

Review

Advances in Photocatalytic Degradation of Crystal Violet Using ZnO-Based Nanomaterials and Optimization Possibilities: A Review

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Abstract

The photocatalytic degradation of Crystal Violet (CV) using ZnO-based nanomaterials presents a promising solution for addressing water pollution caused by synthetic dyes. This review highlights the exceptional efficiency of ZnO and its modified forms—such as doped, composite, and heterostructured variants—in degrading CV under both ultraviolet (UV) and solar irradiation. Key advancements include strategic bandgap engineering through doping (e.g., Cd, Mn, Co), innovative heterojunction designs (e.g., n-ZnO/p-Cu₂O, g-C₃N₄/ZnO), and composite formations with graphene oxide, which collectively enhance visible-light absorption and minimize charge recombination. The degradation mechanism, primarily driven by hydroxyl and superoxide radicals, leads to the complete mineralization of CV into non-toxic byproducts. Furthermore, this review emphasizes the emerging role of Artificial Neural Networks (ANNs) as superior tools for optimizing degradation parameters, demonstrating higher predictive accuracy and scalability compared to traditional methods like Response Surface Methodology (RSM). Potential operational challenges and future directions—including machine learning-driven optimization, real-effluent testing potential, and the development of solar-active catalysts—are further discussed. This work not only consolidates recent breakthroughs in ZnO-based photocatalysis but also provides a forward-looking perspective on sustainable wastewater treatment strategies.

Keywords: ZnO; crystal violet; photocatalytic degradation; advanced oxidation processes; artificial neural networks; wastewater treatment



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1. Introduction

Water pollution has emerged as one of the most pressing threats to sustainable development and human prosperity, due to rising industrial activity and population growth. According to reports by the United Nations, over two billion people worldwide lack access to safe drinking water, with contaminated water sources contributing to millions of deaths annually [1]. Harmful contaminants such as heavy metals, pesticides, pharmaceutical residues, and various organic compounds negatively impact ecosystems and public health. Thus, developing efficient and sustainable wastewater treatment and recycling methods is crucial for safeguarding the planet's future [1,2].

Agricultural and industrial expansion has become a major driver of freshwater resource depletion and degradation. Pollution from organic compounds, industrial discharge, farming practices, and urban waste presents a severe worldwide challenge. At

the same time, poor regulation and inefficiencies in the global textile industry result in nearly 200,000 tons of synthetic dyes being released into the environment each year. Dyeing wastewater is particularly problematic due to its complex composition, intense coloration, and high pollutant concentration [3].

Among numerous hazardous effluents from various industries, textile wastewater, in particular, contains toxic dyes that endanger aquatic life and human health [4]. Among these, triphenylmethane dyes like crystal violet (CV)—widely used in food, cosmetics, leather, paper, and pharmaceuticals—pose severe environmental risks. Due to their low biodegradability, conventional treatment methods often fail to remove them effectively. When discharged into water systems, these dyes inhibit photosynthesis, reduce oxygen levels, and cause endocrine disruption, feminization in aquatic species, and bioaccumulation in the food chain [5].

Cationic dyes such as CV are, in general, especially harmful due to their ability to bind to cell membranes, penetrate tissues, and accumulate in organisms. Even at 1 ppm, CV can block light transmission, disrupting aquatic ecosystems. In humans, exposure leads to eye/skin irritation, nausea, respiratory distress, and potential carcinogenic effects, with an oral LD₅₀ of 1.2 g/kg in mice [4]. Despite its widespread use as a disinfectant, pH indicator, and biomedical marker, CV is a proven mitotic poison, tumor promoter, and clastogen. Since replacing CV entirely is impractical, developing efficient degradation methods—breaking it into non-toxic compounds like CO₂ and H₂O—is critical before wastewater discharge [6].

Addressing the long-term presence of synthetic dyes in ecosystems is critical, yet the degradation of these compounds remains highly challenging due to their stable aromatic molecular structures [1]. Various conventional and advanced techniques are employed to remove dyes from wastewater, including physicochemical methods (coagulation, membrane filtration, activated carbon adsorption, electrochemical oxidation, wet oxidation), biological treatments (aerobic/anaerobic degradation), and chemical processes (oxidation). These approaches are often combined depending on contamination levels and specific requirements [3]. For textile wastewater, common treatments like flocculation, coagulation, adsorption, and membrane filtration primarily transfer pollutants from liquid to solid phases without full degradation, merely concentrating contaminants rather than eliminating them. While effective for heavy metals and some dyes, such methods fail to completely neutralize persistent toxins like CV due to its high stability and resistance to biological breakdown (a trait largely attributed to the presence of its stable dimethylamino groups). For example, with the usage of activated carbon, high removal efficiencies can be achieved; however, a contaminant is not degraded, and this necessitates costly regeneration processes for the spent adsorbent and creates a risk of secondary pollution. Chemical oxidation with agents like chlorine or ozone can achieve high rates of decolorization and even mineralization, the excessive oxidant demands required to treat CV make this approach economically unsustainable for large-scale implementation.

Advanced oxidation processes (AOPs) have become recognized as a highly effective wastewater treatment technology. In these processes, highly reactive radicals are produced, such as hydroxyl radicals, that break down dyes into water, carbon dioxide, and less toxic byproducts. Compared to traditional methods, AOPs provide better efficiency in breaking down stubborn compounds like CV, making them a practical alternative despite higher initial costs [3,7,8].

AOPs rely on homogeneous and heterogeneous photocatalysis for water treatment due to their high efficiency, environmental compatibility, and ability to degrade persistent pollutants. Molecular or inorganic catalysts (transition-metal complexes, dyes, and pigments) dissolve completely in wastewater, in systems where homogeneous photocatalysis

occurs, enabling rapid reaction kinetics and high conversion rates per catalytic molecule. A significant drawback in this case is the complex and costly catalyst recovery [6,9,10]. Heterogeneous photocatalysis overcomes these limitations by employing solid-phase catalysts that remain separable from the liquid reaction medium. This method allows pollutants to adsorb onto the catalyst surface, where they undergo efficient degradation under solar/UV light. This catalytic approach offers significant practical advantages, primarily through its use of stable, non-toxic catalysts (e.g., metal oxides) that maintain high reusability with minimal activity loss. Its key strength is the complete mineralization of dyes into CO_2 , which effectively eliminates secondary pollution. Furthermore, the reliance on commercially available materials ensures the process is both cost-effective and readily scalable. Heterogeneous systems are particularly promising for dye removal, as they operate under ambient conditions while maintaining catalytic performance over multiple cycles [8,11–13].

In the case of heterogeneous photocatalysis, recent research has focused on developing efficient photocatalysts—including TiO_2 , ZnO , CdS , Ag_3PO_4 , WO_3 , $\text{g-C}_3\text{N}_4$, and metal–organic frameworks (MOFs)—to degrade synthetic dyes in aqueous environments. These materials exhibit exceptional photocatalytic activity, chemical stability, and broad-spectrum solar light utilization, making them ideal for sustainable wastewater remediation. By optimizing these materials—through doping, heterojunction design, or hybrid composites—researchers aim to overcome limitations (e.g., electron-hole recombination, durability) while maximizing degradation rates for industrial-scale applications [14]. ZnO stands out as a premier photocatalyst due to its exceptional stability, high electron mobility ($200\text{--}1000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), and strong oxidative potential (+2.7 V vs. SHE—Standard Hydrogen Electrode). As an n-type semiconductor with a large exciton binding energy (60 meV) and a 3.3 eV bandgap, it offers remarkable photosensitivity and sustained adsorption efficiency. These properties, combined with its eco-friendly nature and various doping strategies, make ZnO ideal for photocatalytic applications [15–20].

Solar energy in the photocatalytic degradation of various pollutants, as the optimal choice for driving eco-friendly chemical processes, offers a clean, renewable, and cost-effective solution for photocatalytic applications [21]. With an irradiance of $1.8\text{--}2.6\text{ kW/m}^2$ (depending on location), solar power far exceeds global energy demands when efficiently converted. Its growing adoption addresses critical environmental challenges—reducing reliance on fossil fuels while mitigating CO_2 emissions [22]. Compared to conventional methods like adsorption or ozonation, solar-driven processes provide superior sustainability for pollutant degradation.

This review provides a comprehensive analysis of recent advances in ZnO nanoparticle-based photocatalysts (pristine, doped, and structurally modified) for degrading CV under UV and natural sunlight. By evaluating material composition, synthesis methods, and modifications, the paper presents the factors that govern degradation efficiency. With growing emphasis on sustainable wastewater treatment, this work highlights ZnO -based nanomaterials as promising solar-driven photocatalysts for the degradation of CV and similar pollutants. While numerous studies assess ZnO performance under controlled UV irradiation, significant gaps remain when it comes to limited comparative studies on doped ZnO -based composites in solar photocatalysis, insufficient data on synthesis methods on photocatalytic activity and reusability in these cases and/or lack of machine learning applications for optimizing sunlight-driven processes.

Latest reviews on ZnO -based photocatalysts reveal a mixture of valuable contributions and notable shortcomings. Many papers provide a broad overview and succeed in presenting ZnO photocatalysts as a promising platform for water treatment, but the analysis remains largely descriptive, offering limited methodological depth [23]. Even with a more constructive approach, highlighting preparation methods and applications with

clear emphasis on advantages and potential impacts, though at times the discussion leans toward enumeration of results rather than interpretive synthesis [24]. Additionally, there is an inability to establish in-depth comparisons between catalytic performances reported in the literature [25], coupled with a relative lack of focus on the mechanistic insights underlying photocatalytic processes [26]. Some studies strictly discuss experiments with model pollutants under controlled conditions, while real effluent treatment still poses challenges due to complex chemistries and fluctuating parameters such as pH, ionic strength, and temperature [26,27]. Although the body of literature on ZnO photocatalysts is growing and increasingly diverse, many reviews tend to favor descriptive compilation without addressing toxicological assessment of intermediates, scalability challenges, underexplored operational parameters, real effluent challenges, and other potential novel insights. Focusing on specific pollutants and the latest research on degradation in the presence of novel catalysts, this paper integrates three key, previously disconnected areas: Advanced ZnO material engineering, the complex degradation pathway of CV, and ANN-based optimization. Presented information should provide a clear, organized, and critical overview of this landscape as a valuable contribution that establishes the necessary groundwork for future quantitative modeling efforts. This review bridges these gaps by analyzing degradation kinetics and catalyst stability, evaluating practical feasibility for water remediation, and providing guidelines for developing application-ready photocatalytic systems.

2. General Principles of Heterogeneous Photocatalysis

The exceptional stability of solid photocatalysts enables their long-term use in demanding conditions without significant activity loss, ensuring extended catalyst lifespan, consistent performance across multiple cycles, and reduced replacement frequency. From an environmental perspective, heterogeneous systems minimize wastewater contamination by catalytic residues, simplifying regulatory compliance, lowering post-treatment needs, and enhancing the safety of treated water. Key industrial advantages include scalability for large-volume treatment, compatibility with existing infrastructure, and flexible integration into diverse plant designs [26].

Zinc oxide (ZnO) has emerged as a promising semiconductor photocatalyst due to its exceptional chemical, thermal, and mechanical stability, non-toxic nature, and cost-effectiveness. However, its photocatalytic activity remains constrained to the UV spectrum because of its wide bandgap (~ 3.3 eV) and rapid charge-carrier recombination [28]. To enhance solar-driven applications, ideal photocatalysts require bandgap tuning to match the solar spectrum and suppressed electron-hole recombination for improved efficiency. These limitations underscore the need for advanced material engineering (e.g., doping, heterostructures) to optimize ZnO's performance in real-world conditions [29].

Both homogeneous and heterogeneous photocatalysis begin with photon absorption, generating electron-hole pairs. In heterogeneous systems, these charge carriers migrate to surface reaction sites, where they drive redox reactions with target pollutants. However, rapid charge recombination significantly limits solar conversion efficiency. The process effectiveness depends critically on two factors—charge diffusion length (determining how many carriers reach active sites) and reaction pathway (influencing product selectivity and degradation rates). Optimizing these parameters is essential for enhancing photocatalytic performance in practical applications [30].

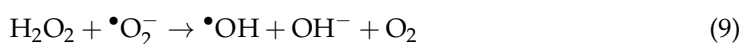
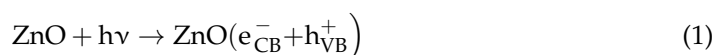
To overcome the limitations of conventional photocatalysts, researchers have developed several innovative material science approaches [18–20,31,32]:

- Semiconductor heterojunctions—Combining ZnO with other semiconductors (e.g., TiO_2) creates charge-separation interfaces that reduce electron-hole recombination.

- Z-Scheme photocatalytic systems—These systems synergistically pair two semiconductors to preserve high redox potentials while minimizing recombination.
- Noble metal nanoparticle incorporation—Adding silver or gold nanoparticles forms electron traps (Schottky barriers), delaying charge recombination.
- Non-metal and transition metal doping—Nitrogen or transition metal doping modifies bandgap structures to enhance visible-light absorption.
- Graphene-based hybridization—Graphene derivatives improve charge mobility and prevent recombination through efficient electron transfer.
- Dye sensitization—Organic dyes expand light absorption range, though stability remains a challenge under operational conditions.

Following photoexcitation, electrons and holes become mobile charge carriers within the semiconductor material. These carriers can undergo three primary processes [33]: Recombination—electrons return to the valence band, releasing energy as light or heat, reducing photocatalytic efficiency; surface reactions—carriers migrate to particle surfaces, driving redox reactions with adsorbed molecules (the desired photocatalytic process); and defect trapping—charge carriers become temporarily immobilized at crystal defects, potentially participating in later reactions.

When carriers reach the material's surface, they exhibit enhanced redox properties, enabling two critical processes [11,27]: Oxidation, where holes react with $\text{H}_2\text{O}/\text{OH}^-$ to generate $\bullet\text{OH}$ radicals; and reduction, where electrons convert O_2 to superoxide radicals ($\bullet\text{O}_2^-$). This light-to-chemical energy conversion forms the basis of photocatalytic systems. Understanding these pathways is essential for designing efficient photocatalysts. When exposed to light, ZnO generates excited electrons in the conduction band (e^-) and holes in the valence band (h^+). These charge carriers tend to recombine, releasing energy as heat Equation (2). However, the presence of molecular oxygen (O_2) acts as an electron acceptor, preventing recombination and creating superoxide radicals ($\bullet\text{O}_2^-$) Equation (3) [34].



Simultaneously, the valence band holes react with hydroxyl ions (OH^-) to form highly reactive hydroxyl radicals ($\bullet\text{OH}$) with an oxidation potential of +3.06 V Equation (4). These radicals can completely mineralize organic compounds Equation (5). Additionally, the holes themselves can directly oxidize organic molecules into reactive intermediates Equation (6). The superoxide radicals further react to form hydroperoxyl radicals ($\text{HOO}\bullet$) and hydrogen peroxide (H_2O_2), which participate in additional hydroxyl radical generation. These species act as electron scavengers, thereby helping to slow down charge carrier recombination Equations (7)–(9) [34].

2.1. Modifications for Enhancing the Activity of ZnO-Based Catalysts

ZnO offers a cost-effective production advantage over TiO₂, making it a more viable option for large-scale water treatment. Additionally, ZnO exhibits superior light absorption capabilities, capturing a broader spectrum of sunlight and a higher number of photons compared to other metal oxides. However, ZnO has limitations, including a wide bandgap and susceptibility to photocorrosion, which reduce its efficiency under visible light [34]. Beyond photocatalysis, ZnO is widely used in UV diodes, photodetectors, solar cells, spintronic devices, biosensors, and other catalytic applications [35]. The properties of ZnO nanostructures—such as bandgap and optical characteristics—can be fine-tuned by controlling particle size, shape, and dopant incorporation. Its wide bandgap makes ZnO an ideal host material for doping with various elements, allowing precise property customization [36,37]. A detailed comparison of two of the most used and researched photocatalysts is shown in Table 1.

Table 1. Overview of ZnO and TiO₂ characteristics as nanomaterial photocatalysts.

Characteristic	ZnO	TiO ₂
Efficiency and performance	- Higher efficiency in some cases and better performance for specific pollutants (dyes) [38,39] - High quantum efficiency [40], easily enhanced via doping [41]	- Reliable photocatalyst with very good overall efficiency under UV light, but inefficient utilization of solar energy, low photocatalytic quantum efficiency due to fast charge carrier recombination [38,42] - Relatively low surface area [43] - Industrial TiO₂ Evonik Degussa P-25, being a mixture of 30% rutile and 70% anatase, is often found to exhibit notably higher photocatalytic activities compared to other phase-pure TiO₂ samples [44]
Charge mobility and recombination rate	- Exceptional charge mobility ($120 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) with a possibility of significant enhancement via doping [45] or synthesis technique [46]	- Low mobility ($0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), with anatase phase having better charge carrier capability than the rutile phase [47] - Faster recombination of charge carriers [43]
Synthesis and feasibility	- Low-cost material [48] with facile and eco-friendly fabrication techniques, with the possibility of obtaining various nanostructures and morphologies even at lower temperatures [23]	- In various approaches (chemical, hydrothermal, solvothermal), there are imitations of cost effectiveness, high temperature and pressure, high energy, and eco-toxicity and environmental sustainability; while sol-gel and similar methods are regarded as cost-intensive [49]
Biocompatibility	- Non-toxic [48] - Excellent biocompatibility [24]	- Low toxicity [43] - Biocompatible [50]
Stability	- Excellent physical stability [24] - Thermal stability, and chemical stability [48] - Susceptible to photocorrosion (reduced stability in acidic environments) or disintegration [48,51]	- Long term stability [43] - Poor thermal stability of the photocatalytically most active anatase phase is another main disadvantage of the TiO₂ photocatalyst [44]
Light absorption and visible light activation	- Inability to utilize visible light due to its wide band gap of 3.3–3.4 eV [48] - ZnO absorbs UV light more efficiently than TiO₂ because of its higher binding energy [51] - Visible light activation can be achieved through band gap reduction with non-metal doping (S, F, and N) [31] - Metal (Sn, Ag, Cu, W) and rare earth element dopants (Nb, Eu) can be used for creating the charge carrier traps, generation of crystal defects, generation of acceptor mid-gap levels, and increased surface area [31,32]	- TiO₂ photocatalysts are limited by their wide band gap (anatase ~3.2 eV, rutile ~3.0 eV), which restricts activity mainly to UV light (<5% of solar radiation). Rutile absorbs slightly longer wavelengths but suffers from weaker reduction potential and faster electron–hole recombination, hindering practical commercialization [44]. - Visible-light absorption of TiO₂ is achieved by monodoping with Ca [52], N, Co, or Na dopant [53]

Doping is an effective method to modify ZnO's physical properties, particularly its optical and electrical performance, to meet specific application requirements [16–18]. For instance, incorporating Group III elements significantly enhances ZnO's optical and electrical properties [35]. These modifications not only alter particle structure and morphology but also introduce structural defects, such as zinc and oxygen vacancies, further influencing

material behavior [54]. Transition metals and non-metals can be integrated into ZnO's crystal lattice to shift its bandgap from the UV to the visible range, expanding its photocatalytic utility [55]. Common dopants include noble metals (Ag, Au), non-metal elements (B, S, F, and N), transition metals (Fe, V), and rare-earth elements (Nb, Eu), which enhance optical absorption, electrical conductivity, and magnetic properties [56–60].

Tin (Sn) doping has emerged as particularly effective, narrowing the bandgap while boosting electron-hole pair generation and suppressing charge carrier recombination. This approach simultaneously improves material morphology. Conversely, non-metal dopants like boron, carbon, fluorine, nitrogen, and sulfur are gaining traction for their ability to reduce recombination losses, enhance grain size, and increase surface area—all contributing to superior photocatalytic efficiency [57].

Zinc oxide inherently exhibits n-type conductivity due to native defects such as oxygen vacancies (V_o), zinc interstitials (Zn_i), and zinc vacancies (V_{Zn}), which critically influence its optoelectronic properties. Higher V_o concentrations can elevate charge carrier density. Despite the well-established and straightforward synthesis of n-type ZnO, the development of stable and reproducible p-type material continues to pose a significant scientific hurdle. This fundamental doping asymmetry is primarily rooted in the material's inherent properties. Firstly, ZnO exhibits a strong native tendency for n-type conductivity, especially under zinc-rich growth conditions. Secondly, attempts to achieve p-type conduction through native defects, such as zinc vacancies or oxygen interstitials, have proven insufficient and unreliable. Furthermore, these defects can introduce compensating recombination centers; for instance, electron-hole recombination at oxygen vacancy sites is a well-known source of the characteristic green luminescence in ZnO, which can be detrimental to optoelectronic performance. This combination of intrinsic n-type dominance and the instability of acceptor doping makes the pursuit of p-type ZnO a major challenge in the field [58].

In zinc-rich environments, self-compensation occurs as donor defects (V_o , Zn_i) neutralize acceptor defects (O_i or V_{Zn}), reinforcing n-type characteristics. For applications demanding high radiation stability, p-type ZnO is ideal. Among synthesis methods—mono-doping, co-doping, and dual-doping—dual-doping has proven exceptionally effective. Co-doping is also gaining attention for its precision in tuning photocatalyst optical properties through strategic combinations of dopants [58].

Doping ZnO with cationic elements (K, Ni, Cu, Pd, Cd) significantly alters its photocatalytic properties by modifying electron transfer rates and reducing charge recombination. These dopants incorporate at surface sites, zinc lattice positions, or interstitial locations, leading to increased surface area, lower electrical resistance, and reduced activation energy while narrowing the bandgap compared to pure ZnO. Anionic dopants like nitrogen, carbon, and sulfur demonstrate unique advantages—nitrogen doping introduces isolated 2p orbitals that enhance light absorption alongside Zn 3d sublevels, while carbon doping creates oxygen vacancy-induced energy sublevels that generate additional charge carriers without increasing recombination. Co-doping strategies have proven particularly effective, outperforming single-dopant systems in degrading various dyes, including methylene blue and naphthol blue black. This enhanced activity stems from the co-dopants' ability to simultaneously trap photogenerated electrons from ZnO's conduction band, effectively suppressing recombination and improving photocatalytic efficiency [34]. The strategic incorporation of different dopants enables precise tuning of ZnO's electronic and optical properties for optimized photocatalytic performance.

Semiconductor materials for photocatalytic systems must satisfy specific energy requirements. Their bandgap (E_g) needs to be sufficiently wide to enable electron generation (typically > 2.0 eV) yet narrow enough for efficient solar light absorption (< 3.0 eV). Beyond energy considerations, effective charge transport and separation mechanisms are crucial.

Optimal photocatalytic performance requires a tight integration of semiconductors with suitable redox catalysts, along with protection against undesirable electrochemical reactions to maintain stability. Since single materials rarely meet all these demands, contemporary research increasingly focuses on heterogeneous photocatalytic systems [59]. Composite formation with WO_3 , NiO_2 , Fe_2O_3 , MoS_2 , TiO_2 , and reduced graphene oxide enables more efficient degradation of organic pollutants, with each component contributing unique properties—from enhanced charge separation to increased surface activity [60].

ZnO's versatility extends beyond material composites to diverse nanostructural forms, including nanorods, nanorings, nanowires, nanobelts, nanocages, and nanocombs. These tailored morphologies not only enhance surface area but also enable precise tuning of optical and charge transport properties. This dual advantage—compatibility with heterostructures and structural diversity—positions ZnO as a leading material for advanced photocatalytic applications [61].

Photocatalyst development has evolved through three generations. First-generation single semiconductors (e.g., CdS, WO_3) faced limitations from rapid electron-hole (e^-/h^+) recombination and suboptimal band alignment. Second-generation composites (e.g., $\text{Fe}_2\text{O}_3/\text{TiO}_2$ - WO_3 n-n heterojunctions) improved visible-light absorption and charge separation. The current third-generation incorporates supported catalysts, enhancing both stability and performance [60].

In the field of photocatalysis, three fundamental types of heterojunctions exist with distinct charge transport mechanisms [60]:

1. Type I (“Straddling band alignment”)

Characterized by overlapping energy bands where the valence band (VB) and conduction band (CB) of one semiconductor lie entirely within the energy range of another. This configuration leads to a high recombination rate of electron-hole pairs, limiting photocatalytic efficiency.

2. Type II

Spatial separation of charge carriers between two semiconductors occurs in this type, widening the bandgap and reducing recombination. However, repulsive interactions between electrons (e^-/e^-) and holes (h^+/h^+) diminish overall photocatalytic performance.

3. Type III (Z-scheme system)

Representing the most advanced configuration, repulsive interactions are avoided through a Z-transfer mechanism. Here, electrons from the conduction band of one semiconductor recombine with holes in the valence band of another. Two variants exist: Metal-mediated Z-scheme (uses metal nanoparticles as bridges) and direct Z-scheme (no metal mediators).

Z-scheme systems are particularly noteworthy because they preserve the strong oxidation and reduction potentials of both semiconductors while minimizing recombination. This feature makes them ideal for advanced photocatalytic wastewater treatment applications.

The photocatalytic efficiency of pure ZnO is limited by its wide bandgap between the valence band (composed of O 2p orbitals) and conduction band (formed by Zn 4s orbitals), which restricts visible light absorption. To achieve effective visible-light adsorption and photocatalytic activity, the formation of metal oxide heterojunctions becomes essential. Such engineered interfaces significantly enhance solar energy utilization while boosting the material's overall photocatalytic performance [62].

Composite photocatalysts combine semiconductors with wide and narrow band gaps, enabling electron transfer from materials with higher conduction band minima to those with lower minima. Heterojunction formation facilitates efficient inter-catalyst electron transfer,

improving charge separation while reducing electron-hole recombination, thereby enhancing photocatalytic activity [22]. Key heterostructures include binary systems: TiO_2/ZnO , SnO_2/ZnO , $\text{ZnO}/\gamma\text{-Mn}_2\text{O}_3$, $\text{ZnO}/\text{Mn}_3\text{O}_4$, ZnO/MnO_2 , $\text{ZnO}/\text{Fe}_2\text{O}_3$; and ternary systems: $\text{ZnO}/\text{Fe}_2\text{O}_3/\text{MnO}_2$, $\text{SnO}_2/\text{ZnO}/\text{TiO}_2$, $\text{ZnO}/\text{Ag}_2\text{O}/\text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CoWO}_4$, $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{NiWO}_4$ [34]. These systems demonstrate superior performance compared to pure ZnO [34], with TiO_2/ZnO , SnO_2/ZnO , $\text{SnO}_2/\text{ZnO}/\text{TiO}_2$, and $\text{Co}_3\text{O}_4/\text{ZnO}$ being the most extensively studied [58]. The main strategies for modifying ZnO to overcome its limitations (wide bandgap, rapid recombination) are summarized in Table 2, providing a concise comparative overview.

Table 2. Summary of modification strategies for enhancing ZnO photocatalytic performance.

Modification Strategy	Key Examples	Primary Effects & Advantages	Key Challenges/Considerations
Cationic doping	Transition metals (Mn, Co, Ni, Fe), Rare earths (Eu, Nb), Cd, Sn	- Reduces bandgap for visible light absorption - Suppresses charge carrier recombination - Alters morphology (surface area, particle size)	- Potential toxicity (e.g., Cd) - Risk of introducing recombination centers at high doping levels
Anionic doping	N, C, S, F, B	- Creates new energy levels for visible light response - Often generates oxygen vacancies - Typically uses abundant, less toxic elements	- Can be complex to control the exact incorporation into the lattice
Co-doping	e(Al + Mn), (N + Gd)	- Synergistic effects; overcomes limitations of single doping - Enhanced charge separation and stability - Can enable p-type conductivity	- More complex synthesis process - Requires precise control of dopant ratios
Heterojunction formation	Binary: ZnO/TiO_2 , $\text{ZnO}/\text{g-C}_3\text{N}_4$, $\text{n-ZnO}/\text{p-Cu}_2\text{O}$ Ternary: $\text{ZnO}/\text{Fe}_2\text{O}_3/\text{MnO}_2$	- Dramatically improves charge separation (Type II, Z-scheme) - Extends light absorption range - Combines the advantages of different materials	- Synthesis complexity increases - Interface stability can be an issue
Morphological Control	Nanorods, nanowires, nanoflowers, etc.	- Increases surface area for adsorption & reaction sites - Tunes charge transport properties	- Morphology can be sensitive to synthesis conditions

While high degradation efficiency is a key metric, the practical deployment of photocatalysts still hinges on overcoming challenges related to catalyst stability and scalability. Deactivation from fouling by dye intermediates and difficulties in maintaining efficiency and uniform illumination at scale remain significant hurdles.

To address these, future research must prioritize simple, scalable synthesis routes (e.g., co-precipitation) for doped ZnO over complex composites, and develop continuous-flow reactor designs suitable for industrial use. Enhancing catalyst longevity through magnetic recovery or immobilization on substrates to facilitate separation and reuse might also be crucial, thereby improving cost-effectiveness. While cadmium offers performance benefits, its environmental risk necessitates a preference for abundant, non-toxic alternatives (e.g., Fe, Mn) or strategies to prevent metal leaching [51].

Different synthesis routes for doped ZnO influence the structure of doped ZnO, alongside crystallinity and defect density, all of which impact its electrical and optical performance. Also, various dopants and their concentrations immensely affect the properties of ZnO nanoparticles, leading to varying improvements or even antagonistic effects on efficiency depending on the application [17,63].

The introduction of multiple dopant species—particularly rare-earth elements—induces significant structural reorganization in zinc oxide matrices. These alterations drive a multifaceted evolution in material characteristics, often yielding a broad and sometimes unpredictable range of functional outcomes [64]. This issue only becomes more complex when taking into consideration mixing with other nanocatalysts in various ratios of doped ZnO in order to obtain heterojunctions.

A higher dopant concentration in ZnO does not guarantee higher efficiency because excessive doping introduces defects, increases electron-hole recombination [16], introduces impurities and promote the formation of secondary phases [65], or causes agglomeration [66], all of which can degrade material properties like luminescence, charge carrier mobility, or optical absorption [67], leading to reduced overall performance in devices [68]. In the context of thin-film systems, properties such as layer thickness and crystalline orientation are crucial determinants of performance. This is clearly demonstrated in aluminum-doped zinc oxide (AZO), where such parameters govern charge carrier mobility and ultimately define the material's conductive properties [69].

Ultimately, the choice of photocatalyst for the CV degradation (most desirably simple, low cost, and/or “green”) involves a trade-off between efficiency, cost, scalability, and environmental footprint.

Another major challenge is wide-scale heterojunction usage, due to the high cost of raw materials, the complexity of synthesis methods, and their limited scalability. Large-scale production is also limited due to extended reaction durations and energy consumption [43].

With its narrow 2.2 eV bandgap, Cu₂O—for example—emerges as an excellent candidate for visible-light photocatalysis and photoelectric conversion [70]. Its p-type conductivity originates from copper vacancies (V_{Cu}) that generate charge carriers through low ionization energy. Researchers particularly value Cu₂O for its exceptional charge mobility, making it ideal for solar cells, sensors, and photocatalytic systems [71]. The n-ZnO/p-Cu₂O heterojunction demonstrates remarkable synergistic effects: Enhanced sunlight absorption and utilization, accelerated electron transfer, efficient charge carrier separation, and improved dye degradation efficiency. Under UV-visible light, both semiconductors become photoactive. The 0.5 eV lower conduction band of ZnO facilitates electron migration from Cu₂O, effectively preventing recombination [70,72], as illustrated in Figure 1.

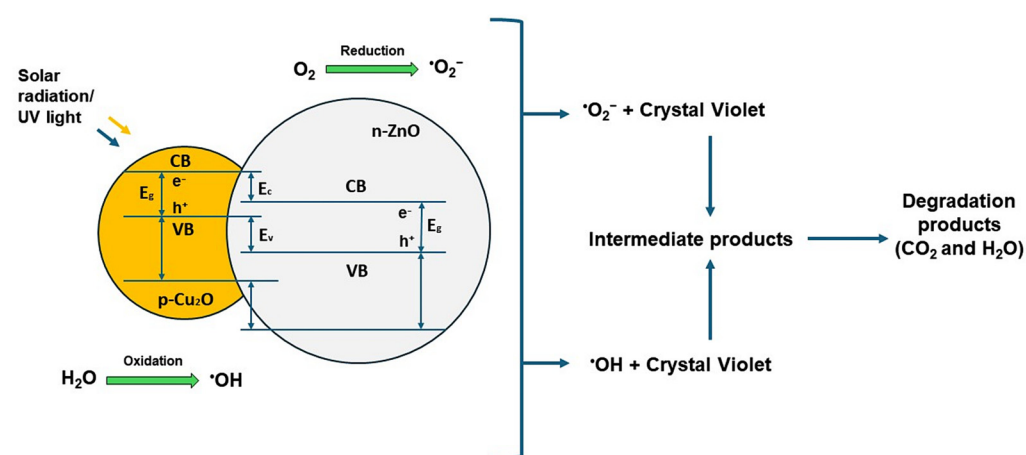


Figure 1. Crystal violet degradation in the presence of n-ZnO/p-Cu₂O type catalyst.

Both ZnO and Cu₂O feature conduction band potentials more negative than the standard O₂/•O₂⁻ redox potential (−0.33 eV vs. SHE), enabling electron transfer to adsorbed oxygen and subsequent superoxide radical (•O₂⁻) formation. While ZnO's valence band holes can oxidize OH⁻ groups to generate hydroxyl radicals (•OH), Cu₂O

lacks this capability. The superoxide radicals further react with H^+ ions to form $HO_2^\bullet$ and H_2O_2 , which then interact with electrons to produce additional $^\bullet OH$ radicals [70,72].

2.2. Wide-Scale and Real-Effluent Testing Challenges

The application of photocatalysis to real-world effluent treatment presents significant challenges that are not encountered in controlled laboratory studies. Real industrial wastewater, such as that from aluminum anodizing, is a complex matrix containing a mixture of dyes, chemical additives, organic compounds, and various inorganic ions. These constituents can severely hinder the process; anions like chloride (Cl^-) act as scavengers for hydroxyl radicals, while other compounds can adsorb to and poison the catalyst's active sites, effectively blocking its activity. Furthermore, the often dark color and high turbidity of real effluent impede light penetration, limiting the catalyst's activation and the subsequent generation of reactive oxygen species. The inherent variability of parameters like pH, temperature, and ionic strength in real systems also makes performance more difficult to predict and reproduce reliably [73]. Additional insufficiently researched issues are catalyst reusability and deactivation caused by the adsorption of pollutants on the catalyst surface or reactions with interfering substances in the effluent [74]. Alongside these issues, separation, and regeneration, as well as the agglomeration tendency of catalyst particles, as technical challenges that remain rarely discussed [75].

The transition from laboratory research to industrial-scale implementation faces significant hurdles. Key among these are scale-up difficulties, where issues with uniform light distribution, inefficient mass transfer, and complex reactor design impede performance at larger volumes. This is compounded by low light efficiency, as the ineffective utilization of visible sunlight due to scattering, combined with the prohibitive energy costs of powerful artificial light sources, severely impacts the economic viability of the process. Furthermore, mass transfer limitations can create a bottleneck, where the inefficient diffusion of pollutants to the active catalyst surface stifles the overall reaction rate [76–78].

As real effluents are characterized by their complex compositions, containing intricate mixtures of dyes, heavy metals, and pharmaceutical residues, these compounds and elements can compete for active sites, absorb light intended for the catalyst, or even act as scavengers for reactive species, thereby inhibiting the degradation process. Moreover, the variable operating conditions of real-world environments—such as unpredictable fluctuations in light intensity, temperature, pH, and ionic strength—make it exceptionally challenging to maintain consistent and reliable photocatalytic performance [73,79].

A gap in the literature concerns the long-term reusability and stability of photocatalysts under non-laboratory conditions, where factors like catalyst fouling, poisoning, and difficult separation might lead to rapid deactivation. However, a study by Ngan et al. (2025) [80] directly addresses this challenge by rigorously evaluating a commercial TiO_2 photocatalyst under environmentally relevant conditions. The research employed a synthetic complex matrix with high concentrations of sulfate and nitrate co-contaminants to mimic the harsh reality of industrial wastewater. Remarkably, without any washing or regeneration between cycles, the catalyst was reused for 15 consecutive treatment cycles while maintaining a selenium removal efficiency exceeding 99.3%. Research by Ramesh et al. (2024) [81] synthesizes findings from multiple lab-scale studies, which indicate that Ag-doped TiO_2 catalysts exhibit promising reusability and stability in a controlled environment. Testing typically involves recovering the catalyst post-reaction via centrifugation or filtration and subjecting it to multiple degradation cycles. Results from these studies show that Ag-doped TiO_2 can maintain photocatalytic efficiency above 85% even after five cycles, with minimal silver leaching observed. This durability is attributed to the formation of a stable Schottky barrier at the Ag- TiO_2 interface, which helps maintain the catalyst's integrity. However, the

authors emphasize that challenges such as catalyst recovery, prevention of photocorrosion, and scalability of synthesis methods remain significant barriers to practical implementation in real-world wastewater treatment systems [81]. Findings like these provide a critical counterpoint to the commonly cited challenges of catalyst reusability and deactivation in complex effluents.

The release of nanoparticles into ecosystems poses significant and multifaceted risks due to their unique physicochemical properties. Their minute size, high surface area-to-volume ratio (most notably ZnO and TiO₂), and reactivity enable them to easily penetrate biological membranes, disrupt cellular structures, and induce oxidative stress through the generation of reactive oxygen species. This can lead to DNA damage, protein denaturation, and mitochondrial impairment in a wide range of organisms, from soil bacteria and plants to aquatic invertebrates and fish [82].

According to the classification by Nthunya et al. (2025) [83] nanowaste is categorized into five classes (I–V) based on its risk profile. Class II nanowaste, exemplified by Zinc Oxide (ZnO) nanoparticles from products like sunscreens and paints, is characterized by a low to medium exposure level and slight toxicity. Its overall risk is considered low to medium, with the primary health concern being the induction of oxidative stress, inflammation, and cytotoxicity in skin cells.

This places ZnO nanowaste in a middle tier of risk. It is less hazardous than Class I materials like SiO₂ (very low toxicity) but significantly safer than the higher classes. Classes III–V represent increasingly severe categories, including the very toxic silver (Ag) nanoparticles (Class III), the highly exposed and toxic titanium dioxide (TiO₂) nanoparticles (Class IV), and the extremely toxic cadmium-based quantum dots (Class V), which pose the highest risks [83].

For example, nanoparticles cause limited growth, reduced reproduction, and negative impacts on food assimilation for *Daphnia magna* [82]. Nanoparticles have been shown to inhibit the growth of algae like *Chlorella vulgaris* by adsorbing to cell surfaces and blocking nutrient access [84]. ZnO nanoparticles can undergo various transformations, including dissolution, aggregation, sedimentation, and adsorption onto organic matter. Their behavior and toxicity are influenced by factors such as particle size, shape, ionic strength, pH, and the presence of natural organic materials like humic acids. A key concern is their dissolution, which releases Zn²⁺ ions—a known toxicant to aquatic life—with smaller nanoparticles dissolving faster. Furthermore, redox reactions on the surface of ZnO nanoparticles can generate reactive oxygen species, leading to oxidative stress in organisms. This raises additional concerns due to further bioaccumulation in tissues such as the liver, gills, brain, and muscle, with a potential for trophic transfer [85]. Some of the toxic effects of zinc oxide nanoparticles (ZnO NPs) were confirmed in *Perna viridis* [86].

Furthermore, nanoparticles can act as carriers for other environmental contaminants, potentially leading to synergistic toxic effects that are greater than the sum of the individual pollutants [82]. A major concern is their ability to evade conventional water treatment processes like coagulation and filtration, allowing them to enter drinking water supplies. Chronic exposure, even to low concentrations (e.g., <0.1 µg/L), can lead to bioaccumulation in humans and wildlife, potentially causing inflammation, organ dysfunction, and long-term health issues [84].

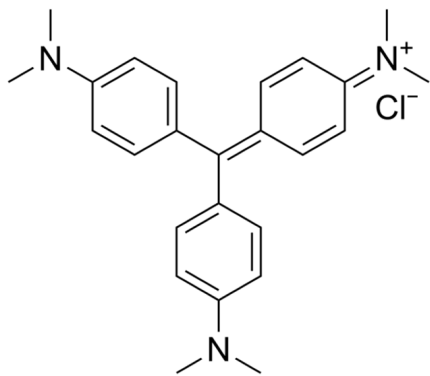
A major ecological concern is the potential for nanoparticles to bioaccumulate in organisms and biomagnify up the food chain, threatening higher trophic levels, including humans. Their environmental behavior and toxicity are not static; factors like exposure to sunlight (photoactivation), changes in pH, salinity, and the presence of organic matter can alter their stability, aggregation state, and surface chemistry, thereby modifying their bioavailability and ecological impact over time. The complex and variable nature of real-

world ecosystems, combined with a current lack of comprehensive data on the long-term fate and exposure concentrations of NPs, makes it challenging to predict and mitigate these risks, highlighting an urgent need for robust environmental monitoring and tailored regulatory frameworks [84].

3. Crystal Violet—Kinetics and Degradation Mechanism

With its distinctive structure featuring three phenyl rings each bearing a dimethylamino group, CV (International Union of Pure and Applied Chemistry—IUPAC name: tris(4-(dimethylamino)phenyl)methylium chloride) represents an important cationic dye. This synthetic triarylmethane compound demonstrates both cost-effective production and excellent dyeing efficiency, though approximately 10–20% of global CV production is lost during synthesis and processing [8]. Regulatory agencies have prohibited its use in aquaculture and the food industry due to its health risks. Table 3 summarizes its key physicochemical properties [87].

Table 3. Physicochemical properties of crystal violet [87].

Physicochemical Properties	Data/Value
Formula	C ₂₅ H ₃₀ ClN ₃
Structural formula	
Molar mass	407.98 g/mol
Number of heavy atoms	29
Number of aromatic heavy atoms	12
Fraction Csp ³	0.24
Number of rotatable bonds	4
Number of H-bond acceptors	0
Number of H-bond donors	0
Molar Refractivity	128.45
Topological Polar Surface Area	9.49 Å ²
Log Po/w (iLOGP)	−3.09
Log S (ESOL)	−2.88
Solubility	-
Class	Soluble
Log S (Ali)	−0.52

The degradation process critically depends on the energy required for water molecule dissociation or hydroxyl radical generation. The energy required for water molecule dissociation or hydroxyl radical generation is directly related to the band gap energy of the

photocatalyst (e.g., ~ 3.2 eV). This energy corresponds to a wavelength of approximately 388 nm, which is in the UV range [88–90]. The fact that CV absorbs strongly in the visible region (590 nm), far from the catalyst's activation wavelength, helps establish that the dye's degradation is not mediated by a direct photoexcitation process (where the dye would act as a photosensitizer) but is instead primarily driven by the photocatalyst itself upon UV excitation. When MO_x materials are irradiated, electron excitation creates active holes in the valence band. These holes interact with water molecules, triggering ionization into protons (H^+) and hydroxyl radicals ($\text{OH}^\bullet$). Simultaneously, conduction band electrons react with oxygen to form superoxide radicals ($^\bullet\text{O}_2^-$), which subsequently protonate into hydroperoxyl radicals ($\text{HOO}^\bullet$) and additional $\text{OH}^\bullet$ radicals. For efficient water splitting (0–1.23 eV), the MO_x bandgap must encompass this energy range. However, charge carrier recombination often limits photocatalytic efficiency. While Fe_2O_3 , CuO , and Cu_2O fall outside the optimal range for water splitting, which makes them inactive for photocatalysis, TiO_2 and ZnO demonstrate superior performance in CV degradation [6].

3.1. Overview of CV Degradation Mechanism

The exact degradation mechanism remains under investigation, with studies employing scavengers like EDTA-2Na (h^+ scavenger), IPA ($\text{OH}^\bullet$ scavenger), and p-BQ ($^\bullet\text{O}_2^-$ scavenger). These reagents help identify radical contributions, revealing that H^+ and $\text{OH}^\bullet$ radicals play pivotal roles [87,91,92], whereas $^\bullet\text{O}_2^-$ has minimal impact. Although $^\bullet\text{O}_2^-$ conversion to $\text{HOO}^\bullet$ is non-preferred, its presence alone shows limited catalytic influence compared to $\text{H}^+/\text{OH}^\bullet$ [6]. Mass spectrometry analyses at pH 10–12 detected key intermediates within 30 min, confirming multi-pathway bond cleavage (Figure 2). These findings underscore the complexity of CV degradation, involving diverse reactive intermediates and fragmentation routes [87].

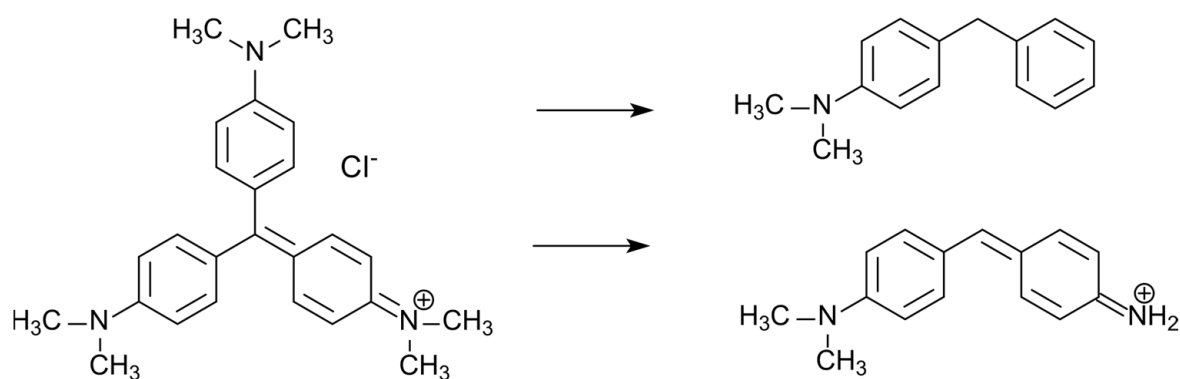


Figure 2. Proposed degradation pathways of CV.

The degradation of CV strongly depends on pH. Crystal violet dye belongs to the triphenylmethane group and has a cationic nature, which favors degradation in alkaline solutions [93,94]. In an acidic environment, deposition of crystal Violet dye on the catalyst surface is difficult, resulting in low degradation [92]. In alkaline solution, the catalyst surface becomes negatively charged due to interaction with OH^- ions, which strongly attracts CV cations to the catalyst surface, creating conditions for more intensive dye decomposition [87]. A high amount of adsorbed hydroxyl ions on the catalyst surface promotes the formation of $\text{OH}^\bullet$ radicals, leading to higher degradation of CV [95]. $\text{OH}^\bullet$ species cause CV dye decoloration through chromophore group decomposition and conversion into aromatic intermediate compounds (Figure 2) [87,94,96,97].

Sanakousar et al. (2021) [87] evaluated compound toxicity using EPA-TEST software and the EPA-CompTox database across three organisms: *Fathead minnow* (fish), *D. magna*

(water flea), and *T. pyriformis* (protozoan). In their purely computational study, researchers have presented key findings based on lethal concentration 50% —“LC50” values, revealing that the parent compound (C1, CV) and its transformed molecule “TM2” ($C_{15}H_{18}N_2$) exhibited comparable toxicity levels. However, TM1 ($C_{15}H_{17}N$) demonstrated significantly higher toxicity toward the *Fathead minnow* compared to the other compounds. Both transformation products (TM1 and TM2) exhibited substantially lower toxicity to *D. magna* than to fish, indicating species-specific effects. Overall, the composite ecotoxicological analysis identified TM2 as the most favorable transformation product due to its relatively lower toxicity across multiple species [87].

Fan et al. (2009) [98] confirmed that primary degradation pathways involve N-demethylation and cleavage of the conjugated chromophore structure, leading to a series of aromatic amines and phenolic compounds. Key toxic intermediates identified include: N-demethylated derivatives, which retain the triphenylmethane structure and may exhibit similar or enhanced toxicity due to increased bioavailability or reactivity; benzophenone derivatives, formed through chromophore cleavage, which can be persistent and toxic; aminophenols, such as 4-aminophenol, known for their toxicity and potential carcinogenicity; and aromatic amines like N-methylaminobenzene and aminobenzene (identified by gas chromatography-mass spectrometry—GC-MS), which are recognized carcinogens and mutagens [98].

Aliphatic degradation products were also detected (e.g., acetic acid, 1-hydroxy-2-propanone), which are less toxic but indicate incomplete mineralization. The persistence of aromatic intermediates—even after significant decolorization—highlights the risk of releasing more harmful compounds into aquatic environments if degradation is not complete [98].

During the photodegradation of crystal violet (CV) assisted by the hybrid photocatalyst, intermediate products are formed whose toxicity may exceed that of the original dye. Theoretical and experimental analyses indicate the formation of pararosaniline (PR) via N-demethylation, as well as phenolic and benzophenone derivatives resulting from central carbon cleavage. An ECOSAR software-based ecotoxicity assessment revealed that PR, for which the European Chemicals Agency has confirmed potential human carcinogenicity, exhibits the highest toxicity among the compounds investigated. Similarly, Michler’s ketone (MK) also displayed high toxicity. Although some degradation products (such as demethylated derivatives and p-aminophenol) are less toxic than the precursor, their presence still poses harm to the aquatic ecosystem. These findings emphasize the critical need to monitor degradation processes in order to identify and quantify toxic intermediates, with surface-enhanced Raman spectroscopy emerging as a key technique for their detection and real-time monitoring [99].

While the recent literature seems to lack intermediate and degradation by-product toxicological assessment, a study by Liu and Wang (2024) [100] has identified key intermediates, including partially N-demethylated compounds and aromatic fragments resulting from central carbon cleavage. Toxicity assessments using ECOSAR and TEST software revealed that most of these intermediates are more poisonous than CV itself. For instance, fully demethylated CV (compound similar to Basic Red 9) and other aromatic by-products retain toxic properties and may exhibit enhanced bioavailability or reactivity. Only small carboxylic acids (e.g., formic acid) and fully mineralized end products showed low or negligible toxicity. The persistence of toxic aromatic intermediates underscores the importance of achieving complete mineralization rather than mere decolorization to avoid introducing more harmful substances into aquatic ecosystems [100].

To assess the potential ecological impact of CV degradation using the medical waste-derived carbon/ZnO (MWC/ZnO) composite under visible light and persulfate (PS) acti-

vation, a toxicological evaluation was conducted by Ramanathan et al. (2024) [101] using both plant and aquatic animal models. The water quality before and after photocatalytic degradation of CV was compared by examining seed germination and seedling viability in *Vigna mungo*, as well as embryonic development and adult health in zebrafish (*Danio rerio*). These intermediates result from processes such as N-demethylation, decarboxylation, and ring-opening reactions [101].

Phytotoxicity tests on *Vigna mungo* seeds showed that seeds exposed to the degraded CV solution had a germination rate of >95%, similar to the control (water), while the untreated CV solution resulted in <10% germination. Seedling growth (root and stem length) and cellular morphology (e.g., vascular bundle integrity in roots and mesophyll development in leaves) were normal in the degraded CV group, but severely impaired in the CV-treated group. Zebrafish embryotoxicity tests further confirmed the safety of the degraded products. Embryos exposed to degraded CV solution showed no developmental defects, normal hatchability, and no increase in mortality, unlike those exposed to untreated CV, which exhibited lethal coagulation, bent tails, cardiac edema, and significant mortality at higher concentrations [101].

Experimental studies demonstrated that 0.5 mol% cadmium doping in ZnO substantially improved photocatalytic activity. The Cd modification altered ZnO's optical bandgap, facilitating $\bullet\text{O}_2^-$ radical generation and significantly enhancing degradation efficiency [87]. Complementary research by Ameen et al. (2013) reported rapid CV degradation (96% within 80 min) using synthesized ZnO nanoparticles [102]. Reactive species on ZnO surfaces promoted CV breakdown into less harmful organic/mineral products. Mass spectrometry confirmed complete mineralization after 80 min, evidenced by the disappearance of the primary $m/z = 372.2$ signal and the emergence of lower-mass fragment signatures.

While Ameen et al. (2013) [102] did not extensively examine the mechanistic and toxicological aspects of CV degradation, Liao et al. (2011) [103] provided a comprehensive analysis of intermediate products and proposed degradation pathways. Using HPLC-ESI (High-Performance Liquid Chromatography-Electrospray Ionization), they identified multiple degradation intermediates, including: **A**—N,N,N',N',N'-hexamethyl-pararosaniline, **B**—N,N-dimethyl-N',N'-dimethyl-N''-methyl-pararosaniline, **C**—N,N-dimethyl-N'-methyl-N''-methyl-pararosaniline, **D**—N,N-dimethyl-N',N'-dimethyl-pararosaniline, **E**—N-methyl-N'-methyl-N''-methyl-pararosaniline, **F**—N,N-dimethyl-N'-methyl-pararosaniline, **G**—N-methyl-N'-methyl-pararosaniline, **H**—N,N-dimethyl-pararosaniline, **I**—N-methyl-pararosaniline, **J**—Pararosaniline, **a**—4-(N,N-dimethylamino)-4'-(N',N'-dimethylamino)benzophenone, **b**—4-(N,N-dimethylamino)-4'-(N'-methylamino)benzophenone, **c**—4-(N-methylamino)-4'-(N'-methylamino)benzophenone, **d**—4-(N,N-dimethylamino)-4'-aminobenzophenone, **e**—4-(N-methylamino)-4'-aminobenzophenone, **f**—4,4'-bis-aminobenzophenone, α —4-(N,N-dimethylamino)phenol, β —4-(N-methylamino)phenol, and γ —4-Aminophenol [103].

The degradation occurs through two primary pathways: N-demethylation and chromophore cleavage. Hydroxyl radicals, generated when photogenerated holes (h^+) react with surface-adsorbed water or hydroxide ions, predominantly drive the process by attacking N,N-dimethyl groups to form progressively demethylated intermediates from hexamethyl-pararosaniline (**A**) to pararosaniline (**J**). Simultaneously, these radicals may cleave the central carbon bond, producing benzophenone derivatives (**a**–**f**) and phenolic compounds (α – γ). The positively charged dye molecules initially adsorb to Bi_2WO_6 surfaces via their diethylamine groups. Subsequent reactions involve cationic radical ($\text{CV}^{\bullet+}$) formation through $\bullet\text{OH}$ attack, followed by either hydrolysis or deprotonation. Notably, each demethylation step (e.g., intermediate **B**→**C**→**D**) requires fresh radical attacks until complete N-demethylation occurs. While superoxide radical formation proves less favor-

able under UV light, the study confirmed complete chromophore breakdown through mass spectral data showing sequential fragmentation patterns. These findings demonstrate that CV degradation involves complex, competing pathways of N-dealkylation and conjugated structure cleavage, with hydroxyl radicals playing the dominant role compared to other reactive oxygen species [103].

Research has revealed that CV molecules adsorb onto photocatalyst surfaces through both functional groups and conjugated chromophore structures. When hydroxyl radicals ($\bullet\text{OH}$) attack the adsorbed dye, carbon-centered radicals form and subsequently react with molecular oxygen, yielding intermediates **a** (4-(N,N-dimethylamino)-4'-(N',N'-dimethylamino)benzophenone) and **α** (4-(N,N-dimethylamino)phenol). These intermediates undergo progressive transformations on Bi_2WO_6 surfaces. First, intermediate **a** reacts further with $\bullet\text{OH}$ via attack, deprotonation, or oxygen incorporation, generating the di-N-demethylated derivative **b**. This is then followed by an intermediate **α** who follows a parallel pathway to form **β** (4-(N-methylamino)phenol). Finally, a complete N-demethylation ultimately produces fully demethylated products **f** (4,4'-bis-aminobenzophenone) and **γ** (4-aminophenol). Concurrently, N-hydroxymethylated intermediates emerge through N-methyl group hydroxylation. All fragments eventually mineralize to simple organic compounds (e.g., N,N-dimethylaminobenzene, acetic acid) and inorganic ions (CO_3^{2-} , NO_3^-), as confirmed by Liao et al. (2011) [103].

3.2. ZnO-Based Nanomaterials—Degradation Experiments and Kinetics

The photocatalytic breakdown of CV has been systematically investigated using diverse catalyst materials. Key parameters evaluated include degradation efficiency, process duration, light source characteristics, and operational conditions. Table 4 summarizes the photocatalytic ZnO-based materials tested for CV degradation, along with their synthesis methods and performance metrics.

Table 4. Literature review of CV degradation experiments in the presence of ZnO-based photocatalysts.

Catalyst	Synthesis Method	Degradation Efficiency (%)	Experiment Parameters	Illumination Time (min)	Reference
ZnO	Spray pyrolysis on polyetherimide substrate (PEI) at 250 °C	86	12.5 mg/L CV solution, UV exposure	210	[104]
ZnO		78	12.5 mg/L CV solution, solar exposure		
Co (1%)-ZnO		91.3	12.5 mg/L CV solution, UV exposure		
Co (1%)-ZnO		85	12.5 mg/L CV solution, solar exposure		
In (1%)-ZnO		85	12.5 mg/L CV solution, UV exposure		
In (1%)-ZnO		88.5	12.5 mg/L CV solution, solar exposure		
ZnO	Co-precipitation ($\text{ZnSO}_4 + \text{NaOH}$, calcination at 600 °C for 4 h)	82	80 mg of catalyst, 100 mL of 5 mg/L CV solution, UV exposure (25 W Hg lamp at $\lambda = 406\text{--}580$ nm)	240	[105]
ZnO/Graphene-oxide (GO)	Solid state reaction (mixing ZnO and GO at a ratio of 1000:3, calcination at 300 °C for 2 h)	99		240	
ZnO	Co-precipitation (30 min) + calcination (300 °C)	82	100 mg of catalyst, 200 mL of 10 mg/L CV solution, UV lamp (450 W)	150	[15]
	Co-precipitation (60 min) + calcination (300 °C)	81		150	
	Co-precipitation (90 min) + calcination (300 °C)	99		150	
	Co-precipitation (120 min) + calcination (300 °C)	72		150	

Table 4. Cont.

Catalyst	Synthesis Method	Degradation Efficiency (%)	Experiment Parameters	Illumination Time (min)	Reference
Mn (1%) doped + (1%) polyvinylpyrrolidone (PVP) capsulated ZnO	Co-precipitation (Zn-acetate, NaOH, Mn-acetate), calcination at 300 °C	99.1	0.25 g of catalyst, 100 mL of 10 mg/L CV solution, UV-VIS exposure (Hg lamp), 1500 rpm	180	[106]
Mn (2%) doped + PVP (1%) capsulated ZnO		97.5		180	
Undoped ZnO + PVP (1%)		79.5		180	
Mn (1%) ZnO (re-use)	First usage + washing and recalcination at 300 °C	~100		180	
ZnO	Commercial (size: <5 µm, purity: ≥99%)	98	25 mg of catalyst, 50 mL of 10 ^{−5} M CV solution, UV exposure (365 nm), mixing at 200 rpm	120	[6]
ZnO	Hydrothermal method	~88	25 mg of catalyst, 25 mL of 20 ppm CV solution, solar exposure	180	[107]
g-C ₃ N ₄ /ZnO	Melamine pyrolysis and hydrothermal synthesis of heterostructure	97		180	
0.5 mol% Cd-ZnO	Polyvinyl alcohol (PVA)—assisted precipitation	100	2 mg of catalyst, 10 mg/L CV solution, pH = 10–12, UV lamp (6 W)	30	[87]
0.5 mol% Cd-ZnO		94	2 mg of catalyst, 10 mg/L CV solution, pH = 8, UV lamp (6 W)	60	
1.0 mol% Cd-ZnO		73.94	2 mg of catalyst, 10 mg/L CV solution, UV lamp (6 W)	90	
1.5 mol% Cd-ZnO		71.01	2 mg of catalyst, 10 mg/L CV solution, UV lamp (6 W)	90	
2.0 mol% Cd-ZnO		77.24	2 mg of catalyst, 10 mg/L CV solution, UV lamp (6 W)	90	
Pure ZnO		85.17	2 mg of catalyst, 10 mg/L CV solution, UV lamp (6 W)	90	
SA-g-poly(AA-co-CA)/ZnO/GO nanocomposite (S3)	Copolymerization (Graft) of sodium-alginate (SA) with acrylic acid/cinnamic acid (AA/CA) + incorporation of ZnO nanorods i graphene oxide (GO—made via Hummers method) layers through sonication	94 (sunlight)	0.1 g of catalyst, 50 mL of 30 mg L ^{−1} CV solution, pH = 5, 40 °C	300	[108]
SA-g-poly(AA-co-CA)/ZnO nanocomposite (S2)		87 (sunlight)		300	

Ben Ameer et al. (2019) [104] demonstrated that cobalt (Co) and indium (In) doping significantly improves the photocatalytic activity of ZnO thin films. Under UV irradiation, Co-doped ZnO (CZO) achieved 91.3% CV degradation efficiency, while In-doped ZnO (IZO) showed superior performance (88.5%) under solar light. These enhancements were attributed to doping-induced structural and optical modifications, including reduced bandgap energy (IZO) and improved crystallinity (CZO). The films were deposited on flexible polyetherimide (PEI) substrates, enabling versatile applications across different reactor geometries. Remarkably, all samples maintained high degradation efficiency (>89%) after three photocatalytic cycles, confirming their stability and reusability. The CV degradation kinetics followed a pseudo-first-order Langmuir-Hinshelwood model [104]. Cobalt doping is known to significantly alter the structural, optical, and other properties of ZnO nanoparticles, as shown by Naik et al. (2021) [109]. Successful substitution of Co²⁺ into the ZnO lattice without phase segregation maintained the hexagonal wurtzite structure, while reducing crystallite size from 35 nm (undoped) to 21 nm (10% Co). Optical studies revealed a redshift in the bandgap (3.33 eV to 3.17 eV) due to sp-d exchange interactions between Co²⁺ d-electrons and ZnO band electrons, enhancing visible-light absorption. Photoluminescence spectra showed increased defect-related emissions, indicating higher oxygen vacancies, which further confirms the catalyst efficiency [109]. Indium doping, on the other hand, significantly enhances the structural, optical, and photosensing properties

of ZnO thin films [110]. The incorporation of In^{3+} into the ZnO lattice at optimal doping at 2.5% results in improved crystallinity, evidenced by increased crystallite size and reduced microstrain, while higher concentrations (7.5%) induced lattice disorder.

The combination of zinc oxide (ZnO) with graphene oxide (GO) or reduced graphene oxide (RGO) significantly enhances photocatalytic performance by addressing key limitations of pure ZnO, such as rapid electron-hole recombination, photocorrosion, and low photostability. Additionally, RGO provides a large surface area for pollutant adsorption and active sites for photocatalytic reactions, making this combined catalyst a promising and economic choice for the photocatalytic degradation processes due to the good recyclability and long lifetime [111]. Puneetha et al. (2021) [105] developed a ZnO/graphene oxide (GO) hybrid with a reduced bandgap (2.71 eV vs. ZnO's 2.81 eV), enabling 99% CV degradation under visible light within 4 h—a 17% improvement over pure ZnO. The enhanced performance stemmed from Zn-O-C bond formation and defect generation, where GO served as an electron transporter to suppress charge recombination. Photoluminescence spectroscopy confirmed reduced electron-hole recombination rates in the hybrid. The composite's specific surface area more than doubled ($1.553 \text{ m}^2/\text{g}$ vs. $0.657 \text{ m}^2/\text{g}$ for ZnO), improving CV adsorption. The material retained high activity over four cycles, with an X-ray diffraction (XRD) confirming structural stability post-reaction. Notably, the solvent-free synthesis method proved more energy-efficient than conventional hydrothermal/sol-gel approaches [105].

The co-precipitation method is a cost-effective, energy-efficient, and scalable technique for synthesizing ZnO nanoparticles. It offers advantages such as rapid preparation, control over particle size and composition, and minimal surface defects [112]. The study by Yelpale et al. (2024) [15] revealed that co-precipitation time, in this synthesis route, critically determines ZnO morphology and photocatalytic performance. ZnO_90 (synthesized for 90 min) achieved 99% CV degradation in 150 min due to its porous, spindle-like structure with high surface area ($28 \text{ m}^2/\text{g}$), facilitating CV adsorption and reactive species generation under UV. The process followed pseudo-first-order kinetics, with ZnO_90 showing the highest rate constant (0.018 min^{-1}). It retained excellent activity through 4 reuse cycles [15].

Mittal et al. (2014) [106] found that 1% Mn doping dramatically improved ZnO's photocatalytic activity (99.1% CV removal in 3 h), attributed to reduced bandgap (2.94 eV vs. undoped ZnO), smaller particle size (15–20 nm), and enhanced visible light absorption.

Higher doping (2%) increased the bandgap (3.24 eV, Burstein-Moss effect), reducing efficiency. PVP (1%) capping prevented agglomeration and improved surface hydrophilicity, boosting CV adsorption. The process followed pseudo-first-order kinetics with the highest rate constant (0.02078 min^{-1}) for 1% Mn-ZnO, confirmed by photoluminescence spectroscopy showing reduced charge recombination [106]. Senol et al. (2015) [113] have reported that manganese doping in ZnO nanoparticles significantly influenced both structural and magnetic properties. Scanning electron microscopy (SEM) revealed porous morphologies with random agglomeration, while energy dispersive X-ray spectroscopy (EDS) confirmed successful Mn substitution [113]. Magnetic measurements demonstrated that all Mn-doped ZnO samples exhibited clear ferromagnetic behavior at room temperature, in contrast to the paramagnetic nature of undoped ZnO. Structurally, Mn incorporation preserves the wurtzite phase but seems to introduce lattice distortions and variations in crystallite size, reflecting increased microstrain and defect density [35,113]. Belkhaoui et al. (2019) [35] have reported that Mn doping has induced a red shift in the absorption edge and reduced the band gap, which might be attributed to sp-d exchange interactions between the Mn ions and ZnO host lattice, thereby enhancing visible light absorption. However, excessive Mn content led to pronounced defect states that could act as non-radiative recombination centers, diminishing optical quality [35]. Low Mn doping levels improved

conductivity due to enhanced carrier concentration, while higher doping introduced scattering centers that suppressed mobility. Thus, Mn plays a dual role—beneficial at low concentrations for tailoring ZnO's multifunctional properties, but detrimental at higher levels where structural disorder and defect-driven recombination dominate [35,113,114].

Graphitic carbon nitride (g-C₃N₄) is recognized as a promising metal-free photocatalyst widely used for degrading organic pollutants (e.g., dyes like methyl orange and rhodamine B), hydrogen evolution, CO₂ reduction, and organic synthesis. Its advantages include low-cost synthesis, excellent thermal and chemical stability, and a suitable bandgap (~2.7 eV) that enables visible-light absorption. Additionally, its eco-friendly nature makes it a sustainable alternative to metal-based photocatalysts. Considering these advantages, this material might also be very efficient when it comes to CV degradation, especially in combination with ZnO due to improved charge separation by leveraging the visible-light response of g-C₃N₄ and the wide bandgap of ZnO [60]. The study by Sifat et al. (2024) [6] highlighted the exceptional photocatalytic efficiency of ZnO and TiO₂, achieving 98% and 95% CV degradation, respectively, within just 2 h under UV light (365 nm). This high degradation activity was attributed to their optimal bandgap values (~3.2 eV), which corresponds well with UV radiation energy, along with their ability to facilitate water molecule decomposition—a crucial process for generating reactive hydroxyl radicals [6]. Commercial ZnO demonstrated better performance than TiO₂, which was ascribed to its larger specific surface area (12.1 m²/g compared to 5 m²/g for TiO₂). The CV degradation followed first-order kinetics, with ZnO showing a significantly higher rate constant (0.036 min^{−1}) than TiO₂ (0.028 min^{−1}). Mechanism analysis revealed hydroxyl radicals as the key reactive species, while superoxide radicals had a lesser impact.

The g-C₃N₄/ZnO nanocomposite showed substantially better CV degradation efficiency (97%) compared to pure g-C₃N₄ and ZnO (88% for each material individually). This improvement was attributed to the formation of a heterojunction between g-C₃N₄ and ZnO, which enables better separation of photo-generated charge carriers (electrons and holes) and reduces their recombination. XRD analysis confirmed successful nanocomposite synthesis, showing the characteristic (002) peak for g-C₃N₄ in the sample. Field emission SEM (FESEM) images revealed that ZnO had a hexagonal rod structure, while the composite formed multi-layered rod-like structures. Ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) spectra showed a shift in the absorption profile of the composite toward the visible region (2.7 eV), explaining its better efficiency under solar light. The nanocomposite maintained high efficiency (94%) after five usage cycles, with CV degradation following pseudo-first-order kinetics and a rate constant (k) of 0.014 min^{−1} for the composite. Scavenger experiments demonstrated that photo-generated holes (h⁺) played a key role in CV degradation, along with superoxide and hydroxyl radicals [107]. Future research should focus on advanced nanostructuring, doping strategies, and computational modeling to optimize g-C₃N₄-based photocatalysts. Improving heterojunction designs and exploring scalable synthesis methods might be crucial for practical applications in wastewater treatment and renewable energy.

Cobalt doping represents another promising doping solution, significantly impacting the structural, optical, and magnetic properties of zinc oxide nanoparticles, as reported by [114,115]. Experiments showed that 0.5 mol% Cd-ZnO achieved the best efficiency (100% CV degradation in 30 min under alkaline conditions), while higher Cd concentrations (1.0–2.0 mol%) reduced performance due to electron-hole recombination, indicating the critical role of doping balance in improving charge carrier separation. Alkaline conditions (pH 10–12) were found to significantly accelerate the process, enabling complete degradation in just 30 min, which was attributed to increased generation of hydroxyl radicals identified as the primary reactive agents. The study also noted that cadmium doping

reduced ZnO's bandgap from 3.11 eV to 2.75 eV, extending the material's absorption capabilities into the visible spectrum. XRD and energy-dispersive X-ray spectroscopy analyses confirmed successful cadmium incorporation into the ZnO lattice, while FESEM revealed morphological changes (hexagonal rod structures). Density functional theory (DFT) calculations (B3LYP/6-31G) showed that cadmium doping modified HOMO-LUMO ranges, consistent with experimental UV-DRS results. Additionally, liquid chromatography–mass spectrometry and Fourier-transform infrared spectroscopy analyses confirmed complete CV degradation into less toxic intermediates, supported by toxicological predictions (EPA-TEST). The 0.5 mol% Cd catalyst maintained 95% efficiency after 5 cycles [87].

Zinc oxide/sodium alginate (ZnO/SA) nanocomposite was also recognized as a promising catalyst for photocatalytic removal of dyes, such as Direct Yellow 44. Sodium alginate (SA) was chosen as a polymer matrix for ZnO nanoparticles due to its biodegradability, non-toxicity, and carboxyl-rich structure, which enhances pollutant adsorption. Its film-forming ability and pH sensitivity facilitated nanocomposite synthesis and dye removal. However, SA's mechanical weakness may limit long-term stability, and its hydrophilic nature could reduce catalyst recovery efficiency [116]. The combination of adsorption (using grafted alginate) and photocatalysis (ZnO/GO) demonstrated significant improvement in CV removal. The SA-g-poly(AA-co-CA)/ZnO/GO composite (S3) achieved 94% efficiency under sunlight, which was 10% higher than the same process in darkness (84%). This confirms that sunlight activates photocatalytic degradation alongside parallel adsorption. The incorporation of graphene oxide sheets with ZnO nanoparticles in the polymer matrix caused a bandgap shift from 3.39 eV (UV) to 2.99 eV (visible light), enabling utilization of a broader solar spectrum and explaining S3's superior performance compared to S2 (ZnO alone). Adsorption followed pseudo-second-order kinetics, indicating chemisorption as the rate-limiting step. Intraparticle diffusion was a multi-stage process involving three phases (surface adsorption, matrix diffusion, and equilibrium). Isotherm data best fit the Freundlich model, suggesting heterogeneous surface multilayer adsorption. Although the S3 composite showed impressive efficiency, its weak desorption (maximum 5.7% in HNO₃) limits reusability [108].

3.3. Non-ZnO-Based Nanomaterials—Degradation Experiments and Kinetics

It is important to consider other catalysts that have demonstrated effective results in the degradation of CV. For comparison with ZnO-based materials, Table 5 summarizes various photocatalytic materials tested for CV degradation, along with their synthesis methods and performance metrics.

Table 5. Literature review of CV degradation experiments in the presence of various photocatalysts.

Catalyst	Synthesis Method	Degradation Efficiency (%)	Experiment Parameters	Illumination Time (min)	Reference
Zn ₃ V ₂ O ₈	Co-precipitation	94.52	0.1 g/L of catalyst, 200 mL of 10 ppm CV solution, pH = 6, UV exposure	150	[14]
SrFeO ₃ /g-C ₃ N ₄ (4 wt%)	Sintering of mixed components at 500 °C for 2 h	95	10 mg of catalyst, 100 mL of 10 ppm CV solution, VIS exposure (150 W Xe lamp at $\lambda \geq 422$ nm, intensity: 31.2 W/m ²)	96	[117]
TiO ₂ /Montmorillonite	Impregnation method (TiCl ₄) + calcination at 350 °C	97.1	0.08 g of catalyst, 500 mL of 10 ^{−4} mol/L CV solution, UV-A lamp (365 nm, 100 W/m ²)	360	[118]

Table 5. Cont.

Catalyst	Synthesis Method	Degradation Efficiency (%)	Experiment Parameters	Illumination Time (min)	Reference
BiSI/MoS ₂	Hydrothermal method (30 wt% BiSI on MoS ₂ nano-flowers)	90	50 mg of catalyst, 100 mL of 5 ppm CV solution, VIS exposure (250 W Hg lamp)	250	[119]
BiSI	Hydrothermal method (Bi(NO ₃) ₃ ·5H ₂ O + (NH ₂) ₂ CS + I ₂ in ethanole, 160 °C/30 h)	~30 (approx.)			
MoS ₂	Hydrothermal method (Na ₂ MoO ₄ ·2H ₂ O + NH ₂ CSNH ₂ + oksalna kiselina, 180 °C/24 h)	~20 (approx.)			
No catalyst (photolysis only)	/	<5	100 mL of 5 ppm CV solution, VIS exposure		
TiO ₂	Commercial (purity: ≥ 99%)	95	25 mg of catalyst, 50 mL of 10 ^{−5} M CV solution, UV exposure (365 nm), mixing at 200 rpm	120	[6]
g-C ₃ N ₄	Melamine pyrolysis	~88	25 mg of catalyst, 25 mL of 20 ppm CV solution, solar exposure	180	[107]
SA-g-poly(AA-co-CA) (S1)	Copolymerization (Graft) SA with AA/CA without photocatalyst	84 (in dark; adsorption, without photocatalysis)	0.1 g of catalyst, 50 mL of 30 mg L ^{−1} CV solution, pH = 5, 40 °C	300	[108]
Ce ₂ (MoO ₄) ₃ -CTAB	Microemulsion with cetyltrimethylammonium bromide (cationic surfactant), n-butanol (co-surfactant), isooctane (oil phase)	89	0.04 g of catalyst, 100 mL of 5 ppm CV solution, pH = 6, room temperature	300	[120]
Ce ₂ (MoO ₄) ₃ -TX-100	Microemulsion with TX-100 (non-ionic surfactant), 2-propanol (co-surfactant), cyclohexane (oil phase)	89			
Fe ₃ O ₄ /SnO ₂ (FS3—1:1)	Hydrothermal method (at 200 °C for 8 h) with FeCl ₂ and SnCl ₂ ·2H ₂ O in ratio of 1:1, calcination at 450 °C	83	500 mg of catalyst/500 mL of 2 × 10 ^{−5} mol/L CV solution, pH = 6, 30–33 °C, UV exposure (365 nm)	180	[121]
Fe ₃ O ₄ /SnO ₂ (FS1—1:4)	Hydrothermal method—higher SnO ₂ content (1:4)	83			
Fe ₃ O ₄ /SnO ₂ (FS2—4:1)	Hydrothermal method—higher Fe ₃ O ₄ content (4:1)	78			
Pure Fe ₃ O ₄	Hydrothermal method (180 °C, 12 h) iz FeCl ₂ i NaOH	76			
Pure SnO ₂	Hydrothermal method—SnCl ₂ ·2H ₂ O and NaOH	81			
Bismuth ferrite doped with gadolinium-Gd(0):BFO	Auto-combustion	35.8	0.2 g of catalyst, 20 ppm CV solution, Hg lamp (250 W)	180	[122]
Gd(2):BFO		84.5			
Gd(5):BFO		72			
Gd(10):BFO		61			
3D MnO ₂ nanofiber net	Hydrothermal method (180 °C, 24 h)	97	15 mg of catalyst, 15 mL of 40 ppm CV solution; UV exposure (Hg lamp, λ = 254 nm; 160 W)	90	[123]
3D MnO ₂ nanofiber net		99	40 mg of catalyst, 40 mL of 40 ppm CV solution; Sunlight exposure + H ₂ O ₂ (0.04 mL)	60	
3D MnO ₂ nanofiber net		84	15 mg of catalyst, 15 mL of 40 ppm CV solution, UV exposure (Hg lamp, λ = 254 nm; 160 W), pH = 3	280	
MnFe ₂ O ₄	Co-precipitation (MnCl ₂ ·4H ₂ O i FeCl ₃ at pH 10–11, at 80 °C)	25.13	1 g/L of catalyst, 20 mL of 10 ppm CV solution, pH = 6, sunlight exposure (75 W/cm ²)	120	[124]
g-C ₃ N ₄	Thermal decomposition of melamine at 550 °C for 3 sata	58.11			
g-C ₃ N ₄ @MnFe ₂ O ₄ (80:20 wt%)	Thermal decomposition of melamine + co-precipitation (MnFe ₂ O ₄)	98.42			
MoS ₂ /ZnS	Hydrothermal method	98.5	0.5 g/L of catalyst, 10 mg/L CV solution, pH = 7, VIS exposure (Xenon lamp, 300W), 25 °C, mixing at 300 rpm	40	[125]
MoS ₂		60			
ZnS		49			
Ag ₃ PO ₄ /Bi ₂ WO ₆ -0.3	Hydrothermal method + mixing (Bi ₂ WO ₆ nanoflakes + Ag ₃ PO ₄ nanospheres)	~100	200 mg of catalyst, 220 mL of 50 ppm CV solution, 25 °C, Xe lamp (λ > 410 nm, 400 W)	120	[30]

Table 5. Cont.

Catalyst	Synthesis Method	Degradation Efficiency (%)	Experiment Parameters	Illumination Time (min)	Reference
α -ZrP	Precipitation of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ using H_3PO_4 (at 650 rpm, 80 °C, HF controlled pH)	41.3	0.4 g/L of catalyst, 50 mL of 10 ppm CV solution, pH: 7, sunlight exposure	90	[126]
g- C_3N_4	Thermal decomposition of melamine at 550 °C for 3 h	64.7			
α -ZrP/g- C_3N_4 (2:1)	Direct precipitation of α -ZrP at g- C_3N_4 with mixing at 80 °C for 2 h	97.8			
TDB (TiO_2 /raw diatomite)	Solvothermal-hydrolysis sol-gel method (TiCl_4 + sirov diatomit, 70 °C/24h, kalcinisan na 350 °C)	99.996	150 mL of 25 ppm CV solution, pH = 10, room temperature, UV exposure (365 nm)	210	[127]
TDS (TiO_2 /acid treated diatomite)	Solvothermal-hydrolysis sol-gel method (TiCl_4 + acid treated diatomite, 70 °C/24 h, calcined at 350 °C)	99.96		390	
TiO_2	Solvothermal-hydrolysis sol-gel method (only TiCl_4 , 70 °C/24 h, calcined at 350 °C)	99.17		735	

Bimetallic oxide nanocomposites offer significant advantages over single-metal oxides, such as ZnO, primarily due to their enhanced light absorption, reduced band gap, and improved charge carrier separation. The incorporation of a second metal oxide (e.g., NiO with ZnO) shifts absorption into the visible range, enabling efficient sunlight-driven photocatalysis [128]. BMOs also exhibit higher surface areas and better adsorption capabilities, crucial for concentrating pollutants near active sites. However, their synthesis, especially via green routes, may introduce variability in morphology and composition, potentially affecting reproducibility. While BMOs like NiO–ZnO show superior activity and reusability, their environmental safety and long-term stability in real wastewater matrices require further investigation [128].

Druzian et al. (2023) [129] report that bimetallic oxides TiO_2/ZnO deposited on montmorillonite (MMT) exhibit better photocatalytic performance than single metal oxides due to synergistic effects. In addition, the role of montmorillonite as a substrate was recognized, which increases the specific reaction area and enhances the photocatalytic activity. Bimetallic oxide nanocomposite $\text{Fe}_3\text{O}_4/\text{SnO}_2$ combines magnetite with n-type semiconductor, resulting in a catalyst with novel physicochemical properties that improve the efficiency of the catalyst. The $\text{Fe}_3\text{O}_4/\text{SnO}_2$ heterostructure enhances charge carrier (electron-hole) separation, reducing recombination and increasing hydroxyl radical generation [121]. It would be particularly interesting to explore the development of a ternary nanocomposite based on $\text{Fe}_3\text{O}_4/\text{SnO}_2$ integrated with rGO, as such a structure could provide pronounced synergy effects between the components for CV degradation. While Fe_3O_4 and SnO_2 individually contribute to magnetic separability and high adsorption capacity, respectively, their combination with rGO provides a conductive scaffold with a large surface area that mitigates agglomeration and promotes better dispersion of nanoparticles. The synthesized mixed oxides of vanadium and zinc ($\text{Zn}_3\text{V}_2\text{O}_8$) catalyst demonstrated exceptional photocatalytic activity, achieving 94.52% CV degradation (Table 5). Optimal degradation occurred at a pH = 4, where the electrostatic attraction between positively charged CV molecules and the catalyst was enhanced [14].

Graphite nitrogen carbide is a semiconductor with a p-conjugated structure that has been used with other photocatalysts to synthesize heterojunctions that promote photocatalytic activity. The development of perovskite-type $\text{SrFeO}_3/\text{g-C}_3\text{N}_4$ composites presents an interesting heterojunction that exhibits improved charge separation, broader optical absorption, and enhanced stability. The perovskite component contributes high thermal stability, low cost, and promising catalytic activity, while g- C_3N_4 , as a metal-free polymeric semiconductor, provides structural tunability and visible-light activity but typically re-

quires coupling to overcome rapid electron–hole recombination [130]. Lin et al. (2016) [117] developed a $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ photocatalyst heterojunction by sintering for the photocatalytic degradation of crystal violet under visible irradiation. The photocatalytic degradation was evaluated by measuring the degradation efficiency, which confirmed an efficiency of over 95% (Table 5). According to the results presented by Rathore and coworkers [124], the nanocomposite $\text{g-C}_3\text{N}_4/\text{MnFe}_2\text{O}_4$ exhibited exceptional photocatalytic activity and achieved 98.42% degradation of CV dye upon exposure to sunlight, which significantly exceeded the performance of the individual components. This improved performance was attributed to the formation of a p–n heterojunction, which suppressed electron–hole recombination and improved the efficiency of charge separation, enabling better utilization of solar energy. Gupta et al. (2024) [126] investigated an $\alpha\text{-ZrP}/\text{g-C}_3\text{N}_4$ nanocomposite as a photocatalyst for the degradation of crystal violet synthetic dye under visible light and achieved a degradation efficiency of 97.8%. The authors reported that maximum efficiency was observed at pH = 6, attributed to favorable surface charge interactions between the catalyst and the dye molecules. At lower pH values, the positively charged surface repels the cationic CV dye, while at higher pH, the reduced generation of hydroxyl radicals lowers degradation efficiency [126].

The synthesized TiO_2 -montmorillonite composite ($\text{TiO}_2\text{-M}$) demonstrated exceptional photocatalytic efficiency, achieving 97.1% (Table 5). This superior performance stems from a dual mechanism combining strong dye adsorption with subsequent photocatalytic degradation, which is a result of the composite structure [118]. The study of immobilization of TiO_2 nanoparticles on natural minerals such as diatomite was performed in the context of photocatalytic performance in the degradation of CV dye. Diatomite prevented the agglomeration of TiO_2 nanoparticles and improved the thermal stability of the composite. Also, diatomite facilitated better dispersion of TiO_2 particles and stronger electrostatic interactions with CV dye molecules [127]. According to the literature review, the BiSI/MoS_2 heterostructure shows strong photocatalytic activity due to a synergistic effect. MoS_2 has already proven itself as a photocatalyst that can drive hydrogen evolution, nitrogen fixation, water electrolysis and the degradation of various pollutants. The low toxicity and ability to form heterojunctions make MoS_2 attractive as a co-catalyst. BiSI has desirable optical properties and a suitable band gap [131,132]. Bargozideh and Tasviri (2018) [119] reported in their study that a BiSI/MoS_2 nanocomposite achieved 90% CV degradation under visible light, significantly higher than the individual components (BiSI ~30%, MoS_2 ~20%). This improvement is based on synergistic effects resulting from the high electron conductivity of the MoS_2 nanoflowers in combination with the photocatalytic activity of BiSI . Metal molybdates are also an interesting group of inorganic compounds that have been reported to have catalytic activity. Dargahi et al. (2020) [120] show that $\text{Ce}_2(\text{MoO}_4)_3$ nanoparticles, combined with cationic and nonionic surfactants to realize stabilized nanoparticles, achieved 89% degradation of crystal violet under visible light.

Kossar et al. (2020) [122] investigated the influence of Gd doping on the catalytic properties of BiFeO_3 and reported that doping reduces the band gap of BiFeO_3 from 2.21 eV to 2.17 eV, thereby improving the absorption of visible light. The authors also suggest that there is an optimal doping concentration beyond which overdoping leads to increased charge recombination (electron–hole pairs) and reduced surface interactions, thereby impairing photocatalytic activity. Rahmat et al. (2019) [123] synthesized and evaluated MnO_2 nanofiber networks and achieved 97–99% CV degradation efficiency (Table 5) under UV and solar irradiation, which significantly outperformed conventional photocatalysts such as TiO_2 and ZnO . The superior performance was attributed to the unique three-dimensional network of the nanofibers, which provided a large surface area for dye adsorption and facilitated efficient electron transport. Experiments revealed

that acidic conditions (pH = 3) significantly improved the degradation efficiency, while neutral (pH = 7) and alkaline (pH = 10) environments resulted in lower efficiencies due to the increased formation of hydroxyl radicals in acidic media. Several studies have described the strong catalytic effect of ZnS/MoS₂ heterojunctions when irradiated with visible light [125,133]. Rao Akshatha et al. (2020) [125] reported degradation efficiency of 98.5% within just 40 min under visible light irradiation, representing an improved efficiency over pure MoS₂ (60%) and ZnS (49%). Synergistic enhancement was attributed to the optimal alignment of energy levels between the two components, wherein ZnS acts as an efficient electron donor, while MoS₂ provides abundant active sites for catalytic reactions. The characteristic interwoven morphology facilitated rapid charge carrier transport and significantly suppressed electron–hole recombination. In comparison with ZnO, a widely used photocatalyst, the ZnS/MoS₂ composite exhibits a narrower bandgap (2.91 eV) and enhanced visible light absorption. However, it requires additional steps for heterostructure fabrication and may be more susceptible to deactivation over prolonged use due to pore blockage or loss of active sites [133].

Heterostructures like Ag₃PO₄/Bi₂WO₆ have shown remarkable efficiency in degrading organic pollutants, including crystal violet, and achieved complete degradation under visible light. This performance was attributed to the enhanced spectral responsiveness and minimized recombination of the photogenerated charge carriers (e[−]/h⁺) [30]. Based on a literature review, ZnO and its advanced nanocomposites emerge as a superior and highly competitive class of photocatalysts for the degradation of CV, offering a compelling combination of efficiency, versatility, and practicality. In the CV degradation experiments, ZnO-based materials have demonstrated exceptional and tunable photocatalytic efficiency. Pure ZnO itself achieves impressive degradation rates (often above 82–98%), but its true strength lies in its highly modifiable properties. Strategic doping with elements like Cobalt (Co), Indium (In), Manganese (Mn), or Cadmium (Cd) fine-tunes the optical and electronic properties of doped photocatalysts to achieve a higher level of efficiency (Table 4). These modifications successfully narrow the bandgap, extend light absorption into the visible spectrum, and most critically, suppress the rapid electron-hole recombination that typically plagues pure ZnO. The formation of ZnO-based heterostructures and nanocomposites creates powerful synergistic effects. Combining ZnO with materials like graphene oxide (GO), graphitic carbon nitride (g-C₃N₄), or polymers (e.g., sodium alginate) seems to address its inherent limitations. The ZnO/GO hybrid, for example, achieved 99% degradation by leveraging GO as an electron transporter to minimize charge recombination. Similarly, the g-C₃N₄/ZnO nanocomposite outperformed its individual components by forming a heterojunction that enhanced charge separation. These composites often benefit from doubled surface areas, providing more active sites and improved adsorption capacity for the target pollutant. Compared to some novel and more advanced catalysts, ZnO-based catalysts exhibit remarkable stability and reusability. Multiple studies have confirmed that these materials maintain high efficiency after 3–5 photocatalytic cycles [87,104,107]. This confirms not only their catalytic robustness but also their economic viability, as they can be recovered and reused without a significant loss in performance, a key advantage over many single-use adsorbents or less stable catalysts. While other photocatalysts like TiO₂ or novel perovskites have their merits, ZnO and its nanocomposites offer an unmatched balance of high performance, structural versatility, cost-effectiveness, and stability. Their capacity for targeted modification allows them to be engineered for specific conditions, whether under UV or solar light, making them a premier and future-proof choice for advanced photocatalytic degradation processes.

While photocatalytic studies frequently employ controlled, artificial lighting systems, a significant knowledge gap remains regarding their performance under the variable and

spectrally complex conditions of natural sunlight. Factors such as fluctuating intensity, spectral shifts, and competing environmental influences necessitate more extensive investigation to assess real-world applicability and efficiency [134,135].

Furthermore, the intricate composition of real wastewater, comprising a diverse mixture of organic matter, inorganic ions, and suspended solids, presents a substantial challenge. The synergistic or antagonistic interactions between the photocatalyst, target pollutants, and this complex aqueous matrix are not yet fully understood, yet they are critical determinants of the overall degradation efficacy and practical viability of the process [136]. This challenge is compounded by the common research approach of optimizing individual parameters—such as pH, catalyst loading, or light intensity—in isolation. In actual application environments, these factors operate within a dynamic and interconnected system. A more holistic understanding of their combined and interactive effects is essential for accurate prediction and scaling of photocatalytic performance [137].

To bridge the identified gaps between laboratory research and real-world application, a structured and comprehensive research roadmap is proposed. This plan addresses the critical challenges of environmental complexity, economic viability, and fundamental mechanistic understanding.

1. Development of a standardized multi-variable testing template: A pivotal initial step involves creating a robust laboratory-based testing protocol designed to evaluate photocatalysts under a wide array of variable conditions simultaneously. This template would systematically combine factors like pH, initial pollutant concentration, catalyst loading, light intensity, and the presence of common inorganic ions and organic scavengers. By testing catalysts against this comprehensive matrix of conditions, researchers can generate a rich, comparable dataset. This “catalyst fingerprint” would then serve as a powerful benchmark, allowing for direct and meaningful comparison of new materials or new environmental conditions against established baselines, significantly accelerating the screening and development process.
2. Holistic performance optimization under real conditions: Moving beyond isolated parameter studies, future work must adopt a systems approach to understand the dynamic interactions between key variables (e.g., pH, catalyst loading, fluctuating light intensity) within complex environments. This is essential for developing robust models that can predict performance in real-world settings, not just idealized laboratory systems.
3. Validation under natural solar irradiation: A critical step is to transition from artificial light sources to validation under natural sunlight. Research must compare degradation kinetics and photonic efficiency with Light Emitting Diode (LED)-based systems while quantitatively measuring the impact of solar spectral shifts and intensity fluctuations (as well as UV index) on catalytic performance and energy balance.
4. Advanced water matrix interaction studies: To address the complexity of real effluents, a systematic investigation using both authentic wastewater samples and designed synthetic matrices is crucial. This will isolate the effects of individual inorganic and organic constituents, moving beyond Cl^- and HCO_3^- to understand how a diverse mix of compounds synergistically or antagonistically impacts photocatalytic efficiency and catalyst stability.
5. Catalyst longevity and reusability assessment: Practical application demands catalysts that are not only effective but also durable. Rigorous testing over 3–5 consecutive reaction cycles must be conducted, coupled with thorough post-cycle surface analysis (X-ray photoelectron spectroscopy—XPS, Brunauer-Emmett-Teller—BET, SEM) to quantify activity loss, identify deactivation mechanisms (e.g., fouling, poisoning, structural change), and develop effective regeneration protocols.

6. Comprehensive by-product profiling and toxicity evaluation: Ensuring environmental safety requires moving beyond parent pollutant removal. Advanced non-targeted liquid chromatography-mass spectrometry—LC-MS/MS analysis is needed to identify transformation products, complemented by a battery of bioassays to track the evolution of toxicity throughout the treatment process and perform a complete ecological risk assessment.
7. Techno-economic and scaling analysis: A definitive feasibility study is paramount. This requires a full economic and energy analysis comparing LED systems to conventional UV lamps, calculating metrics like electrical energy per order. Furthermore, process modeling must be employed to assess scalability, operational costs, and capital expenditures for potential pilot-scale and full-scale implementation.
8. Mechanistic elucidation via in situ spectroscopy: To fundamentally understand the interactions within complex matrices, in situ spectroscopic techniques (electron paramagnetic resonance—EPR, Fourier transform infrared—FTIR, Raman) must be applied. These methods will allow for the direct observation of reactive species generation, surface reaction pathways, and the real-time impact of water matrix components on catalytic mechanisms, informing more effective catalyst and process design.

Despite the significant progress in ZnO-based photocatalysis for CV degradation, analysis of the literature reveals a critical challenge: the vast diversity of synthesis methods and experimental conditions severely hinders the direct comparison of photocatalytic performance across different studies. To address this issue and foster more reproducible and comparable research, recommendations for a standardized experimental framework were proposed:

1. Benchmarking: Studies should include a well-established reference catalyst under identical conditions to serve as an internal benchmark for relative performance assessment.
2. Light source characterization: The light source must be precisely characterized. Reports should include the type (e.g., UV-A LED, solar), peak wavelength(s), irradiance (W/m^2) measured with a calibrated radiometer, and the distance to the reactor.
3. Standardized reaction Conditions: While specific research questions may require deviation, we suggest an initial set of standard conditions for screening purposes: Catalyst loading: 0.5–1.0 g/L; initial CV concentration: 10 or 20 mg/L; pH: Report performance at the solution's natural pH and at a controlled pH. Also, a mandatory dark adsorption period to establish adsorption–desorption equilibrium before illumination should be implemented, and the adsorption efficiency should be reported separately.
4. Performance metrics: Beyond percentage degradation, studies should report kinetic metrics and the initial reaction rate to allow for more robust quantitative comparisons.

Adopting such a framework could enhance the coherence of future research and accelerate the development of efficient photocatalytic systems for practical applications.

3.4. Optimization of Photocatalytic Degradation Experiments on ZnO-Based Nanomaterials

Assessing the performance of photocatalytic materials requires a detailed analysis of degradation kinetics following nanomaterial characterization. However, the complex interplay of multiple experimental variables often makes it challenging to isolate and understand the specific contribution of each parameter. This complexity has led researchers to increasingly adopt advanced computational approaches, particularly machine learning techniques and ANN, to enhance data interpretation and process optimization [138].

Within the field of engineering, ANNs have established themselves as versatile and robust computational tools. These systems represent just one approach among many in machine learning, which also includes adaptive neuro-fuzzy systems, decision trees, support vector machines, and deep learning architectures. Drawing inspiration from

biological neural networks, these computational models have evolved far beyond their original theoretical foundations. Modern implementations can identify intricate patterns in complex datasets, generate accurate predictive models, and support data-driven decision-making across various scientific and industrial applications [139].

Compared to conventional modeling methods, neural networks demonstrate superior pattern recognition in complex, nonlinear datasets, enabling more precise trend analysis [140–142]. Their architecture consists of interconnected artificial neurons organized in layers, where input layers receive experimental data, hidden layers process patterns (typically one suffices), and output layers produce predictions. The universal approximation theorem confirms that a single sufficiently large hidden layer can model any input-output relationship, with neuron count being a key design parameter for prediction accuracy [138].

Adjusting the number of hidden layers and neurons within them is critical to avoiding underfitting and overfitting. Underfitting occurs when the network has too few neurons or layers to learn complex data patterns, while overfitting arises from excessive neurons or layers, leading to poor generalization on new data. Regularization techniques like L1 (Lasso), L2 (Ridge), or Elastic Net can mitigate overfitting by penalizing large weights and improving classification performance [142]. For convolutional ANNs, optimized learning with regularization boosts accuracy by 4 percentage points while minimizing both underfitting and overfitting [143].

Adaptive neuron pruning has been shown to effectively reduce both issues [144]. Additional strategies like early stopping and dropout in deep neural networks further enhance performance and curb overfitting [145]. Dynamic regularization outperforms static methods by adaptively adjusting regularization strength during training, improving generalization [146]. Bias terms, added to neuron outputs before activation, are essential for architectural flexibility. They enable neurons to adjust outputs independently of inputs, enhancing the network's ability to learn complex patterns.

The training phase in the ANN optimization concludes when the mean squared error is minimized across all training experiments. Once trained, the ANN demonstrates strong predictive capability, accurately describing surface responses without requiring insight into the system's physicochemical basis. ANNs provide an alternative to polynomial regression for modeling, unlike traditional RSM, which requires predefined polynomial functions (linear, first-order interaction, or quadratic) to be fitted. ANNs can model complex, nonlinear relationships without explicit equations. Additionally, RSM is constrained by the number of experimental design points, and each response requires its own polynomial equation. In contrast, ANN methodology is highly flexible, accommodating varied data structures and allowing for less formal experimental designs compared to statistical approaches. ANNs often outperform regression models in predictive power, as regression relies on predetermined statistical significance thresholds, excluding less significant terms. ANNs utilize all available data, potentially enhancing model accuracy [147].

Limited research has been conducted on the optimization of CV degradation using ANN, although existing studies on other dyes have demonstrated promising results. Table 6 provides a literature review of ANN optimization in photocatalytic degradation experiments, highlighting key parameters.

Studies presented in Table 6 reveal that ANN models can effectively predict and optimize degradation conditions, offering a robust alternative to traditional experimental methods.

Table 6. Literature review of ANN optimization of dye removal experiments on ZnO-based nanomaterials.

Catalyst	Pollutant	Illumination	Degradation Efficiency (%)	Most influential Parameter	ANN Architecture	R ²	Reference
ZnO	Crystal violet	Without illumination (adsorption only)	99.82%	-	4-4-1	0.9998	[148]
ZnO-NP-AC and Na, K-doped ZnO-NP-AC	Crystal violet	Without illumination (adsorption only)	99.1%	-	5-15-1	0.984	[149]
Cu-doped ZnO	Reactive black 5	UV	-	Dye concentration	4-6-1	0.94	[150]
ZnO, and TiO ₂ -ZnO—synthesized via the impregnation method with the addition of 1.5% and 2.5% of Fe	Maxilon blue 5G	UV	100%	Dye concentration	3-3-1	0.99	[151]
Ni-doped ZnO	Acid orange 7	UV	93%	-	4-7-1	0.991	[152]
ZnO on light expanded clay aggregate	Reactive Yellow 84	UV	-	Time (for the first 30 min); UV intensity /lamp power (after 30 min)	5-9-9-1	0.9708	[153]
ZnO/Mg-Al layered double hydroxide	Methyl orange	UV	91.21%	Calcination temperature	4-5-1	0.968	[154]
B-doped ZnO	Methyl orange	UV	99.94%	-	4-14-1	0.991	[155]
PUM-ZnO (pumice with zinc oxide); synthesised via the impregnation method with a calcination (900 °C, 4 h)	Organic pollutants in textile effluent	Sunlight	99.46%	-	3-10-1	0.993	[156]
ZnO/MMT (zinc oxide with montmorillonite); ZnO synthesized on the surface of montmorillonite (MMT) with the aid of a surfactant	Disperse red 54	UV-C	99.92%	Catalyst dosage	3-10-1	0.9998	[157]
ZnO/AC; ZnO synthesized on activated carbon (AC) through alkaline precipitation and post-thermal treatment	Sunset yellow	Without illumination (adsorption only)	98.81%	Catalyst dosage	3-6-1	0.9988	[158]
ZnO and ZnO/SnO ₂	Eosin Y	UV	-	Reaction time	6-12-18-1	0.9993	[159]

A direct bridge between artificial neural network (ANN) modeling and ZnO-based photocatalytic systems has already been demonstrated in a study by Dil et al. (2015) [148], who successfully applied a 3-layer feed-forward ANN with a Levenberg–Marquardt backpropagation algorithm to predict the removal efficiency of CV using ZnO nanorods. Their optimized ANN with a 4–4–1 architecture achieved a determination coefficient of $R^2 = 0.98\text{--}0.99$ with minimal mean square error (MSE) for both training and testing datasets, accurately correlating four input parameters—initial dye concentration, pH, adsorbent dosage, and sonication time—with the removal percentage. The removal efficiency of crystal violet reached 99.82% under optimal conditions. The model not only reproduced experimental results with high fidelity but also revealed nonlinear dependencies consistent with physicochemical mechanisms of ZnO-based adsorption and photocatalysis.

The study by Karimi et al. [149] successfully developed and characterized zinc oxide nanoparticles loaded on activated carbon (ZnO-NP-AC), both with and without Na and K doping, for the simultaneous ultrasound-assisted removal of Crystal Violet (CV) and Quinoline Yellow (QY) dyes. The optimal conditions for maximum removal efficiency were identified using Central Composite Design (CCD) as follows: a pH of 7, an adsorbent mass of 0.02 g, a sonication time of 4 min, and initial dye concentrations of 15 mg L^{−1} for CV and 10 mg L^{−1} for QY. Under these optimized conditions, exceptional removal percentages of 99.1% for CV and 90.16% for QY were achieved.

Crucially, an ANN model was developed to predict the experiment outcome, demonstrating an outstanding predictive capability for CV removal. The ANN model for CV achieved a high coefficient of determination (R^2) of 0.984 and a very low Absolute Average Deviation (AAD%) of 1.06%, indicating a strong agreement between the model's predictions and the experimental data. When compared to the CCD model, which had an R^2 of 0.974 and an AAD% of 1.87% for CV, the ANN proved to be the superior predictive tool due to its lower error. The ANN was structured with 5 input parameters, a single hidden layer containing 7 neurons for CV, and one output, trained using the Levenberg–Marquardt backpropagation algorithm.

An ANN model was also used to predict experimental outcomes for using ZnO-based nanomaterial photocatalysts for the removal of different azo dyes [150–155]. Salehi et al. (2015) [150] compared ANN with Multiple Linear Regression (MLR), a form of RSM, for modeling the photocatalytic degradation of azo dye using Cu-doped ZnO nanoparticles. The ANN model demonstrated superior predictive capability for the training, validation, and test datasets, respectively, as well as enhanced ability to capture the complex, non-linear relationships between process variables, such as dye concentration, pH, UV intensity, and contact time, which were identified as the most influential parameters through sensitivity analysis. The findings confirm that ANN is a more robust and accurate modeling tool than traditional MLR for optimizing this photocatalytic process. Lenzi et al. (2015) modeled and optimized the photocatalytic degradation of the textile dye Maxilon Blue 5G using ZnO based catalyst by an ANN model—a multilayer perceptron with three layers, backpropagation algorithm, and sigmoid activation function—achieved high prediction accuracy ($R^2 = 0.98$ – 0.99), confirming its suitability for degradation process modeling and parameter optimization [151]. Pirshab et al. (2019) [152] demonstrated ANN performance in modeling the photodegradation of Acid Orange 7 using Ni-doped ZnO nanoparticles under sunlight and ultraviolet irradiation. The ANN model achieved a coefficient of determination of 0.991 and 0.981 for the process under sunlight and ultraviolet irradiation, respectively.

Moradi et al. [153] used and compared four distinct machine learning approaches—Multilayer Perceptron (MLP), Gaussian Process Regression (GPR), Radial Basis Function (RBF), and Adaptive Neuro-Fuzzy Inference System (ANFIS) to predict the photocatalytic degradation efficiency based on five input parameters: initial dye concentration, pH, decolorization time, catalyst concentration, and UV lamp power. A dataset of 221 experimental points, validated as reliable by the Leverage method, was used for model training and testing. Among the models, the GPR-based approach demonstrated superior predictive performance, achieving the best metrics on the test dataset. Hosseini and Akbari (2016) [154] designed the experimental process using Response Surface Methodology (RSM) and modeled with an ANN to predict and optimize the methyl orange removal efficiency in the presence of ZnO-based nanocatalyst. The ANN model demonstrated superior predictive capability compared to the RSM model, effectively capturing the complex, non-linear relationships of the photocatalytic system. The developed ANN was a feed-forward multilayer perceptron (MLP) trained with the Levenberg–Marquardt algorithm, featuring an architecture with one hidden layer containing 5 neurons. This model achieved an overall coefficient of determination (R^2) of 0.968, confirming its high accuracy in simulating the dye removal process. Nedelkovski et al. (2025) [155] developed a predictive ANN model built entirely in Python (version 3.10). This model was designed to forecast photocatalytic efficiency based on four key experimental parameters, creating a powerful tool for optimization without the need for extensive lab work. The model's architecture was a feed-forward neural network (FFNN) with 4 input neurons (dopant content, mixing time, calcination temperature, photocatalysis time), one hidden layer with 14 neurons using a sigmoid activation function, and a single linear output neuron (degradation efficiency).

Trained on experimental data, the model demonstrated exceptional predictive accuracy, achieving a coefficient of determination of $R^2 = 0.9810$ on the test set and $R^2 = 0.991$ on new, unseen data.

Literature data show that ANN architecture has been employed to optimize the photodegradation of organic pollutants in real textile effluents [156], DR54 [157], Sunset Yellow [158], and Eosin Y. [159] dyes using ZnO-based nanomaterials. Additionally, similar successful optimization results have been reported in experiments on non-ZnO materials [160–162].

In the study by Kıranşan et al. (2014) [157], a 3-10-1 ANN architecture was employed, based on minimal mean squared error, with 10 hidden-layer neurons providing the most accurate predictions. Relative importance analysis revealed the ZnO/MMT catalyst dosage as the most critical factor. The model's exceptional predictive capability confirms its robustness for industrial wastewater treatment design, while its parameter quantification feature enables precise process scaling. Maghsoudi et al. (2015) [158] developed an ANN model to optimize dye adsorption on ZnO nanorods/activated carbon. The optimal 3-6-1 topology was chosen based on minimal MSE and high correlation. Trained on 270 experimental datasets using the Levenberg–Marquardt algorithm for rapid convergence, the model identified catalyst dosage as the most influential parameter.

An efficient eosin Y dye removal via photodegradation was achieved in the presence of ZnO/SnO₂ nanocomposites [159]. A predictive ANN model was created using six key inputs. The model achieved outstanding accuracy, with a correlation of 0.999 and a low ~4% error, identifying reaction time as the most critical factor.

The current literature, with a focus on photodegradation experiments, consistently demonstrates the superiority of ANN over traditional statistical optimization approaches such as Response Surface Methodology (RSM) and Box–Behnken Design (BBD) in modeling and predicting photocatalytic dye degradation processes [77,163,164].

However, several critical considerations must be addressed. While ANNs excel in system-specific optimization (e.g., phenol, azo dyes), their predictive accuracy for CV—a structurally distinct triarylmethane dye—may require tailored architectures. The non-linear interactions of CV's cationic structure with catalysts (e.g., TiO₂, ZnO) might demand multiple hidden layers or alternative activation functions to capture its unique degradation pathways.

Current models rely on controlled parameters (pH, catalyst dosage), but CV degradation often involves competing factors (e.g., dye aggregation, light absorption interference). ANNs trained on narrow experimental ranges may fail under real-world variability unless augmented with noise-injection techniques or adversarial training.

High R^2 values may reflect over-optimization for specific systems. For CV, cross-validation with diverse datasets (e.g., mixed pollutants, natural water matrices) is essential to ensure generalizability. ANNs' nature limits insight into CV's degradation mechanisms (e.g., N-demethylation vs. chromophore cleavage). Hybrid approaches coupling ANNs with kinetic modeling (e.g., pseudo-first-order fits) could bridge this gap. Most studies use lab-scale reactors. For CV treatment in industrial effluent, ANNs must integrate hydrodynamic parameters (e.g., flow rates, reactor geometry), requiring convolutional or recurrent architectures.

4. Conclusions

This literature review highlights key aspects of the photocatalysis of CV, emphasizing the role of ZnO and ZnO-based nanomaterials as highly efficient photocatalysts due to their tunable bandgap, stability, and ability to generate reactive species. Experimental results demonstrate that ZnO under UV irradiation is exceptionally effective in degrading CV,

achieving high rates of decolorization and mineralization. The degradation mechanism involves the formation of hydroxyl and superoxide radicals, which attack the conjugated structures of the dye, leading to molecular fragmentation into less toxic intermediates and, ultimately, into CO_2 and H_2O . Under optimal conditions (appropriate pH, catalyst dosage, light intensity), complete degradation of CV can be achieved in a relatively short time. A comparison between UV-A and natural sunlight reveals that while UV-A is more efficient due to a higher number of photons with sufficient energy for catalyst activation, sunlight demonstrates significant photocatalytic activity, alongside advantages in energy sustainability and cost-effectiveness. However, challenges such as charge carrier recombination in ZnO and the potential formation of toxic intermediates require further investigation.

There is a pronounced lack of feasible information on photocatalytic processes at the pilot or industrial scale for applications beyond basic water treatment. Some recent reviews call for more studies focused on continuous experimental processes in pilot-scale units and strategies for scaling up. This is crucial to move beyond model systems and understand real-world performance, including the lifecycle, reproducibility, and long-term stability of photocatalytic materials under realistic conditions. For any novel system, such as one guided by artificial neural networks (ANN) for optimization, validation in a pilot plant is an essential step to assess its true potential, economic impact, and environmental sustainability before commercial deployment. In conclusion, despite the advanced potential of ANN-guided designs to optimize parameters, the fundamental engineering challenges of photoreactor scale-up, light distribution, mass transfer, and system integration remain. Therefore, pilot-scale validation is indispensable to translate the theoretical benefits of these advanced photocatalysts into practical, industrially relevant technologies.

The photocatalytic degradation of CV using these nanomaterials holds great potential for industrial wastewater treatment. Nevertheless, further optimization of the catalysts (through synthesis conditions and structural modifications) and process parameters (via machine learning modeling) is necessary to achieve commercial applicability. It is important to note that, compared to traditional optimization methods like RSM, ANNs exhibit superior performance in predicting and modeling the photocatalytic degradation of organic dyes and other substances. ANNs can process a wide range of input parameters (pH, catalyst concentration, light intensity, time) and more accurately predict output parameters (degradation efficiency, kinetic constants). While RSM relies on statistical polynomial equations to approximate nonlinear processes, ANNs can recognize complex, nonlinear patterns in data without predefined mathematical forms, which is crucial for intricate photocatalytic systems.

To monitor the efficiency of the ANN model in the degradation of CV, traditional metrics such as R^2 and root mean square error (RMSE) should be complemented with normalized errors (nRMSE, MAE) to ensure reliability across varying concentrations. Statistical tests (e.g., Wilcoxon, Bland–Altman) can reveal systematic biases, while dynamic metrics like mean absolute percentage error (MAPE) enable real-time monitoring, which is particularly important for continuous systems. The Levenberg–Marquardt (LM) algorithm is efficient but prone to overfitting when applied to small datasets. Bayesian Regularization can enhance generalization, while adaptive algorithms perform better under dynamic conditions. Hybrid approaches, such as combining genetic algorithms (GA) with ANN, can optimize hyperparameters and improve model accuracy.

Given the complex structure of CV, a configuration with multiple hidden layers containing 10–20 neurons might be optimal. Swish or LeakyReLU activation functions in the hidden layers capture nonlinearity more effectively, while the output layer can employ a sigmoid function (for percentage outputs) or a linear function (for kinetics). Dropout layers (with rates between 0.1 and 0.3) help mitigate overfitting, especially in noisy

data environments. Min-Max scaling is suitable for a wide range of CV concentrations. Feature engineering should include interaction terms (e.g., pH $\times$ time) and additional parameters such as absorbance at characteristic wavelengths, which can enhance the predictive capability of the model. Applying 10-fold cross-validation and nested cross-validation increases model reliability. Regularization techniques (such as L1/L2 penalties and early stopping) prevent overfitting, while D-optimal experimental design allows for the generation of informative data at minimal cost.

Finally, tools like SHAP values and LIME assist in identifying key parameters (e.g., pH, catalyst dosage) and explain the model's decisions under specific conditions. This is critical for practical deployment, as it links ANN predictions to real-world chemical processes. A hybrid approach that integrates ANN with kinetic models (e.g., Langmuir-Hinshelwood) enables more accurate prediction of rate constants and provides a deeper understanding of the degradation mechanism. This is particularly beneficial for scaling the process from laboratory to industrial scale.

In conclusion, future research directions should include:

- Modifications of ZnO (doping and forming heterostructures with Cu₂O) to enhance visible-light absorption and reduce charge carrier recombination.
- Exploring the application of synthesized materials under sunlight and in real effluents, where the presence of other organic and inorganic compounds may affect efficiency.
- Optimizing experiments using machine learning techniques to reduce the number of required experiments while evaluating the influence of various operational parameters.

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Abbreviations

The following abbreviations are used in this manuscript:

CV	Crystal Violet
UV	Ultra Violet
ANN	Artificial Neural Network
RSM	Response Surface Methodology
AOP	Advanced Oxidation Processes
EDS	Energy-Dispersive Spectroscopy
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction

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