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ARTICLE

MOFs as Environmentally Friendly Photocatalysts for Organic Pollutants Degradation

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ABSTRACT

Metal–organic frameworks (MOFs) have gained significant attention as advanced photocatalysts for the degradation of organic pollutants due to their unique structural versatility, high surface area, tunable porosity, and customizable metal–ligand coordination. This review highlights the environmental challenges posed by persistent organic contaminants and the shortcomings of conventional treatment methods. It emphasizes photocatalysis as a sustainable alternative to the currently used methods. The principles of MOF-photocatalysis, including light absorption, charge separation, and the formation of reactive oxygen species, are discussed, along with factors affecting performance, such as pH, temperature, light source, and pollutant type. MOF classes, composites, and hybrids are also investigated as methods to increase photocatalytic performance, stability, and recyclability. There are case studies of the degradation of dyes, phenolics, pharmaceuticals, and pesticides. The aspects of environmental sustainability, such as environmentally friendly synthesis, non-toxic constituents, and life-cycle, are also discussed. Lastly, future research areas and present challenges are described, supporting the idea that MOFs have great potential as an efficient and environmentally friendly tool to fix the problem of water pollution.

Keywords: Metal–Organic Frameworks; Photocatalysis; Organic Pollutant Degradation; Environmental Sustainability; Water Treatment

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1. Introduction

1.1. Environmental Challenges Posed by Organic Pollutants

One of the current challenges facing the environment is the persistence, toxicity, and ubiquitous nature of organic pollutants in the natural environment, which have produced severe effects. The common sources of these contaminants, which include textile dyes, pesticides, pharmaceuticals, phenolic compounds, and solvents used in industries, are industrial runoff, agricultural runoff, petrochemical industries, and local sewage. Due to either the stable aromatic structure or the presence of a halogenated functional group, many of these compounds cannot be readily broken down by natural degradation processes. Consequently, they tend to concentrate in water bodies, sediments, and biota, resulting in long-term contamination. Their invasion of the waters causes an ecological imbalance that affects the primary producers, aquatic invertebrates, and fish populations, disturbing the entire food webs. Moreover, some of these pollutants are mutagenic, carcinogenic, or endocrine-disrupting, posing a potent threat to human health due to the consumption of contaminated drinking water and bioaccumulation in the food chain [1,2].

The problem of organic pollutants in the environment is further aggravated by the drawbacks of traditional wastewater treatment systems, which are quite inefficient in decomposing such recalcitrant compounds. As an illustration, biological treatment processes can partially decompose some organics, leading to the production of other harmful products. In addition, when these pollutants are constantly released, albeit in small quantities, a cumulative toxic effect may be experienced in the long run. The problem could be intensified by climate change and the growing water shortage, which decreases natural water availability, leading to higher pollutant concentrations and diminished natural dilution. To overcome these environmental problems, it is necessary to develop new, sustainable, and cost-effective remedial technologies that degrade a wide variety of organic pollutants into harmless end products, generating no secondary pollution. The problem of eradicating the dreadful condition of pathogens and viruses that plague our world today can therefore be alleviated by photocatalysis, especially with new forms of materials that hybridize with known photocatalysis, such as metal-organic frameworks [3–5].

1.2. Limitations of Conventional Treatment Technologies

Traditional wastewater treatment processes, such as adsorption, coagulation, flocculation, biological degradation, and chemical oxidation, are highly limited in treating persistent organic pollutants. Even though the adsorption methods are effective in extracting contaminants from water, they only shift the pollutants to another medium, thus forming secondary wastes that need further treatment or disposal. Biological oxidation is typically slow and inefficient with recalcitrant compounds that have complex aromatic or halogenated structures, and can require a lot of energy or generate dangerous by-products in chemical oxidation procedures. Most common systems also struggle to efficiently treat low-concentration pollutants in large water volumes, and their effectiveness may be limited by changes in pH, temperature, and the presence of co-contaminants. **Table 1** presents a summary of the shortcomings of traditional wastewater treatment technologies in relation to persistent organic pollutants. The limitations given above indicate the necessity of modern sustainable treatment technologies that can completely mineralize organic pollution without additional impacts on the environment [6].

Table 1. Limitations of conventional wastewater treatment technologies for persistent organic pollutants.

Treatment Technology	Main Mechanism	Key Limitations
Adsorption	Transfer of pollutants to adsorbent surface	Creates secondary waste; requires regeneration or disposal of adsorbent
Coagulation–Flocculation	Aggregation and sedimentation of suspended particles	Ineffective for dissolved organic pollutants; sludge generation
Biological Degradation	Microbial breakdown of contaminants	Slow process; poor efficiency for recalcitrant/halogenated compounds
Chemical Oxidation	Oxidative breakdown using chemical agents	High energy/chemical demand; possible hazardous by-products
Conventional Combined Systems	Multi-stage physical, chemical, and biological steps	Limited efficiency for low-concentration pollutants; sensitive to pH, temperature, and co-contaminants

1.3. Photocatalysis as a Sustainable Degradation Approach

It is an eco-friendly and viable method for degrading organic pollutants, reducing all harmful substances to inorganic salts, carbon dioxide, and water as final products. This is, in turn, based on light excitation of a photocatalyst, especially by solar light or visible light, in order to produce reactive oxygen species (ROS) that can degrade even the most recalcitrant and stable organic species. In contrast to traditional processes, the photocatalysis process not only splits or relocates pollutants but also oxidizes them through oxidation-reduction reactions, thereby eliminating the likelihood of secondary contamination. In addition, photocatalysis is energy efficient since it uses copious solar energy that can be renewed easily, therefore cutting the operational expenses and reliance on fossil-based electricity sources [7].

From an environmental standpoint, photocatalysis offers versatility and adaptability, as it can be integrated into existing water treatment systems or deployed in decentralized applications for rural and industrial wastewater treatment. Its ability to operate under mild conditions—ambient temperature and pressure—further enhances its sustainability profile, minimizing energy requirements and chemical usage. Advances in photocatalyst materials have expanded the applicability of the process, enabling activity under visible light and improving degradation efficiency for a wide range of pollutants, including dyes, pharmaceuticals, pesticides, and industrial chemicals. As research continues to refine catalyst design and improve charge separation efficiency, photocatalysis is poised to become a key technology in achieving sustainable, large-scale water purification in alignment with global environmental protection goals [8]. **Figure 1** summarizes the major advantages of photocatalysis.

Figure 1. Major advantages and efficiency of photocatalysis technologies for wastewater treatment [8].

1.4. Why MOFs? – Unique Properties and Advantages

Metal–organic frameworks (MOFs) possess a unique set of properties that make them particularly attractive for environmental photocatalysis. Structurally, MOFs are crystalline porous materials composed of metal ions or clusters coordinated to organic linkers, creating an extended, highly ordered network. This architecture results in exceptionally high surface areas—often exceeding 1000 m^2/g—and tunable pore sizes, which facilitate efficient adsorption of pollutants and provide abundant active sites for photocatalytic reactions. Furthermore, the modular nature of MOFs allows precise control over their composition and functionality by selecting appropriate metal centers and organic

linkers. This tunability enables the integration of light-absorbing chromophores, redox-active metals, and catalytic functional groups directly into the framework. Additionally, MOFs can be engineered to possess band gaps suitable for visible light absorption, thereby maximizing solar energy utilization in photocatalytic processes [9–11]. Research on MOF-based photocatalysis has demonstrated significant growth over time, as illustrated in **Figure 2**, highlighting the expanding scope and relevance of this field.

The advantages of MOFs over traditional photocatalysts stem from their multifunctionality and adaptability. Unlike conventional semiconductors such as TiO_2 or ZnO, MOFs can simultaneously act as adsorbents and photocatalysts, enhancing pollutant degradation by combining pre-concentration of contaminants with catalytic breakdown. Their design flexibility allows for the incorporation of multiple components—such as semiconductor nanoparticles, carbon-based materials, or plasmonic metals—within the porous framework to improve charge separation and extend light absorption. MOFs also offer structural diversity, which can be exploited to create composites tailored for specific pollutant types or environmental conditions. Importantly, certain MOFs can be synthesized from environmentally benign metals like iron, zirconium, or titanium, aligning with the principles of green chemistry. These advantages position MOFs as next-generation materials capable of overcoming many limitations faced by conventional photocatalysts in sustainable water treatment applications [12,13].

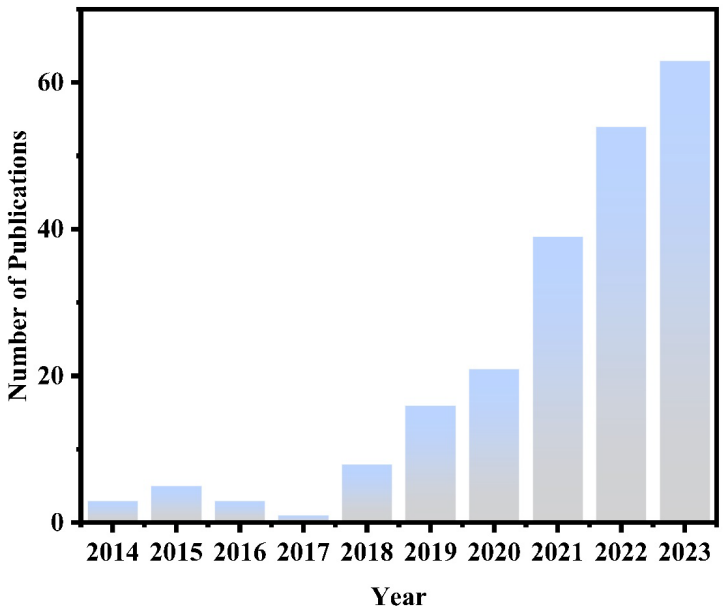

Figure 2. Number of articles published articles on MOFs based photocatalysis.
Source: The information is retrieved from scopus with a keyword "Photodegradation organic pollutants by MOFs" on 12 August 2023.

1.5. Scope and Objectives of the Review

This review aims to provide a comprehensive and critical overview of recent advancements in the use of metal–organic frameworks as environmentally friendly photocatalysts for the degradation of organic pollutants in water. It begins by outlining the fundamental principles of photocatalysis and the structural features of MOFs that make them suitable for such applications. The review then discusses various categories of MOF-based photocatalysts, including pristine MOFs, MOF composites, and hybrid systems, with emphasis on their mechanisms of action and performance against different classes of organic contaminants. Environmental sustainability aspects, including green synthesis routes, reusability, and potential ecological impacts, are also addressed. By consolidating current knowledge and identifying key research trends, the review seeks to highlight the potential of MOFs to meet global water treatment challenges, while outlining the limitations and future directions needed to advance their practical implementation [3].

2. Fundamentals of Photocatalysis for Organic Pollutant Degradation

2.1. Principles of Photocatalysis

Photocatalysis is a light-driven process in which a photocatalyst absorbs photons with energy equal to or greater than its band gap, promoting electrons from the valence band to the conduction band and leaving behind positively charged holes in the valence band. These photogenerated charge carriers migrate to the catalyst surface, where they participate in redox reactions: electrons typically reduce dissolved oxygen to form reactive oxygen species such as superoxide radicals ($O_2^{\bullet-}$), while holes oxidize water molecules or hydroxide ions to produce hydroxyl radicals (•OH). Both radicals are highly reactive and capable of breaking down complex organic molecules into smaller, less harmful intermediates, ultimately mineralizing them into carbon dioxide and water. The efficiency of the process depends on effective light absorption, rapid charge separation, and minimal recombination of electron–hole pairs, all of which are influenced by the structural and electronic properties of the photocatalyst [14].

2.2. Photocatalytic Degradation Mechanisms for Organic Pollutants

Photocatalytic degradation of organic pollutants generally proceeds through a series of interconnected mechanisms, each contributing to the overall mineralization of contaminants. The first step involves the adsorption of pollutant molecules onto the surface of the photocatalyst, which is facilitated by a high surface area and suitable surface chemistry. For example, in dye degradation, molecules such as methylene blue or rhodamine B can be adsorbed into the pores or onto active sites of the catalyst, bringing them into close contact with photogenerated reactive species. Effective adsorption not only concentrates the pollutants near the reaction sites but can also influence selectivity and reaction kinetics [15].

Once adsorbed, the photoexcitation process begins when the photocatalyst absorbs photons with energy equal to or exceeding its band gap. This excites electrons to the conduction band, leaving behind holes in the valence band. In Ti-based MOFs, for instance, Ti–O clusters act similarly to TiO_2, generating electron–hole pairs under UV or visible light. The charge separation and migration mechanism then becomes crucial—electrons move toward the surface to reduce oxygen molecules into superoxide radicals ($O_2^{\bullet-}$), while holes oxidize water or hydroxide ions to form hydroxyl radicals (•OH). In Fe-based MOFs, the Fe^{3+}/Fe^{2+} redox cycle can further facilitate electron transfer and radical generation.

The reactive oxygen species (ROS) attack is the next mechanism, where superoxide radicals, hydroxyl radicals, and other oxidizing species, such as singlet oxygen ($^1O_2$) or hydrogen peroxide (H_2O_2), directly react with pollutant molecules. For example, in the photocatalytic degradation of phenol, hydroxyl radicals attack the aromatic ring, leading to ring opening and formation of short-chain organic acids before complete mineralization. Equally, during the degradation of medicines, including tetracycline, ROS decomposes the medicine into small non-toxic molecules. Lastly, the mineralization process occurs, releasing organic pollutants in the form of CO_2, H_2O, and inorganic ions, seemingly without forming dangerous residues. Photocatalysis not only purifies, but also eliminates the possibility of secondary pollution, as the reaction also undergoes complete degradation of contaminants, which is guaranteed by this mechanism [16,17].

2.3. Key Performance Parameters

The efficiency of photocatalytic degradation is strongly influenced by several key performance parameters, each of which governs a critical stage in the process.

Band Gap Energy: The band gap is the amount of energy needed by the photons in order to excite the electrons between the valence and the conduction bands. A narrow energy-level band gap enables the absorption of visible light by the photocatalyst, which comprises most of the solar radiation, thus enhancing photocatalysis driven by sunlight. As an example, the visible light absorption in Ti-based MOFs can be tuned by changing the organic linkers or adding chromophore functionalities, enabling the degradation of pollutants under ambient sunlight without the need for UV light. However, an excessively small band gap may lead to enhanced electron-hole recombination, so a compromise must be made between charge stability and

the range of light absorption.

Surface Area and Porosity: A large surface area and extensively developed porosity contribute to increased adsorption of contaminants, keeping them near the catalytically active sites where ROS are produced. MOFs perform well in this regard, and surface areas of more than 1000 m^2/g are possible, which enables them to adsorb weights of dyes such as methylene blue or drugs such as ibuprofen prior to photocatalytic degradation. The volume of the pores and the ability to enlarge and reduce them further increase accessibility to larger organic molecules.

Charge Separation Efficiency: ROS generation is highly dependent on the lifetime of the photogenerated electron-hole pair. High recombination is reduced due to efficient charge separation, resulting in the production of more reactive species that can be degraded. To accelerate charge migration, MOFs may be designed to contain internal electron acceptors, conducting linkages, or heterojunctions. As an example, Zr-based MOFs and graphitic carbon nitride ($g\text{-}C_3N_4$) have higher electron transfer, leading to an increased degradation rate of pollutants such as bisphenol A.

Chemical and Structural Stability: The Photocatalyst cannot be disintegrated under long-term illumination, changing pH, or contact with pollutants. Aqueous applications are especially sensitive to stability issues, such as the hydrolysis of metal ions or the washing out of ions. Zr-based MOFs like UiO-66 are renowned for their outstanding hydrolytic stability, allowing them to be used thousands of times without a loss in performance.

Reusability and Regeneration: A photocatalyst ought to be recyclable and reusable with minimal reduction in its activity so that it can be practically used in water treatment. This minimizes operational costs and footprint. Other MOFs are relatively easily removed through either filtration or sedimentation of treated water and regenerated by simple washing or gentle heating/cooling, factors that qualify them to be used in continuous treatment systems [18–20].

2.4. Environmental Advantages Over Conventional Oxidation Processes

Photocatalysis has some environmental benefits over the traditional oxidation process; therefore, it will become the solution for sustainable water treatment. In contrast to other chemical oxidation techniques whose processes usually necessitate the use of huge quantities of oxidizing reagents such as chlorine, ozone, or permanganate, many of which form toxic sub-products, photocatalysis can be used to in situ generate reactive oxygen species with the use of non-toxic amounts of light energy, ideally in the form of sunlight. This eliminates the risk of secondary pollution and reduces chemical handling and disposal issues. Moreover, photocatalytic systems operate under mild conditions, typically at ambient temperature and pressure, which minimizes energy consumption compared to high-temperature or high-pressure oxidation methods. The process can achieve complete mineralization of organic pollutants into harmless end-products like CO_2 and H_2O, rather than producing partially oxidized intermediates that may still pose environmental hazards. Additionally, photocatalysis can be coupled with adsorption, filtration, or biological processes to create integrated treatment systems with enhanced efficiency and reduced environmental impact, making it a greener alternative to conventional oxidation-based approaches [21,22]. These advantages are summarized in **Table 2**.

Table 2. Environmental advantages of photocatalysis over conventional oxidation processes.

Advantage	Photocatalysis	Conventional Oxidation Processes
Chemical use	No need for external harmful oxidants; generates ROS in situ	Requires large amounts of chemicals (e.g., chlorine, ozone, permanganate)
By-product formation	Produces harmless end-products (CO_2, H_2O)	May produce toxic or hazardous by-products
Operating conditions	Mild (ambient temperature and pressure)	Often requires high temperature or pressure
Energy demand	Can utilize renewable sunlight; low overall energy use	Higher energy requirements for heating, pressurizing, or oxidant production
Secondary pollution	Minimal risk; no chemical disposal needed	Risk of secondary pollution from chemical residues
Process integration	Can be combined with adsorption, filtration, or biological treatment	Limited integration potential without additional complexity

3. Metal–Organic Frameworks (MOFs): Structure, Properties, and Classification

3.1. Overview of MOFs: Composition and Topology

Metal–organic frameworks (MOFs) are crystalline porous materials constructed from metal ions or clusters coordinated to organic linkers, forming extended three-dimensional networks. The metal nodes act as connectors, while the organic linkers serve as bridges, resulting in highly ordered structures with tunable pore sizes and exceptionally high surface areas. MOFs exhibit diverse topologies—such as cubic, hexagonal, or layered frameworks—depending on the choice of metal center, ligand geometry, and synthesis conditions. This structural versatility allows precise control over their physicochemical properties, enabling the design of MOFs with specific functionalities for targeted applications, including photocatalysis, gas storage, and pollutant removal [23].

3.2. Classification based on metals (e.g., Ti-, Zr-, Fe-based MOFs)

MOFs can be classified based on the type of metal ions or clusters used as their structural nodes, with the choice of metal significantly influencing their stability, electronic properties, and photocatalytic performance.

Ti-based MOFs are among the most studied for photocatalysis due to titanium's strong oxidative potential and ability to form Ti–O clusters, which behave similarly to TiO_2. For example, MIL-125(Ti) exhibits good photocatalytic activity under UV light and can be modified with linkers or dopants to extend its response into the visible spectrum for degrading dyes such as methylene blue. Zr-based MOFs, such as UiO-66 and its derivatives, are renowned for their exceptional chemical and hydrothermal stability, which makes them ideal for aqueous photocatalytic applications. Their tunable band gaps and the possibility of incorporating photosensitizers enable efficient degradation of pollutants like bisphenol A and pharmaceuticals under visible light.

Fe-based MOFs offer photocatalytic behaviors together with redox action due to the Fe 3plus /Fe 2plus cycle, which can promote an electron transfer to carry out Fenton-like reactions under visible light irradiation. As an example, the radical decomposition of organic dyes and antibiotics in MIL-53(Fe) and MIL-101(Fe) was achieved by forming reactive oxygen species more effectively. In addition to these, other metals destined to be included in MOFs include but are not limited to Al, Cu, or Co, which introduce new photocatalytic characteristics, further enhancing the prospect of such materials whenever employed in specific projects aiming to clean up the environment [24–26].

3.3. Tailorable Porosity, Surface Area, and Light Absorption

These include the highly designable porosity and surface area, making MOFs one of the most appealing materials. Porosity and surface area can be customized to an extreme level by using specific types of metal nodes, organic linkers, and synthesis parameters. Their pore sizes may vary from extremely narrow (microporous < 2 nm) to mesoporous (2–50 nm), allowing them to absorb a large number of organic pollutants, including both small molecules (aromatic molecules and aromatic growths) and bulky molecules (large-scale dyes). The extremely low surface areas—usually much more than 5000 m^2/g—not only contribute to the pre-concentration of pollutants in the vicinity of active sites but also increase access to active catalytic sites. Moreover, MOFs can be designed to enhance light absorption by adding photoactive metals and 2-conjugated linkers/chromophoric groups, allowing them to efficiently utilize both visible and UV light. As one example, the addition of porphyrin-based linkers may expand absorption into the visible region, which can accelerate solar-to-fuel photocatalytic dye and drug degradation. The combination of tunable porosity, high surface area, and optical properties makes MOFs uniquely advantageous over traditional photocatalysts in terms of their potential for water treatment [27,28].

3.4. Stability and Recyclability in Aqueous Environments

Two essential issues to consider for rationalizing the use of MOFs as photocatalysts in aqueous systems (e.g.,

exposure to water, changes in pH, and constant light irradiation) include stability and recyclability. Though certain MOFs, especially those with weak metal-ligand bonds, are susceptible to hydrolysis, others are extremely hydrolytically and thermally stable, especially those structured with strong metal-oxygen bonds of coordination compounds of Zr (like the UiO-66 MOF), Ti (such as the MIL-125 MOF), or Fe (in a few instances). Such sturdy MOFs could maintain their crystallinity and photocatalytic performance through numerous use cycles, making them ideal for long-term water treatment. Their solid-state nature also enhances recyclability by allowing easy separation from treated water through filtration, centrifugation, or magnetic recovery using magnetic nanoparticles. Such a combination of structural stability and reusability not only guarantees reasonable efficiency in degrading pollutants but also reduces the operating costs and waste produced in the environment, as well as corresponding with the principles of sustainable material design [26].

3.5. Comparison with Other Photocatalysts (TiO_2, g-C_3N_4, and ZnO)

MOFs have special advantages over traditional photocatalysts, such as TiO_2, g-C_3N_4, and ZnO, due to their adjustable framework and multifunctional characteristics. Though TiO_2 and ZnO are both recognised to have high oxidation-reduction potential and stability, their large band gaps minimise the absorption of visible light and therefore frequently need UV illumination. g-C_3N_4 can spread visible light more readily but has a small surface area and quick charge recombinative behavior, making it an inefficient light collector. Instead, MOFs have high surface areas and variable pore width, thus making them capable of performing adsorption and photocatalysis together, which locally concentrates the pollutants closer to the reactive areas and, therefore, accelerates their degradation. They will have band gaps that can be finely tuned by metal node selection, modification of organic linkers, or inclusion of photosensitizers, to enable efficient usage of visible light. MOFs may also be combined with conventional photocatalysts in hybrids with heterojunctions to enhance charge separation and extend the absorption range to a wider spectrum of light than many single-component systems. This leads to them surpassing many single components in the removal of a wide range of organic pollutants.

4. MOFs as Photocatalysts for Organic Pollutant Degradation

Various perturbations to structure, optical properties, and porosity have made MOFs an interesting and flexible type of organic pollutant-degrading photocatalyst. In **Figure 3**, some applications of MOF-based photocatalysts in photodegrading various pollutants are listed. Their highly structured platforms can be designed to accommodate photoactive metal centers or light-harvesting organic bridges to efficiently generate electron-hole pairs under UV/visible light. The exterior surface area leads to intense adsorption of pollutants, placing them in proximity to available active sites. Additionally, the bandgap can be adjusted to suit any specific energy demands of the photocatalytic reaction process. MOFs can degrade a wide range of contaminants, including dyes, pharmaceuticals, pesticides, and phenolic compounds, through oxidative pathways involving hydroxyl radicals and superoxide species. Moreover, their structural versatility enables the creation of composites and heterojunctions with other semiconductors, carbon materials, or plasmonic nanoparticles, further enhancing charge separation and light absorption. This adaptability positions MOFs as a promising next-generation platform for sustainable and efficient organic pollutant removal from water and air [2].

4.1. Direct Photocatalytic Activity of Pristine MOFs

Pristine MOFs, without any post-synthetic modification or composite formation, can exhibit significant photocatalytic activity owing to their intrinsic photoactive components. In such systems, the metal nodes—such as Ti^{4+}, Zr^{4+}, or Fe^{3+}—and conjugated organic linkers act synergistically to absorb light and generate electron–hole pairs that drive redox reactions for pollutant degradation. For example, Ti-based MOFs like MIL-125 and NH_2-MIL-125 can utilize both UV and visible light due to their tailored linkers, effectively degrading dyes and phenolic compounds. The ordered pore channels of pristine MOFs facilitate pollutant diffusion to the active sites, while their high surface areas ensure maximum contact between the catalyst and contaminants. Although pristine MOFs sometimes

suffer from limited conductivity and rapid charge recombination, their ability to integrate adsorption and photocatalysis in a single material makes them highly effective for organic pollutant removal, especially when the framework is optimized for both light harvesting and stability in aqueous environments [29].

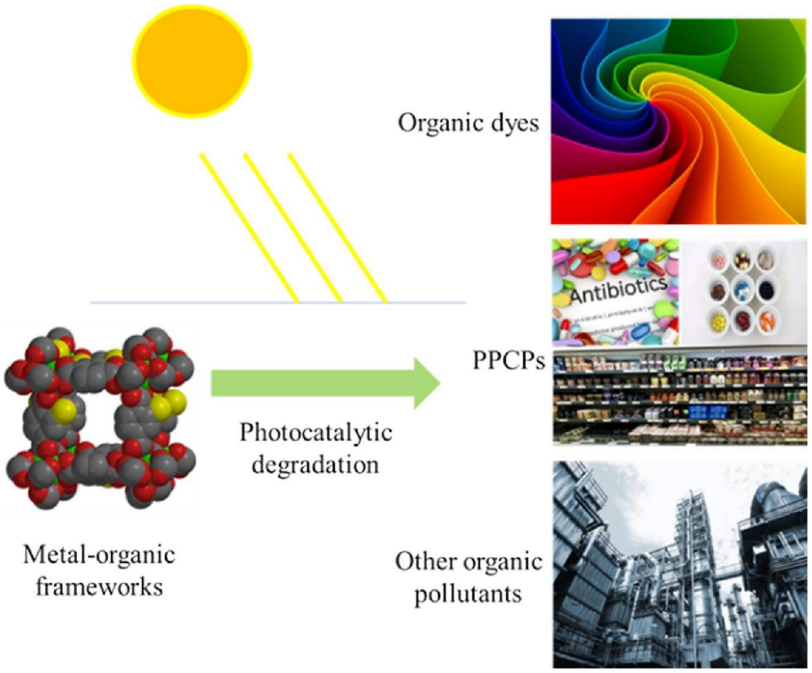

Figure 3. Application of MOFs-based photocatalyst for degradation of organic pollutants [2].

4.2. MOF Composites and Hybrids

Combining MOFs with other functional materials has emerged as an effective strategy to overcome the intrinsic limitations of pristine MOFs, such as low electrical conductivity and rapid charge recombination. These composites and hybrids integrate the structural tunability of MOFs with the complementary properties of semiconductors, carbon-based materials, or metal nanoparticles to enhance photocatalytic efficiency and stability.

4.2.1. MOF–Semiconductor Composites

MOF–semiconductor composites couple the tunable porosity and pollutant adsorption ability of MOFs with the superior light absorption and charge transport properties of inorganic semiconductors. For example, TiO_2/MOF composites such as TiO_2@NH_2-MIL-125 exhibit extended light absorption into the visible region and improved charge separation through heterojunction formation. The semiconductor component generates electron–hole pairs under light irradiation, while the MOF acts as a pollutant concentrator and electron mediator, enhancing reaction rates. This synergy not only increases degradation efficiency but also broadens the photocatalytic activity to different light spectra, making these composites highly effective for diverse organic pollutants [30,31].

4.2.2. MOF–Carbon-Based Composites (Graphene, CNTs, Biochar)

Incorporating carbon-based materials like graphene, carbon nanotubes (CNTs), or biochar into MOFs significantly improves photocatalytic performance by enhancing electrical conductivity and charge mobility. Graphene/MOF composites, for instance, facilitate rapid electron transfer from photoexcited MOFs, reducing recombination losses. CNTs provide 1D conductive pathways and mechanical strength, while biochar offers a sustainable, low-cost option with high surface area and adsorption capacity. These carbon frameworks also contribute to light absorption and pollutant pre-concentration, enabling more efficient degradation under visible light. The strong interfacial contact between the MOF and carbon phase ensures synergistic effects that outperform either component alone [32,33].

4.2.3. MOF–Metal Nanoparticle Hybrids

Embedding noble or transition metal nanoparticles (e.g., Au, Ag, Pt, Cu) into MOF structures introduces plasmonic or catalytic effects that enhance photocatalytic degradation. Plasmonic metals like Au and Ag can absorb visible light and generate hot electrons, which are injected into the MOF's conduction band to boost redox activity. Meanwhile, metals like Pt and Pd act as co-catalysts, trapping electrons and promoting the formation of reactive oxygen species. The MOF matrix not only stabilizes these nanoparticles but also ensures their uniform dispersion, maximizing the available active surface area. Such hybrids are particularly effective for rapid degradation of dyes, antibiotics, and persistent organic pollutants under solar or artificial light [34].

4.3. Role of Organic Linkers and Metal Nodes in Photocatalytic Efficiency

The photocatalytic efficiency of MOFs is strongly influenced by the nature of their organic linkers and metal nodes, which together define the material's electronic structure, light absorption capacity, and redox potential. The conjugated aromatic systems or functional groups ($-NH_2$, -OH) present in the organic linkers can extend light absorption to the visible range as well as provide charge transfer pathways, whereas Ti, Zr, or Fe metal nodes offer active sites on which redox processes and electron-hole pair generation processes occur. The maximisation of light harvesting, charge separation, and the overall degradation rate of organic pollutants can be achieved by optimising aspects of the coordination environment, functionalising the linkers, or selecting the metal [9].

4.4. Case Studies

Case studies examining the use of MOF-derived photocatalysts illustrate that the technology is versatile in degrading organic pollutants under environmentally friendly conditions. Their performance regarding the following types of pollutants is presented below, demonstrating their applicability as an effective solution to wastewater treatment in practice [10].

4.4.1. Dye Pollutants

MOFs have also been shown to be highly efficient in degrading synthetic dyes such as methylene blue (MB) and rhodamine B (RhB), which are common industrial wastewater pollutants in photocatalysis processes. For example, NH_2-MIL-125 (Ti) also degraded MB under visible light, as it retained an amino-functionalized linker that enhanced light absorption and charge separation. By the same token, MOFs based on Zr, such as UiO-66-NH_2, have shown high rates of RhB removal due to their stability in water and adsorption capacity. These MOFs have porous channels that allow rapid migration of dye molecules to the photocatalyst's active sites [35,36].

4.4.2. Phenolic Compounds

Phenolic Pollutants: Phenolic pollutants are mostly by-products of the petrochemical, pharmaceutical, and paper industries and are toxic and resistant to conventional degradation. Metal-organic frameworks based on Fe, such as MIL-53(Fe) and MIL-101(Fe), mineralize phenol and its analogs under visible light. They are metal-containing photoactive centers that form hydroxyl radicals, which can cleave aromatic rings. The large surface area and adjustable band gaps make these MOFs effective adsorbents for phenolic compounds and for breaking them down into safe end products such as CO_2 and water [37].

4.4.3. Pharmaceutical Contaminants

Pharmaceutical residues, such as antibiotics and analgesics, are also harmful to the environment due to bioaccumulation and persistence. Ti-based MMOFs like NH_2-MIL-125 (Ti) are, in fact, photocatalytically excellent for treating antibiotics such as tetracycline, taking advantage of their visible-light-responsive properties and structural stability. Zr-based MOFs combined with plasmonic nanoparticles have also shown enhanced degradation of anti-inflammatory drugs, such as diclofenac. These systems leverage both adsorption and advanced oxidation processes, ensuring effective mineralization and minimizing the formation of harmful intermediates [38].

4.4.4. Pesticides and Herbicides

Pesticides and herbicides, often persistent in agricultural runoff, are challenging to remove using traditional methods. MOF-based photocatalysts, such as MIL-125(Ti) and UiO-66-NH_2, have been successfully employed to degrade chlorpyrifos, atrazine, and other agrochemicals under sunlight. The porous structure aids in capturing pesticide molecules, while photo-generated reactive species break down their complex molecular structures into biodegradable forms. Incorporating visible-light-absorbing linkers or metal nanoparticles can further enhance their degradation rates, making MOFs a promising tool for sustainable management of agricultural wastewater [39].

5. Photocatalytic Mechanisms in MOFs

5.1. Light Absorption and Electron–Hole Generation

The photocatalytic activity of MOFs is based on fundamental processes such as light absorption and the generation of electron-hole pairs. Upon illumination with light of the appropriate energy, an adequate MOF in the energy range corresponding to a suitable band gap causes electrons in the valence band (highest occupied molecular orbital, HOMO) to get excited to the conduction band (lowest unoccupied molecular orbital, LUMO), leaving behind positively charged holes. The organic linkers tend to be light-harvesting units, with the metal nodes providing an efficient path for charge transfer and thus effectively separating photo-generated electron-hole pairs. This greatly helps avoid recombination and enables electrons and holes to reduce and oxidize bound pollutants. As an example, in NH_2-MIL-125(Ti) of amino-functionalized Ti-based MOFs, the NH_2 groups are found to increase the visible light absorption and favor the charge transfer process, leading to greater sensitivity in its function as a photocatalyst [40].

5.2. Charge Separation and Transfer Pathways

The directions by which separated charges in MOFs travel through the material are decisive to well-defined photocatalytic properties, namely, how efficiently the photogenerated electrons and holes will migrate to active sites without being recombined. The metal-organic nodes and ligand molecules in properly constructed MOFs result in well-defined conduction paths, with electrons generally moving along the metal clusters, and holes along the π-conjugated or π-conjugated linkers. Improved charge mobility can also be achieved through strategies such as adding electron-withdrawing or donating groups to linkers, forming heterojunctions with semiconductors, or adding conductive materials as additives, e.g., graphene. As an illustration, with Zr-based MOFs composite-g-C_3N_4, the directional transfer of electrons between g-C_3N_4 and the conduction band of MOFs is realized in a type-II heterojunction, where the direction of electron transfer and hole transfer is opposite so that the recombination is inhibited and the performance of degrading persistent organic pollutants is enhanced [40].

5.3. Reactive Oxygen Species (ROS) Generation and Their Role in Degradation

Reactive oxygen species (ROS) generation is a critical step in MOF-based photocatalysis, as these highly reactive intermediates are primarily responsible for breaking down organic pollutants. Upon light irradiation, photogenerated electrons in the conduction band can reduce dissolved oxygen (O_2) to form superoxide radicals ($\bullet O_2^-$), while holes in the valence band can oxidize water (H_2O) or hydroxide ions (OH^-) to produce hydroxyl radicals (•OH). These ROS, along with singlet oxygen ($^1O_2$) and hydrogen peroxide (H_2O_2), possess strong oxidative potential, enabling the cleavage of complex organic molecules into smaller, less toxic fragments, and ultimately mineralizing them into CO_2 and H_2O. For example, in Fe-based MOFs, the photo-Fenton-like mechanism accelerates ROS production, enhancing the degradation efficiency of dyes, pharmaceuticals, and pesticides even under visible light [41,42].

Representative ROS generation reactions:

$$MOF + h\nu \rightarrow e_{CB}^- + h_{VB}^+$$
$$e_{CB}^- + O_2 \rightarrow {}^{\bullet}O_2^-$$
$${}^{\bullet}O_2^- + 2H^+ + e^- \rightarrow H_2O_2$$
$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^-$$

$h_{VB}^{+} + H_2O \rightarrow {}^{\bullet}OH + H^{+}$

Organic pollutant + ROS → CO_2 + H_2O + mineral acids

Figure 4 can simply demonstr.ate the mechanism of photodegradation of dye over the UiO-66_GO composite catalyst.

5.4. Structure–Activity Relationship in MOFs for Photocatalysis

The structure–activity relationship in MOFs for photocatalysis highlights how their crystal architecture, metal node identity, and organic linker chemistry collectively determine light absorption, charge transport, and active site availability. The metal nodes act as catalytic centers and influence the electronic structure, thereby tuning the band gap to match the solar spectrum, while organic linkers can be modified to extend π-conjugation for enhanced visible-light harvesting. Pore size and topology govern the diffusion of pollutants and reactive species, ensuring effective contact between active sites and substrates. Furthermore, structural features such as mixed-metal frameworks, defect engineering, and heteroatom-doped linkers can promote charge separation and suppress recombination, directly boosting photocatalytic efficiency. This synergy between structural design and functional performance allows MOFs to be tailored for targeted degradation of diverse organic pollutants under sustainable conditions [9].

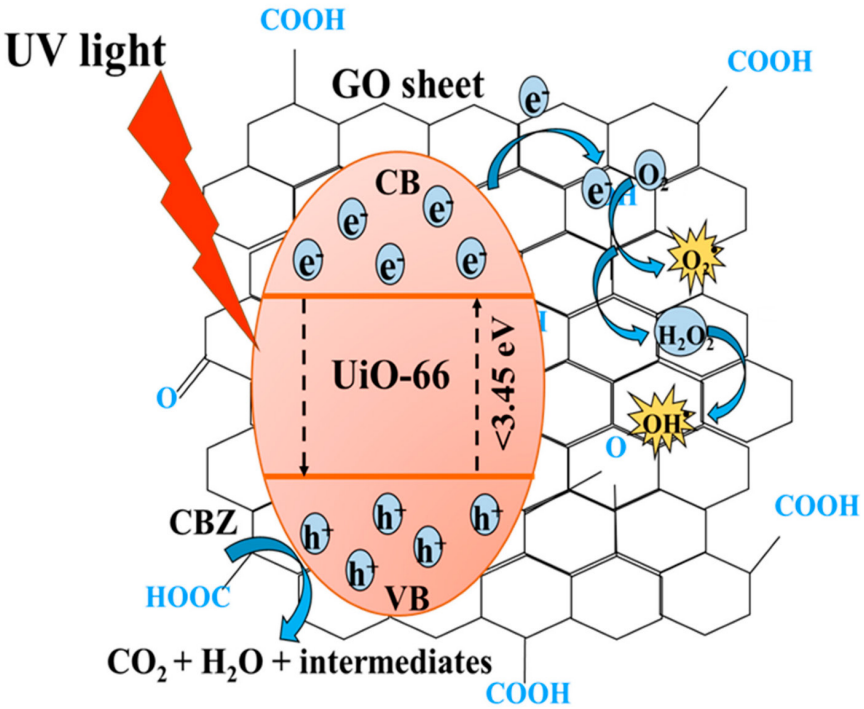

Figure 4. Schematic diagram of the proposed mechanism for the enhanced photocatalytic oxidation over the UiO-66_GO composite catalyst [42].

5.5. Factors Influencing Performance (pH, Temperature, Light Source, Pollutant Type)

Several environmental and operational factors influence the photocatalytic performance of MOFs.

- **pH** affects both the surface charge of the catalyst and the ionization state of pollutants, which can alter adsorption and ROS generation efficiency.
- **Temperature** can accelerate reaction kinetics but may also destabilize certain MOF structures if too high.
- **Light source** type, intensity, and wavelength determine the excitation efficiency, with visible-light-responsive MOFs benefiting from solar or LED sources matching their band gaps.

- **Pollutant type**—including molecular structure, solubility, and chemical stability—affects degradation rates, as some compounds are more resistant to ROS attack or require specific active sites for breakdown [43].

6. Environmental Sustainability and Life-Cycle Aspects

MOFs as photocatalysts offer significant environmental sustainability benefits, not only through their ability to degrade hazardous organic pollutants under mild conditions but also by enabling solar-driven processes that minimize energy consumption. Their high reusability and stability in aqueous environments reduce the need for frequent material replacement, lowering operational costs and resource usage. From a life-cycle perspective, the environmental impact of MOFs depends on factors such as the sustainability of raw materials, the efficiency of synthesis methods, and the recyclability of spent catalysts. Advances in green synthesis—using renewable feedstocks, water-based solvents, and energy-efficient methods—are helping to reduce the carbon footprint of MOF production. When integrated into wastewater treatment systems, MOFs can replace or complement conventional oxidation technologies, contributing to circular water management and reduced chemical waste generation [44].

6.1. Green Synthesis Routes for MOFs

MOF production via green synthesis strategies focuses on reducing environmental burden by substituting toxic reagents and energy-intensive chemical reactions with ecologically safe alternatives. These procedures frequently do not use toxic organic solvents but rather use water or bio-based solvents, renewable feedstocks, and are carried out at ambient conditions of temperature and pressure, therefore, lowering energy requirements. Methods such as mechanochemical, microwave-assisted, and ultrasound-assisted synthesis also reduce reaction time and increase yield while avoiding the production of toxic byproducts. In other cases, the organic natural linkers are derived from biomass or extracted from plants, making the material more sustainable overall. The environmental safety of MOF production is achieved through the application of green technologies, therebythereby providing a basis for the feasibility of a large-scale, mass- and economically viable orientation applicable in practice for the use of photocatalysis [45].

6.2. Avoiding Toxic Metals and Organic Linkers

Avoiding toxic metals and organic linkers in MOF design is essential to ensure their safe use in environmental applications, particularly in water treatment, where leaching risks can pose secondary pollution hazards. By selecting biocompatible and non-toxic metals such as iron, zirconium, titanium, or magnesium, and using environmentally benign linkers derived from natural or food-grade sources, the potential for ecological and human health risks is significantly reduced. This approach not only improves the safety profile of MOFs during use but also facilitates their disposal or recycling at the end of their life cycle. Additionally, replacing hazardous ligands with sustainable alternatives maintains or even enhances photocatalytic performance while meeting green chemistry principles, making such MOFs more suitable for large-scale and long-term environmental remediation [46].

6.3. Recyclability and Reusability of MOF Photocatalysts

Recyclability and reusability are critical attributes for MOF-based photocatalysts to ensure their economic and environmental viability in large-scale pollutant degradation. An ideal MOF photocatalyst should retain its structural integrity, surface area, and photocatalytic efficiency over multiple operational cycles without significant leaching of metal ions or decomposition of organic linkers. High-quality coordination bonds and hydrolysis resistance have enabled the production of many stable MOFs, which, with Zr-based frameworks (e.g., UiO-66) as prime examples, have been shown to sustain reuse through multiple cycles. Their ease of use, even after simple recovery procedures such as filtration or centrifugation, also adds to their usefulness. Recyclable MOF photocatalysts minimize operational costs by allowing multiple rounds to be performed simultaneously without generating secondary waste, making them environmental-

ly friendly in line with the sustainable principles of environmental remediation [47].

6.4. Environmental Risks and Safe Disposal Considerations

Safe disposal and environmental risks associated with MOF photocatalysts should also be noted as important aspects to prevent unintended ecological effects upon reaching the end of their service life. Although many MOFs are designed to be stable, when kept for longer periods under environmental conditions, they can rupture, releasing metal ions or degradation products that can be potentially harmful to both terrestrial and aquatic life. As such, used MOFs must be archived diligently and discarded safely, or reused in an eco-friendly manner, such as thermodynamic activation to recover metals, chemical treatment to extract components, or reuse in other useful materials. Further, the use of low-toxicity metals (e.g., Fe, Zr, Ti) and biodegradable linkers during MOF design can also reduce any risk. Such advanced materials can become environmental sustainability factors, as their overall management, use, and end-of-life should be based on a life-cycle approach that does not generate secondary pollution issues [48].

6.5. Life-Cycle Assessment (LCA) Perspectives

The LCA perspective provides a holistic account of MOF photocatalysts, covering environmental impacts from raw-material extraction through synthesis, application, and end-of-life treatment. Such a strategy can be used to identify hotspots of energy use, greenhouse gas emissions, and waste production across the production and operation lines. For example, LCA can compare the environmental footprint of different synthesis methods, such as solvothermal versus green aqueous processes, highlighting trade-offs between performance and sustainability. Incorporating durability, recyclability, and safe disposal into the LCA framework ensures that MOF-based photocatalytic systems deliver net environmental benefits. Ultimately, LCA-guided design promotes the development of truly eco-friendly MOFs that address pollution challenges without shifting the burden to other parts of the environment.

7. Challenges and Future Directions

Despite significant progress in MOF-based photocatalysts for the degradation of organic pollutants, several challenges remain that must be addressed to enable practical, large-scale applications. Future research should focus on improving stability, enhancing activity under natural light, lowering costs, and enabling multifunctional capabilities for real-world water treatment systems.

7.1. Improving Stability Under Aqueous and UV/Visible Irradiation

Many MOFs suffer from hydrolytic instability and structural degradation when exposed to aqueous environments and prolonged UV/visible light irradiation. Enhancing their durability can be achieved through the selection of high-valence metal nodes (e.g., Zr^{4+}, Ti^{4+}), the use of hydrophobic linkers, surface passivation, or post-synthetic modifications to strengthen metal–ligand bonds. Stable MOFs such as UiO-66 and MIL-125 have demonstrated long-term photocatalytic performance without significant loss in crystallinity, indicating that rational design can overcome instability issues.

7.2. Enhancing Photocatalytic Activity Under Visible and Solar Light

To effectively utilize the abundant solar spectrum, MOFs must be engineered to absorb a broader range of visible wavelengths. This can be achieved through linker functionalization with chromophoric groups, incorporation of narrow-band-gap semiconductors, or metal doping to reduce band gaps. For example, amino-functionalized UiO-66-NH_2 exhibits strong visible-light absorption, enabling the efficient degradation of dyes such as rhodamine B under simulated sunlight.

7.3. Large-Scale Synthesis and Cost Reduction

The practical deployment of MOF photocatalysts requires scalable, low-cost production methods that maintain structural and functional integrity. Traditional solvothermal methods are often energy-intensive and solvent-heavy, prompting interest in green synthesis approaches such as mechanochemical, microwave-assisted, or aqueous-based

processes. Utilizing abundant, inexpensive precursors and minimizing solvent waste can further reduce costs, making MOF production more economically feasible for industrial applications.

7.4. Integration into Water Treatment Systems

For real-world pollutant remediation, MOFs must be effectively integrated into water treatment systems, such as fixed-bed reactors, membranes, or coated supports, to enable continuous operation and easy recovery. Immobilization strategies can prevent particle loss, enhance catalyst stability, and allow for modular designs that fit existing infrastructure. MOF-based coatings on ceramic or polymeric supports, for instance, have shown promise in coupling high photocatalytic efficiency with operational practicality [49,50].

7.5. Prospects for Multifunctional MOFs (Simultaneous Adsorption + Photocatalysis)

Multifunctional MOFs that combine strong adsorption with efficient photocatalysis can enable synergistic pollutant removal by concentrating contaminants near active sites prior to degradation. Designing such materials involves optimizing pore structures for selective adsorption while maintaining high surface activity for photocatalytic reactions. For example, Fe-based MOFs with tailored porosity have demonstrated simultaneous adsorption and photodegradation of dyes, achieving faster and more complete pollutant removal than single-function materials [3,4,47].

8. Conclusions

Metal–organic frameworks (MOFs) have emerged as highly versatile and tunable photocatalysts for the degradation of a wide range of water pollutants, offering distinct advantages over conventional oxidation processes due to their high surface area, adjustable porosity, and customizable metal–linker coordination. They can consume light, produce reactive oxygen species, and catalyze efficient charge separation to mineralize common wastewater pollutants, including dyes, phenolic compounds, pharmaceuticals, and pesticides. Fine-tuning of photocatalytic activity, stability, and visible-light utilization has also improved with advances in composite and hybrid MOF systems. Major decisions should be made to facilitate sustainable application by employing environmentally friendly strategies, such as green synthesis, avoidance of toxic reagents, and recyclability. Nevertheless, there are drawbacks when it comes to enhancing long-term stability, amplifying cost-efficient production, and incorporating MOFs into realistic water-cleaning arrangements. As innovations continue and more emphasis is placed on multi-use designs, MOFs have a good chance of becoming an adaptive and effective solution for massive-scale environmental remediation.

Author Contributions

All authors contributed equally to the conception, design, data collection, analysis, and writing of this study. All authors have read and agreed to the published version of the manuscript.

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The authors declare that there is no conflict of interest.

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