

Biogenic Synthesis of ZnO-CuO Heterojunction Nanoparticles Using *Callistemon Citrinus* Plant Extract and Evaluation of Photocatalytic Activity

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Abstract: The present study reports the biogenic synthesis of ZnO, CuO, and ZnO-CuO heterojunction nanoparticles using aqueous leaf extract of *Callistemon citrinus* as a reducing and stabilizing agent. The green synthesis approach was adopted as an environmentally friendly and sustainable alternative to conventional chemical methods. The synthesized nanoparticles were characterized using UV-Visible (UV-Vis) and Fourier Transform Infrared (FTIR) spectroscopy. UV-Vis analysis confirmed the formation of ZnO, CuO, and ZnO-CuO nanoparticles through their characteristic absorption features, while FTIR studies revealed the presence of phytochemical functional groups responsible for nanoparticle stabilization and confirmed the formation of Zn-O and Cu-O bonds. The photocatalytic performance of the synthesized materials was evaluated through the degradation of Methylene Blue (MB) dye under natural sunlight irradiation. Among the investigated photocatalysts, the ZnO-CuO heterojunction nanoparticles exhibited superior photocatalytic activity, achieving a maximum degradation efficiency of 85.87% after 120 min of irradiation, compared to 61.88% and 59.64% for ZnO and CuO nanoparticles, respectively. The enhanced photocatalytic performance of the heterojunction nanocomposite was attributed to improved charge separation, reduced electron-hole recombination, and enhanced visible-light absorption. The results demonstrate that biogenically synthesized ZnO-CuO heterojunction nanoparticles are efficient photocatalysts with significant potential for environmental remediation and wastewater treatment applications.

Keywords: Nanotechnology, Green synthesis, Heterojunction Nanoparticles, *Callistemon citrinus*, Photocatalytic activity

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Conflict of interest: None

Introduction

By making it possible to design materials at the atomic and molecular levels, nanotechnology has revolutionized modern science and engineering [1]. However, because of the excessive use of harmful reducing agents, toxic solvents, and high energy requirements of the production processes, the rapid development of nanomaterial production has brought serious environmental and health issues. In accordance with global environmental goals, the conventional physical and chemical procedures typically result in hazardous byproducts and use a significant amount of energy, creating a sustainability risk [2].

Metals and alloys that produce nanocrystalline grains with particle sizes ranging from 5 to 100 nm are known as nanometallic materials [3]. The surface area of nanoscale metals is greater than that of their bulk or non-nano equivalents. Furthermore, they have unique physical and chemical characteristics not found in non-nano metals because of the tiny size effect, surface effect, interface effect, and quantum impact. Numerous types of nanoscale metals have broad uses in engineering, biology, and medicine [4,5]. The synthesis of nanoscale metals using chemical, physical, and green synthesis techniques is the subject of a growing amount of research these days [6,7]. Green synthesis techniques are progressively replacing chemical and physical processes [4,8].

Compared to their bulk counterparts, nanoparticles (NPs) are incredibly strong mechanically, chemically reactive, and optically active, making them essential in cutting-edge technology [9]. Green synthesis is a paradigm change in the synthesis of nanoparticles, whereby ecologically friendly materials can be created instead of using conventional chemical and physical methods [1].

It has been suggested that the biosynthesis of nanoparticles provides an economical and eco-friendly substitute for chemical and physical processes. One green chemistry technique that links nanotechnology and plants is plant-mediated production of nanoparticles. It is therefore believed that new techniques for producing NPs at room temperature, neutral pH, cheap cost, and in an environmentally benign manner are ideal. Nanomaterials have been produced in a number of ways with these objectives in mind. Plants and plant extracts appear to be the greatest biological substitute. Nature's "Chemical factories" are plants. They are inexpensive and require little upkeep [10].

EPA scientists Paul Anastas and John C. Warner laid the groundwork for green chemistry in the early 1990s. Paul Anastas and John Warner first presented the 12 principles of green chemistry in 1998. These guidelines concentrate on reducing or doing away with the use of hazardous solvents in chemical reactions and avoiding the production of waste as a result of these reactions. [Figure 1] illustrates the 12 principles of green chemistry [47].

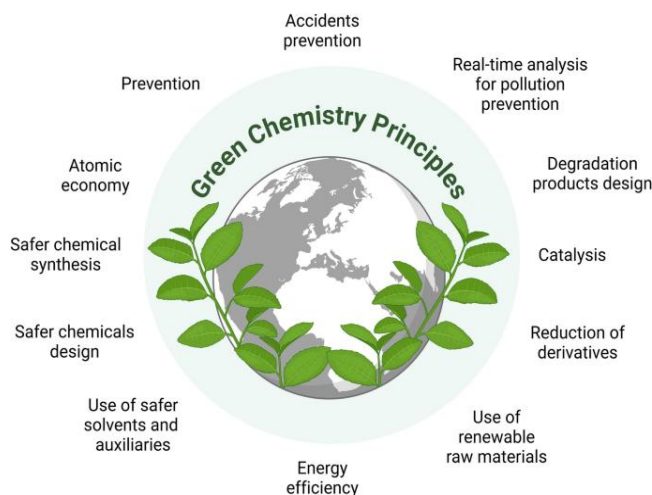


Figure 1: The 12 principles of green chemistry

In addition to metal oxides like Pt, Cu, Ag, Pd, NiO, CuO, Au, TiO₂, and ZnO, other metals can also be used to create nanoparticles [11]. Among these metal oxide and metal nanoparticles, Zinc oxide (ZnO) NPs have garnered a lot of interest in recent years due to their wide range of applications in biological systems, electronics, and optics, as well as their low cost of manufacturing, ease of preparation, and safety [11-15]. ZnO is an n-type semiconductor with a crystallizing wurtzite structure and hexagonal unit cell. In addition to its wide and straight band gap (3.36 eV), ZnO possesses a high exciton binding energy (60 meV) at room temperature, a strong electrochemical coupling coefficient, low toxicity, biocompatibility, and excellent photostability [11,16]. Because of their potent photodegradation activity directed at a variety of organic dyes, ZnO NPs are frequently employed in well-known photocatalytic applications [11,17,18].

Because of their unique anti-inflammatory, anti-bacterial, and environmentally friendly qualities, Copper oxide (CuO) nanoparticles (NPs) are p-type semiconductor materials with small band gaps that have been widely exploited for a range of applications [19-23]. The photocatalytic degradation of industrial dyes like Rhodamine B (RhB), which are challenging to eliminate using traditional biological treatments, is a well-known environmental use of green-synthesized CuO nanoparticles [24]. CuO nanoparticles may effectively absorb visible light and produce electron-hole pairs because of their narrow bandgap and high surface reactivity. Reactive oxygen species produced by these charge carriers break down dye molecules into less dangerous compounds, providing a clean and energy-efficient solution [24-27].

Different types of mixed metal oxides (MO) NPs have drawn a lot of attention because of the promising uses of NPs in science and technology. By incorporating metals into an oxide matrix, prospective materials' chemical and physical characteristics can be enhanced, improving their performance in a variety of applications [19,28]. This could greatly enhance the material's functioning and charge separation efficiency [19,29]. Understanding that most single-phase mixed oxides exhibit constituent oxide properties is crucial [19,30]. Multiphase nanocomposite materials have been used in electrochemical sensors, photocatalysis, antibacterial activity, and other applications [19,20,31-34]. Several research groups have used different synthesis techniques to create metal oxide nanoparticles (NPs) as ZnO-MgO [35], CuO-ZnO [36], and ZnO-NiO [37]. It is well known that ZnO is a large direct band gap material with flaws like photo-generated electron and hole recombination efficiency. It can only absorb ultraviolet light with energy greater than its band gap value. These barriers must be eliminated in order to boost ZnO NPs' photocatalytic efficiency in breaking down water pollutants. Numerous modification strategies, including doping and coupling with other semiconductors, have been reported to enhance ZnO NPs' photocatalytic efficiency toward the degradation of water contaminants [48]. The coupling with a p-type metal nanoparticles such as CuO nps prepared via a green method is preferable to improve the photocatalytic degradation efficiency of ZnO NPs by preventing charge carrier recombination and extending the absorption of light to the visible region, due to the low band gap of the CuO NPs, which is in the visible range (1.2-2.4 eV) and also improved in surface area [49-52].

The leather, textile, food, and plastic industries use a wide range of natural and synthetic colors. Aquatic and marine species are seriously threatened by dye-contaminated water, which has emerged as a significant industrial pollution. Therefore, it is crucial to reduce the primary effluent colors before the hazardous water reaches aquatic bodies. One of the frequently used dyes, methyl red, is discharged into water reservoirs and contaminates the water [19,38-43].

Callistemon citrinus is a member of the Myrtaceae family, which has around thirty species. Although it is currently distributed worldwide, the plant is most common in moist tropics, particularly in Australia, South America, and tropical Asia [44]. It is frequently referred to as lemon bottlebrush, red bottlebrush, and crimson bottlebrush. Flavonoids, alkaloids, terpenoids, sterols, and tannins are among the many

phytochemicals found in *Callistemon citrinus* extract [45]. Green production of several stable metallic nanoparticles has been successfully described using bottlebrush extracts [44,46].



Figure 2: *Callistemon citrinus* plant

In this paper, *Callistemon citrinus* plant is used for green synthesis of ZnO, CuO, and ZnO-CuO nanoparticles. Phytochemicals are abundant in the plant and can act as reducing and stabilizing agents. The synthesized ZnO, CuO NPs, and ZnO/CuO nanocomposite were investigated as a potential photocatalyst against Methylene Blue dye [19].

Material and Methodology

Materials:

For preparation of plant extract fresh leaves of *Callistemon citrinus* were collected and thoroughly washed with tap water followed by distilled water to remove dust and other impurities. To prepare 0.1 M solution of Zinc Acetate salt, 2.195 g of Zinc Acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, MW: 219.49, FINAR) was dissolved in 100 mL of distilled water. 0.1 M solution of Copper Acetate was made by dissolving 1.995 g of Copper(II) Acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, MW: 199.65, Oxford Lab Fine Chem LLP) in 100 ml of distilled water.

All chemicals applied in this research study, including Zinc Acetate extrapure ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, MW: 219.49, FINAR), Copper(II) Acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, MW: 199.65, Oxford Lab Fine Chem LLP), Sodium hydroxide pellets (NaOH, MW: 40, Oxford Lab Fine Chem LLP) and Methylene Blue (MB) staining solution (aqueous, Oxford Lab Fine Chem LLP) were of analytical grade and used as received commercially without further purification. Distilled water was used throughout the experiment wherever required.

Preparation of Plant Extract:

Collected cleaned leaves of *callistemon citrinus* were crushed using a pestle and mortar to obtain a fine paste. The prepared paste was wrapped in filter paper and placed in the thimble of a Soxhlet apparatus. Distilled water was used as the extraction solvent. The extraction process was carried out at 100°C for approximately 5–6 hours until the solvent in the siphon tube became colorless, indicating complete extraction of phytochemicals. The obtained extract was allowed to cool to room temperature and then filtered using Whatman filter paper. The filtered extract was stored for further nanoparticle synthesis.

Synthesis of ZnO Nanoparticles:

For the synthesis of ZnO nanoparticles, 100 mL of 0.1 M Zinc Acetate solution was prepared. To this solution, 100 mL of the prepared leaf extract was added under continuous magnetic stirring at 60°C for 1 hour. Subsequently, 0.1 M NaOH solution was added dropwise to maintain the pH in the range of 9–10, as alkaline conditions favor the formation of ZnO nanoparticles. The reaction mixture was then centrifuged at 7000 rpm for 10 minutes, and the precipitate obtained was collected. The precipitate was washed several times with distilled water and ethanol to remove impurities and unreacted materials. The washed product was dried on a water bath and further calcined in a muffle furnace at 450°C for 2 hours to obtain ZnO nanoparticles.

Synthesis of CuO Nanoparticles:

For the synthesis of CuO nanoparticles, 100 mL of 0.1 M Copper Acetate solution was prepared. Then, 100 mL of the prepared leaf extract was added to the Copper Acetate solution under continuous magnetic stirring at 60°C for 1 hour. After that, 0.1 M NaOH solution was added dropwise to maintain the pH between 9 and 10. The formation mixture was centrifuged at 7000 rpm for 10 minutes, and the precipitate formed was collected. The obtained precipitate was washed repeatedly with distilled water and ethanol to remove impurities. The washed sample was dried on a water bath and calcined in a muffle furnace at 450°C for 2 hours to obtain CuO nanoparticles.

Synthesis of ZnO–CuO Heterojunction Nanoparticles:

For the synthesis of ZnO–CuO heterojunction nanoparticles, 100 mL of 0.1 M Zinc Acetate solution and 100 mL of 0.1 M Copper Acetate solution were prepared separately and mixed together under magnetic stirring. Subsequently, 200 mL of the prepared leaf extract was added while maintaining a 1:1 ratio between the precursor solution and plant extract. The reaction mixture was continuously stirred at 60°C for 1 hour. Thereafter, 0.1 M NaOH solution was added dropwise to maintain alkaline pH conditions (9–10), which facilitate nanoparticle formation. The resulting mixture was centrifuged at 7000 rpm for 10 minutes, and the precipitate obtained was collected and washed thoroughly with distilled water and ethanol. Finally, the product was dried on a water bath and calcined in a muffle furnace at 450°C for 2 hours to obtain ZnO–CuO heterojunction nanoparticles.

Characterization:

The synthesized ZnO, CuO, and ZnO–CuO nanoparticles were characterized using UV-Visible (UV-Vis) spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy. UV-Vis spectroscopy was performed in the wavelength range of **200–800 nm** to confirm nanoparticle formation and investigate their optical properties through characteristic absorption peaks. The obtained absorption spectra also provided information regarding the light absorption behavior and band-gap characteristics of the synthesized nanoparticles, which are important for photocatalytic applications.

FTIR spectroscopy was carried out in the wavenumber range of **4000–400 cm⁻¹** to identify the functional groups present on the nanoparticle surface and to confirm the formation of metal-oxygen bonds (Zn–O and Cu–O). FTIR analysis also helped in identifying the phytochemical compounds from the plant extract that acted as reducing and stabilizing agents during the green synthesis process. Together, these characterization techniques provided valuable information regarding the optical properties, surface chemistry, chemical composition, and successful synthesis of the nanoparticles.

Application of Synthesized Nanoparticles: Photocatalytic degradation of MB dye

The photocatalytic efficiency of biosynthesized ZnO, CuO, and ZnO–CuO nanoparticles for the degradation of MB dye was evaluated under sunlight at pH 4. The MB solution was prepared by diluting 1 mL of aqueous Methylene Blue staining solution (Oxford Lab Fine Chem LLP) with 99 mL of distilled water to obtain a 100 mL dye solution. For the photocatalytic degradation experiments, 0.05 g of ZnO, CuO,

and ZnO-CuO nanoparticles were separately dispersed in 100 mL of the prepared MB solution. The resulting suspensions were magnetically stirred in the dark for 30 min to achieve uniform dispersion of the nanoparticles and to establish adsorption-desorption equilibrium between the dye molecules and the catalyst surface. After dark equilibration, the suspensions were exposed separately to natural sunlight for photocatalytic degradation studies. At regular irradiation intervals of 30, 60, 90, and 120 min, aliquots of the reaction mixture were collected. The collected samples were filtered to remove the suspended nanoparticles and obtain clear solutions. MB degradation was examined by measuring the absorbance of the dye solution at $\lambda = 585\text{nm}$ using a UV-Vis spectrophotometer. The percentage of MB degradation was determined by the following equation:

$$\eta = A_0 - \frac{A_t}{A_0} \times 100 \quad (1)$$

In equation (1), η is the degradation percentage and A_0 and A_t are the absorbances of MB dye solution at $t=0$ and after time t , respectively.

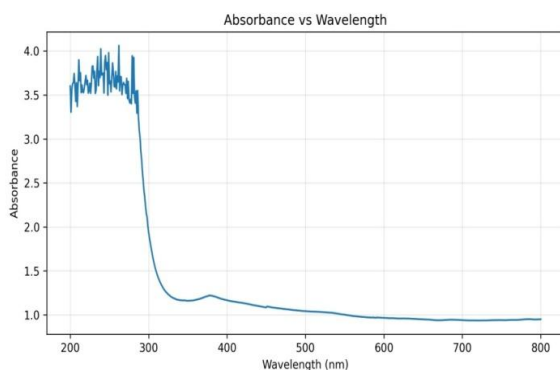
Results and Discussion

Visual confirmation of nanoparticle synthesis:

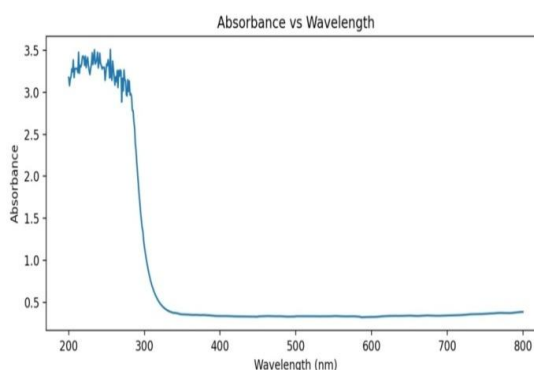
The successful synthesis of ZnO, CuO, and ZnO-CuO nanocomposite nanoparticles was initially confirmed through observable color changes and precipitate formation during the reaction process. In the ZnO synthesis, the reaction mixture gradually became turbid and developed a pale cream to yellowish-white color, resulting in a white to pale-yellow powder after calcination. For CuO nanoparticles, the Blue Copper Acetate solution changed to brownish-black with the formation of a dark precipitate, yielding a dark brown to black powder upon calcination. In the case of the ZnO-CuO nanocomposite, the reaction mixture transformed into a brownish suspension with visible precipitate formation, producing a brown to dark brown powder after drying and calcination. These visual observations indicated the successful formation of nanoparticles, which were subsequently confirmed through characterization studies.

UV-Visible Spectroscopic Analysis:

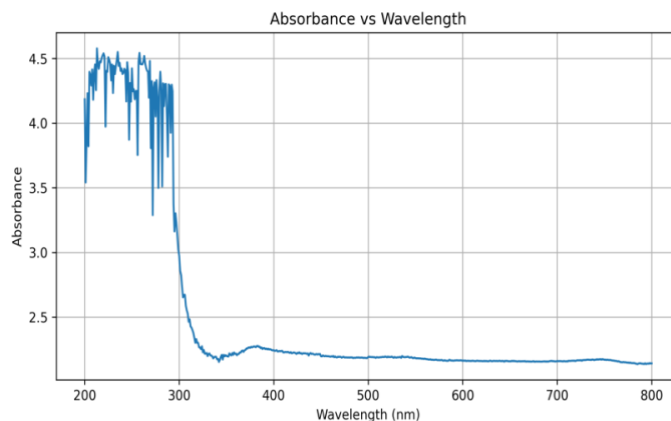
UV-Visible spectroscopy [Figure 3] was employed to confirm the formation and investigate the optical properties of the synthesized ZnO, CuO, and ZnO-CuO heterojunction nanoparticles. The spectra were recorded in the wavelength range of 200–800 nm. The ZnO nanoparticles exhibited a characteristic absorption peak [figure3(a)] at approximately 377 nm, which is attributed to the intrinsic band-gap absorption of ZnO and confirms the successful formation of ZnO nanoparticles. The CuO nanoparticles showed an absorption band [figure 3(b)] in the range of 250–290 nm, indicating the formation of CuO nanoparticles and their characteristic optical response.



(a)



(b)



(c)

Figure 3: (a) UV-Vis characterization of ZnO nanoparticles; (b) UV-Vis characterization of CuO nanoparticles; (c) UV-Vis characterization of ZnO CuO heterojunction nanoparticles

The ZnO–CuO heterojunction nanoparticles displayed a broader absorption region [figure 3(c)] extending from **300–500 nm**, demonstrating enhanced light absorption compared to the individual metal oxides. The broad absorption behavior is attributed to the formation of the ZnO–CuO heterojunction, which facilitates improved charge transfer and extends the absorption of light into the visible region. The observed absorption characteristics confirmed the successful synthesis of the ZnO–CuO nanocomposite and suggested its suitability for photocatalytic applications under sunlight irradiation.

FTIR Spectroscopic Analysis:

FTIR spectroscopy was carried out in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$ to identify the functional groups associated with the synthesized nanoparticles and to investigate the role of *Callistemon citrinus* phytochemicals in nanoparticle formation and stabilization. The FTIR spectra of ZnO, CuO, and ZnO–CuO nanoparticles exhibited broad absorption bands around $3400\text{--}3450\text{ cm}^{-1}$, corresponding to O–H stretching vibrations of phenolic and alcoholic compounds present in the plant extract. Peaks observed in the $2920\text{--}2850\text{ cm}^{-1}$ region were attributed to C–H stretching vibrations of aliphatic compounds, while bands near $1620\text{--}1650\text{ cm}^{-1}$ were assigned to C=O stretching or N–H bending vibrations associated with proteins and other biomolecules. Additional peaks in the $1030\text{--}1100\text{ cm}^{-1}$ region corresponded to C–O stretching vibrations of flavonoids, tannins, and other phytochemicals.

For ZnO nanoparticles, the characteristic Zn–O stretching vibration was observed in the range of $450\text{--}550\text{ cm}^{-1}$ [table 1], confirming the formation of ZnO. For CuO nanoparticles, the Cu–O stretching vibration appeared between $520\text{--}620\text{ cm}^{-1}$ [table 2], confirming the formation of CuO nanoparticles.

In the case of the ZnO–CuO heterojunction nanoparticles, the simultaneous presence of both Zn–O ($450\text{--}550\text{ cm}^{-1}$) and Cu–O ($520\text{--}620\text{ cm}^{-1}$) vibration bands confirmed the coexistence of ZnO and CuO phases. Furthermore, the broad band observed in the $430\text{--}650\text{ cm}^{-1}$ region was attributed to Zn–O–Cu interactions [table 3], providing evidence for the successful formation of the ZnO–CuO heterojunction structure. The presence of phytochemical functional groups in the FTIR spectrum indicates that biomolecules from *Callistemon citrinus* acted as reducing, capping, and stabilizing agents during the green synthesis process. These FTIR results collectively confirm the successful biosynthesis and stabilization of ZnO, CuO, and ZnO–CuO heterojunction nanoparticles using *Callistemon citrinus* leaf extract.

Table 1: FTIR Analysis of Green-Synthesized ZnO Nanoparticles

FTIR Peak (cm ⁻¹)	Functional Group	Assignment
3400–3450	O–H stretching	Phenols and alcohols from plant extract
2920–2850	C–H stretching	Alkanes/terpenoids
1630–1650	C=O stretching / N–H bending	Amide groups of proteins
1380–1420	C–N stretching	Amines
1020–1100	C–O stretching	Alcohol and flavonoids
450–550	Zn–O vibration	Confirmation of ZnO nanoparticle formation

Table 2: FTIR Analysis of Green-Synthesized CuO Nanoparticles

FTIR Peak (cm ⁻¹)	Functional Group	Assignment
3400–3450	O–H stretching	Hydroxyl groups from phytochemicals
2920–2850	C–H stretching	Aliphatic compounds
1600–1650	C=O stretching	Carbonyl groups
1380–1450	C–N stretching	Amines
1030–1100	C–O stretching	Polyphenols and flavonoids
520–620	Cu–O vibration	Confirmation of CuO nanoparticle formation

Table 3: FTIR Analysis of Green-Synthesized ZnO–CuO Heterojunction Nanoparticles

FTIR Peak (cm ⁻¹)	Functional Group	Assignment
3400–3450	O–H stretching	Hydroxyl groups from phytochemicals
2920–2850	C–H stretching	Organic capping molecules
1620–1650	C=O stretching / N–H bending	Proteins and polyphenols
1380–1450	C–N stretching	Amines
1030–1100	C–O stretching	Flavonoids and tannins
450–550	Zn–O vibration	ZnO phase present
520–620	Cu–O vibration	CuO phase present
430–650	Zn–O–Cu interaction	Evidence of heterojunction formation

Assessment of the photocatalytic activity

The photocatalytic degradation of Methylene Blue (MB) in the presence of biosynthesized ZnO, CuO, and ZnO–CuO heterojunction nanoparticles was investigated under sunlight irradiation. The extent of degradation was monitored by measuring the absorbance of MB solution using UV–Visible spectroscopy at regular time intervals. The results revealed that the degradation efficiency increased progressively with increasing irradiation time for all the synthesized photocatalysts. The phenomenon of photodegradation of MB takes place when sunlight is irradiated on the photocatalyst (ZnO, CuO and ZnO/CuO), which leads to the generation of electron–hole pairs in conduction/valence bands (VBs) simultaneously on the surface of the photocatalyst [eq. (2)]. In the conduction band (CB), oxygen on the surface of the photocatalyst combines with the excited electron and forms $\cdot^- \text{O}_2$ [superoxide radical; eq. (3)]. This radical checks the recombination of e^-/h^+ pairs by converting into $\cdot\text{OH}$ radicals through hydroperoxyl radicals ($\text{HOO}\cdot$) and H_2O_2 intermediates [eq. (4)]. Simultaneously, holes produced in VB react with the surface water to produce hydroxyl radicals [$\cdot\text{OH}$; eq. (5)]. The hydroxyl radicals produced in CB and VB, on the surface of photocatalyst, act as a strong oxidizing agent, which in turn degrade MB molecules into simple inorganic molecules, such as H_2O , CO_2 , and inorganic ions [eq. (6)]. The survey of literature also reveals that O_2

(superoxide) radicals and hydroxyl radicals ($\cdot\text{OH}$) are the leading reactive species for the photodegradation of MB dye [53]. The photocatalytic mechanism based on the generation of reactive species was described in Figure 4.

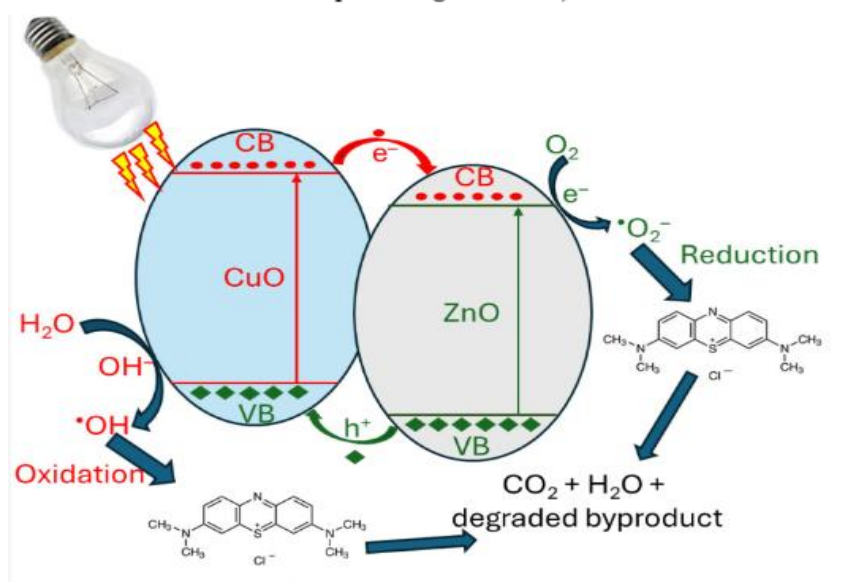
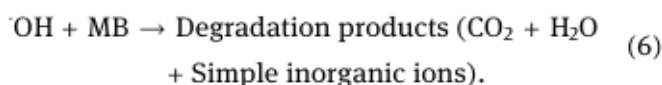
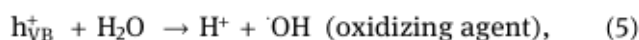
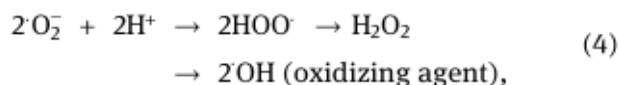
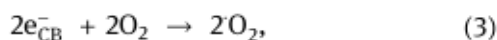
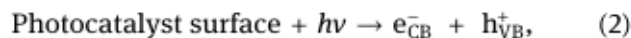


Figure 4: Photocatalytic mechanisms for the degradation of MB by Green Semiconductor CuO/ZnO nanocomposites [54]

ZnO nanoparticles are n-type semiconductor with wide band gap (3.2-3.4 eV), usually works better in UV region (200-400 nm). When ZnO is exposed to UV light, it produces electron-hole pairs that react with oxygen and water to form superoxide radicals ($\text{O}_2^{\cdot-}$) and hydroxyl radicals ($\cdot\text{OH}$). However, the practical efficiency of ZnO is limited by its wide band gap and rapid electron-hole recombination. CuO nanoparticles are p-type semiconductor with narrow band gap (1.2-2.0 eV), making it more suitable for visible light. CuO nanoparticles also exhibit a photocatalytic degradation mechanism similar to ZnO nanoparticles. Nevertheless, CuO alone may exhibit lower photocatalytic efficiency due to charge carrier recombination and lower surface activity compared to ZnO.

The ZnO-CuO nanocomposite creates a heterojunction structure by combining the benefits of both semiconductors. This heterojunction facilitates efficient separation of photogenerated electrons and holes, thereby reducing their recombination rate. Consequently, more reactive oxygen species are created. The synergistic interaction between ZnO and CuO improves visible-light absorption, increases photocatalytic activity, and accelerates dye degradation compared to the individual metal oxides.

The absorbance spectra (Figure 5) showed a continuous decrease in the characteristic absorption peak of Methylene Blue, indicating the gradual degradation of dye molecules. Among the investigated photocatalysts, ZnO–CuO heterojunction nanoparticles exhibited the highest photocatalytic activity, whereas ZnO and CuO nanoparticles showed comparatively lower degradation efficiencies. The enhanced photocatalytic performance of the heterojunction nanocomposite clearly demonstrates the beneficial effect of combining ZnO and CuO into a single semiconductor system.

The photocatalytic degradation efficiency obtained after 120 min of sunlight irradiation followed the order:

$$\text{ZnO–CuO} > \text{ZnO} > \text{CuO}$$

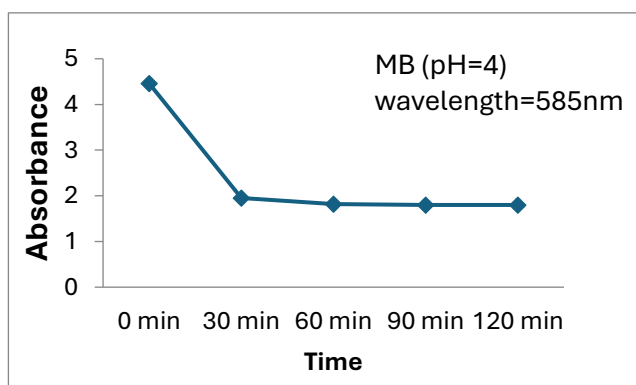
The ZnO–CuO heterojunction nanoparticles achieved a maximum degradation efficiency of 85.87%, while ZnO and CuO nanoparticles exhibited degradation efficiencies of 61.88% and 59.64%, respectively, shows in Table 5. These results indicate that the formation of the heterojunction significantly improves photocatalytic performance compared to the individual metal oxide nanoparticles.

Table 4: Variation in absorbance of CuO, ZnO and ZnO/CuO nanoparticles treated MB dye solution under sunlight with time.

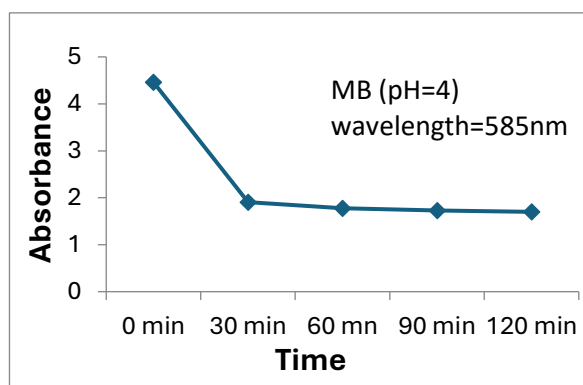
Time	CuO (Absorbance)	ZnO (Absorbance)	ZnO/CuO (Absorbance)
0 min	4.46	4.46	4.46
30 min	1.95	1.908	0.71
60 min	1.85	1.78	0.67
90 min	1.80	1.73	0.64
120 min	1.80	1.70	0.63

Table 5: % Degredation of MB dye with time when treated with synthesized nanoparticles.

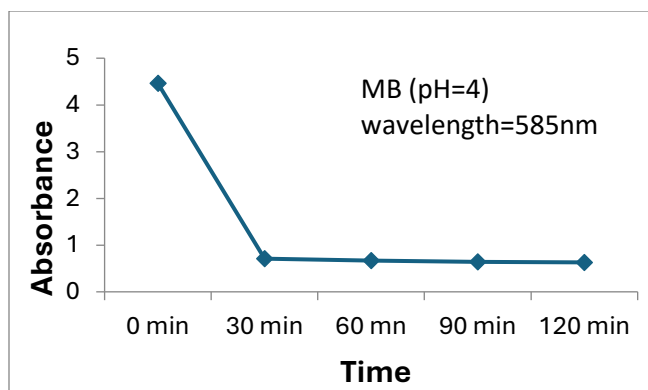
Time	CuO (% Degredation)	ZnO (% Degredation)	ZnO/CuO (% Degredation)
30 min	56.27	57.21	84.08
60 min	58.52	60.08	84.97
90 min	59.64	61.21	85.65
120 min	59.64	61.88	85.87



(a)



(b)



(c)

Figure 5: Absorbance spectra of a 100mL solution of Methylene Blue dye containing 0.05g each of: (a) CuO nanoparticles (b) ZnO nanoparticles (c) ZnO-CuO heterojunction nanoparticle

The superior photocatalytic activity of ZnO-CuO heterojunction nanoparticles can be attributed to the synergistic interaction between ZnO and CuO. The heterojunction interface facilitates efficient separation of photogenerated charge carriers and suppresses electron-hole recombination, thereby increasing the availability of reactive species responsible for dye degradation. Furthermore, the incorporation of CuO enhances visible-light absorption, resulting in improved utilization of solar energy and accelerated degradation of Methylene Blue. Figure 6 shows Variation of absorbance at 585 nm with sunlight exposure time.

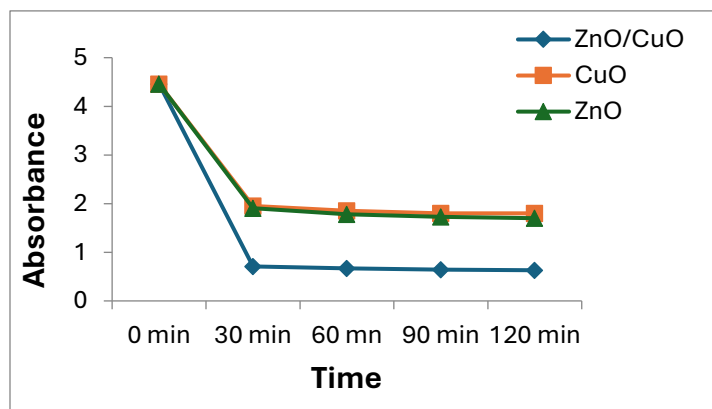


Figure 6: Variation of absorbance at 585 nm with sunlight exposure time

The obtained results demonstrate that the biogenically synthesized ZnO-CuO heterojunction nanoparticles are highly efficient photocatalysts and possess significant potential for the removal of organic dye pollutants from wastewater under sunlight irradiation.

Conclusion

In this study, ZnO, CuO, and ZnO-CuO heterojunction nanoparticles were successfully synthesized using *Callistemon citrinus* leaf extract through a simple, cost-effective, and eco-friendly green synthesis route. Visual observations, UV-Visible spectroscopy, and FTIR analysis confirmed the successful formation of the nanoparticles and the involvement of plant-derived phytochemicals in their synthesis and stabilization. UV-Vis analysis revealed characteristic absorption behavior of the synthesized nanomaterials, while FTIR

spectra confirmed the presence of functional groups and metal-oxygen bonds associated with ZnO and CuO formation.

The photocatalytic activity of the synthesized nanoparticles was evaluated using Methylene Blue dye under sunlight irradiation. All photocatalysts exhibited dye degradation capability; however, the ZnO-CuO heterojunction nanoparticles demonstrated significantly enhanced photocatalytic performance compared to the individual ZnO and CuO nanoparticles. The heterojunction nanocomposite achieved a maximum degradation efficiency of 85.87%, whereas ZnO and CuO nanoparticles exhibited degradation efficiencies of 61.88% and 59.64%, respectively. The improved photocatalytic efficiency of the ZnO-CuO heterojunction is attributed to enhanced charge carrier separation and improved utilization of visible light.

Overall, the findings of this study demonstrate that *Callistemon citrinus*-mediated ZnO-CuO heterojunction nanoparticles are promising photocatalytic materials for the degradation of organic dye pollutants. The developed green synthesis approach provides a sustainable pathway for producing efficient nanomaterials with potential applications in environmental remediation and wastewater treatment.

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