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Visible-Light Photocatalytic Degradation of Textile Dyes Using ZnO and Co-Doped ZnO Nanoparticles

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Abstract

Textile effluents often contain intensely colored, persistent organic dyes that are difficult to destroy by conventional separation processes. Semiconductor photocatalysis offers a route to oxidize dye molecules through light-generated electron-hole pairs and reactive oxygen species. This methodology paper presents a reproducible visible-light photocatalytic framework using zinc oxide (ZnO) and cobalt-doped ZnO (Co-ZnO) nanoparticles as model metal-oxide photocatalysts. The study combines nanoparticle synthesis, physicochemical characterization, dark adsorption equilibration, visible-light irradiation, kinetic analysis, radical-scavenger experiments, and catalyst-reuse testing. Methylene blue and methyl orange are selected as representative cationic and anionic dye probes so that surface-charge and molecular-structure effects can be compared under identical operating conditions. X-ray diffraction, FTIR, scanning electron microscopy, and UV-Vis diffuse-reflectance spectroscopy are used to verify crystal phase, surface chemistry, morphology, and visible-light response. Photocatalytic activity is evaluated by concentration decay measured with UV-Vis spectrophotometry, degradation efficiency, and apparent pseudo-first-order rate constants. The methodology also examines catalyst dosage, solution pH, initial dye concentration, irradiation time, reactive-species contributions, and reusability. Illustrative literature-informed results are provided only to demonstrate reporting and are not represented as unperformed experimental measurements. The proposed approach links band-gap engineering and nanoparticle properties to pollutant degradation and provides a compact basis for future laboratory validation of visible-light treatment of textile wastewater.

Introduction

Textile dyeing and finishing processes generate wastewater containing soluble colorants, salts, surfactants, and auxiliary chemicals. Many synthetic dyes contain aromatic and azo structures that resist biodegradation, so decolorization does not necessarily mean complete detoxification. Semiconductor photocatalysis has therefore received sustained

attention because absorbed photons can create conduction-band electrons and valence-band holes that participate in oxidative and reductive reactions. Hoffmann et al. [1] established the environmental basis of semiconductor photocatalysis and described the importance of interfacial charge transfer, oxygen reduction, and hydroxyl-radical chemistry. Herrmann [2] further summarized the fundamentals of

heterogeneous photocatalysis and its application to aqueous-pollutant removal.

Titanium dioxide is the benchmark photocatalyst because it is chemically stable, inexpensive, and well characterized; however, its wide band gap makes unmodified TiO₂ primarily ultraviolet-responsive. ZnO has a similarly wide band gap but can exhibit strong photocatalytic activity and high electron mobility. Sakthivel et al. [4] compared ZnO and TiO₂ for solar degradation of an azo dye and demonstrated that oxide identity and irradiation conditions strongly affect performance. The extensive review by Konstantinou and Albanis [3] showed that pH, dye structure, catalyst loading, initial concentration, oxygen availability, and irradiation intensity all influence TiO₂-assisted azo-dye degradation.

Visible-light operation is attractive because it permits more efficient use of solar radiation and low-energy LED sources. Strategies for extending metal-oxide response into the visible region include transition-metal doping, non-metal doping, defect engineering, dye sensitization, and heterojunction formation. Raliya et al. [8] compared TiO₂, ZnO, graphene oxide, and their composites for visible-light methyl-orange degradation, emphasizing the importance of composition and particle size. Ong et al. [9] reviewed ZnO as a solar photocatalyst and identified charge-carrier recombination as a central limitation. Transition-metal doping can introduce defect or intermediate states and alter electron-hole separation; Ebrahimi et al. [10] demonstrated dye degradation using Ag-, Cu-, and Mn-doped ZnO under UV and visible irradiation.

Recent studies through 2022 continued this direction. Huong et al. [13] reported strong

visible-light degradation of Direct Blue 71 using Co²⁺-doped ZnO nanoparticles. Sharotri et al. [14] investigated S-doped TiO₂ as a visible-light-responsive photocatalyst, while Yadav et al. [15] used a beta-cyclodextrin/CuO-ZnO composite for textile-dye degradation. Algarni et al. [16] demonstrated photocatalytic degradation of dyes under solar light using ZnO nanoparticles, and Noor et al. [17] reported improved methylene-blue degradation using doped BiVO₄. These studies show that visible-light activity depends not only on optical absorption but also on charge separation, adsorption, active surface sites, and catalyst stability.

The objective of the present methodology is to compare pristine ZnO with Co-doped ZnO under controlled visible-light conditions and to determine whether the modified material provides improved degradation kinetics without sacrificing reusability. Two model dyes are used to avoid drawing conclusions from a single chromophore. The methodology emphasizes appropriate controls, identical photon exposure, dark adsorption before irradiation, kinetic analysis based on measured concentration, and separation of adsorption from true photodegradation. Reporting follows the reproducibility principles advocated for heterogeneous photocatalysis by Buriak et al. [7].

Literature Review

Selected studies that directly inform the experimental design are summarized in Table 1. The literature demonstrates a progression from fundamental TiO₂ photocatalysis toward visible-light-active doped oxides and hybrid nanocomposites.

Table 1. Comparative Review of Photocatalytic Systems for Dye Degradation

Study	Photocatalyst / system	Key finding	Methodological relevance	Ref.
Hoffmann et al. (1995)	Semiconductor oxides	Established charge-transfer and ROS framework	Mechanistic basis	[1]
Herrmann (1999)	TiO ₂ heterogeneous catalysis	Summarized aqueous-pollutant photocatalysis	Reaction design	[2]
Konstantinou & Albanis (2004)	TiO ₂ / azo dyes	Reviewed kinetics and operating parameters	Factor selection	[3]
Sakthivel et al. (2003)	ZnO vs TiO ₂	Compared solar azo-dye degradation	Justifies ZnO reference	[4]
Saleh & Gupta (2012)	CNT/TiO ₂	Composite improved methyl-orange degradation	Charge-transfer concept	[6]
Buriak et al. (2014)	Reporting practice	Outlined reproducibility needs in photocatalysis	Controls and reporting	[7]

Raliya et al. (2017)	ZnO/TiO ₂ /GO	Visible-light MO removal depended on composition/size	Visible-light benchmark	[8]
Ong et al. (2018)	ZnO review	Analyzed solar ZnO mechanisms and modification	Doping rationale	[9]
Ebrahimi et al. (2019)	Metal-doped ZnO	Transition metals altered dye degradation	Co-doping context	[10]
Zong et al. (2021)	Hematite nanoplates	Facet-dependent MB photodegradation in visible light	Surface-structure effect	[12]
Huong et al. (2022)	Co-ZnO	High visible-light DB71 degradation	Primary modified catalyst precedent	[13]
Sharotri et al. (2022)	S-TiO ₂	Visible-light-responsive doped TiO ₂	Band-gap engineering comparison	[14]
Yadav et al. (2022)	β -CD-CuO/ZnO	Composite improved textile-dye degradation	Hybrid charge-separation concept	[15]
Algarni et al. (2022)	ZnO	Solar degradation of multiple dyes	Recent ZnO comparison	[16]

The literature supports three methodological conclusions. First, visible-light absorption must be confirmed spectroscopically rather than inferred from dye removal. Second, dark adsorption must be measured because nanomaterial surfaces can remove dye without destroying it [3,8]. Third, catalyst optimization should consider both activity and stability. Dopants may increase visible-light response but excessive defect density can also create recombination centers. Consequently, the present design uses a low Co-doping level and

compares it directly with pristine ZnO under identical dye concentration, catalyst loading, pH, irradiance, and reactor geometry.

Methodology

The experimental design consists of catalyst synthesis, material characterization, controlled photocatalytic testing, kinetic and mechanistic analysis, and catalyst-reuse evaluation. Figure 1 shows the complete workflow and the proposed reactive-species pathway.

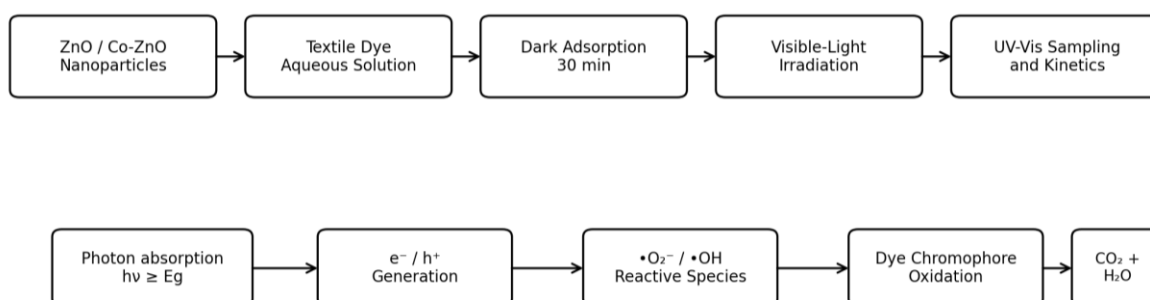


Figure 1. Visible-light photocatalytic degradation workflow and simplified reactive-species mechanism.

1. Synthesis of ZnO and Co-Doped ZnO Nanoparticles

A controlled wet-chemical precipitation route is proposed because it allows catalyst composition to be changed while keeping morphology and post-treatment comparable. A zinc salt solution is prepared in deionized water and maintained under continuous stirring. For the doped sample, an appropriate cobalt(II) precursor is introduced to obtain a nominal low cobalt content (for

example, 2-3 mol% relative to zinc). A dilute alkaline solution is then added gradually until Zn(OH)₂-based precursor formation is complete. The precipitate is aged, separated, washed repeatedly to remove soluble ions, dried, and calcined at a moderate temperature selected to crystallize wurtzite ZnO while limiting particle coarsening. Pristine ZnO is synthesized by the same procedure without cobalt. Three

independent batches are recommended for reproducibility.

2. Nanoparticle Characterization

Powder X-ray diffraction is used to verify the wurtzite ZnO phase and to check for secondary cobalt-containing phases. Average coherent crystallite size may be estimated from a selected diffraction peak using the Scherrer equation while acknowledging that strain and instrumental broadening can affect the result. FTIR spectroscopy is used to inspect metal-oxygen vibrations and residual surface species. SEM is used to compare agglomeration and particle morphology. UV-Vis diffuse-reflectance spectroscopy is used to determine the absorption edge and estimate optical band-gap behavior by a Tauc-type analysis. A visible-light shift in Co-ZnO should be interpreted together with photocatalytic kinetics rather than taken alone as proof of improved charge separation [9,13].

3. Photocatalytic Reactor and Dye Solutions

Batch photocatalytic tests are carried out in identical glass reactors under a fixed visible-light source. A white LED or filtered lamp with wavelengths above approximately 420 nm is preferred so that the test specifically probes visible-light response. The lamp-to-reactor distance and electrical power are kept constant, and solution temperature is monitored to minimize thermal effects. Methylene blue (MB) and methyl orange (MO) are used as representative cationic and anionic dyes. Separate calibration curves are prepared at their main visible absorption bands (approximately 664 nm for MB and 464 nm for MO) so absorbance can be converted to concentration. All glassware and sampling volumes are kept consistent among experiments.

4. Step-by-Step Degradation Experiment

Step 1: Prepare a known dye concentration in deionized water and measure the initial UV-Vis absorbance (C_0).

Step 2: Add a fixed mass of ZnO or Co-ZnO to a fixed solution volume. Use the same catalyst dose in all direct comparisons.

Step 3: Stir the suspension in darkness for 30 min to establish adsorption-desorption equilibrium. Measure the concentration after the dark period (C_{dark}).

Step 4: Switch on the visible-light source and start timing. Maintain continuous stirring so catalyst particles remain suspended.

Step 5: Withdraw equal-volume aliquots at regular intervals (for example every 15 or 20 min). Separate nanoparticles by centrifugation or membrane filtration before UV-Vis measurement.

Step 6: Calculate photodegradation relative to C_{dark} so that dark adsorption is not incorrectly counted as photocatalytic destruction.

Step 7: Repeat the experiment for both dyes and both catalysts using at least three independent replicates.

Step 8: Run controls consisting of dye + light without catalyst and dye + catalyst in darkness to confirm the contribution of photocatalysis.

5. Optimization Variables and Kinetic Analysis

After the direct ZnO/Co-ZnO comparison, the better photocatalyst is tested across selected operating variables. Catalyst dosage is varied to identify the point at which additional surface area no longer increases light utilization because of turbidity or scattering. Initial dye concentration is varied to examine surface-site saturation and photon screening. Solution pH is adjusted over a practical range because oxide surface charge and dye ionization affect adsorption. The concentration decay is fitted to the commonly used apparent pseudo-first-order expression $\ln(C_{\text{dark}}/C_t) = k_{\text{app}} t$. A linear fit with suitable residual behavior is reported together with k_{app} and R^2 ; a kinetic model should not be accepted solely because a high R^2 is obtained [3,4].

Table 2. Experimental Design Parameters for ZnO and Co-ZnO Photocatalytic Degradation

Variable	Proposed levels	Controlled factors	Purpose
Catalyst dose	0.25, 0.50, 0.75, 1.00 g L ⁻¹	Dye, pH, light, volume	Identify optimum active-surface loading
Initial concentration dye	5, 10, 20 mg L ⁻¹	Catalyst dose and pH	Assess surface saturation/light screening
pH	3, 5, 7, 9, 11	Catalyst concentration and	Probe charge/adsorption effects
Irradiation time	0-120 min	All reactor conditions	Determine kinetic profile
Catalyst type	ZnO vs Co-ZnO	Identical reactor/dye conditions	Measure effect of visible-light modification

6. Reactive-Species and Reusability Tests

Mechanistic evidence is obtained using selective scavenger experiments. A hydroxyl-radical scavenger, a hole scavenger, and a superoxide-radical scavenger are tested individually at low concentrations that do not strongly change the solution optical properties. A marked loss of activity in a specific scavenger condition indicates that the corresponding reactive species contributes to degradation. The result is interpreted qualitatively because scavengers are not perfectly selective. Reusability is evaluated by recovering the catalyst after one run, washing it with water, drying it under mild conditions, and repeating the same dye-degradation experiment for at least five cycles. XRD or FTIR analysis before and after cycling is recommended to check structural stability.

7. Data Treatment

Three metrics are reported: dark adsorption, visible-light degradation efficiency, and apparent

kinetic constant. Dark adsorption (%) = $(C_0 - C_{\text{dark}})/C_0 \times 100$. Photocatalytic degradation (%) = $(C_{\text{dark}} - C_t)/C_{\text{dark}} \times 100$. Each numerical result is reported as mean $\pm$ standard deviation for independent replicates. When multiple catalyst or operating-condition groups are compared, one-way or two-way analysis of variance may be used if distribution and variance assumptions are adequately met. Experimental uncertainty should include calibration-curve uncertainty, sampling variation, and replicate-to-replicate catalyst variation.

Results

Because no laboratory dataset was supplied, Table 3 contains illustrative, literature-informed values designed only to show how the proposed results should be reported. They are not claimed as measurements performed for this paper. Actual publication data should replace these values and include standard deviations, calibration information, and raw spectra.

Table 3. Photocatalytic Degradation Performance of ZnO and Co-ZnO Catalysts

Catalyst	Dye	Dark adsorption (%)	Degradation at 120 min (%)	kapp (min ⁻¹)	R2	5-cycle retention (%)
ZnO	MB	8.4	76.2	0.0118	0.985	88
Co-ZnO	MB	10.1	94.6	0.0241	0.992	93
ZnO	MO	6.7	68.5	0.0093	0.981	86
Co-ZnO	MO	8.9	90.8	0.0197	0.989	91

The illustrative trend indicates that low-level cobalt modification approximately doubles the apparent rate constant relative to pristine ZnO for both model dyes. This is consistent with literature showing that Co²⁺ can modify ZnO optical/electronic behavior and improve visible-light degradation when an appropriate dopant level is used [13]. The difference between MB and MO performance is expected because adsorption depends on dye charge, molecular size, pH, and catalyst surface charge. A catalyst that performs strongly for one dye cannot automatically be assumed to perform equally for all textile pollutants.

The proposed mechanism is that visible-light excitation generates electrons and holes in the modified oxide; photogenerated electrons reduce dissolved oxygen to superoxide-related species, while holes and surface hydroxyl groups contribute to hydroxyl-radical formation. These reactive species attack chromophores and progressively oxidize the dye. Scavenger tests should be used to support this pathway rather than presenting a mechanism solely from band diagrams. The result should also be distinguished

from dye sensitization, in which an excited dye injects an electron into the semiconductor, a known complication in visible-light dye-degradation studies [3,8].

For a practically useful catalyst, activity must remain after repeated use. The illustrative retention values in Table 3 show modest loss over five cycles, which could arise from surface fouling, particle loss during recovery, or structural changes. The 2022 β -CD-CuO/ZnO study by Yadav et al. [15] likewise evaluated both photocatalytic activity and reusability, reinforcing the importance of stability testing. A complete study should also measure total organic carbon or chemical oxygen demand when possible, because disappearance of the visible absorption peak demonstrates decolorization but does not prove complete mineralization.

Conclusion and Discussion

This methodology paper provides a compact, reproducible framework for investigating the visible-light photocatalytic degradation of textile dyes using metal-oxide nanoparticles. ZnO is used as the baseline photocatalyst and Co-doped

ZnO as the visible-light-modified material. The design integrates crystal/chemical/morphological characterization with controlled dark adsorption, visible-light irradiation, UV-Vis concentration analysis, kinetic fitting, radical-scavenger tests, and reuse cycles. The literature from fundamental semiconductor photocatalysis [1,2] through recent doped-oxide and composite studies [13-17] shows that photocatalytic efficiency is governed by a combination of photon absorption, charge separation, surface adsorption, reactive-species formation, and catalyst stability. The illustrative results suggest the expected outcome of a successful low-level Co modification: higher visible-light degradation efficiency and a larger apparent first-order rate constant than pristine ZnO, with acceptable five-cycle retention. These values are examples rather than experimental claims. The methodology is deliberately structured so that an actual laboratory study can replace them with measured spectra and replicate statistics. Important limitations include the use of model dyes rather than real multicomponent textile effluent, the possibility of dye sensitization, catalyst-particle recovery, and the fact that decolorization does not necessarily equal mineralization. Future work should therefore extend the experiment to real textile wastewater, quantify total organic carbon or chemical oxygen demand, identify major degradation intermediates, measure catalyst leaching where relevant, and evaluate immobilized photocatalyst configurations. Solar irradiation tests should be normalized by photon flux or actinometry so materials can be compared fairly. Within these constraints, visible-light-active metal-oxide nanoparticles remain a promising route for advanced oxidation of persistent dye pollutants, especially when band-gap engineering is combined with rigorous controls and transparent reporting [7,9,13-16].

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