and hybrid filtration technologies for the treatment of textile effluents, pharmaceutical wastewater, petrochemical waste, mining wastewater, and municipal sewage. In chemical manufacturing, MOFs function as heterogeneous catalysts for oxidation, hydrogenation, esterification, and carbon dioxide conversion while minimizing waste generation and improving reaction efficiency. Gas separation industries employ highly porous MOFs for selective capture of carbon dioxide, methane, hydrogen, sulfur dioxide, and volatile organic compounds. Carbon capture and storage technologies have particularly benefited from amino-functionalized frameworks exhibiting high CO_2 adsorption capacity and excellent regeneration characteristics. Petrochemical industries utilize MOFs for hydrocarbon separation, sulfur compound removal, and purification of industrial gases. Similarly, food processing and pharmaceutical industries employ coordination materials for purification, contaminant monitoring, and controlled release applications. Environmental sensing has also emerged as an important industrial application, with luminescent MOFs capable of detecting toxic metal ions, pesticides, explosives, antibiotics, and organic pollutants at extremely low concentrations. Pilot-scale demonstrations indicate that hybrid MOF membranes, magnetic nanocomposites, and structured adsorbent columns possess considerable potential for commercialization. However, continued optimization of production costs, mechanical stability, scalability, and regeneration efficiency remains essential for widespread industrial implementation.

7. Recent Advances in Metal–Organic Frameworks and Coordination Polymers for Environmental Remediation

The past decade has witnessed remarkable progress in the design and application of metal–organic frameworks (MOFs) and coordination polymers (CPs), driven by advances in coordination chemistry, nanotechnology, materials science, computational chemistry, and environmental engineering. Researchers are increasingly developing multifunctional coordination materials capable of simultaneously adsorbing, catalytically degrading, sensing, and recovering pollutants from complex environmental matrices. These next-generation materials exhibit improved chemical stability, enhanced photocatalytic efficiency, greater adsorption capacity, and excellent recyclability compared with earlier generations of coordination compounds. One of the most significant developments is the emergence of water-stable MOFs based on zirconium, titanium, aluminum, and chromium. Early MOFs frequently suffered from structural degradation in aqueous environments due to hydrolysis of metal–ligand bonds. However, highly stable frameworks such as UiO-series, MIL-series, PCN-series, and CAU-series now maintain excellent crystallinity and catalytic activity under acidic, neutral, and alkaline conditions, making them suitable for long-term wastewater treatment.

Nanotechnology has substantially expanded the environmental applications of MOFs and CPs through the fabrication of hybrid nanocomposites. Integration with graphene oxide, reduced graphene oxide, carbon nanotubes, activated carbon, biochar, silica nanoparticles, titanium dioxide, zinc oxide, cellulose nanofibers, and magnetic iron oxide nanoparticles enhances electron transport, increases active surface area, improves mechanical stability, and facilitates magnetic recovery after pollutant removal. These multifunctional composites often exhibit synergistic effects that significantly outperform individual components. Photocatalytic technology has experienced rapid advancement through the development of visible-light-responsive coordination materials capable of utilizing solar energy for pollutant degradation. Incorporation of photosensitizers, plasmonic nanoparticles, semiconductor heterojunctions, and mixed-metal catalytic centers has improved charge separation efficiency while reducing electron–hole recombination. Consequently, photocatalytic degradation rates for pharmaceuticals, pesticides, dyes, antibiotics, endocrine-disrupting chemicals, and volatile organic compounds have increased substantially, involves sustainable and green synthesis of coordination materials. Renewable organic ligands derived from lignin, cellulose, amino acids, plant polyphenols, tannins, chitosan, and other naturally occurring biomolecules are increasingly replacing petroleum-derived synthetic ligands. Environmentally benign solvents, microwave-assisted synthesis, mechanochemical synthesis, and solvent-free approaches further reduce energy consumption and hazardous waste generation while maintaining excellent structural and catalytic properties.

Recent innovations have also focused on multifunctional environmental systems integrating adsorption, photocatalysis, electrochemical oxidation, antimicrobial activity, and pollutant sensing within a single coordination material. Such integrated platforms provide efficient treatment of complex wastewater containing mixtures of heavy metals, pharmaceuticals, dyes, microorganisms, and persistent organic pollutants, thereby supporting sustainable water management strategies.

9. Conclusion

Metal–organic frameworks and coordination polymers have emerged as one of the most promising classes of porous coordination materials for sustainable environmental remediation. Their exceptionally high surface areas, tunable pore architectures, structural diversity, adjustable functionality, and excellent catalytic properties enable efficient removal of a broad range of environmental contaminants, including heavy metals, synthetic dyes, pharmaceuticals, pesticides, endocrine-disrupting compounds, radionuclides, volatile organic compounds, and greenhouse gases. Recent advances in coordination chemistry have significantly expanded the capabilities of these materials through rational design strategies, ligand functionalization, defect engineering, mixed-metal synthesis, nanocomposite fabrication, and post-synthetic modification. These innovations have improved adsorption capacity, catalytic efficiency, hydrolytic stability, photocatalytic performance, selectivity, and recyclability, making MOFs and coordination polymers increasingly suitable for practical water purification, wastewater treatment, gas separation, environmental sensing, and pollution control applications. The incorporation of graphene-based materials, biochar, magnetic nanoparticles, semiconductors, biodegradable polymers, and renewable bio-based ligands has further enhanced mechanical strength, environmental compatibility, and operational stability. Simultaneously, artificial intelligence, machine learning, computational chemistry, and high-throughput materials screening are accelerating the discovery of next-generation coordination materials with optimized environmental performance.

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