Photocatalytic Degradation of Methylene Blue Dye Using Green-Synthesized Zinc Oxide from Terminalia catappa Leaf Extract

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Abstract. This study presents a sustainable route for synthesizing zinc oxide (ZnO) materials using zinc sulfate heptahydrate and *Terminalia catappa* leaf extract via a low-temperature precipitation method. The biosynthesis leveraged phytochemicals as natural reducing and stabilizing agents, eliminating the need for hazardous chemicals. Energy-dispersive X-ray spectroscopy (EDS) indicated the presence of Zn and O elements, with notable oxygen enrichment (68.49 atom %), which may be associated with surface-bound organic species. The photocatalytic performance of the synthesized ZnO was evaluated through the degradation of methylene blue (MB) dye under UV irradiation. A maximum degradation efficiency of 75.35 % was achieved with 15 mg of ZnO after 60 minutes. Visual trends confirmed significant MB removal across ZnO-treated groups compared to the control, although inter-dosage differences showed a plateauing behavior beyond the 5 mg dosage. While detailed crystallinity and optical properties were not assessed, these findings underscore the potential of *T. catappa*–mediated ZnO as a low-cost, eco-friendly photocatalyst for dye-contaminated wastewater. The synthesis approach supports green chemistry goals and contributes to the development of sustainable functional materials for environmental remediation.

1 Introduction

The textile industry is a primary contributor to global water pollution due to its immense water consumption and the discharge of untreated synthetic dye effluents into aquatic ecosystems, posing severe environmental and human health risks [1]. Methylene blue (MB), a commonly used cationic dye, is particularly problematic due to its chemical stability, persistence, and toxicity, which can cause adverse effects on human health and aquatic ecosystems [2].

Among various treatment methods, photocatalytic degradation has gained attention as an efficient and environmentally compatible approach for removing organic pollutants. This process utilizes semiconductor materials to generate reactive species under light irradiation,

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enabling the breakdown of complex dye molecules into less harmful compounds [3]. Zinc oxide (ZnO) is widely studied as a photocatalyst due to its strong activity under UV light, chemical stability, low cost, and low toxicity [4].

However, conventional synthesis methods for ZnO often involve hazardous chemicals and energy-intensive processes, limiting their environmental sustainability. As a result, green synthesis using plant extracts—specifically *T. catappa*, which is rich in phenolics and flavonoids that act as natural reducing and stabilizing agents—has emerged as a promising alternative to facilitate the formation of metal oxide nanomaterials. While previous studies have primarily explored *T. catappa*-mediated ZnO for antimicrobial applications, its use in photocatalytic dye degradation remains comparatively underexplored [5].

In this study, ZnO was synthesized using *T. catappa* leaf (TCL) extract via a green precipitation method and evaluated for its photocatalytic performance in degrading methylene blue under UV irradiation. The effects of catalyst dosage and reaction time were investigated to assess its feasibility as a low-cost and environmentally sustainable photocatalyst for wastewater treatment.

2 Experimental Rationale

Conventional treatment methods for dye-contaminated wastewater, including adsorption and chemical oxidation, may be limited in fully addressing persistent compounds such as methylene blue [2]. These limitations support the use of photocatalytic approaches as an alternative treatment strategy.

ZnO is widely utilized in photocatalytic applications due to its chemical stability, low cost, and effectiveness under UV irradiation [4]. However, its performance is influenced by operational parameters such as catalyst dosage and surface characteristics, which are critical in determining degradation efficiency.

To improve the sustainability of ZnO synthesis, green approaches using plant extracts have gained attention. Phytochemicals present in these extracts can facilitate nanoparticle formation under mild conditions [6]. In this context, TCL extract was selected as a biogenic precursor due to its potential to support material synthesis while maintaining low processing requirements.

Based on these considerations, this study employs a green precipitation method to synthesize ZnO and evaluates its photocatalytic performance for methylene blue degradation under UV irradiation. The experimental design focuses on the effects of catalyst dosage and reaction time to assess its feasibility as a low-cost and sustainable treatment approach.

3 Materials and Methods

3.1 Preparation of *Terminalia catappa* Leaf Extract

T. catappa leaves were collected from Cabuyao, Laguna, and thoroughly washed with distilled water to remove any surface contaminants. The cleaned leaves were then dried and ground into a fine powder using a mortar and pestle. The resulting powder was sieved using a 200 μm mesh to ensure uniform particle size. 25 grams of the sieved TCL powder was boiled in 50 mL of distilled water for 15 minutes to extract bioactive compounds. The mixture was filtered using Whatman No. 1 filter paper to separate the liquid extract from the solid residues. This aqueous extract was then used as a stabilizing and reducing agent in the green synthesis of zinc oxide.

3.2 Green Synthesis of ZnO Nanomaterial

The synthesis of ZnO followed a precipitation method adapted from Azimpanah et al. [7] with a few modifications to suit the objectives of this study. The process began by dissolving 17.25 grams of $ZnSO_4 \cdot 7H_2O$ in 150 mL of distilled water in a 250 mL Erlenmeyer flask. While heating and stirring the solution at 60 °C and 600 rpm, 50 mL of *TCL* extract was added gradually. The pH of the resulting mixture was adjusted to 9 using 1 M sodium hydroxide (NaOH). Once the desired pH was reached, the solution was left to cool at room temperature and aged for 24 hours. The aged mixture was then transferred to test tubes and centrifuged at 5000 rpm for 10 minutes to separate the precipitate. The collected solid was washed with distilled water, followed by a second centrifugation step. Afterward, the precipitate was rinsed with ethanol and dried in an oven at 100 °C for 12 hours. The resulting ZnO powder was stored in a labelled container for subsequent characterization and photocatalytic degradation testing.

3.3 Material Characterization

The morphology and elemental composition of the synthesized ZnO were analyzed using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). The analyses were conducted at De La Salle University (DLSU) – Laguna Campus using a field-emission SEM system equipped with an EDS detector. SEM was used to examine the surface morphology and particle features of the synthesized material, while EDS was employed to determine elemental composition and identify any residual elements associated with the synthesis process.

3.4 Photocatalytic Degradation Experiment

Aqueous MB solutions with an initial concentration of 5 parts per million (ppm), equivalent to 5 mg/L, were prepared using distilled water. For each experiment, 250 mL of the MB solution was treated with green synthesized ZnO at dosages of 5 mg, 10 mg, and 15 mg, corresponding to catalyst concentrations of 20 mg/L, 40 mg/L, and 60 mg/L, respectively. An untreated solution was used as the control.

All photocatalytic experiments were conducted under fixed ambient temperature conditions (approximately 25 ± 1 °C) to eliminate thermal variability and isolate the effect of ZnO loading. This design is supported by prior work such as by Rafaie et al., [8], and aligns with findings by Mosoarca et al. [3], who reported that temperature exerts comparatively lower influence on dye degradation efficiency than catalyst dosage or pH.

Prior to irradiation, all suspensions were kept under dark conditions without agitation to allow molecular diffusion and establish adsorption equilibrium. Photocatalytic degradation was carried out by exposing the ZnO–MB suspensions to UV-A irradiation within a wavelength range of 365 to 390 nm. Each 250 mL beaker containing the MB solution was placed directly below the UV lamp to ensure uniform illumination across the liquid surface. This configuration replicates typical UV-assisted photocatalytic conditions described in the literature. For instance, Rafaie et al. [8] reported using a UV source positioned directly above the sample to initiate photocatalytic activity, while Islam et al. [4] utilized a UV box reactor that directed light from the top surface to ensure consistent activation of the catalyst. All photocatalytic reactions were performed in cylindrical, food-grade glass containers whose exterior surfaces were coated with matte black spray paint to block ambient light and ensure consistent exposure from the UV lamp positioned above. The experimental system was operated under open-air conditions, with evaporation controlled by loosely covering the

reaction vessels using transparent laboratory film during the irradiation period. At predetermined degradation times of 0, 20, 40, and 60 minutes, 2 mL aliquots were withdrawn from each suspension and centrifuged at 5000 rpm for 10 minutes to separate the ZnO particles. The absorbance of the resulting supernatant was measured using a UV–Vis spectrophotometer at 660 nm (within the methylene blue absorption band) for consistent concentration tracking. The degradation efficiency was calculated from the relative decrease in absorbance with respect to the initial concentration.

3.5 Degradation Efficiency Calculation

The degradation efficiency was calculated based on the relative decrease in absorbance:

$$\text{Degradation (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

where $A_0$is the initial absorbance and $A_t$is the absorbance at time t.

4 Results and Discussion

4.1 SEM-EDS Results

SEM analysis revealed that the green synthesized ZnO consisted of irregularly shaped particles with pronounced agglomeration, as shown in Figure 1. This morphological feature is characteristic of plant mediated synthesis routes and is likely influenced by phytochemical constituents from the *TCL* extract, which can act as capping or binding agents during particle formation. The lack of well-defined spherical or rod-like structures indicates that particle growth was governed by organic constituents rather than high-temperature crystallization processes, consistent with the low energy synthesis approach employed.

Complementary EDS analysis conducted at a representative point of the sample, with results summarized in Table 1 and the corresponding spectrum shown in Figure 2, confirmed the presence of zinc and oxygen. The deviation of the Zn to O atomic ratio from the ideal stoichiometric value is attributed to surface-bound phytochemicals and oxygen-containing functional groups retained from the plant extract, which is consistent with the observed agglomerated morphology.

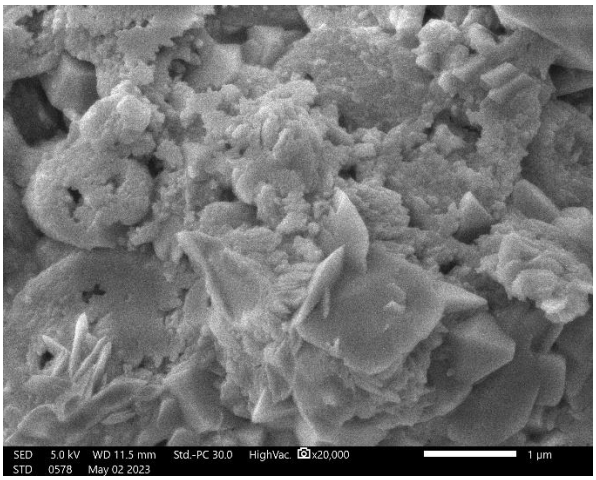

Fig. 1. SEM analysis of the green-synthesized ZnO powder.

In comparison, Pai et al. [9] synthesized ZnO nanoparticles using aqueous leaf extract of *Peltophorum pterocarpum* and reported an elemental composition of 73.65 wt% zinc and 17.41 wt% oxygen, as confirmed by EDS analysis. This relatively zinc-rich surface composition may contribute to their high photocatalytic degradation performance, which reached 95% methylene blue removal under natural sunlight irradiation after 120 minutes. The discrepancy in elemental distribution compared to our study may be attributed to differences in plant source, synthesis protocol, and purification strategy. Notably, both studies detected minor traces of sodium, further supporting its common occurrence in ZnO materials derived via green synthesis.

These observations are supported by Wan et al. [10], who demonstrated that residual precursors and incomplete purification in green synthesis protocols can skew elemental quantification in EDS. Their findings indicated that retained organic components from plant extracts, as well as residual sodium and other elements, influenced the atomic percentage readings in biosynthesized nanoparticles. In the present study, the presence of sodium and sulfur in the EDS spectrum likely originates from the use of sodium hydroxide as the precipitating agent and zinc sulfate heptahydrate as the zinc precursor. Additionally, trace detection of lead may be attributed to minor environmental or laboratory contamination. Although present in small quantities, these elements can bias atomic percentage readings and complicate compositional interpretation. As emphasized in the literature, the use of high-purity reagents and rigorous washing procedures is essential to improve the compositional reliability of biosynthesized ZnO.

Table 1. Material Composition from EDS Analysis

Element	Line	Mass %	Atom %
O	K	46.84±1.46	68.49±2.13
Na	K	15.25±0.93	15.52±0.95
S	K	10.09±0.58	7.36±0.42
Zn	K	22.41±3.06	8.02±1.10
Pb	M	5.40±0.94	0.61±0.11
Fitting Ratio: 0.0908			

Calcination was intentionally excluded in this study to evaluate the photocatalytic potential of ZnO synthesized under mild, low-temperature conditions. While limited access to equipment during the post-pandemic recovery phase partially influenced this decision, the exclusion also aligned with the research objective of exploring a more accessible, low-energy, and environmentally sustainable synthesis route. Nevertheless, this choice may have contributed to the oxygen-rich elemental profile observed. Abdelbaky et al. [11], for instance, reported that applying calcination at 400 °C to ZnO synthesized from *Pelargonium odoratissimum* leaf extract resulted in highly crystalline, phase-pure material with minimal organic residues. Their findings underscore the role of thermal treatment in enhancing material purity and stoichiometric balance in green synthesis protocols.

Future efforts to improve ZnO crystallinity and eliminate residual organics may benefit from incorporating calcination or adopting advanced purification strategies. However, the present findings affirm that even in the absence of such post-treatment, it is feasible to generate functional ZnO using low-cost, eco-friendly methods that support sustainable materials development.

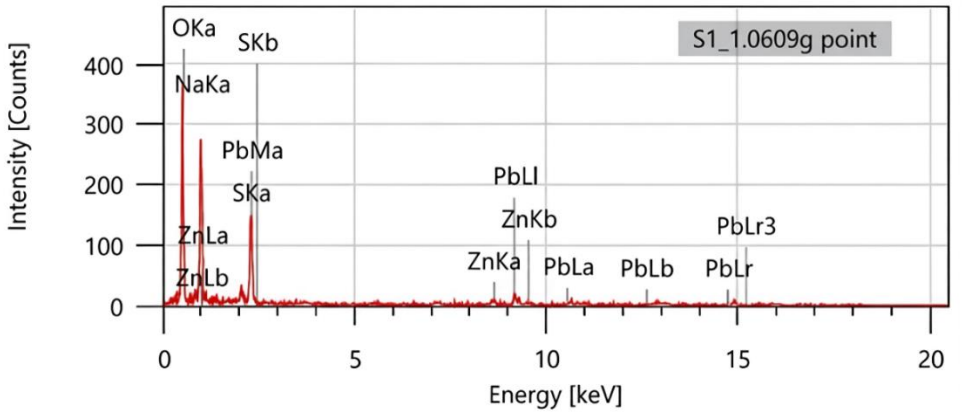

Fig. 2. Energy-Dispersive X-ray Spectroscopy analysis of green-synthesized ZnO powder.

4.2 Photocatalytic Degradation Results

Prior to evaluating photocatalytic performance, the stability of methylene blue under UV irradiation in the absence of ZnO was examined to establish a baseline for natural photolysis. The absorbance values remained essentially constant over the 60-minute irradiation period, decreasing only marginally from 0.7586 at 0 minutes to 0.754 at 60 minutes. Correspondingly, calculated degradation percentages remained below 2% throughout the experiment (1.40% at 20 minutes, 0.87% at 40 minutes, and 0.61% at 60 minutes), indicating that direct UV exposure alone was insufficient to induce meaningful dye degradation. This confirms that any substantial reduction in methylene blue concentration observed in subsequent experiments can be attributed primarily to ZnO-mediated photocatalytic activity rather than photolysis or dye instability.

As illustrated in Figure 3, the degradation efficiency clearly increased with both treatment time and ZnO dosage, demonstrating dose-dependent photocatalytic degradation behavior. At the highest catalyst dosage of 15 mg, MB degradation reached 75.35% after 60 minutes, marking the most effective condition tested. The increased surface area and higher density of active sites at this dosage likely enhanced the generation of reactive oxygen species, facilitating dye breakdown. Similarly, the 10 mg and 5 mg dosages showed moderate efficiencies of 64.79% and 59.67%, respectively, confirming the correlation between catalyst quantity and degradation performance.

The control group, which did not receive ZnO treatment, served to establish the baseline absorbance and assess natural photolysis or dye instability under UV light. As expected, negligible change was observed in control across all time points, reinforcing that the dye degradation was driven by the photocatalytic activity of the ZnO material rather than light exposure alone or in experimental conditions.

Following the initial increase in degradation efficiency, the rate of improvement between 20 and 60 minutes became comparatively modest across all ZnO-treated samples. This trend indicates that a substantial fraction of the readily degradable methylene blue was removed during the early irradiation period, after which further degradation progressed more gradually as residual dye concentration decreased. Similar plateau-like behavior has been reported in ZnO-based photocatalytic systems and is commonly observed once the reaction approaches a practical degradation limit under fixed irradiation and catalyst loading conditions [8].

Compared to related studies, the photocatalytic degradation efficiency achieved in this work was moderate. Pai et al. [9], using ZnO synthesized from *Peltophorum pterocarpum* extract, reported higher methylene blue removal, which they attributed to a zinc-rich

composition. In our case, the elemental profile indicated a lower zinc content, which may reflect retained phytochemicals or the absence of thermal treatment. These factors could reduce surface reactivity and active site availability, thereby limiting degradation performance despite the successful formation of ZnO.

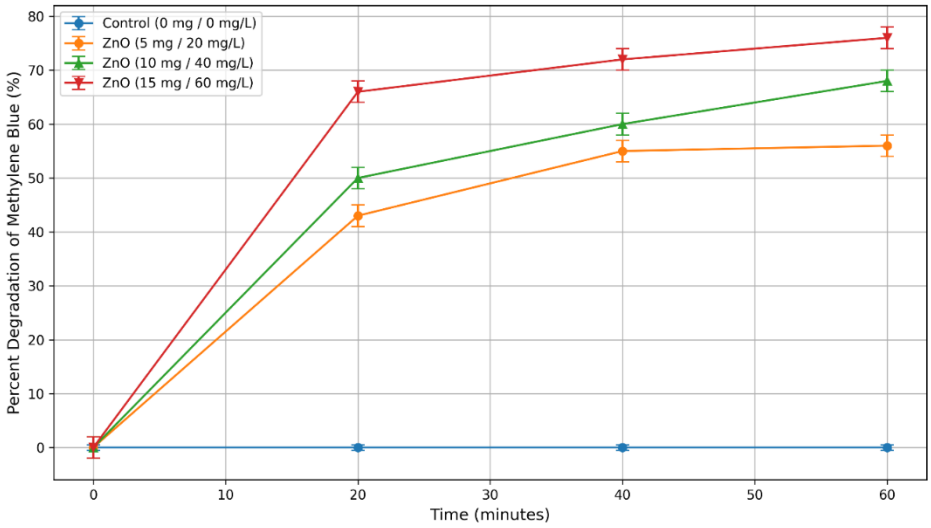

Fig. 3. Photocatalytic degradation efficiency of methylene blue (MB) over time using green-synthesized ZnO at varying dosages.

To further contextualize the photocatalytic performance of the TCL-derived ZnO, comparative studies on biogenic nanoparticles indicate that plant-mediated synthesis avoids high-temperature calcination and can yield high-purity nanostructures with MB degradation efficiencies generally reported at moderate to high levels, depending on irradiation conditions and surface composition [6]. The TCL-based ZnO in this study, while demonstrating slightly lower performance, offers a low-energy synthesis route and potential phytochemical stabilization effects that contribute to its applicability within sustainable photocatalytic systems.

Although the present study did not directly quantify synthesis yield, comparison with reported literature highlights the advantages of green synthesis routes relative to conventional chemical methods. Studies have shown that green synthesized ZnO can achieve synthesis efficiencies comparable to chemically synthesized counterparts while operating under milder conditions and avoiding toxic reagents and high energy inputs. Deger et al. [12] reported that plant mediated ZnO synthesis provides effective precursor utilization and material formation comparable to chemical routes, while significantly reducing processing severity and environmental burden. Similarly, Upadhyay et al. [13] demonstrated that green synthesis approaches can yield ZnO with favorable material characteristics using lower temperatures and fewer chemical additives, indicating efficient conversion despite simplified processing conditions. In contrast, conventional chemical synthesis often relies on excess reagents, strong bases, and elevated temperatures to drive reaction completion, which may increase apparent yield at the cost of sustainability and additional post-treatment steps.

4.3 Limitations and Future Outlook

This study focused on demonstrating the feasibility of a plant mediated, low energy synthesis route for ZnO and its application in photocatalytic degradation of methylene blue. Within this scope, several limitations are acknowledged.

Structural characterization in this study was limited to SEM and EDS due to financial and equipment access constraints. Higher-resolution techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy, which confirm crystallinity, lattice structure, and vibrational modes, were not performed. Additionally, optical characterization such as band gap analysis via UV-Vis diffuse reflectance spectroscopy was not included, which would have provided insights into the electronic properties of the synthesized ZnO and its suitability for photocatalytic activation under UV or visible light. These techniques are therefore identified as priorities for future work to enable deeper structural validation and strengthen correlations between material features and photocatalytic performance. Consequently, interpretations related to crystallinity or residual organic content are presented as plausible considerations rather than experimentally verified conclusions, and their validation is deferred to future studies employing XRD, FTIR, or thermogravimetric analysis. Future work will also include replicate syntheses, multi-point EDS mapping, and procedural blanks to verify whether trace Pb signals are reproducible or attributable to incidental contamination. In addition, future work will quantify key phytochemical groups in the TCL extract (e.g., total phenolics and flavonoids or spectral profiling) to support synthesis reproducibility across locations and batches.

No thermal post treatment was applied following synthesis to preserve the low energy nature of the process. Future work may incorporate controlled calcination to reduce residual organic constituents and enhance material quality, allowing assessment of its effect on photocatalytic efficiency and stability.

Photocatalytic experiments were conducted at a single initial dye concentration with time resolved monitoring and were not designed for adsorption isotherm or kinetic modeling. In addition, adsorption–desorption equilibrium behavior and solution pH variation were not explicitly investigated in this study. However, while photolysis control (MB + UV without catalyst) was conducted and confirmed negligible degradation, the dark adsorption control (MB + ZnO without UV) was not performed as part of the study design. This omission precludes quantification of the adsorptive contribution to dye removal and is therefore acknowledged as a study limitation. Although dark equilibration was applied prior to irradiation, quantitative adsorption analysis and pH monitoring before and after photocatalytic treatment were beyond the scope of the present work, which was designed as an initial performance evaluation under controlled baseline conditions. Future investigations should incorporate systematic adsorption controls and continuous pH monitoring to better understand surface charge dynamics, dye–catalyst interactions, and their influence on degradation mechanisms. Moreover, expanding the experimental matrix to include multiple initial dye concentrations and extended sampling intervals would enable kinetic modeling using frameworks such as pseudo-first-order or Langmuir–Hinshelwood models. Finally, catalyst reusability and photostability were not assessed; future studies should evaluate performance over repeated photocatalytic cycles to establish long-term operational stability and practical applicability.

5 Conclusion

This study demonstrated the successful green synthesis of zinc oxide powder using zinc sulfate heptahydrate and *Terminalia catappa* leaf extract through a precipitation method. Elemental analysis via Energy-Dispersive X-ray Spectroscopy confirmed the formation of ZnO, with zinc and oxygen detected as the principal components, although the elevated oxygen content suggested the retention of residual phytochemicals from the plant extract. The synthesized ZnO exhibited promising photocatalytic activity, achieving a maximum degradation efficiency of 75.35% for methylene blue at a dosage of 15 mg after 60 minutes of UV exposure. While a clear dose-dependent degradation trend was observed, even the

lowest ZnO dosage resulted in a pronounced improvement over the untreated control. However, minimal differences between higher dosages suggest a saturation effect. These findings highlight the potential of *T. catappa*-mediated ZnO as an efficient, low-cost, and sustainable photocatalyst for methylene blue removal from dye-contaminated wastewater.

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