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Occurrence, ecotoxicological aspects, and removal of pharmaceutical contaminants Using MOF-Based composite materials: A review

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Abstract

Background: Pharmaceutical contamination of water resources from industries and domestic discharges poses a major global challenge due to its harmful effects on ecosystems and human health. Metal–organic frameworks (MOFs), a newly developed class of versatile porous materials, show great potential for photocatalytic pharmaceuticals removal. This review explores the occurrence and ecotoxicological impacts of pharmaceutical and discusses recent advances in its photocatalytic removal using advanced MOF-based composites.

Methods: A comprehensive review of peer-reviewed literature published before March 2025 was conducted using renowned bibliographic databases, including Web of Science and Scopus. Electronic databases were thoroughly searched using Medical Subject Headings (MeSH). The search included terms such as water, wastewater, water pollutants, ecotoxicology, pharmaceutical preparations, water purification, catalysis, photolysis, and metal–organic frameworks, along with their related synonyms.

Result: Recent research highlights the potential of MOF-based composites as highly effective catalysts for the photocatalytic degradation of pharmaceutical contaminants. The efficacy of this process, however, hinges on several critical factors, including the amount of catalyst used, the initial concentration of the pollutants, and the pH level of the medium. Fine-tuning these parameters is vital to optimizing performance and ensuring consistent, reliable results.

Conclusion: By efficiently decomposing pharmaceutical compounds when exposed to light, MOF-based composite materials play a crucial role in reducing their concentration within aquatic environments. MOFs serve as optimal platforms for developing a wide range of nanomaterials derived from their structures. In conclusion, their versatility and unique properties make them indispensable for advancing innovation across various scientific and technological domains.

Keywords: Water pollutants, Ecotoxicology, Pharmaceutical, Metal organic frameworks

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Introduction

Water contamination is a critical, pressing global challenge that has drawn significant attention from researchers worldwide. This has spurred extensive studies aimed at understanding the presence of pollutants, developing precise methods to measure their concentrations, and creating innovative techniques to efficiently eliminate these contaminants from diverse water systems (1–3). In this regard, the presence of pharmaceutical compounds, as a subclass of organic contaminants, in water bodies worldwide has become a significant concern (4). These compounds include hormones, antibiotics, and other compounds, all of which have the potential to cause severe health problems and environmental damage (5). For example, the release of hormones such as 17α-ethynylestradiol has been shown to have endocrine-disrupting effects, even at minute concentrations (6). In addition, antibiotics are widely used in human and animal healthcare, and can have both bactericidal and bacteriostatic effects on microbial populations (7). These can reduce microbial diversity and have detrimental effects on the ecological functioning of the environment (8). These chemicals are transported and released to the environment by a variety of sources, including manufacturing plants, wastewater treatment plants, hospitals, individual households, and more, resulting in degraded water quality (9). As a result, identifying the potential risks posed by pharmaceuticals in the environment is a global concern. Therefore, it is urgent to remove pharmaceutical compounds from water systems to decrease harm to people and lower environmental hazards.

Advanced oxidation processes (AOPs) are recognized as critical components of chemical purification techniques, with the potential to oxidize various pollutants (10,11) non-selectively. Photocatalysis, as one of the various AOPs, has attracted considerable scholarly attention for its proven ability to degrade a broad spectrum of organic compounds, coupled with its high efficiency and the potential to harness light energy as a renewable, free resource (12). Upon the absorption of light with energy equal to or exceeding the band gap energy, a semiconductor generates a hole (h^+) in the valence band (VB) and an electron (e^-) in the conduction band (CB). The generation of such charge carrier is imperative for initiating the photocatalytic reaction and significantly enhances photocatalytic performance (13). Throughout the pollutant degradation process, photo-induced charges may migrate to the semiconductor surface, enabling their participation in oxidation and reduction reactions (14).

Over the past two decades, metal–organic frameworks (MOFs) have attracted considerable attention in photocatalysis. This surge in attention can be attributed to their extensive surface area, meticulously organized porous structures, and the ability to tune their organic linkers and metal clusters, which collectively impart remarkable photophysical and chemical properties (15). These materials have spurred innovative applications across multiple domains, such as gas storage, separation, catalysis, and drug delivery (16). An interesting aspect is that MOFs can function as semiconductors and facilitate charge-carrier transport under specific conditions, especially when the organic linkers or metal clusters are photoactivated (17). MOFs offer several advantages over traditional semiconductors like TiO_2 and ZnO for the photodegradation of pharmaceuticals: MOFs often exhibit broader light-absorption spectra, including the visible range, whereas TiO_2 and ZnO primarily operate in the ultraviolet region (18). The extended absorption range leads to greater efficiency in capturing solar energy for photocatalytic purposes. Also, due to their porous nature and high surface area, MOFs provide more active sites for photocatalytic reactions. These result in improved pollutant adsorption and degradation rates compared to the typically lower surface area of TiO_2 and ZnO. To date, a range of different MOFs have been synthesized, including Materials Institute Lavoisier (MILs) (19), zeolitic imidazolate frameworks (ZIFs) (20), University of Oslo frameworks (UiOs) (21), Christian-Albrechts-University frameworks (CAU) (22), Dresden University of Technology frameworks (DUT) (23), porous coordination networks (PCNs) (24), Hong Kong University of Science and Technology frameworks (HKUST) (25), to name only a few. MOFs have been widely explored as potential materials for the photodegradation of pharmaceuticals due to their unique properties and capabilities (26,27). Using MOFs as photocatalysts reveals limitations similar to those of conventional photocatalysts (28). A significant concern is the insufficient absorption of visible light, which significantly reduces the effectiveness of MOFs in photocatalytic applications (29,30). Additionally, rapid carrier recombination poses another critical challenge, further diminishing the photocatalytic activity of these materials. Together, these factors highlight the need for advancements in MOF technology to enhance their photocatalytic performance. The use of conventional MOFs in photocatalysis is constrained by challenges that mirror those of traditional photocatalytic materials, including durability and light-harvesting capabilities. To address MOF drawbacks and improve performance, a variety of components, including metal oxides, metal sulfides, metal-free carbonaceous materials, noble metals, two-dimensional $Ti_3C_2T_x$ (MXene), perovskites, etc., were used. The aims of this study were as follows: (1) to conduct a review of the literature on the occurrence and ecotoxicological risk assessment of pharmaceuticals, (2) to provide current information on the application of MOF-based composite materials for the photodegradation of pharmaceuticals in aquatic media, and (3) to explore semiconductors derived from MOF materials to foster further improvements.

Materials and Methods

A comprehensive assessment of scholarly literature from peer-reviewed and indexed sources was conducted, focusing on publications published up to March 2025. This analysis relied heavily on reputable bibliographic databases, including Web of Science and Scopus. These online resources were thoroughly explored using Medical Subject Headings (MeSH). The search methodology incorporated terms such as water, wastewater, water pollutants, ecotoxicology, pharmaceutical, water purification, catalysis, photolysis, and metal–organic frameworks, along with related synonyms, to ensure an exhaustive review of relevant literature. The selection criteria specified that only literature published in English and featuring at least one keyword matching the core terms under review in their titles, abstracts or keywords were eligible for inclusion. Furthermore, the study considered only works that had undergone rigorous peer review and were published in peer-reviewed journals. literature published after March 2025, along with those written in languages other than English, were excluded to maintain relevance and consistency. This approach was designed to ensure a thorough and representative review of relevant studies. Subsequently, the data extracted from the selected literature were systematically categorized, synthesized, and integrated into the results and discussion sections of this analysis. The compiled and organized data were subsequently integrated into this study, contributing to the results and discussion sections, and were visually depicted through figures and tables for clarity and impact.

Results

Presence and ecological risk assessment of pharmaceuticals in the aqueous environment

While pharmaceuticals can treat illnesses, improper disposal and release into water bodies can result in serious environmental hazards and health risks (31). These compounds fall into many classes, including analgesics and anti-inflammatories, antibiotics, β-blockers, blood lipid regulators, contrast media, cytostatics, hormones, and psychiatric drugs (32). The presence of pharmaceuticals in wastewater from pharmaceutical manufacturers, municipal wastewater treatment plants (WWTPs), hospitals, and livestock farms has been reported in almost all regions of the world. Based on the collected data, Table 1 shows the presence of pharmaceutical compounds in water/wastewater samples.

Definitions of the analytical instrument abbreviations used in this table are as follows:

- **UPLC/TQD-MS:** Ultra-high-performance liquid chromatography coupled with tandem quadrupole mass spectrometry.
- **UPLC-Q Exactive Orbitrap-HRMS (HESI):** Ultra-performance liquid chromatography coupled with a Q-Exactive Plus Orbitrap high-resolution mass spectrometer equipped with heated electrospray ionization (HESI).
- **LC-MS/MS:** Liquid chromatography coupled with tandem mass spectrometry.
- **HPLC-MS/MS:** High-performance liquid chromatography coupled with tandem mass spectrometry.

On the other hand, the presence of pharmaceutical compounds in the environment has been linked to significant ecological disturbances. Therefore, the Risk Quotient (RQ) methodology has been employed in numerous studies worldwide to assess the risks posed by pharmaceutical residues to aquatic organisms. The RQ methodology has been extensively applied in a range of aqueous environments, including wastewater, groundwater, lake water, drinking water and so on. When RQ is less than 1, the environmental risk from pharmaceuticals is minimal; however, when RQ is equal to/or greater than 1, adverse effects on organisms are expected (40). Table 2 shows the ecological risk assessment of pharmaceutical compounds in different regions of the world.

Photocatalytic degradation of Pharmaceuticals by MOFs

MOFs are a group of porous crystalline materials that consist of metal ions or clusters and organic linkers. Compared to traditional semiconductor photocatalysts, MOFs exhibit structural flexibility and unique physicochemical properties, making them particularly effective for degrading organic pollutants. Furthermore, one of the most impressive features of MOFs as photocatalysts is their large surface area and porosity. When MOFs are irradiated with illumination (UV/Vis/natural sunlight) with energy equal to or greater than the MOF bandgap, the photogenerated electrons transfer from the VB to the CB, resulting in the formation of h^+in the VB (45–47).

Table 1. The occurrence of pharmaceutical compounds in water/wastewater samples.

Name	Sampling point	Country	Concentration (ng/L)	Analytical method	Ref.
Acetaminophen	River water	India	6.81–247	UPLC/TQD-MS	(33)
Acetaminophen	Surface water	Nigeria	1–12430	UPLC-Q Exactive Orbitrap-HRMS	(34)
Acetaminophen	Groundwater	Nigeria	< 0.5–349	UPLC-Q Exactive Orbitrap-HRMS	(34)
Acetaminophen	River water	India	6.81–247	UPLC/TQD-MS	(33)
Carbamazepine	WWTP effluent	New Zealand	595–793	LC-MS/MS	(35)
Ciprofloxacin	River water	China	ND–415	HPLC-MS/MS	(36)
Ciprofloxacin	Lake water	Uganda	2.0–41.0	LC-MS/MS	(37)
Ciprofloxacin	River water	China	ND–185.14	HPLC-MS/MS	(38)
Ciprofloxacin	River water	China	ND–35.68	HPLC-MS/MS	(39)
Diclofenac	WWTP effluent	New Zealand	152–561	LC-MS/MS	(35)
Norfloxacin	River water	China	ND–26.74	HPLC-MS/MS	(39)
Sulfamethoxazole	WWTP effluent	New Zealand	160-398	LC-MS/MS	(35)
Tetracycline	River water	China	ND–227	HPLC-MS/MS	(36)
Tetracycline	River water	India	1.25–98.6	UPLC/TQD-MS	(33)
Tetracycline	Lake water	Uganda	2.7–70.0	LC-MS/MS	(37)
Tetracycline	River water	China	ND–28.65	HPLC-MS/MS	(38)

Photogenerated holes can directly decompose pollutants and react with water and/or hydroxyl ions to produce hydroxyl radicals, a strong oxidizing species (48,49). Also, the photogenerated electrons may react with oxygen to form superoxide radicals (50). These oxidizing species can react with organic pollutants, degrading them into non-toxic or less toxic products such as carbon dioxide and water (51). A study conducted by Gao et al reported the synthesis of a Zeolite Imidazole Framework-8 (ZIF-8) for the photocatalytic degradation of oxytetracycline under visible light (52). According to experimental data, 90% of oxytetracycline can be degraded by ZIF-8 after 180 min when exposed to visible light, and the degradation rate reaches 69% after the fourth cycle. In a study by Wang et al (53), zirconium butoxide was used as a precursor for metal clusters. It successfully synthesized a novel UiO-66-based photocatalyst with different functional groups on the organic ligand, including UiO-66, UiO-66-NH_2, and UiO-66-$(OH)_2$. The findings revealed that the key role of the functional group-modified UiO-66-based photocatalyst is for acetaminophen degradation under simulated solar irradiation. It was determined that UiO-66-NH_2 displayed the best performance, with acetaminophen removal > 90% after 360 min of irradiation, exceeding the corresponding values for UiO-66 and UiO-66-(OH_2). On the other hand, numerous studies have investigated MOF-based composite materials for their potential to generate oxidizing species, which have been used to degrade antibiotics such as $BaTi_{0.85}Zr_{0.15}O_3$/MOF-5 (54), BiOBr/MIL-101(Cr) (55), and Bi_2S_3/MIL-53(Fe) (56). Table 3

Table 2. Ecological risk assessment of pharmaceuticals in aquatic environments in different regions of the world.

Country	Environment analyzed	Highlight	Ref.
Bangladesh	River	The levels of sulfamethoxazole, erythromycin-H_2O and tylosin in rivers were medium in terms of ecological risk.	(41)
Malaysia	Drinking water	There was no potential health risk from pharmaceuticals exposure for either adults or children.	(42)
Portuguese	Seawaters	Diclofenac poses a potential risk to aquatic organisms.	(43)
China	River	Ofloxacin showed RQ values above 1, indicating potential risk to aquatic organisms.	(44)

Table 3. Recent studies on the photodegradation of pharmaceuticals by MOFs- semiconductor composites and related materials.

Photocatalyst	Target	Light Source	Conditions	Optimal degradation efficiency	Ref.
CeO_2/MIL101(Fe)	Tetracycline	300 W Xe lamp (λ > 420 nm)	Volume solution: 100 mL Dosage: 0.3 g/L C_0: 20 mg/L Time: 120 min	83.5%	(57)
SnO_2/MOF-199	Metronidazole	75 W Hg lamp (λ ≈ 365.4 nm)	Volume solution: 20 mL Dosage: 2 g/L, C0: 40 mg/L, Time: 240 min	≈ 81%	(58)
DUT-5/Bi_2MoO_6	Tetracycline	300 W XL (λ ≥ 420 nm)	Volume solution: 100 mL Dosage: 0.1 g/L C_0: 20 mg/L Time: 60 min	84.2%	(59)
Bi_2MoO_6/NH_2-UiO-66	Oxytetracycline	350 W XL	Volume solution: 40 mL Dosage: 0.5 g/L C_0: 10 mg/L Time: 150 min	93.7 %	(60)
Bi_2WO_6/ZIF-8	Tetracycline	300 W mercury lamp	Volume solution: 100 mL Dosage: 0.2 g/L C_0: 20 mg/L Time: 80 min	97.8%	(61)
MOF-808/AgI	Tetracycline Hydrochloride	300 W XL	Volume solution: 100 mL Dosage: 0.2 g/L C_0: 20 mg/L Time: 80 min	93.65%	(62)
MIL-125(Ti)/GO	Tetracycline	250 W Xe lamp(-)	Volume solution: 100 mL Dosage: 0.1 g/L C_0: 20 mg/L Time: 90 min	90.1%	(63)
g-C_3N_4/NH_2-MIL-88B(Fe)	Ofloxacin	300 W Xe lamp (λ > 420 nm)	Volume solution: 50 mL Dosage: 0.25 g/L C_0 (OFL): 10 mg/L Time: 150 min	96.5%	(64)
g-C_3N_4 @MIL-101(Fe)	Oxytetracycline Hydrochloride	300 W Xe lamp (λ > 420 nm)	Volume solution: 40 mL Dosage: 0.5 g/L C_0 10 mg/L Time: 300 min	87.68	(65)

lists MOF-based composite materials used to degrade pharmaceutical pollutants.

Discussion

Occurrence and ecological risk assessment of pharmaceuticals in the aqueous environment

The data in Table 1 highlights the widespread occurrence of pharmaceuticals in water bodies, raising concerns about their ecological and health impacts. In addition, the presence of pharmaceuticals in aquatic environments has been reported in other parts of the world. For example, in Tunisia, antibiotics such as cefalexin and spiramycin were reported at concentrations ranging from 7.5 to 370 ng/L in WWTP effluent (66). Also, Younes et al reported high levels of sulfamethoxazole (1.72 µg/L), ciprofloxacin (0.31 µg/L), and azithromycin (0.25 µg/L) in municipal WWTP effluent in Beni-Suef, Egypt (67). Al-Maadheed et al detected the highest concentrations of metronidazole (5.46 µg/L) and ciprofloxacin (1.99 µg/L(68). A study conducted in Kenya showed that hospital wastewater could contain concentrations of pharmaceutical antibiotics 3–10 times higher than those measured in surface water and WWTPs (69). The measured mean concentrations of sulfamonomethoxine, penicillin G, and doxycycline in cattle wastewater in Yunnan (China) were 150.49, 91.71, and 49.00 µg/L, respectively (70). Overall, due to the continuous release of pharmaceutical residues from untreated or insufficient wastewater treatment, they have been widely detected in receiving aquatic ecosystems, including surface waters, groundwater, and treated water.

So far, several investigations have focused on the risks associated with pharmaceutical residues in water bodies, as shown in Table 2. Apart from these, a study conducted by Paíga et al in Portugal identified the potential risks associated with the release of human pharmaceuticals into rivers as an increasingly critical environmental health issue (71). It was determined that the RQs in WWTP effluent were higher than those present in the river. A variety of pharmaceuticals have been shown to pose risks to non-target species, with RQ values exceeding 1. The pharmaceuticals of concern include sulfamethoxazole, clarithromycin, azithromycin, fluoxetine, acetaminophen, ibuprofen, and diclofenac. They found algae to be the most sensitive species.

Additionally, ibuprofen and diclofenac appeared to have a greater impact on fish species. An RQ level exceeding 1 was also observed in daphnids exposed to acetaminophen. According to a study by Lei et al (72), 15 antibiotics from five classes were monitored in the surface waters of the Haihe River sub-catchment in North China. The risk was assessed using the calculated RQ, and amoxicillin, anhydro erythromycin, ofloxacin, norfloxacin, and enrofloxacin were identified as having the potential to pose high ecotoxicological risks that could negatively impact the aquatic ecosystem.

The rising frequency of pharmaceuticals detected in the environment is a significant and escalating concern. These substances, once introduced into natural ecosystems, can pose serious risks not only to various forms of wildlife but also to human health. To tackle this escalating issue, innovative strategies are essential, with advanced degradation methods, such as photocatalysis, emerging as promising solutions for dismantling pharmaceutical contaminants. The focus on photocatalyst degradation has intensified, primarily due to the continuous release of pharmaceutical residues into the environment, which poses a significant challenge to ecological balance.

Photocatalytic degradation of Pharmaceuticals by MOFs

To date, several studies have applied MOF in photocatalytic reactions (see Table 3). In this regard, MOFs composites with metal oxide/metal sulfide, such as Cu_2O (73), CeO_2 (57), BiOBr (74), In_2S_3 (75), and MoS_2 (76), have been widely used as photocatalysts for the degradation of pharmaceutical compounds owing to their unique properties. Among them, MOF/TiO_2-based composites are among the most commonly employed photocatalysts for this purpose. For instance, He et al recently synthesized a novel magnetic composite, MIL-101(Fe)/TiO_2, as a modified photocatalyst and evaluated its potential for tetracycline elimination (77). According to experimental results, the composite exhibited excellent tetracycline removal efficiency (92.76% in 10 min) under solar irradiation. Furthermore, the composite could be easily separated from aqueous solution with a magnet. Therefore, it can be reused multiple times, making it cost-effective and environmental-friendly. In a similar study, He et al successfully synthesized MIL-100(Fe)/TiO_2 composites via growing MIL-100(Fe) crystals on TiO_2, using surface-coated FeOOH as a precursor and utilized them for the degradation of tetracycline under light irradiation (78). Among them, all MIL-100(Fe)/TiO_2 photocatalyst composites showed greater photocatalytic activity than pristine TiO_2. Thus, the enhanced photocatalytic activity of the composites is attributed to a decrease in the optical band gap relative to pristine TiO_2. Also, the Fe–O clusters in MIL-100(Fe) not only effectively separate charge carriers but also promote photocatalytic activity via the Fe^{3+}/Fe^{2+} redox cycle. He et al prepared a MIL-101(Fe)/TiO_2 composite via solvothermal synthesis. They tested a combination of persulfate activation and photocatalysis for the removal of tetracycline, a pollutant model, under visible-light illumination (79). It was demonstrated that combining MIL-101(Fe)/TiO_2 and persulfate, not only led to generate sulfate radicals by enhanced persulfate activity via the synergistic effect between MIL-101(Fe) and TiO_2, but also enhances the separation of photo-generated charge carriers, which enhances the photocatalytic performance, improves the activation effect of persulfate, and eventually achieves the remarkably efficient degradation of the target pollutants. A work by Wu et al explored the formation of a novel TiO_2@UiO-66-NH_2 nanocomposite via in situ solvothermal methods and demonstrated its application for tetracycline elimination (80). Owing to its effective charge separation and improved photocatalytic performance, the resulting nanocomposite exhibits superior photocatalytic activity for tetracycline decomposition compared with the single material. Interestingly, the nanocomposite exhibits outstanding recyclability even after the fourth cycle. These results highlight its potential for valuable applications.

Furthermore, Nazari et al successfully synthesized WO_3/ZIF-67 via the sol-gel method (81). Experimental results showed that WO_3/ZIF-67 composites exhibited remarkable removal efficiency for oxytetracycline under visible-light irradiation. The photocatalytic efficiency of WO_3/ZIF-67 against oxytetracycline could reach 91.5% within 60 min. Besides, the photocatalytic mechanism of WO_3/ZIF-67 composites was explored and proposed, showing the vital roles of active species, including $\bullet O_2^-$, $\bullet$OH, and h^+, in the degradation of oxytetracycline during the photocatalytic reaction. Additionally, the photocatalyst reaction is as follows:

$$WO_3/ZIF\text{-}67 + hv \rightarrow e^- + h^+ \quad (1)$$

$$h^+ \left(WO_3\right) + H_2O \rightarrow \bullet OH + H^+ \quad (2)$$

$$e^- \left(ZIF-67\right) + O_2 \rightarrow \bullet O_2^- \quad (3)$$

$$\text{Oxytetracycline} + \bullet O_2^- / \bullet OH / h^+ \rightarrow CO_2 + H_2O + \text{Harmless Products} \quad (4)$$

Recently, there has been an increase in the use of MOF/bismuth-based semiconductor composites for the degradation of pharmaceutical pollutants (82,83). For instance, Tang et al focused on the fabrication of a Bi_2O_3@UiO-66 heterojunction photocatalyst via a solvothermal route for tetracycline degradation. The improved visible-light absorption and enhanced charge separation were responsible for the increased photocatalytic activity of Bi_2O_3@UiO-66 (84). Zhang et al synthesized a BiOI@PCN-222 composite photocatalyst with a mesoporous nanostructure. They discussed its synergy in enhancing the separation efficiency of photogenerated electron–hole pairs, as well as its self-decontamination and photocatalytic tetracycline degradation under visible-light irradiation (85). Also, Wang et al used one-step hydrothermal methods to prepare novel flower-like MIL-100(Cr)/BiOCl heterojunction photocatalysts with varying MIL-100(Cr) mass (86). Accordingly, the formation of a heterostructure between MIL-100(Cr) and BiOCl played a crucial role in enhancing photocatalytic performance by enabling intense interfacial contact between the two components, thereby accelerating carrier migration. Besides, the composite photocatalysts also yielded a higher photo-current intensity and a smaller arc radius in the EIS Nyquist plot than pure MIL-100(Cr) and BiOCl. The photocatalytic performance of the MIL-100(Cr)/BiOCl composite was evaluated by the photodegradation of oxytetracycline under visible-light illumination. The optimized MIL-100(Cr)/BiOCl composite demonstrated significantly accelerated oxytetracycline degradation rate constant compared with pure MIL-100(Cr).

To date, several studies have confirmed that combining MOFs with bismuth molybdate to construct heterojunctions improves their photocatalytic activity (60,61,87). Su et al successfully designed a Bi_2MoO_6/UiO-66-NH_2 (BUN-x, where x denotes the amount of added UiO-66-NH_2) heterojunction Z-scheme photocatalyst (51). The photocatalytic performance was determined under visible-light irradiation. Meanwhile, the excessive incorporation of UiO-66-NH_2 did not improve Bi2MoO6's ability to degrade ofloxacin and ciprofloxacin. The highest photocatalytic degradation removal efficiencies of ofloxacin and ciprofloxacin were observed in BUN-100, 100.0% and 96.0%, respectively, within 90 min. Also, the BET specific surface area of the BUN-100 composites was higher than that of pure Bi_2MoO_6 and displayed a narrower band gap. Moreover, Wu et al successfully fabricated a series of MIL-100(Fe) photocatalysts decorated with $Bi_2Sn_2O_7$, denoted as BMx (x = 1, 3, 5, 7), and investigated their photocatalytic performance for ciprofloxacin degradation (88). They found that the photocatalytic activity followed the order of BM5 > BM3 > BM1 > BM7 > MIL-100(Fe) > $Bi_2Sn_2O_7$. Zhang et al reported an efficient $CuBi_2O_4$@UiO-66-NH_2 core–shell nanostructures (89). They achieved this by decorating thin-layered UiO-66-NH_2 on the surface of $CuBi_2O_4$ nanorods under solvothermal conditions. The formation of heterogeneous contacts between $CuBi_2O_4$ and UiO-66-NH_2 played a vital role in enhancing photocatalytic performance. It provides significant advantages, including fast charge-carrier transfer and efficient utilization of visible light. The optimized $CuBi_2O_4$@UiO-66-NH_2 composition ($CuBi_2O_4$@UiO-66-NH_2(0.2)) delivers the fastest tetracycline hydrochloride photo-degradation kinetics among the tested catalysts, with a rate constant of 0.0126 min^{-1}.

In recent years, research on integrating MOFs with metal sulfides (including monometallic, bimetallic, and polymetallic sulfides) as photocatalysts to eliminate organic (90–92). This is because of its attractive features, including its response to visible light (93). In view of this, Chaturvedi et al (94) reported a CdS/MIL-53(Fe) photocatalyst synthesized by a two-step ultrasonic-assisted solvothermal method. They examined its photocatalytic activity under visible-light illumination using ketorolac tromethamine as a model pollutant. The high degradation level they obtained was 80% in 330 min, which was ascribed to the high charge separation, retarded electron–hole recombination, and better visible light response of the prepared CdS/MIL-53(Fe) photocatalyst. The process of photocatalytic degradation of the tested pollutants was shown as follows (Equations 5– 8):

$$\text{Cds/MIL - 53(Fe)} + hv \rightarrow \text{Cds}(h^+)\ \text{MIL - 53(Fe)}(e^-) \quad (5)$$

$$e^-\left(\text{MIL} - 53\left(\text{Fe}\right)\right) + O_2 \rightarrow \bullet O_2^- \quad (6)$$

$$h^+\left(\text{MIL} - 53\left(\text{Fe}\right)\right) + H_2O \rightarrow \bullet OH + H^+ \quad (7)$$

$$\bullet OH + \text{Ketorolac tromethamine} \rightarrow \text{Smaller molecules} \quad (8)$$

In another work, He et al examined the photocatalytic degradation of tetracycline, a model substrate, using the In_2S_3/MIL-100(Fe) photocatalyst (91). Characterization was performed, and factors affecting photocatalyst performance, including photocatalyst loading, initial tetracycline concentration, and pH, were investigated. To assess the phase of the used photocatalyst, XRD was performed on the In_2S_3/MIL-100(Fe) photocatalyst after three cycles. They observed that the intensity of the characteristic peaks and the phase structure of the catalyst showed no noticeable change before and after the photocatalytic reaction, indicating no deviation from the fresh In_2S_3/MIL-100(Fe) composite. In addition to metallic sulfides, zinc indium sulfide ($ZnIn_2S_4$), a bimetallic sulfide, has been widely used to construct heterojunctions with MOFs to promote carrier separation. For example, a study by Zhang et al reported that $ZnIn_2S_4$/MOF-525 prepared via a one-step solvothermal method could be used for degrading tetracycline via photocatalytic experiments (95). Their structural attributes were identified using techniques such as XRD, FT-IR, SEM, and TEM. The research results showed that the composite's photocatalytic activity enhancement was much higher than that of the pure component. Furthermore, the composite's stability was examined through a five-run cycling test, and its photocatalytic degradation efficiency showed no noticeable changes after five reuse cycles.

Recently, metal-free carbonaceous materials, such as carbon nitride, graphene oxide (GO), and carbon nanotubes, have attracted significant interest in photocatalysis (96,97). Wu et al examined MOF-801/GO composites and reported that they possessed excellent photocatalytic adsorption activity for the degradation of tetracycline (98). In the photocatalytic degradation process, h^+plays a key role. Also, the reaction of $h^+$with H_2O led to $\bullet OH$ formation. In another research work by Mi et al UiO-66 (Ce)/GO composites were synthesized via an in-situ growth method (99). The highest photocatalytic degradation rate of sulfamethoxazole was achieved over GO@UiO-66(Ce)-5, exhibited a markedly improved reaction rate constant relative to pure UiO-66(Ce) and pristine GO.

It is important to note that, when using photocatalysis to degrade pharmaceutical compounds, various intermediates may form (100). For the identification of intermediate compounds during photocatalytic degradation, liquid chromatography-mass spectrometry (LC-MS) is commonly employed. It is worth noting that some intermediate compounds may exhibit more undesirable effects than the parent compound (101). Therefore, in studies of the photo-degradation of pharmaceutical contaminants, toxicity evaluation is considered as necessary step, for which MTT assay is widely applied (102). In this regard, we have designed MIL-125(Ti) mixed linker/g-C_3N_4 for the removal of cefixime (103). The composite suppresses the recombination of electrons and holes, resulting in high photocatalytic activity. In addition, the cytotoxicity of the treated water sample was evaluated using human peripheral blood lymphocytes, the MTT assay results indicated negligible cytotoxic effects. Also, Cao et al synthesized a g-C_3N_4/MIL-68(In)-NH_2 heterojunction composite using an in situ solvothermal method assisted by ultrasonication for the photocatalytic degradation of ibuprofen (104). Under visible-light irradiation for 120 min, the 10 wt% g-C_3N_4/MIL-68(In)-NH_2 composite achieved 93% ibuprofen degradation, compared with only 9% for pure g-C_3N_4 and 68% for MIL-68(In)-NH_2. The heterojunction formed between g-C_3N_4 (Eg = 2.70 eV) and MIL-68(In)-NH_2 (Eg = 2.81 eV) led to the restriction of the recombination rate of charge carriers, which enhanced the photodegradation of ibuprofen. This, in turn, led to the generation of h^+, $\bullet OH$ and $\bullet O_2^-$, which were the main active species that play a vital role in the degradation of ibuprofen molecules.

In recent years, the use of noble metals and materials containing them to enhance MOF photocatalytic activity has attracted special attention owing to their excellent photoelectrochemical properties (105–107). Muelas-Ramos et al prepared and characterized NH_2-MIL-125 loaded with Pd, Pt, and Ag and investigated its activation under solar irradiation for acetaminophen degradation (108). All synthesized samples were more active than the pure UiO-66-NH_2, with Pt/NH_2-MIL-125 showing a high acetaminophen removal efficiency and rapid kinetics, as reflected by its rate constant (*k*). Additionally, the effects of various inorganic ions, such as NO_3^-, NO_3^-, SO_4^{2-}, and HCO_3^-, on acetaminophen degradation by Pt/NH_2-MIL-125 have been evaluated. Among them, HCO_3^- tended to react with the $\bullet O_2^-$, which could reduce the photocatalytic activity. The Pt/NH_2-MIL-125 photocatalyst maintained its high photocatalytic activity and structural morphology after three reuses, as confirmed by SEM and XRD analysis. In contrast, the formation of reaction by-products may block some pores in the material. In another work, the Pd/UiO-66 photocatalyst was synthesized by Yang et al for the removal of tetracycline from a water solution (109). Under simulated solar irradiation, the modified UiO-66 exhibited significantly greater photodegradation activity toward tetracycline than pure UiO-66. Nyquist plots results confirmed that Pd/UiO-66 is an effective photocatalyst material owing to the increased mobility of photogenerated carriers. Table 3 lists MOFs composed of noble metals and related materials used to degrade pharmaceuticals.

Recently, MOF-on-MOF materials have attracted broad attention due to their ability to enhance the combination of the intrinsic physical/chemical properties and performance of individual compartments (110). For example, Zhang et al synthesized NH_2-MIL-88B(Fe)@MIL-100(Fe) by internal expansion growth for photocatalytic removal of tetracycline (100). The best-performing 0.5-bi-MOFs sample achieved 99% pollutant degradation in 90 min. The study found that degradation efficiency is influenced by catalyst dose, the initial tetracycline concentration, and solution pH. The photocatalyst also demonstrated high stability in tetracycline degradation over five consecutive reaction cycles. In a research study conducted by Zhao et al, a novel MOF-on-MOF composite, PCN-134/PCN-222 (coded as P21-X, where X represents the ratio of PCN-222 to PCN-134), was obtained for the first time via an epitaxial growth strategy (111). As a result, the composition (P21-3) exhibited the highest nizatidine degradation efficiency, reaching 90.81% within 120 minutes under light irradiation. Moreover, the composite photocatalysts showed a decrease in nizatidine photodegradation in water samples, in the following order: distilled water > tap water > river water > sea water. The authors attributed the drop to turbidity. In addition, the synthesized composite shows good reusability over five consecutive runs. Gao et al designed a NH_2-MIL-125@MIL-88B heterostructure for efficient tetracycline removal by solvothermal epitaxial growth of MIL-88B crystals onto the NH_2-MIL-125 surface (112). Almost all NH_2-MIL-125@MIL-88B heterostructures exhibited higher removal rates than pure NH_2-MIL-125 or MIL-88B. The performance was due to the synergistic effect between NH_2-MIL-125 and MIL-88B, as well as the electron-transfer facility between them.

Transition-metal carbides and carbonitrides (MXene) are a new class of two-dimensional nanomaterials mapped by the general formula $M_{n+1}X_nT_x$ ($n=1$–3), wherein M represents an early transition metal, X is either carbon or nitrogen, T represents surface termination groups (–O, –OH, and/or –F), and x denotes the number of functional termination groups. MXene materials exhibit unique properties, including strong light absorption across a broad spectral range, a high specific surface area, and excellent electrical and optical properties. These features make them excellent candidates for combination with MOFs. For instance, Wu et al successfully designed a Ti_3C_2-modulated MIL-125-NH_2 (*MTx*, where *x* denotes the amount of added Ti_3C_2) dual-heterojunction photocatalyst via a one-step hydrothermal method (113). They found that adding Ti_3C_2 into the precursor solution of NH_2-MIL-125(Ti) can significantly increase TiO_2 formation on the surface of NH_2-MIL-125(Ti). The optimum photocatalyst exhibited superior photocatalytic activity for tetracycline degradation. Accordingly, the MT5 sample exhibits 82.80% degradation of tetracycline in 60 minutes under visible-light irradiation, which was 11.43-fold higher than that of pure NH_2-MIL-125(Ti).

In recent years, applications of MOFs composed of perovskite materials, such as lanthanum ferrite ($LaFeO_3$) and cesium lead bromide ($CsPbBr_3$), have attracted significant attention. In a study conducted by Younes et al, the photocatalytic properties of MIL-125-NH_2, $LaFeO_3$, and $LaFeO_3$/MIL-125-NH_2 were investigated for the degradation of carbamazepine and caffeine (114). The results of the study indicated that the combination of $LaFeO_3$ and MIL-125-NH_2 ($LaFeO_3$/MIL-125-NH_2) demonstrated the highest photocatalytic performance. This finding suggests a synergistic effect between the two materials, where their combined properties enhanced the degradation of carbamazepine and caffeine. Asadi et al synthesized a novel $CsPbBr_3$/MOF-808 composite using a simple solvent-free mechanochemical grinding method (115). The photocatalytic degradation ability was assessed using three pharmaceutical compounds: ceftriaxone, vancomycin, and ceftazidime. The $CsPbBr_3$/MOF-808 photocatalyst composite showed degradation efficiencies of 97% and 87% for ceftriaxone and ceftazidime, respectively, whereas vancomycin displayed 12% degradation despite its strong adsorption capacity. The study concluded that the $CsPbBr_3$/MOF-808 sample showed a longer charge-carrier lifetime and greater e^-/h^+ pair separation, thereby exhibiting higher photocatalytic activity.

In recent years, nanomaterials derived from MOFs have attracted significant attention for their stable performance and unique structures. These materials offer a promising solution to the problem of secondary pollution arising from the potential leaching of metal ions. Additionally, their porous carbon structure makes them highly effective photocatalysts for the treatment of pollutants. In a study by Cao et al, researchers successfully prepared novel nitrogen-doped carbon-supported cadmium sulfide (CdS/NC–T) composites via a facile in situ carbonization method (116). The researchers utilized cadmium MOFs as precursors for the synthesis of these composites. The CdS/NC–T composites were highly effective as photocatalysts for tetracycline degradation under visible irradiation (83% in 60 min). In their research, they found that the improved performance is attributed to the efficient production and transport of photogenerated carriers. The study found that the photocatalyst exhibited remarkable stability and reusability. After four rounds of recycling reactions, the catalyst retained over 80% of its initial catalytic capacity.

This finding demonstrates the photocatalyst's potential for practical applications, as it maintains its effectiveness across multiple cycles. The stability and reusability of the photocatalyst make it a promising candidate for sustainable and efficient photocatalytic degradation of tetracycline. Wang et al employed ZIF-8 as a sacrificial template and precursor to synthesize a nitrogen-doped ZnO carbon skeleton, denoted N-ZnO/C (117). Subsequently, hierarchical Bi_2MoO_6 nanosheets (BiM) were grown in situ on the surface of the N-ZnO/C material, forming a core-shell N-ZnO/C@BiM heterojunction. They successfully employed this photocatalyst for the removal of sulfamethoxazole

According to Table 3, several factors, including catalyst dose, initial pollutant concentration, and pH, are reported to affect performance in pharmaceutical photocatalytic degradation.

- **Catalyst dose:** Previous studies found that increasing the photocatalyst dosage positively affects the percentage of pharmaceutical degradation (118). This could be attributed to an increase in the number of active sites on the catalyst surface and the generation of more radicals at the surface, which substantially enhances photocatalytic activity (119). The solution becomes turbid beyond a specific limit of catalyst dosage, thereby hindering light penetration and reducing the degradation rate (120).
- **Initial pollutant concentration:** The initial concentration of organic pollutants plays an important role in tuning the photocatalytic activity (121). As the initial pharmaceutical concentration increases, the photocatalyst's active sites become saturated with target molecules, reducing light penetration. Consequently, degradation efficiency would decline.
- **Initial pH values:** pH is an important factor that affects the photocatalyst's adsorption capacity and degradation efficiency in the reaction system (55). Alterations in pH lead to changes in the catalyst's surface charge and the ionic forms of the pollutant molecules (122). It is worth noting that the photocatalyst surface carries a positive charge at pH values below the point of zero charge (pHzpc) and a negative charge at pH values above pHzpc (123). It can be concluded that similar charges on the target molecule and the catalyst result in low degradation efficiency.

Conclusion

The occurrence and ecological risk assessment of pharmaceutical residues have become critical topics due to their potential threats to the environment and human health. The application of advanced degradation techniques, such as photocatalytic processes, has attracted significant attention as an effective means of mitigating these risks. Photocatalysts, such as MOFs, have demonstrated high efficiency under suitable conditions, offering a promising pathway for sustainable pollutant management. MOFs have demonstrated remarkable potential for degrading pharmaceutical pollutants in water/wastewater due to their exceptional surface area, tunable porosity, and chemical versatility. MOF materials, in particular, have emerged as a promising solution for improving catalytic performance in water treatment processes. Recent studies have also focused on MOFs, known for their abundant pores and efficient light-harvesting abilities. However, the majority of pristine MOFs exhibit insufficient photocatalytic performance, primarily because of their low visible-light response and wide band gaps. To solve these problems, various composite system have been developed by integrated MOFs with metal oxides, metal sulfides, metal-free carbonaceous materials, noble metals, MXenes, and perovskites have been proposed to improve the photocatalytic performance of single MOF photocatalysts, thus opening new possibilities for pharmaceutical degradation.

Nevertheless, most studies using MOFs and MOF-based composite materials as photocatalysts for the degradation of pharmaceutical pollutants are still in their infancy and far from practical. Therefore, more research is needed to develop and optimize more efficient, cost-effective, and environmentally friendly MOF-based photocatalysts for environmental remediation. Also, to apply MOFs and MOF-based composite materials to real water/wastewater treatment, researchers should conduct additional experiments to determine the effects of various water/wastewater properties, such as ionic strength, nutrient content, and organic matter, on photocatalyst performance. To ensure that MOFs and MOF-based composite materials have a sustainable future, research should focus on developing photocatalysts that can be recycled with minimal energy and waste while maintaining chemical and physical stability across multiple photodegradation cycles.

In addition, it is essential to conduct an in-depth investigation into the kinetic and thermodynamic mechanisms that govern the synthesis of MOFs and MOF-based composite materials. Such studies are crucial for facilitating the development of more uniformly distributed active sites within these materials. By achieving greater control over their structural formation processes, it becomes possible to optimize their architecture and significantly enhance their photocatalytic efficiency.

In summary, this review provides a comprehensive overview of current research and development on MOFs and MOF-based composite materials, with a specific focus on their applications for the degradation of pharmaceutical contaminants. Additionally, it seeks to shed light on the key challenges ahead while exploring potential opportunities to advance this field.

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The authors declare that there is no conflict of interest.

Ethical issues
In this manuscript, the authors have considered all ethical considerations related to data collection and affirm that this work is original. All data gathered during the study are accurately represented in the manuscript, and no data from this study has been or will be published separately elsewhere.

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