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Efficiency of photocatalytic processes in the removal of the antibiotic ciprofloxacin from aqueous environments: A systematic review

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Abstract

The widespread presence of the antibiotic ciprofloxacin (CIP) in aquatic environments poses severe ecological and public health risks due to its recalcitrant nature. Advanced oxidation processes, specifically semiconductor-based photocatalysis, have emerged as highly promising strategies for highly efficient CIP removal and mitigation of antimicrobial resistance.

This systematic review evaluates the efficiency of photocatalytic systems in removing CIP from aqueous environments. Following a comprehensive literature search across Scopus, Web of Science, Embase, and PubMed databases for studies published up to September 30, 69 peer-reviewed articles were selected and synthesized for in-depth analysis of operational parameters and degradation mechanisms.

The temporal distribution of the included literature demonstrates a rapid increase in research interest, particularly peaking between 2021 and 2024. Key operational variables governing degradation include optimal catalyst dosages of 0.1–1.0 g/L and reaction times of 60–120 minutes. Recent advancements highlight a shift towards visible-light and solar-driven photocatalysis using advanced Z-scheme and S-scheme heterojunctions. These systems frequently achieve >90% CIP removal, generally following pseudo-first-order kinetics. Mechanistically, reactive oxygen species drive the cleavage of quinolone and piperazine rings, yielding lower-toxicity transformation products. However, discrepancies between rapid parent compound removal and actual total mineralization remain prevalent.

While photocatalytic degradation of CIP is highly effective at the laboratory scale, reliance on synthetic wastewater and powder catalysts in batch slurry reactors hinders industrial scale-up. Future research must prioritize immobilized catalyst systems, continuous-flow reactors, real wastewater matrices, and standardized energy efficiency (EEo) reporting to bridge the gap toward real-world applications.

Keywords: Ciprofloxacin, Photocatalysis, Advanced oxidation processes, Heterojunction, Wastewater treatment, Systematic review.

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Introduction

The uncontrolled dissemination of pharmaceutical compounds in aquatic environments has become a growing global concern (1, 2). Among these pollutants, antibiotics particularly fluoroquinolones such as ciprofloxacin (CIP) are recognized as emerging contaminants due to their persistence, high stability, and resistance to conventional wastewater treatment processes (3-5). The widespread consumption of CIP in human and veterinary medicine has resulted in its frequent detection in surface waters, groundwater, and even drinking water, at concentrations ranging from nanograms to milligrams per liter (3, 6). The incomplete biodegradability and stable quinolone structure of CIP hinder its natural decomposition, facilitating its accumulation in ecosystems and promoting the evolution of antibiotic-resistant bacteria (3). Conventional biological and physicochemical treatment methods including adsorption, chlorination, and ozonation often fail to mineralize such recalcitrant compounds and may produce harmful by-products (7). Consequently, advanced oxidation processes (AOPs), particularly semiconductor-based photocatalysis, have emerged as promising alternatives for the degradation of CIP in aqueous systems (8, 9). These processes rely on the generation of highly reactive oxygen species (ROS), including hydroxyl (•OH) and superoxide ($O_2^{\bullet-}$) radicals, upon photoexcitation of a semiconductor under UV or visible light (10, 11). The ROS oxidize organic molecules, converting them into non-toxic end products such as CO_2 and H_2O (12, 13). Among various semiconductors, TiO_2 has been extensively studied for photocatalytic degradation due to its stability and strong oxidizing potential (14-16). However, its wide bandgap (~3.2 eV) limits activity to the UV region, which represents less than 5% of the solar spectrum, while the rapid recombination of electron-hole pairs further diminishes efficiency (17, 18). To overcome these limitations, doping and heterojunction engineering have been widely adopted to extend light absorption into the visible region and enhance charge separation (16, 19). For instance, Nd_2O_3/TiO_2 nanocomposites exhibited up to eightfold higher photocatalytic activity compared to bare TiO_2, achieving complete CIP degradation within 150 minutes under visible light (20). Beyond TiO_2 systems, perovskite-based materials such as La-doped $NaTaO_3$ (LNTO) have shown excellent photocatalytic performance owing to their tunable electronic structure and chemical stability. Coupling LNTO with narrow bandgap oxides such as α-Fe_2O_3 and Bi_2O_3 efficiently reduced the bandgap energy from 4.4 to ~2.3 eV and significantly improved charge carrier separation, enabling full degradation of CIP within 90–120 minutes under visible irradiation (21, 22). These perovskite systems demonstrated strong recyclability and structural stability, confirming their potential for sustainable water treatment applications. In addition, green-synthesized photocatalysts have gained increasing interest as environmentally friendly alternatives to conventional synthesis routes. For instance, Co_3O_4 quantum dots synthesized using tomato seed extracts successfully degraded CIP under UV light, offering a low-cost and biogenic pathway to produce efficient catalysts (23). Similarly, ZnO-functionalized fly ash composites have been proposed as eco-compatible materials combining industrial waste utilization with effective photocatalytic performance for antibiotic removal (24). Such green and waste-derived materials align with circular economy principles and reduce secondary pollution risks.

Recently, two-dimensional (2D) heterostructures have emerged as advanced platforms for visible-light-driven photocatalysis. Bi-doped NiAl-LDH/g-C_3N_4 composites, for example, displayed 86% CIP removal efficiency within 180 minutes under visible light due to improved charge mobility and interfacial contact between 2D layers (25). Likewise, RGO-bridged $CuFe_2O_4$@Ag_2S S-scheme heterojunctions achieved complete CIP degradation under simulated sunlight, demonstrating excellent mineralization capacity (85% COD reduction) and reusability over six consecutive cycles (26).

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Collectively, these advances highlight a strong research trend toward designing multifunctional, recyclable, and solar-active photocatalysts that combine material innovation, green synthesis, and mechanistic understanding for enhanced degradation of antibiotics.

Given the environmental significance and ongoing technological progress, a comprehensive assessment of photocatalytic efficiency, mechanisms, and influencing parameters across various systems is essential. Therefore, this systematic review aims to synthesize recent findings on ciprofloxacin degradation using diverse photocatalytic materials ranging from metal oxides and perovskites to hybrid and green-synthesized nanocomposites. The review consolidates insights into how structural design, dopants, light sources, and reaction conditions govern the degradation kinetics, stability, and reusability of photocatalysts, providing a holistic understanding of current advances and future prospects in antibiotic removal from aquatic environments.

Materials and Methods

Literature survey and search approach

This systematic review was conducted in accordance with the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) 2020 guidelines. Adherence to this framework ensures that the methodology is transparent, comprehensive, and reproducible. The subsequent sections provide a detailed account of the search strategy, the inclusion and exclusion criteria, the process of data extraction, and the analytical approach employed for the synthesis of the findings.

A systematic search covered four main electronic databases. These included Scopus, Web of Science, Embase and PubMed. The search was conducted with no lower date limit and included all available records up to September 30, 2025. To ensure comprehensiveness, articles formally published in 2025 that were available online as early access by the search date were also included. Search strategies were tailored for each database, and reference lists of eligible articles were manually screened for additional relevant studies.

An example of the search strategy we employed in Scopus is structured as follows:

(photocatal* OR "photo-catal*" OR "photocatal*" OR "photocatalytic" OR photocatalysis OR "heterogeneous photocatalysis" OR "visible light photocatal*" OR "visible-light photocatal*" OR TiO2 OR "titanium dioxide" OR ZnO OR g-C3N4 OR "graphitic carbon nitride" OR photocatalytic) AND (ciprofloxacin OR Cipro OR "ciprofloxacin hydrochloride") AND (water OR aqueous OR wastewater OR "wastewater" OR sewage OR "surface water" OR groundwater OR "drinking water" OR "environmental water" OR "aqueous solution") AND (remov* OR degrad* OR photo degrad* OR photolys* OR mineraliz* OR eliminat* OR "removal efficiency" OR "degradation rate" OR "rate constant" OR kinetics)

Inclusion and Exclusion Criteria

Eligibility criteria for all studies included: (1) experimental studies investigating photocatalytic processes applied for CIP removal from aqueous solution, (2) reports of quantitative results such as removal efficiencies, rate constants, or total organic carbon reductions, (3) reporting in English and (4) published in a peer-reviewed journal. Studies were excluded if they were: (1) a review, conference abstracts, or editorial, (2) an experiment unrelated to CIP or lacked any data/results on CIP, and (3) studies that presented no quantitative results.

Study selection

Two independent reviewers screened titles and abstracts for eligibility. The articles which were eligible for inclusion had their full text screened. A third reviewer mediated any conflicts. The selection process followed the 4 PRISMA phases: identification, screening, eligibility and inclusion. Of 4065 records initially retrieved, 69 studies met all inclusion criteria. A PRISMA flow diagram summarizing the selection process is presented in Figure 1.

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Data extraction

A uniform data extraction instrument was employed to extract: (1) bibliographic information (author, year, country); (2) catalyst type and formulation; (3) experimental conditions (pH, initial CIP concentration, catalyst dosage, method and intensity of irradiation, reaction time); (4) performance outcomes (removal efficiency, rate constants); (5) catalyst stability and reusability; (6) mineralization efficiency (TOC removal); and (7) degradation pathway and toxicity investigations. Two reviewers independently extracted the data, with disagreements reconciled through discussion.

Quality assessment

To evaluate the methodological quality and risk of bias of the included studies, a customized appraisal was conducted. Criteria included the clarity of the experimental setup, inclusion of appropriate control groups (e.g., dark adsorption tests), reproducibility, and proper reporting of parameters. Studies were categorized to ensure that the data synthesized in this review originated from methodologically sound experiments with a low to moderate risk of bias.

Data analysis

Considering the diversity in experimental conditions, results were synthesized descriptively rather than combined into a meta-analysis. Trends in catalyst performance were evaluated in response to catalyst composition, operational conditions, and reported mechanisms of degradation. Wherever possible, ranges and medians were reported to summarize removal efficiencies and mineralization rates.

Results and discussion

Study selection process

The systematic literature search identified 4065 preliminary records in the target databases [Scopus: 1476, Web of Science: 1956, Embase: 305, and PubMed: 328]. After eliminating document duplication, 3129 distinct documents were screened. A total of 2070 articles that were not pertinent to the study were eliminated by evaluating their titles, leaving 1059 articles for abstract screening. Following this, 859 records were excluded because their abstracts did not meet the inclusion criteria, leaving 200 articles for the full-text review. After excluding 131 articles due to insufficient data, unrelated methodologies, or unrelated outcomes, 69 studies were included in the final synthesis. The extensive screening and selection procedures are shown in the PRISMA flow diagram (Figure 1).

Light source publication and distribution

Figure 2 shows the distribution of the selected studies over time. As indicated, the number of publications is overall on an increasing trend with time, which shows the interest in more research in this direction. The peaks included 2024 [n=11], then 2022 [n=10], 2021 [n=10], and 2020 [n=10]. Several studies were also published in 2018 [n=7] and 2023 [n=6]. Few studies were published in 2019 [n=5], 2010 [n=3], 2025 [n=2], 2017 [n=2], 2016 [n=1], 2015 [n=1], and 2014 [n=1].

Figure 3 shows the distribution of light sources used in the studies. It can be seen that most of the research was conducted on visible light irradiation [37.7%], slightly more than UV irradiation [31.9%] and natural or simulated sunlight [30.4%]. This trend implies that research interest is moving toward the utilization of visible light and solar energy to achieve sustainable photocatalytic usage.

Examples of photocatalysts in selected studies

Table 1 presents a comprehensive overview of the main characteristics of the studies reviewed, including the photocatalyst, light source, working conditions, and degradation rate. Various photocatalytic materials with a wide range of diversity have been generated and tested for CIP breakdown in aqueous solutions. These materials can be defined based on their composition and structural design. Photocatalysts based on metal oxides continue to be heavily researched because they are stable and possess strong oxidizing potential. An example would be TiO_2 nanotubes (NTAs) or Nd_2O_3/TiO_2 nanocomposites that

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utilize dopants to extend light absorption into the visible region. Zinc oxide (ZnO) has also been used extensively, commonly in composite types like ZnO@FAU composites or functionalized with fly ash to combine industrial waste utilization with effective performance.

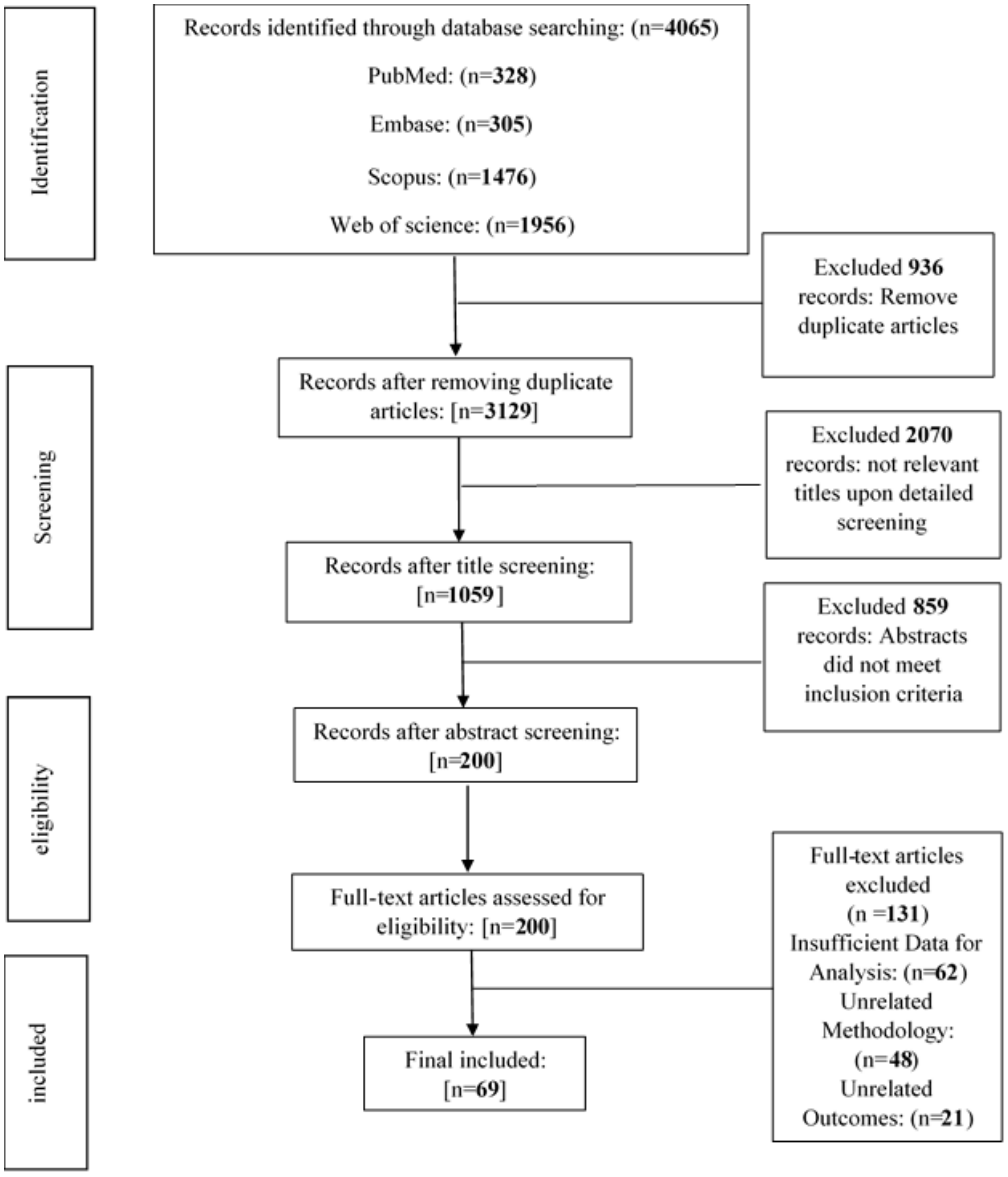

Figure 1. PRISMA diagram for searching resources

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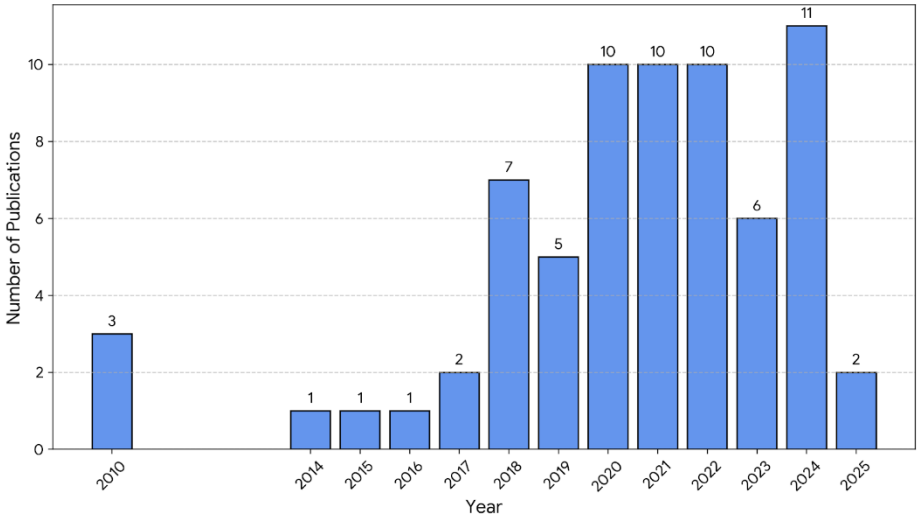

Figure 2. Distribution of the selected studies on the photocatalytic degradation of ciprofloxacin over time (year of publication).

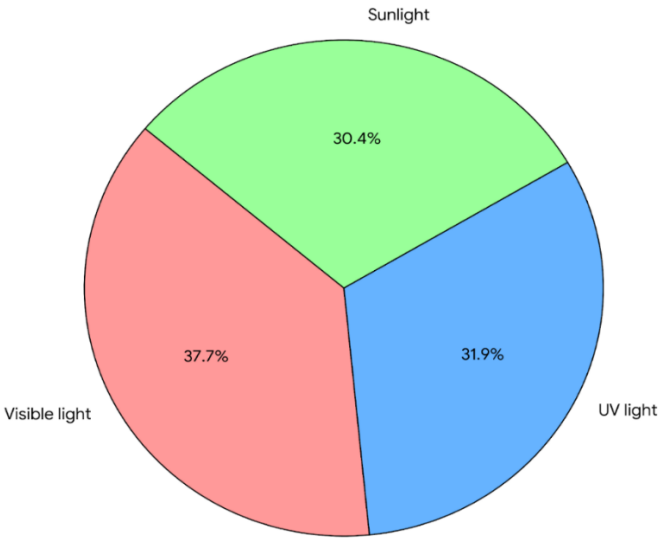

Figure 3. Distribution of the various light sources (visible light, UV irradiation, and natural/simulated sunlight) utilized in the reviewed photocatalytic systems.

Additionally, perovskite-based materials such as La-doped $NaTaO_3$ (LNTO) have been investigated, especially in heterojunction designs with narrow bandgap oxides like α-Fe_2O_3, to enhance the gathering of visible light (22). Another important category includes Metal-Organic Frameworks (MOFs) and biochar composites, which offer high surface areas and sustainable synthesis routes. MOF-based and biochar composites, including PAN@ZnONPs/Bio-MOF and Bi_2MoO_6/Banana Peel Biochar, have been demonstrated to be

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highly effective for CIP degradation (27). Finally, more complex 2D heterojunction systems, including S-scheme and Z-scheme designs, have been engineered so that the charge carriers are spatially separated. Examples include BiOX/GaMOF S-scheme heterojunctions and N-CQDs/TiO_2 S-scheme systems. A critical comparison between these materials reveals a trade-off between activity and stability (28, 29). While advanced heterojunctions generally offer superior visible-light harvesting compared to single metal oxides like bare TiO_2, industrial scale-up often requires mechanically robust and cost-effective synthesis routes.

Operational and reaction conditions

Catalyst dosage [g/L]

The concentration of the photocatalyst is an important factor that varies the quantity of active sites that can be utilized in the reaction and the penetration of light into the solution. The studies reviewed mention a broad spectrum of catalyst dosages ranging between 0.004 g/L and 4 g/L. In most cases, the degradation efficiency increases with increasing catalyst loading to an optimal level, after which light scattering and shielding effects occur owing to solution turbidity, and thus, the photoactivity is reduced. For example, Wei et al. employed a dosage of 0.5 g/L for Bi_2MoO_6/Banana Peel Biochar, and Tang et al. utilized 0.8 g/L for PAN@ZnONPs/Bio-MOF. In contrast, Huang et al. found success using lower amounts (0.2 g/L) for TiO_2@AMSF under UV light (30-32).

PH

- The pH of the solution has a significant effect on the photocatalyst's surface charge and the target molecule, changing the way the pollutant and the catalyst surface interact with each other. The best pH level depends on the material being used.
- **Acidic Conditions:** Numerous studies have indicated a preference for acidic environments. For example, Hayri-Senel et al. found that PS-TiO_2 composites worked effectively at pH=3 (33), while Alam et al. used a Mn/Co oxide nanocomposite optimally at pH=4 (34).
- **Neutral and Alkaline Conditions:** On the other hand, some systems work better in neutral or alkaline conditions. Mohamed et al. achieved efficient degradation at pH=8 utilizing a NiO@g-C_3N_4 nanocomposite (35). Similarly, El-Kemary et al. observed activity at pH=10 for ZnO nanoparticles (36). However, many studies indicated that a neutral pH (around 6-7) is highly effective, such as for the ZnO@FAU composite.
- The reported variation in optimal pH across studies highlights the critical role of electrostatic interactions.

Time [min]

The time it takes to get significant degradation through irradiation depends on how well the catalyst and light source work. Highly efficient catalysts, like the TiO_2 nanotubes (NTAs) that Abromaitis et al. (37), wrote about, broke down completely [100%] in 8 minutes of UV-C light. Similarly, Bouyarmane et al. (37),achieved 100% degradation in 15 minutes of UV light utilizing a TiHAp Nanocomposite. On the other hand, other systems needed more time. For instance, Huang et al. (38), used a 400-450-minute reaction time for TiO_2@AMSF, and Durán-Álvarez et al. (39), used a 300-minute reaction time for Z-scheme AgBr/Ag/Bi_2WO_6. Most studies, on the other hand, say that the best reaction time is between 60 and 120 minutes.

Figure 4 shows how degradation efficiencies are spread out over different reaction times. It shows that shorter times [like 8–30 minutes] can lead to high efficiencies with advanced catalysts, but most systems reach equilibrium in the 60–120-minute range.

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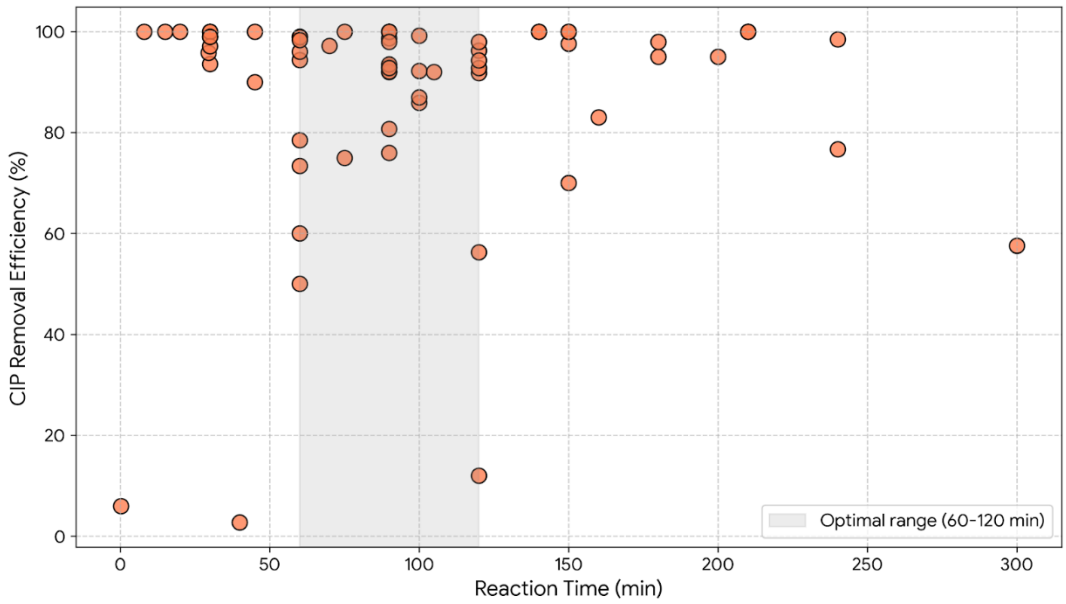

Figure 4. Scatter plot illustrating the relationship between ciprofloxacin removal efficiency (%) and reaction time (min), highlighting the typical equilibrium range of 60–120 minutes.

Concentration [mg/L]

The initial concentration of CIP was inversely related to degradation efficiency. Higher concentrations can saturate the active sites of the catalyst and reduce light penetration in the solution. The reviewed studies investigated a wide range of initial concentrations, from trace levels of 10 µM to higher loads of 50 mg/L. However, most research has focused on concentrations between 5 and 20 mg/L, reflecting typical experimental laboratory conditions. For instance, Chen et al. and Baldez et al. utilized 20 mg/L and 10 mg/L, respectively, achieving high removal rates (40). From a critical engineering perspective, a major limitation in the reviewed literature is the discrepancy between experimental concentrations and real-world conditions. While high concentrations facilitate easier kinetic monitoring in the lab, environmental CIP levels are typically found at concentrations ranging from nanograms to milligrams per liter. Future studies must evaluate photocatalytic performance at trace levels to accurately predict removal behavior in actual wastewater treatment plants.

Degradation efficiency

The reported photocatalysts generally exhibited high degradation efficiencies. Exceptionally high removal rates (100%) have been achieved using advanced composites such as Pt@$BiVO_4$-g-C_3N_4 and 3% CdO/La-$NaTaO_3$. Many other studies have reported efficiencies in the range of 80–99%, including the BiOX/GaMOF S-scheme composite (96.27%) and the PAN@ZnONPs/Bio-MOF catalyst (99.22%). Across all evaluated studies, the median removal efficiency was approximately 95%, with the interquartile range typically falling between 85% and 100%.

Light source

Recent research has focused on visible light and direct sunlight active photocatalysts to use sustainable energy.

- **Visible light:** A considerable number of studies employed visible light sources to

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facilitate the reaction, overcoming the wide bandgap limitations of traditional materials. Examples include Nd_2O_3/TiO_2 nanocomposites and $CoFe_2O_4/ZnO$ systems.

- **Sunlight:** Practical applicability was demonstrated by researchers using natural or simulated sunlight, such as Golmohammadi et al. for Ag/SiO_2 and Cilamkoti & Dutta for p-type $ZnO/N\text{-}SiO_2$ nanorods.
- **UV light:** UV irradiation is still highly effective for wide-bandgap semiconductors, utilized by systems like TiO_2 NTAs and ZnO NPs. A significant limitation in the current literature is the absence of Electrical Energy per Order (EEo) calculations. As indicated in Table 1, nearly all reviewed papers failed to report this metric. For photocatalysis to compete with traditional physicochemical treatments, future research must shift from reporting simple percentage removal to quantifying energy efficiency. Researchers are strongly encouraged to report EEo using the standard equation:

$$EEO = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C0}{Cf}\right)}$$

Where P is the rated power of the system (kW), t is the time (min), V is the volume (L), and C0 and Cf are the initial and final concentrations.

Kinetics

The pseudo-first-order model mostly explains how CIP breaks down over time, yielding observable rate constants (K_{obs}). This model exhibited the optimal fit for data in several studies, including Tang et al. (2.38×10^{-2} min^{-1} for PAN@ZnONPs/Bio-MOF) and Wei et al. (0.0486 min^{-1} for Bi_2MoO_6/Banana Peel Biochar). Exceptionally rapid kinetics were also reported, such as 1.1 min^{-1} for TiO_2 NTAs by Abromaitis et al. The degradation kinetics are strictly governed by structural design, dopants, light sources, and reaction conditions. Overall, the reported pseudo-first-order rate constants (K_{obs}) exhibited a wide range from 0.0034 to 1.1 min^{-1}, with a median value of approximately 0.035 min^{-1}.

Stability and reusability of catalysts

For photocatalysts to be economically viable and sustainable, they must be stable and reusable. Most studies looked at how well the catalyst worked over three to six consecutive cycles.

- **Structural stability:** Characterizations done after the reaction usually showed that the catalysts were structurally sound. For example, Wei et al. reported that Bi_2MoO_6/Banana Peel Biochar endured 5 cycles without efficiency loss, and the RGO-bridged $CuFe_2O_4@Ag_2S$ heterojunction demonstrated excellent reusability over six consecutive cycles.
- **Magnetic/Immobilized recovery:** Systems offering easy separation were highly beneficial for recovery. Radić et al. reported success using an IO-TiO_2 magnetic nanocomposite, and Borges et al. utilized supported TiO_2 on glass rings to sidestep the challenges of powder recovery.

Degradation mechanisms and pathways

The creation of highly reactive oxygen species (ROS) is what makes CIP break down through photocatalysis. A comprehensive overview of this process, illustrating the charge transfer pathways in an advanced heterojunction (e.g., S-scheme) and the subsequent generation of ROS for CIP degradation, is depicted in Figure 5.

- **Active species:** Radical scavenging experiments have consistently identified hydroxyl (OH) and superoxide ($O_2^{\bullet-}$) radicals, as well as photogenerated holes (h^+), as the primary species responsible for oxidizing the organic molecules. This was validated in research conducted by Tang et al. and El Golli et al (32, 41).
- **Charge transfer mechanisms:** New heterojunction designs have been put forward

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to improve charge separation. Multiple studies confirmed S-scheme mechanisms (e.g., BiOX/GaMOF and N-CQDs/TiO_2) which maintain the elevated redox potential of the charge carriers.

- **Intermediates and pathways:** Analyses have clarified degradation pathways that include the cleavage of piperazine and quinolone rings, oxidation, and complete C-F cleavage. Studies like those by Dong et al. confirmed that the biotoxicity of CIP toward E. coli was eliminated following photocatalysis, yielding low-toxicity end products.
- **Chemical specificity of the degradation:** The structural advantage of advanced heterojunctions is directly linked to the chemical stability of ciprofloxacin. CIP possesses an incomplete biodegradability and a highly stable quinolone structure that hinders natural decomposition. Conventional treatment methods and simple single-component oxides often fail to generate ROS with sufficient oxidation potential to break these bonds efficiently. In contrast, advanced systems (e.g., S-scheme) preserve the high thermodynamic potential of photogenerated holes. These potent carriers are energetically capable of initiating ring-opening and defluorination, which are critical steps in CIP mineralization. This explains why heterojunctions consistently achieve strong mineralization capacity and non-toxic end products.

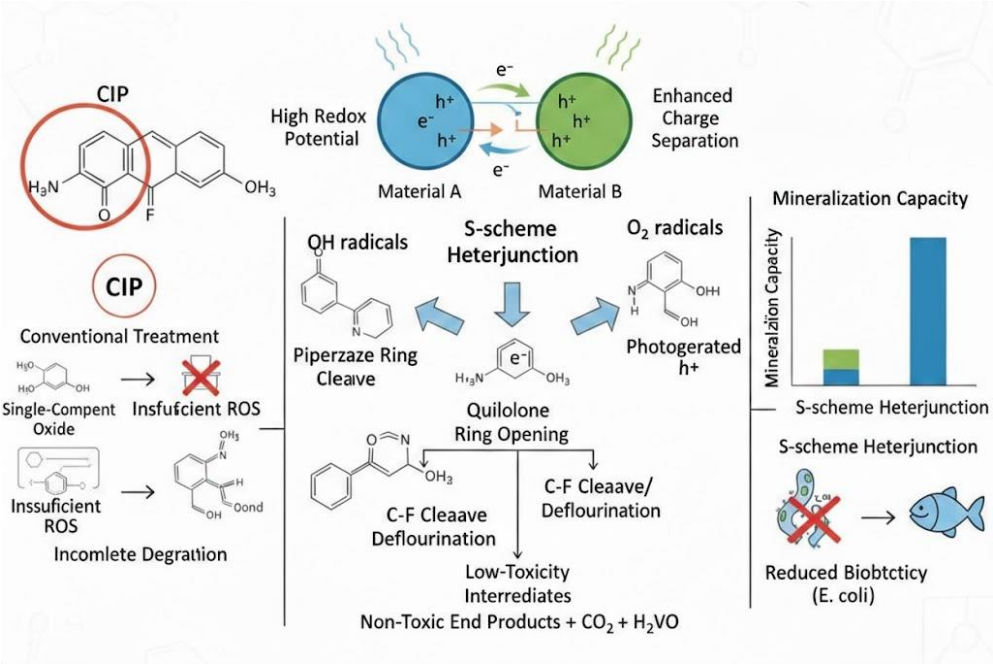

Figure 5. Schematic representation of the charge transfer mechanism in an advanced S-scheme heterojunction and the generation of reactive oxygen species (•OH, O_2•$^-$, h^+) leading to the cleavage and mineralization of ciprofloxacin.

Critical challenges and knowledge gaps

A systematic synthesis of the included studies reveals fundamental hurdles that limit the validity of current laboratory data for real-world applications:

- **The Mineralization paradox and intermediate toxicity:** A major discrepancy exists between parent compound removal and mineralization. While CIP removal efficiencies often exceed 90%, only about 35% of the reviewed studies explicitly quantified mineralization. Among these,

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Total Organic Carbon (TOC) or Chemical Oxygen Demand (COD) removal rates vary significantly, sometimes only reaching 40-50%. This indicates the accumulation of transformation products. Future research must prioritize pathway analysis coupled with stringent toxicity assays rather than relying solely on removal rates.

- **Experimental matrix vs. real effluents:** The overwhelming majority of studies (over 90%) utilize synthetic aqueous environments, whereas fewer than 10% evaluated the photocatalysts in real wastewater or spiked environmental matrices, thereby ignoring the complex chemistry of real effluents. Consequently, the reported degradation efficiencies in laboratory settings likely overestimate the performance expected in real wastewater treatment applications.
- **Reactor configuration:** A significant portion of reviewed studies employ slurry-type batch reactors with powder catalysts. While effective for screening, this configuration faces massive bottlenecks in catalyst recovery and secondary pollution risks. Furthermore, the extreme heterogeneity in reported light sources without standardized metrics makes direct comparisons difficult.

Conclusion

This systematic review evaluated photocatalytic approaches for degrading the antibiotic ciprofloxacin (CIP) in aqueous systems and identified operational variables that govern performance, including catalyst dosage, pH, initial CIP concentration, irradiation source, and contact time. Across the 69 selected studies, effective conditions commonly included catalyst dosages of approximately 0.1–1.0 g/L and reaction times of approximately 60–120 minutes, reflecting a trade-off between active-site availability and optical scattering at higher solid loading. The optimal pH was catalyst-dependent, although many advanced composites maintained strong performance near neutral to mildly alkaline conditions. Mechanistic improvements over the past decade have been consistent across platforms, including S-scheme and Z-scheme heterojunction construction, dopant engineering, and integration with sustainable supports such as biochar or fly ash to increase visible-light absorption and improve charge separation. These designs often achieve >90% CIP removal and frequently follow pseudo-first-order kinetics under the reported test regimes. Studies incorporating MS analysis and toxicity estimation indicate that degradation can proceed beyond parent depletion toward less toxic transformation products via quinolone and piperazine ring cleavage, with partial to complete mineralization reported in a subset of the literature.

This review shows that photocatalytic advanced oxidation processes are promising for the degradation of recalcitrant antibiotics like CIP in aqueous solutions. However, because a large number of research studies are carried out on a laboratory scale using synthetic wastewater, the results may not be directly scalable to pilot applications. Most current studies focus on powder catalysts, which pose challenges for recovery and reuse, although magnetic composites have shown promise in addressing these issues. Furthermore, the predominant use of slurry reactors in current research presents a significant bottleneck for downstream processing. To bridge the gap between laboratory success and industrial application, the focus must shift towards immobilized catalyst supports [e.g., coating on glass rings or membranes], EEo quantification, and the treatment of real effluents containing complex co-existing ions to provide a holistic understanding of antibiotic removal from aquatic environments.

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Table 1. Key characteristics of studies investigating the efficiency of photocatalytic processes for ciprofloxacin removal from aqueous environments

No.	Study specifications	Catalyst type	Operating conditions					CIP removal efficiency	K_{obs} (min^{-1})	Catalyst stability	Mineralization rate	Toxicity and degradation pathway	EEo (Kwh)	References
			pH	Cip (mg/L)	Dose (g/L)	Time (min)	Light Source							
1	Chen et al., 2025, China	BiOX/GaMOF (S-scheme)	7	20	0.4	120	UV	96.27%	0.369	95.79	NR	Four pathways, toxicity reduction	NR	(42)
2	Mohamed et al., 2025, Egypt	NiO@g-C_3N_4 nanocomposite	8	10	1	60	sunlight	78.5%	0.025	>50 % removal after 4 reuse cycles	Effective (S-scheme mechanism)	Not toxic; full photocatalytic oxidation suggested	NR	(35)
3	Ateş et al., 2024, Turkey	N-CQDs/TiO_2 (S-scheme)	5	5	0.4	120	UV-A	91.8%	0.0138	NR	NR	S-scheme mechanism proposed	NR	(43)
4	Abromaitis et al., 2024, Lithuania	TiO_2 nanotubes (NTAs)	NR	5-10	NR	8	UV-C	100%	1.1	96.26% after 5th cycle	57% TOC removal after 30 min	Log-5 bacterial reduction	NR	(37)
5	Cilamkoti & Dutta, 2024, India	p-type ZnO/N-SiO_2 nanorods	6.3	12	0.4	90	sunlight	93%	0.029	88% after 4th cycle	80% degradation, not full mineralization	Two degradation pathways proposed	NR	(44)
6	Ecareño-Torres et al., 2024, Mexico	TiO_2/SnO_2/g-C_3N_4 (composite)	6	10	1	300 (UV), 10 (sunlight)	UV and sunlight	97.87%	0.024	High adsorption (≈ 30 %) + excellent photo-stability over cycles	Significant	Intermediate particles were analyzed, the pathway with reactive oxygen species	NR	(45)
7	Wei et al., 2024, China	Bi_2MoO_6/Banana Peel Biochar	8	10	0.5	90	Vis	98.7 %	0.0486	5 cycles without loss	85 %	•OH, and h^+ dominant; toxicity reduction significantly by LC–MS analysis	NR	(46)
8	Baldez et al., 2024, Brazil	ZnO@FAU Composite	7	10	0.16	90	UV	92%	NA	3 cycles; 75.7 %	NR	h^+ is the dominant active species; •OH minor; direct	NR	(40)

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										removal in cycle 3; FTIR unchanged		oxidation by holes (and indirect via •OH); toxicity not evaluated		
9	Radić et al., 2024, Croatia/Slovenia	IO-TiO2 magnetic nanocomposite	7	8	0.2	150	UV-B	70 %	0.0063	Reused 4 times without activity loss	60 %	Hydroxyl radical oxidation; no residual toxicity after treatment	NR	(47)
10	Tang et al., 2024, China	PAN@ZnONPs/Bio-MOF	7.2	10	0.8	100	Vis	99.22 %	2.38×10^{-2}	Excellent (≥90 % efficiency after reuse)	TOC ≈ 50 %	h^+, •OH, $•O_2^-$ active; stable low-toxicity products	NR	(48)
11	Hayri-Senel et al., 2024, Turkey	PS-TiO_2 Composite	3	5	0.8	180	Vis	95.01%	0.0125	Stable; reusable	85 % (TOC basis)	•OH and $•O_2^-$ radicals; piperazine-ring cleavage	NR	(49)
12	El Golli et al., 2024, Italy	ZnO/g-C_3N_4 (Green Coating)	NR	10	NR	210	sunlight	100 %	0.02113	High 89 % efficiency retained in second cycle	Near-complete decomposition confirmed by HPLC; no CIP peak after 210 min	•OH, and $O_2•^-$ radicals; major pathways: oxidation (+O), decarboxylation ($–CO_2$), H elimination	NR	(50)
13	Machín et al., 2024, Spain	5% (Co_3O_4-gC_3N_4) @ZnONPs	7	10	1.1	60	sunlight	99 %	NR	6 % loss after 15 cycles	NR	By-products via superoxide radicals ($•O_2^-$ dominant)	NR	(51)
14	Fazil & Narayanan, 2023, India	5Ag/ZnO (Mesoporous)	6.5 - 7.5	25	0.2	240	Vis	76.7%	0.0034	Effective after 5 cycles	Not numerical but quinolone-ring breakdown confirmed by LC-MS	CIP quinolone ring cleavage observed → non-toxic products	NR	(52)
15	Golmohammadi et al., 2023, Iran	Ag/SiO_2 (Rice Husk Silica)	6.7	40	0.6	180	sunlight	98%	2.18×10^{-2}	Stable after 3 cycles with no efficiency loss	TOC removal measured	Not toxic after treatment; decomposition confirmed	NR	(53)
16	Ngo et al., 2023, Vietnam	CuFe2O4/rGO/Halloysite	7	20	0.2	60	UV	99	0.006332	> 90 % after 4 runs	78 %	Piperazine and quinolone oxidation → benign products	NR	(54)
17	Kumar, 2023, India	SnS2/BiVO4 nanocomposite	NR	10	0.6	105	sunlight	92%	0.0184	Up to 5 cycles with acceptable efficiency, low % metal emission	Effective, confirmed (ROS generation)	Reduction of toxicity, decomposition pathway involving $•O2^-$ and h+, Z-scheme composition	NR	(55)

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18	Goudarzi et al., 2023, Iran	Mn-Tl_2WO_4 Nanostructures	9	10	0.3	90	UV	76%	NR	Good, the performance decreased by only 1-3% after 3 reuse cycles	NR	A general photocatalytic mechanism involving reactive oxygen species is assumed	NR	(56)
19	Borges et al., 2023, Portugal	Batch Reactor: Powdered TiO_2 (Degussa P25) Packed Bed Reactor: Supported TiO_2 on glass rings/cylinders	NR (ambient)	50	NR	200	Sunlight	95%	NR	reusable supported TiO_2 (glass rings > cylinders)	nearly complete under solar run	The general mechanism involving hydroxyl radicals (˙OH) is assumed; no specific scavenger tests were conducted	NR	(57)
20	García-Reyes et al., 2022, Spain	XGS-Fe-Im	NA	15	1	60	Sunlight	60 %	0.015	> 90 % efficiency after 5 cycles	80 % TOC removal	Superoxide and hydroxyl radicals dominate; non-toxic end-products	NR	(58)
21	Ahmadmoazzam et al., 2022, Iran	Ag_2O-AgI /TiO_2	9.5	10	NA	120	Vis	92.8%	0.021	Catalyst stayed stable for 6 days	51% TOC removal	Proposed degradation pathway based on GC-MS reported	NR	(59)
22	Alam et al., 2022, Pakistan/Saudi Arabia/China	Mn/Co oxide nanocomposite	4	3.31	1	120	Sunlight	56.3%	7.9 x 10^{-2}	Stable for 5 cycles	NR	Identification of active species (•OH, O_2^-, h^+), reaction pathway identified	NR	(34)
23	Shawky & Alshaikh, 2022, Egypt/Saudi Arabia	3% $CoFe_2O_4$/ZnO	NR	10	2.4	45	Vis	100%	0.103	97 % after 5 cycles	85 %	Complete C–F cleavage → CO_2 + H_2O (end non-toxic)	NR	(60)
24	Xiao et al., 2022, China	CNBN (Membrane Loaded)	5.3	10	3.1-3.3 × 10^{-3} (g cm^{-2})	40	sunlight	NR	2.7 × 10^{-3}	Stable > 40 days use	> 80 %	Ring-opening + decarboxylation → low-toxicity products	NR	(61)
25	Alhaddad & Amin, 2022, Saudi Arabia	Pt@BiVO4-g-C3N4	NR	NR	2.4	90	Vis	100 %	NR	maintained after several reuse cycles	nearly complete decomposition confirmed	non-toxic intermediates confirmed via PL and photo-current tests	NR	(62)
26	Batterjee et al., 2022, Saudi Arabia	LP-ZnO NPs	8	6.62	0.1	160	UV	83	0.011	5 cycles with high stability	NR	Dominant species: •OH, presence of h^+ and $•O_2^-$ also confirmed	NR	(63)
27	Thuan et al., 2022, Vietnam	5% ZnO/g-C_3N_4	8	1	0.5	150	Vis	97.6%	0.0281	89.8 % efficiency after 3 cycles (6 cycles tested)	NR	•OH, $•O_2^-$, h^+ active species; benign products	NR	(64)
28	Amir et al., 2022, Pakistan/Australia/ Korea	BCZ-3	7	100	1	240	Vis	98.5%	NA	BCZ-3 showed good stability, degrading 80.3% of CIP after four cycles.	98.1% COD	Radicals break down CIP into intermediates (piperazinyl ring or quinolone part) and then into CO_2 and H_2O.	NR	(65)

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29	Alhaddad et al., 2022, Saudi Arabia/Kuwait	Nd_2O_3/TiO_2 (1.5%)	NR	10	2	150	Vis	100%	0.0086	It retained 93% of its efficiency after five consecutive cycles.	NR	Based on the reported scavenger test results.	NR	(66)
30	Beshkar et al., 2021, Iran	$Cu_2O/Cu_2(PO_4)$ (OH)	NR	10-20	1	120	sunlight	98%	NA	95% after 5 cycles	NR	p-n heterojunction mechanism	NR	(67)
31	Kaur et al., 2021, India	Ag-Fe-TiO2 Composite	3.5	25	100% area covered (120 beads)	60	sunlight	94.4%	0.068	Stable up to 30 reuse cycles	Confirmed via GC-MS intermediates	Detoxified; pathway verified by inhibition-zone test	NR	(68)
32	Alhaddad & Shawky, 2021, Saudi Arabia/Egypt/Japan	3%FO@LNTO	NR	10	2	90	Vis	100%	0.047	It showed remarkable stability, retaining nearly 95% efficiency after five cycles.	NR	Proposed photocatalytic mechanism reported	NR	(22)
33	Akbari et al., 2021, Iran/Spain	S, N-MgO	9	50	0.1	30	UV-A	99%	0.115	The catalyst showed high stability, maintaining over 95% efficiency after four reuses.	The TOC removal, indicating mineralization, reached 92% after 90 minutes of reaction.	Degradation pathway based on LC/MS analysis reported	NR	(69)
34	Basaleh et al., 2021, Saudi Arabia and Egypt	3% CdO/La-$NaTaO_3$	NR	10	2	90	Vis	100%	0.049	97% after 5 cycles	NR	Production of active species •OH and $•O_2^-$, Z-scheme mechanism, complete mineralization	NR	(21)
35	Alshaikh et al., 2021, Saudi Arabia/Egypt/UK	3 wt% Co_3O_4/ZnO	NR	10	2.4	30	Vis	100%	0.2	The catalyst showed high stability, retaining 97.7% of its initial efficiency after five reuses	93.3% TOC removal	Mechanism reported via Scavenger test and p-n heterojunction diagram	NR	(70)
36	Dong et al., 2021, China	PDI/rGO Composite Film	NR	10	5% mass ratio film	120	Vis	94.31 %	NR	excellent after 3 cycles	almost complete (3D-EEM fluorescence loss)	clean water similar to DI water; main radicals h^+ and $•O_2^-$	NR	(71)

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37	Liu et al., 2021, China	Fe_3O_4@SiO_2@$Bi_2O_2CO_3$-Sepiolite	NR	10	1	90	vis	92.1 %	0.03823	reusability & recyclability	Measured TOC removal (value not numerical)	NR	NR	(72)
38	Bouyarmane et al., 2021, Morocco	TiHAp Nanocomposite	6.1	20	2	15	UV	100 %	0.1765	reusable after calcination 500 °C, no activity loss	High, with 98% COD (Chemical Oxygen Demand) removal after 2 hours	no bacterial inhibition post-treatment (E. coli, B. subtilis, S. aureus = 0 mm zones)	NR	(73)
39	Ahamad et al., 2021, Saudi Arabia/Korea/India	$FeWO_4$/NC-800	8	10	NA	100	Vis/sunlight	92.23%	0.0240	Good	TOC removal reached 65.08% after 100 minutes of irradiation	Degradation pathway reported via MS/MS and DFT calculations	NR	(74)
40	Alahmadi et al., 2020, Saudi Arabia/Egypt	0.6 wt.% Pt@ZnO nanorods	NR	10	1.6	75	Vis	100%	NR	98% after 5th cycle	NR	Complete decomposition, referring to hydroxyl radicals and electron transfer	NR	(75)
41	Balta et al., 2020, Turkey/Slovakia	WTC9	6.3	10	0.4	60	Sunlight	96%	0.058	NR	NR	Only charge transfer mechanism reported	NR	(76)
42	Alhaddad et al., 2020, Saudi Arabia/Egypt	7wt% $ZnMn_2O_4$ZnO	NR	10	1.5	30	Vis	100%	NR	remarkable stability, with its efficiency remaining almost unchanged after five reuses	NR	only charge transfer	NR	(77)
43	Bai et al., 2020, China	Bi_2WO_6/CuS/g-C_3N_4	NR	10	0.1	75	Vis	74.94%	0.026	72.47% after 4th cycle	Mineralization suggested, not quantified	Active species e^-, h^+, O_2^-, complete decomposition pathway identified	NR	(78)
44	Jiménez-Salcedo et al., 2020, Spain	g-C3N4 Nanocomposite	NR	4	0.22	150	Vis	100%	0.035	Stable, reusable	Partial; eight intermediat	Piperazine-ring attack by •OH → defluorination → CO_2 + H_2O + NO_3^- + F^-	NR	(79)

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45	Shoueir et al., 2020, Egypt	PAN@ZnONPs/Bio-MOF	NR	5	0.32	70	Vis	97.2%	0.0503	Maintained > 95 % for 4 cycles	80 % (TOC)	C–F and piperazine cleavage → CO_2 + H_2O (end non-toxic)	NR	(27)
46	Ulyankina et al., 2020, Russia	ZnO NPs (Periodic Electrochemical)	6.5	5	0.5	30	UV	93.6 %	NR	Good (ZnO – LiCl synthesis route)	TOC 51 %	h^+ dominant; low toxicity confirmed	NR	(80)
47	Huang et al., 2020, China	TiO_2@AMSF	6-7	50	0.2	400-450	UV	153 (mg/g)	2.1×10^{-4}	Reusable 3 cycles	COD ≈ 70 %	Hydroxyl + superoxide radicals, “capture & destroy” mechanism	NR	(31)
48	Tahir et al., 2020, Pakistan/Saudi Arabia	Bi_2WO_6/PANI (5%)	4	10	0.5	90	Vis	98%	0.041050	The catalyst showed good stability after four reuse cycles.	NR	Degradation pathway based on HPLC/MS analysis reported	NR	(81)
49	Dong et al., 2020, China	ZSO-C	5.9	10	0.5	100	sunlight	85.9%	1.93×10^{-2}	retained > 90 % activity after 4 cycles	onfirmed nearly complete by TOC reduction	Biotoxicity of CIP toward E. coli eliminated after photocatalysis	NR	(82)
50	Durán-Álvarez et al., 2019, Mexico	AgBr/Ag/Bi2WO6 (Z-scheme)	7	30	0.5	300	Vis	57.6	NR	Stable after 4 cycles	38 % TOC (pure water); complete mineralization (tap water)	degradation into non-toxic products, pathway determined by LC-MS	NR	(39)
51	Malakootian et al., 2019, Iran	$ZnFe_2O_4$@CMC	7	5	1	100	UV-C	87 %	0.43	Excellent after five runs	75 % TOC	Complete mineralization to CO_2 + H_2O confirmed	NR	(83)
52	Yan et al., 2019, China	CNT@MIL-101(Fe)	3	1	0.5	45	Vis	90 %	0.0411	Fe leaching ≈ 50 % lower than MIL-101(Fe)	NR	•OH, oxidation dominant, low-toxicity end products	NR	(84)
53	Behera et al., 2019, India	ZFO@3%RGO	NA	20	1	60	Sunlight	73.4%	0.021	Catalyst stability was tested over four cycles.	NA	Mechanism reported based on Scavenger, NBT, and TA tests	NR	(85)
54	Nasiri et al., 2019, Iran	CuFe2O4@methylcellulose	7	3	0.67	90	UV-C	80.74 %	0.0184	4 cycles, ferromagnetic separation	68.26 % COD	Radical oxidation (•OH), non-toxic residues	NR	(86)
55	Hassani et al., 2018, Iran/Turkey	TiO2/MMT nanocomposite	7.16	25.80	0.07	29.48	UV-A	95.78%	NR	NR	high (near-complete)	•OH, $O2^-$, homogeneous and heterogeneous mechanisms of photocatalysis+ozone	NR	(87)

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56	Khoshnamvand et al., 2018, Iran	CuO Nanoparticles	8.17	11.2	0.08	60	UV-C	98.9%	NR	NR	Based on COD removal	NA	NR	(88)
57	Xing et al., 2018, China	N-TiO_2/Glass Spheres	7	20	3	90	Vis	93.5%	0.02859	>90 % activity after 5 cycles	NR	7 degradation products detected; toxicity reduced	NR	(89)
58	Eskandari et al., 2018, Iran	Synthetic ZnO	5	10	0.15	140	UVC	100%	0.037	High (reusable)	NR	no interference from anions (Cl^-, SO_4^{2-}, etc.)	NR	(90)
59	El Bekkali et al., 2018, Morocco/France	25ZnHAp / 40ZnHAp	NR	20	2	20	UV A-B-C	100%	NR	NR	CIP disappeared quickly; intermediates likely stayed on the surface, showing degradation but incomplete mineralization	Proposed degradation pathway based on HPLC data reported	NR	(91)
60	Das et al., 2018, India/Sweden	Fe-ZnO nanoparticles	9	10	0.15	210	sunlight	100 %	NA	Stable under sunlight; reusable	NA	Hydroxyl radical (•OH) and Fenton process	NR	(92)
61	Sayed et al., 2018, Pakistan/China	PVA-assisted TiO2/Ti + PMS	6.3	5	NR	60	sunlight	98.3%	0.0582	> 90 % after 5 cycles	82 % (TOC)	C7–N and piperazine bond cleavage → non-toxic products	NR	(93)
62	Kumar et al., 2017, India	RPC	6.1	20	1	90	sunlight	92.8%	0.026	5 reuse cycles-efficiency dropped slightly from 91.8 → 86.4 %	44 % COD	Non-toxic intermediates; •OH and $O_2^{\bullet-}$ radicals dominate oxidation Pathway leads to ring-opened carboxylic acids and CO_2	NR	(94)
63	Bojer et al., 2017, Denmark	Mesostructured ZnO Nanotubes	8	2×10^{-5} ($Mol.L^{-1}$)	14 (mg)	120	sunlight	12%	9.61×10^{-4}	no catalyst loss in flow operation	confirmed by UV–Vis complete removal	not tested (only noted environmental relevance)	NR	(95)
64	Genç, 2016, Turkey	TiO_2	9	10	0.8	30	UV	97.1 %	0.445	NR	40.3% COD	Two-stage oxidation → non-toxic acids (1,4-benzenedicarboxylic acid, etc.)	NR	(96)
65	Zhang et al., 2015, China	BiOBr	9	5	0.5	140	Vis	100 %	0.037	Bi^{3+} leaching < 2 % after 30 h	TOC 40 %	Low toxicity; main intermediate = desethylene CIP	NR	(97)
66	Lima et al., 2014, Portugal	Fe2+ (homogeneous) / Magnetite nanoparticles (heterogeneous)	2.8 and 6.8	10	4 and 0.004	1.8	sunlight	85% and 55%	NR	Stable, easily magnetically recovered	NR	•OH, radical oxidation; non-toxic effluent	NR	(98)

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67	Paul et al., 2010, United Kingdom	TiO_2 Hombikat UV100 (Anatase)	6	33.1	0.5	25	UV-A	>99%	NA	NR	NH_3 and F^- released; partial mineralization	Transformation products had negligible antibacterial activity	NR	(99)
68	El-Kemary et al., 2010, Egypt	ZnO nanoparticles	10	5	0.02	60	UV	50%	0.004 ±3 0.0023	NR	NR	Removal of functional groups, route based on optical decomposition	NR	(36)
69	An et al., 2010, China	TiO_2 Degussa P25	9	33.1	1.5	30	UV	99%	0.38	NR	NR	Direct photo-hole oxidation and hydroxyl radical (˙OH) attack. Seven intermediates were identified	NR	(100)

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