

Critical review on photocatalytic removal of Ciprofloxacin from water and wastewater: Implications for environmental management and wastewater treatment

Hossein Farash Khayalo^{1,2}, Mojtaba Yeganeh^{1,2}, Ali Esrafil^{*1,2}

¹ Research Center for Environmental Health Technology, School of Public Health, Iran University of Medical Sciences, Tehran, Iran

² Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran

*Corresponding Author Email: a_esrafil@yahoo.com

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Abstract

The increasing contamination of water bodies by fluoroquinolone antibiotics poses severe environmental risks, particularly regarding antibiotic resistance. This critical review evaluates the efficiency of advanced photocatalytic systems for the removal of Ciprofloxacin (CIP) from aqueous matrices, focusing on the transition from laboratory-scale studies to real-world environmental management.

A systematic literature search was conducted across Scopus, Web of Science, PubMed, and Google Scholar databases for peer-reviewed articles published between January 2020 and December 2025. The search was applied to "Title, Abstract, and Keywords" fields. After rigorous screening of 847 initially identified records based on predefined inclusion/exclusion criteria, 94 relevant articles were selected for critical analysis.

The analysis reveals that while traditional metal oxides are limited, novel heterojunctions achieve up to 100% CIP removal under visible light. However, a significant discrepancy exists between parent compound removal (often >90%) and complete mineralization (typically only 40–60%), leading to the accumulation of toxic intermediates. Consequently, relying solely on removal efficiency is insufficient for sustainable environmental management. Future research must prioritize toxicity monitoring and the validation of catalysts in real wastewater matrices to bridge the gap between laboratory success and industrial application.

Keywords: Photocatalysis, Ciprofloxacin, Advanced Oxidation Processes, Wastewater Treatment, Environmental Management, Toxicity Assessment, Emerging Contaminants.

Introduction

The escalating crisis of freshwater scarcity and the deterioration of water quality have become pivotal challenges for sustainable development in the 21st century (1, 2). Among the myriad of emerging contaminants, pharmaceutical active compounds [PhACs] have garnered significant attention due to their continuous release and pseudo-persistence in aquatic ecosystems (3). Antibiotics, in particular, represent a critical class of these pollutants. Their extensive usage in human therapy, veterinary medicine, and aquaculture has led to their ubiquitous presence in surface water, groundwater, and even drinking water sources (4, 5). Fluoroquinolones [FQs] are among the most prescribed antibiotics worldwide (6, 7). Ciprofloxacin [CIP], a second-generation fluoroquinolone, is of particular concern due to its complex chemical structure and high stability (8). Unlike biodegradable organic matter, CIP resists natural attenuation and tends to accumulate in the environment (9, 10). Recent studies indicate that residual concentrations of CIP in water bodies can trigger toxicological effects on aquatic organisms, ranging from inhibition of photosynthesis in algae to genotoxicity in fish (11, 12). More alarmingly, the sub-lethal exposure of bacteria to CIP promotes the proliferation of Antibiotic Resistance Genes [ARGs], which poses a catastrophic threat to global public health (13, 14). Despite the environmental risks, conventional Wastewater Treatment Plants [WWTPs] are not designed to eliminate recalcitrant pharmaceuticals (15, 16). Traditional methods such as biological activated sludge rely on microbial degradation, which is often inhibited by the antibiotic nature of CIP itself (17). Physical separation techniques like adsorption or membrane filtration, while effective in removing the parent compound, often result in the generation of concentrated sludge or secondary pollution without truly destroying the contaminant (18). Thus, there is an urgent need for destructive technologies that can ensure the complete mineralization of CIP into harmless end-products. Advanced Oxidation Processes

[AOPs], specifically heterogeneous photocatalysis, have emerged as a promising technology for the remediation of antibiotic-contaminated water (19). This process utilizes light energy to activate a semiconductor, generating electron-hole pairs that produce reactive oxygen species [ROS], such as hydroxyl radicals [$\bullet\text{OH}$] and superoxide anions [$\bullet\text{O}_2^-$] (20). These radicals are non-selective and capable of attacking the fluoroquinolone ring structure, leading to its degradation (20, 21).

Although Titanium Dioxide [TiO_2] has been the benchmark photocatalyst, its practical application is hindered by its wide bandgap and limited activity under visible light (22). Consequently, recent research [2020–2025] has shifted towards developing visible-light-driven photocatalysts, heterojunctions [e.g., Z-scheme], and magnetic composites to enhance solar energy utilization and catalyst recovery. This review critically analyzes the state-of-the-art photocatalytic systems for CIP removal, focusing on visible-light-driven semiconductors, Z-scheme heterojunctions, magnetic composites (e.g., Fe_3O_4 -based), and carbon-based nanocomposites like CQDs and g-C $_3\text{N}_4$. Unlike previous reviews, this paper focuses on the gap between laboratory efficiency and real-world application, evaluating the toxicity of degradation intermediates, the influence of water matrices, and the economic feasibility of novel catalysts to provide a roadmap for future environmental management.

Review methodology

This critical review was conducted through a systematic literature search to identify relevant studies on the photocatalytic degradation of Ciprofloxacin (CIP). The Scopus, Web of Science, PubMed, and Google Scholar databases were searched for peer-reviewed articles published between January 2020 and December 2025. The following keywords and Boolean operators were applied: ("Ciprofloxacin" OR "CIP") AND ("photocatalysis" OR "photocatalytic degradation" OR "advanced oxidation processes") AND ("wastewater" OR "water treatment") AND ("visible light" OR

"heterojunction" OR "Z-scheme"). The search was specifically applied to the "Title, Abstract, and Keywords" fields within each database to ensure the relevance of the retrieved literature.

The initial search yielded 847 records. After removing duplicates (n=214), 633 articles underwent title and abstract screening. Review articles, conference proceedings, and non-English studies were excluded (n=479). Subsequently, 154 full-text articles were assessed for eligibility. Studies were included if they: (i) reported original experimental data on CIP photocatalytic degradation; (ii) utilized

heterogeneous photocatalysts; and (iii) provided quantitative efficiency data. Studies focusing solely on adsorption or homogeneous photocatalysis were excluded. Finally, 34 articles met the inclusion criteria and were critically analyzed in this review. As shown in Figure 1, a total of 34 articles were eventually selected for critical analysis after removing duplicates and applying eligibility criteria. Data extraction focused on catalyst type, operational parameters, degradation kinetics, mineralization rates, and toxicity assessment.

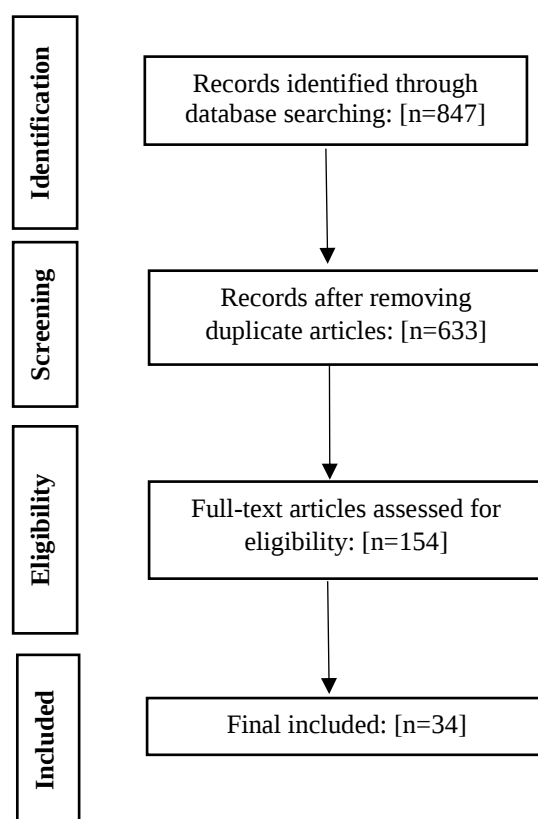


Figure 1. Flowchart of the study selection process based on inclusion and exclusion criteria.

Photocatalytic systems and efficiency

Mechanistically, photocatalysis relies on the excitation of electrons from the valence band to the conduction band upon light absorption, creating reactive holes. These charge carriers interact with water and oxygen to generate reactive oxygen species (ROS), which non-selectively attack the molecular structure of CIP, leading to its degradation.

The development of efficient photocatalytic systems for the removal of Ciprofloxacin [CIP]

has evolved significantly from simple metal oxides to complex nanocomposites. The primary goal of recent research [2020–2025] has been to overcome the wide bandgap limitation of traditional semiconductors and to inhibit the rapid recombination of electron-hole pairs, which severely limits quantum efficiency. To evaluate the performance of the discussed technologies, a comparison of various photocatalytic systems reported in recent literature is presented in Table 1. As shown, composite photocatalysts generally

Table 1. Comparison of photocatalytic degradation efficiency of Ciprofloxacin using different photocatalysts reported in recent studies (22).

Photocatalyst	Light Source	Time (min)	Efficiency (%)
N-Cu-TiO ₂ /CQD	Visible	60	100
Ag/TiO ₂	UV	120	92
Bi ₂ WO ₆ /CNT	Visible	180	85
ZnO/Ag	UV	90	95
g-C ₃ N ₄ /Fe ₃ O ₄	Visible	150	88

exhibit superior degradation efficiency under visible light compared to single-component systems.

Metal oxide-based photocatalysts and their limitations

Titanium dioxide [TiO₂] and Zinc oxide [ZnO] act as the cornerstone of photocatalytic research due to their favorable band-edge positions, non-toxicity, and low cost. However, a critical analysis of recent studies highlights significant drawbacks in their pristine forms.

Bandgap limitation

Pure TiO₂ acts primarily under UV irradiation, which accounts for only 4% of the solar spectrum. This limits its practical application in sustainable, solar-driven treatment plants (22).

Recombination rate

ZnO, despite having higher electron mobility than TiO₂, suffers from fast charge carrier recombination. Furthermore, ZnO is susceptible to photo corrosion in acidic or alkaline environments, leading to the dissolution of the catalyst and secondary pollution by Zinc ions (5, 17). To address these issues, doping with transition metals [e.g., Ag, Fe] has been employed to introduce intermediate energy levels, thereby narrowing the bandgap and extending absorption into the visible region (4).

Novel composites

Heterojunctions and Magnetic Recovery
The most promising advancements involve the

construction of heterojunctions, such as the Z-scheme or S-scheme systems (23). These structures not only broaden the light absorption range but also spatially separate the oxidation and reduction sites, preserving the high redox potential of the charge carriers (24).

Z-scheme systems

Recent work has demonstrated that Z-scheme photocatalysts [e.g., coupling g-C₃N₄ with metal oxides] facilitate efficient charge transfer, significantly enhancing CIP degradation rates compared to single-component systems (3).

Magnetic composites

A major operational challenge in slurry-based photocatalysis is the separation of the catalyst after treatment. Incorporating magnetic nanoparticles [like Fe₃O₄ or CoFe₂O₄] into the catalyst structure allows for easy recovery using an external magnetic field. This innovation is crucial for industrial upscaling and preventing the release of nanoparticles into the ecosystem (8, 21).

Adsorption-photocatalysis synergy

Carbon-based supports, such as Activated Carbon or Graphene Oxide, have been utilized to increase the specific surface area. These composites create a synergistic effect where CIP is first adsorbed onto the carbon surface and subsequently degraded by the photocatalyst, improving mass transfer kinetics.

Influence of operational parameters

Optimizing operational parameters is essential for maximizing removal efficiency while minimizing energy consumption and

Effect of pH and surface charge interactions

The pH of the solution is arguably the most critical parameter as it dictates the surface charge of the photocatalyst [via Point of Zero Charge, PZC] and the speciation of Ciprofloxacin. CIP is an amphoteric molecule with two pKa values [approximately 6.0 and 8.8]. The pH dictates the surface charge of the catalyst through the protonation or deprotonation of surface functional groups. When the pH is below the Point of Zero Charge (PZC), the surface becomes positively charged due to excess protons, whereas at $\text{pH} > \text{PZC}$, it becomes negatively charged. Since CIP speciation also changes with pH (cationic, zwitterionic, or anionic), the solution pH determines the strength of the electrostatic attraction or repulsion between the contaminant and the catalyst, directly influencing the adsorption and subsequent degradation rates.

Electrostatic interactions

In acidic media [$\text{pH} < 6$], CIP exists as a cation, while in alkaline media [$\text{pH} > 9$], it acts as an anion. Maximum degradation is often reported near neutral pH [$\text{pH} 7\text{--}8$], where CIP is in its zwitterionic form. At this range, the electrostatic repulsion between the catalyst surface and the antibiotic is minimized, facilitating better adsorption (11).

Catalyst stability

Extreme pH values can also affect the structural stability of the catalyst. For instance, ZnO-based catalysts may dissolve at very low pH, causing a drastic drop in efficiency (25).

Catalyst dosage and screening effect

Increasing the catalyst dosage initially enhances the degradation efficiency by providing a higher number of active sites for photon absorption and reactant adsorption. However, the relationship is not linear. Beyond an optimal threshold, the suspension becomes overly turbid, leading to a significant "shielding effect." This excess of particles scatters the

costs. The reviewed literature emphasizes the complex interplay between solution chemistry and catalyst properties.

incident light and reduces the optical path length, preventing photons from reaching the catalyst active sites located deeper in the reactor. Consequently, a portion of the catalyst remains unionized, which not only diminishes the specific reaction rate but also renders the process economically inefficient due to material wastage.

The screening effects

Beyond an optimum concentration [typically 0.5 – 1.5 g/L depending on the reactor], the excess catalyst particles cause light scattering and increase the turbidity of the solution. This screening effect prevents light from penetrating deeper into the reactor, reducing the overall photo-activation rate (4, 5).

Initial concentration and active sites saturation

At high initial CIP concentrations, the degradation rate often decreases. This is attributed to the saturation of active sites on the catalyst surface by CIP molecules, which hinders the adsorption of water and oxygen needed to generate hydroxyl and superoxide radicals. Additionally, high concentrations of CIP can absorb photons directly, competing with the catalyst for light energy (17).

Degradation mechanisms and kinetics

A thorough understanding of the reaction mechanism is vital for predicting the fate of the contaminant. Most studies in the reviewed period fit the experimental data to the Langmuir-Hinshelwood pseudo-first-order kinetic model, indicating that the reaction occurs on the surface of the catalyst.

Role of reactive oxygen species [ROS]

To identify the primary active species, radical scavenging experiments using EDTA [for holes], IPA [for $\bullet\text{OH}$], and BQ [for $\bullet\text{O}_2^-$] are standard protocols. As depicted in Figure 2, upon irradiation, electrons are excited to the conduction band, leaving holes in the valence band. These charge carriers react with water

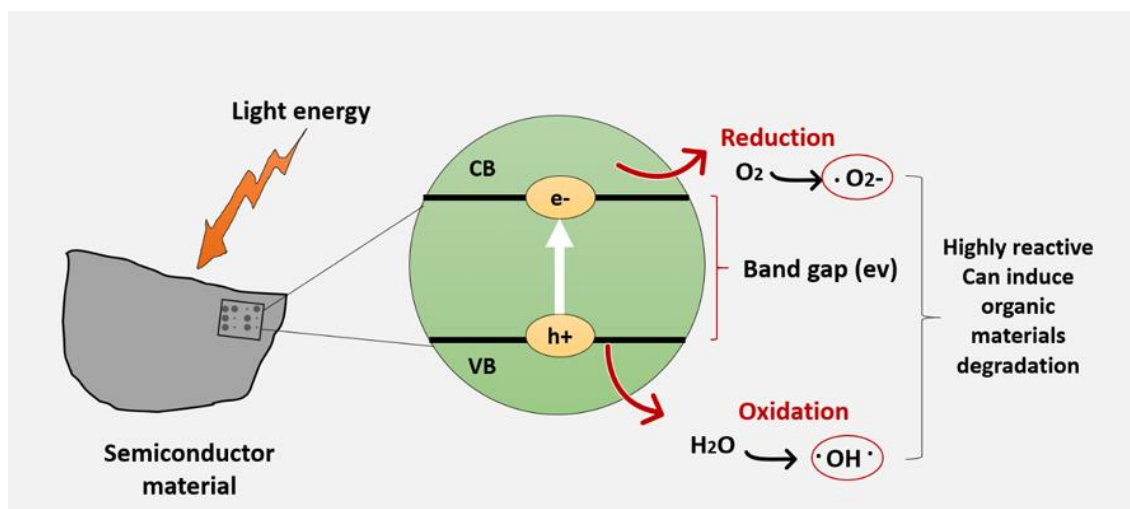


Figure 2. Schematic illustration of the general photocatalytic mechanism involving charge carrier generation and ROS formation upon light irradiation (3).

and oxygen to produce hydroxyl radicals [$\bullet\text{OH}$] and superoxide anions [$\bullet\text{O}_2^-$], which are the primary oxidants for CIP degradation.

Dominant radicals

The reviewed papers consistently identify holes [h^+] and superoxide anions [$\bullet\text{O}_2^-$] as the main drivers for CIP degradation in visible-light systems, while hydroxyl radicals [$\bullet\text{OH}$] play a significant role in UV-based or Z-scheme systems (20).

Mechanism

The photogenerated electrons in the conduction band reduce adsorbed O_2 to $\bullet\text{O}_2^-$, while holes in the valence band oxidize H_2O to $\bullet\text{OH}$. These Reactive Oxygen Species [ROS] then attack the fluoroquinolone ring and the piperazine moiety of CIP (3).

Mineralization vs. primary degradation

A critical gap identified in the literature is the distinction between primary degradation (removal of the parent compound) and complete mineralization (conversion to CO_2 , H_2O , and inorganic ions) (26, 27). While analytical techniques like HPLC or UV-Vis spectrophotometry effectively monitor the

The ultimate goal of wastewater treatment is to protect the aquatic ecosystem. Therefore, evaluating the Green aspect of the

disappearance of the parent Ciprofloxacin molecule, they fail to quantify the remaining organic by-products (28, 29). Complete mineralization is a more accurate indicator of water safety, typically measured by Total Organic Carbon (TOC) analysis. A recurring limitation in the reviewed studies is the significant discrepancy between high CIP removal rates (often >90%) and relatively low TOC removal efficiencies (typically 40–60%). This suggests that stable organic intermediates, such as carboxylic acids or defluorinated derivatives, persist in the treated effluent, indicating that the pollutant has been transformed rather than eliminated.

TOC removal

While HPLC analysis often shows >90% removal of CIP, Total Organic Carbon [TOC] analysis frequently reveals much lower mineralization rates [e.g., 40-60%]. This indicates that the antibiotic is merely broken down into smaller organic intermediates rather than being fully eliminated (13).

Implications for environmental management [Critical analysis]

photocatalytic process is as important as the removal efficiency (30, 31). Toxicity of Intermediate Products One of the most

concerning findings in recent literature is the potential increase in effluent toxicity during treatment (32).

Transformation products [TPs]

The photocatalytic breakdown of CIP involves defluorination and piperazine ring cleavage, which can generate intermediate compounds (33). Some studies utilizing *Vibrio fischeri* or *E. coli* bioassays have reported that these intermediates can be more toxic than the parent CIP molecule, particularly in the early stages of degradation (13, 14). The degradation process leads to the formation of several intermediate products. As shown in Figure 3,

the attack of reactive species results in the cleavage of the piperazine ring and defluorination, producing a variety of transformation products before complete mineralization is achieved. Recent studies using bioassays like *Vibrio fischeri* have demonstrated that intermediates formed via piperazine ring cleavage can exhibit higher genotoxicity and growth inhibition in aquatic organisms than the parent CIP. For instance, defluorinated transformation products can remain bioactive, contributing to the proliferation of antibiotic-resistant genes (ARGs) in the environment, which poses a long-term threat to aquatic biodiversity.

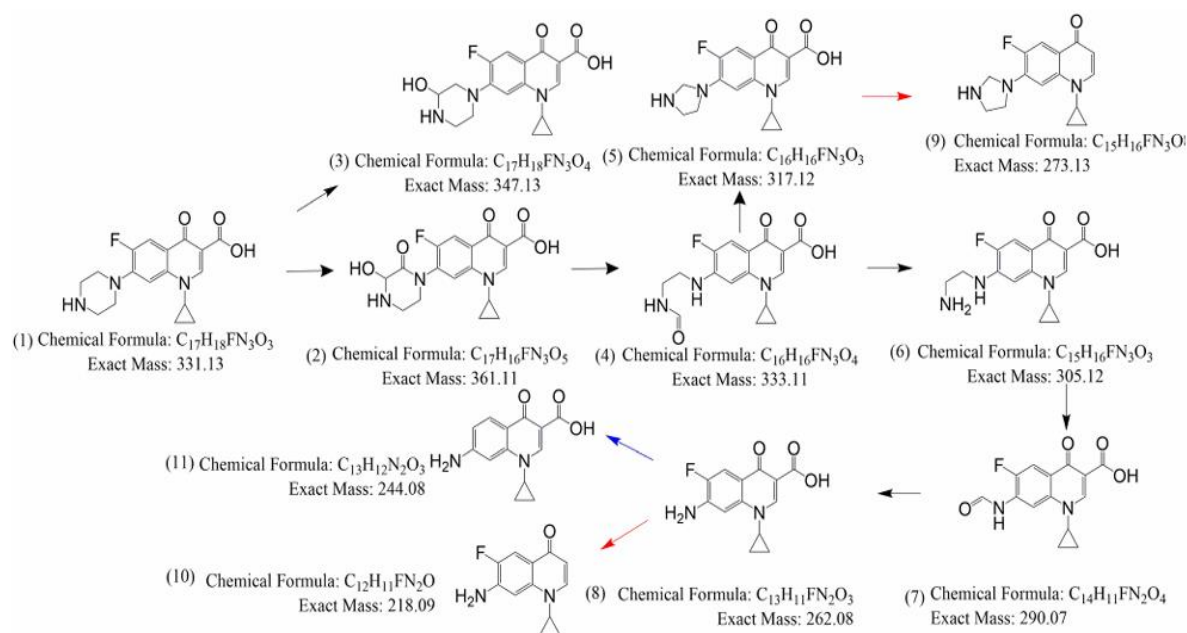


Figure 3. Proposed degradation pathways of Ciprofloxacin showing the formation of various intermediate by-products through piperazine ring oxidation and defluorination steps (18).

Implication

This observation has profound implications for the design and operation of advanced wastewater treatment plants. The results suggest that short hydraulic retention times (HRT) might be detrimental to the environment, as they could release an effluent containing a cocktail of transformation products that are potentially more hazardous

than the original influent. Consequently, an effective environmental management strategy must move beyond simple contaminant removal metrics. Instead, it requires a paradigm shift towards effluent detoxification, ensuring sufficient reaction time to achieve the breakdown of these toxic intermediates. Furthermore, this necessitates the integration of biological toxicity assays alongside standard

chemical analysis in regulatory monitoring protocols to prevent the release of deceptively treated water into aquatic ecosystems.

Matrix effects in real wastewater

While laboratory results in distilled water are promising, the translation to real-world application is severely hindered by the complex chemistry of wastewater matrices. Real effluents contain ubiquitous inorganic anions (e.g., Cl^- , SO_4^{2-} , HCO_3^-) and Natural Organic Matter (NOM). These constituents primarily act as radical scavengers, competing with CIP for the photogenerated holes and hydroxyl radicals. For instance, bicarbonate ions react with $\bullet\text{OH}$ to form carbonate radicals ($\bullet\text{CO}_3^-$), which possess a much lower oxidation potential, thereby retarding the degradation kinetics. Furthermore, the presence of NOM introduces an "inner filter effect", absorbing UV/visible light and reducing photon penetration, while simultaneously fouling the catalyst surface through competitive adsorption. Consequently, efficiency drops observed in real matrices (often 30–50% lower than in Milli-Q water) underscore the necessity of validating photocatalysts under realistic conditions rather than idealized ones.

Radical scavenging

Real wastewater contains inorganic anions [e.g., Cl^- , SO_4^{2-} , HCO_3^-] and Natural Organic Matter [NOM]. These substances act as scavengers for $\bullet\text{OH}$ radicals, significantly reducing the treatment efficiency. For example, chloride ions can react with hydroxyl radicals to form less reactive chlorine species, thereby inhibiting the degradation process (11, 17).

Future direction

Future research must prioritize the testing of photocatalysts in real hospital effluents or municipal wastewater to validate their robustness and viability for large-scale environmental management. Additionally, comprehensive techno-economic analyses are indispensable to assess the cost-effectiveness of these advanced systems compared to established technologies like ozonation. Finally, the transition from batch laboratory experiments to continuous-flow reactor designs

is a prerequisite for bridging the gap between academic research and industrial implementation.

Conclusion

This critical review has systematically evaluated the recent advancements (2020–2025) in photocatalytic systems developed for the removal of Ciprofloxacin from aqueous matrices. The findings demonstrate a significant paradigm shift from traditional wide-bandgap metal oxides toward visible-light-driven heterojunctions and magnetic nanocomposites, which offer enhanced solar energy utilization and improved catalyst recoverability. However, the analysis reveals that operational parameters particularly solution pH and catalyst dosage remain decisive factors governing degradation kinetics, with optimal performance typically observed under near-neutral conditions.

A major concern identified throughout the literature is the substantial discrepancy between parent compound removal and complete mineralization. While numerous studies report >90% CIP degradation within short irradiation times, Total Organic Carbon (TOC) removal rarely exceeds 60–70%, indicating the persistence of stable organic intermediates. More critically, toxicological assessments utilizing *Vibrio fischeri* and *E. coli* bioassays have demonstrated that these transformation products can exhibit higher ecotoxicity than the parent antibiotic itself. This finding fundamentally challenges the adequacy of relying solely on chromatographic removal efficiencies as a metric for treatment success. Furthermore, the translation of laboratory-scale successes to real-world applications remains severely constrained by the complexity of actual wastewater matrices. The presence of inorganic anions and natural organic matter substantially suppresses degradation kinetics through radical scavenging and light attenuation effects factors routinely overlooked in idealized distilled water experiments.

Consequently, future research agendas must prioritize three interconnected frontiers: (i) integration of comprehensive toxicity monitoring into standard photocatalytic

assessment protocols; (ii) validation of catalyst performance under realistic wastewater conditions using continuous-flow reactor configurations; and (iii) rigorous techno-economic analyses to establish the competitiveness of photocatalytic processes against established technologies such as ozonation and activated carbon adsorption. Without such paradigm shifts, the gap between academic innovation and industrial implementation will persist, limiting the contribution of photocatalysis to sustainable environmental management and public health protection.

Furthermore, an often-overlooked dimension in photocatalytic wastewater treatment is the carbon footprint of the technology itself. The synthesis of nanomaterials, operation of high-energy light sources, and catalyst recovery systems contribute to indirect greenhouse gas emissions, potentially undermining the environmental benefits of contaminant

removal. Recent evidence indicates that energy-intensive technologies despite their functional advantages can impose significant hidden climate costs (34). Photocatalysis, particularly under continuous artificial irradiation, faces analogous sustainability challenges. Therefore, future research should integrate life-cycle carbon accounting and energy efficiency metrics into the optimization of photocatalytic systems, ensuring that water remediation technologies align with global decarbonization targets.

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Conflict of interest

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Abbreviations

Abbreviation	Full Form
AOP	Advanced Oxidation Process
ARG	Antibiotic Resistance Gene
CIP	Ciprofloxacin
CQD	Carbon Quantum Dot
FQ	Fluoroquinolone
HPLC	High-Performance Liquid Chromatography
NOM	Natural Organic Matter
PZC	Point of Zero Charge
ROS	Reactive Oxygen Species
TOC	Total Organic Carbon
TP	Transformation Product
WWTP	Wastewater Treatment Plant

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