Research Article

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Recyclability and catalytic characteristics of copper oxide nanoparticles derived from bougainvillea plant flower extract for biomedical application

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Abstract: This work aims to investigate the environmentally sustainable technique to synthesize the copper nanoparticles using bougainvillea flower ethanolic extract at ambient temperature. Copper nanoparticles have considerable potential for reducing the environment's harmful pigments and nitrogen contaminants. The oxidized copper nanoscale catalysts are enclosed inside nanomaterial, which work as a benign and sustainable resource for capping agents. Ultraviolet spectroscopic, transmission electron microscopy (TEM), and X-ray crystallography (XRD) techniques were used to evaluate the produced oxidized copper nanocrystals. The particles produced have been very robust, are cylindrical in form, and have an outer diameter of 12 nm. Furthermore, under normal conditions, copper oxide (CuO) nanomaterials demonstrated strong photocatalytic efficiency in liquid media for the oxidation of Congo red, bromothymol blue, and 4-nitrophenol in an acidic solution acetic anhydride. Moreover, the CuO nanocrystalline enzyme could be readily vortexed or used for five cycles with an exchange rate of even over 90%. The evaporation process caused around 18% of the loss of weight between 25°C and 190°C, while soil organic breakdown caused almost 31% of the loss of weight around 700°C. As a result, the little reduction in enzymatic effectiveness of the recoverable multilayer CuO substrate might be attributed to catalytic degradation throughout spinning and processing.

Keywords: copper oxide, nanoparticles, green synthesis, bougainvillea plant flower extract, catalytic properties

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Abbreviations

CuO	copper oxide
SEM	scanning electron microscope
TEM	transmission electron microscopy
XRD	X-ray crystallography
UVS	ultraviolet spectroscopy
NPs	nanoparticles
$NaBH_4$	sodium borohydride
EDAX	energy-dispersive X-ray spectroscopy
TGA	thermogravimetric analysis
CR	Congo red

MB methylene blue
ICPAES inductively coupled plasma atomic emission spectroscopy

1 Introduction

Currently, nanotechnology is a fast-growing branch of modern technology. Because of their notable and/or diverse characteristics in catalytic reactions, absorbent materials, lubricating oils, ceramic materials, semiconductors, screen equipment, renewable power, medical technology, bioengineering, contaminant detection, and physiological detectors, nanoparticles made of metal oxide have snagged fantastic consideration in all of the major domains of emerging engineering and science [1,2]. Green chemistry concentrates just on the fabrication of nanostructures using non-toxic substances under moderate operational parameters, hence improving the energy conservation of nanostructures. This sector has risen in popularity due to its potential characteristics such as low prices, easy methods, and reasonably large efficiency gains [3]. Although nanostructures are commonly generated at massive distances using a variety of physical and chemical techniques, there is worry about contamination owing to the participation and the emission of dangerous compounds [4]. Organic substances, including colors, are generally harmful, and the majority of harmful toxins constitute a major contributing factor to environmental pollution. Health issues due to the use of bromothymol blue, bromothymol blue, methylation emerald, and Congo red (CR), and other organic contaminants and chemical pigments are extremely evident and adaptable [5]. They are also widely used in pesticides, textiles, medicine, fungal, and other production sectors, and when discharged into systems, they pose significant dangers to humans. Due to expressing personal stabilization, nitrophenols and colorants are challenging to eliminate using pesticide, physiological, and physiological methodologies such as rainfall, adsorbents, ultraviolet light, electrical photocatalyst, and biodegradation, and all these methodologies have innate limits such as high expense and creation of health hazards by merchandise [6]. The breakdown of such harmful contaminants, including colors, in sewage has piqued scientists' curiosity in recent years. As a result, it is critical in the current situation to produce an aqueous medium transformation of these organic contaminants, including colors, under moderate circumstances using the enzymatic segmented image. Municipal potable water has developed as a simple and practical analytical method using nanoscale enzymatic performance [7].

Because of their distinct attributes, nanocrystals of precious metals, including inorganic materials, have seen considerable and exciting uses in recent days. Numerous metallic nanoparticles have also received a lot of attention among numerous metallic nanoparticles since they are highly reactionary, simple p-type metallic transistors to cubic phase, and one's large surface loudness display, having obtained in catalytic reactions, elevated conducting polymers, photovoltaic panels, photonic detectors, and antibacterial, anti-fouling, anti-biotic, and anti-fungal. Furthermore, nanocomposites display a distinctive superhydrophobic characteristic [8,9]. Numerous biophysical techniques are used mostly in the production of CuO nanomaterials, which presents several issues such as high temperatures, reductases, and volatile compounds, among dangerous compounds. This research recommends utilizing houseplants for synthesis to meet the technical needs while minimizing the disadvantages [10]. Furthermore, CuO is a cheap, plentiful, and economical metal with a rapid response time in usual conditions, which is advantageous in sustainable nanomaterials. It developed an environmentally friendly technique for producing copper oxide (CuO) nanoparticles, emphasizing the use of biological factors once more for the production of CuO nanopowder [11].

Yet, given the widespread use of NPs in a variety of industries, there is an urgent need to develop safer, more dependable, non-noxious, simple, and environmentally friendly NP production techniques. Indeed, for the production of less toxic metallic NPs, a wide range of plants, bacteria, biopolymers, fungus, enzymes, and other bio-constituents have been introduced [12,13]. Nevertheless, microbe-assisted myco-synthesis of NPs is neither economically or industrially viable since it requires expensive culture and maintenance under strict sterile conditions. Consequently, research into plant materials has been identified as a possible bioreactor for the production of metal nanoparticles without the use of harmful chemicals. Common methods for producing CuO nanoparticles include chemisorption, depicted, geothermal heat oxidizing, sol-gel, arc discharge in fluid, biochemical method, solitary moist production, solvothermal, supercapacitor heat breakdown, and simple chemical route [14,15]. Robust copper nanoparticles were manufactured using a sustainable technique employing botanical extracts of bougainvillea flowers as just a lowering, stabilizing, and driving sealing reagent [16]. Trees and related items enable transcendental manufacturing that is both environmentally friendly and of low cost [17]. CuO nanoparticles were created by extracting foliage, seeds, stems, spores, branches, stems, peeling, and flowers from species such as Persian walnut, Heaven tree flowers, common mallow, date palm, monkey bush, khat flowers, pinwheel flowers, and *Aloe barbadensis* Miller [18].

Colorant effluent is emitted into the atmosphere by developing manufacturing industries such as textiles, newspapers, rubber, culinary, plastics, and pharmaceutical businesses. Although most pigments are toxic or carcinogenic, contaminants offer a major consequence of exposure damage. As a result, treating wastewater before dumping it into water sources is critical [19]. Rhodamine B is among the most commonly used thiazine pigment in the industry; consequently, it was chosen as a representative contaminant throughout this investigation. It is highly durable with minimal variance in numerous aspects that impact the world's oceans. Due to the toxic and hazardous nature of blue, wastewater from firms using this colorant should be treated prior to release [20]. During decolorization, many approaches such as pharmacological, physiological, and biostimulation are accessible. Furthermore, photocatalyzed pigment breakdown offers several benefits, including a benign procedure, excellent electrocatalytic effectiveness, and low cost, enabling the quick breakdown of several contaminants into innocuous chemicals. Because India is a tropical country, sunshine is plentiful in irradiating photocatalytic activity. Daylight serves as an alternative fuel during pigment breakdown [21,22].

In this light, this research concentrates on the truthful principles of chemical synthesis that were decided to apply in the synthesis of CuO nanoparticles, an eco-friendly strategy using a bougainvillea flower extract, and analyzes their effectiveness for the photocatalytic degradation of deleterious organic contaminants and dyes, notably 4-nitrophenol (4-NP), methylene blue (MB), and CR, from liquid phases by homogeneous and heterogeneous methods. Bougainvillea aqueous extracts include a high concentration of various phenolics and other phytochemicals that really can function as both a capping and reducing agent for CuO NPs. According to the literature, the authors suggest that this is the initial study on CuO NPs generated from bougainvillea flower extracts.

2 Materials and methods

2.1 Materials

Copper nitrate solutions with such a quality of 98.99% were acquired through Modern Industries in India. The violet blossoms of the bougainvillea shrub were obtained from several places in Tamil Nadu, India. Demineralized water was procured from the Madras Pharmaceutical Industry in India.

2.2 Synthesis of CuO nanoparticles

Organic veranera or bougainvillea blossoms were carefully cleaned to remove particulates and dried at 25°C in the laboratories. In such a potato masher, flowers were gently pulverized. In a beaker containing 6–12 g of fine-powdered bougainvillea blossoms, 150 mL of distilled water was added and boiled for 10 min at 80°C before filtering through Whatman No. 1 filtration apparatus material to generate a clear violet solution of veranera flowers. It was then placed in the freezer for later consumption. Figure 1 shows the biosynthesis process of CuO nanoparticles from veranera or bougainvillea flower extract.

Oxalic acid hydrochloride (6–12 g) was mixed in 150 mL of distilled water and mechanically swirled for 5 min at 25°C. Then, veranera flower decoction has been introduced drop by drop while stirring vigorously. Whenever the blossom decoction came into direct contact with metal cations, the blue color of copper ions transformed to a blueish gray under two to three seconds, demonstrating the formation of CuO particles. The dark black fine material was collected and kept in an unbreakable plastic bottle for further characterization and photocatalytic degradation testing. Copper hydroxide was formed on the surface, which was confirmed by the presence of OH groups. This discovery is supported by the occurrence of an asymmetry that is more prominent for CuO. The substantial formation of $Cu(OH)_2$ on the CuO surface indicates a reduced impact of subsequent exposure to ambient moisture and, as a result, limited competition among photochemical processes at an ambient temperature [1,23].

2.3 Nanoparticle characterizations

The CuO nanoparticles produced in this sustainable environment using veranera flowers were subsequently analyzed using X-ray spectrometer. The X-ray wavelengths were 1.521, and the diffractograms were captured at a penetration depth of 2 min. Thermal analysis and differential scanning calorimetric (DSC) have been used to determine the loss weight of CuO nanocatalysts after this sacrificial deployment. Such experiments have been carried out in the presence of an N_2 atmosphere. The specimens were placed and subsequently warmed at a speed of $20°\cdot min^{-1}$

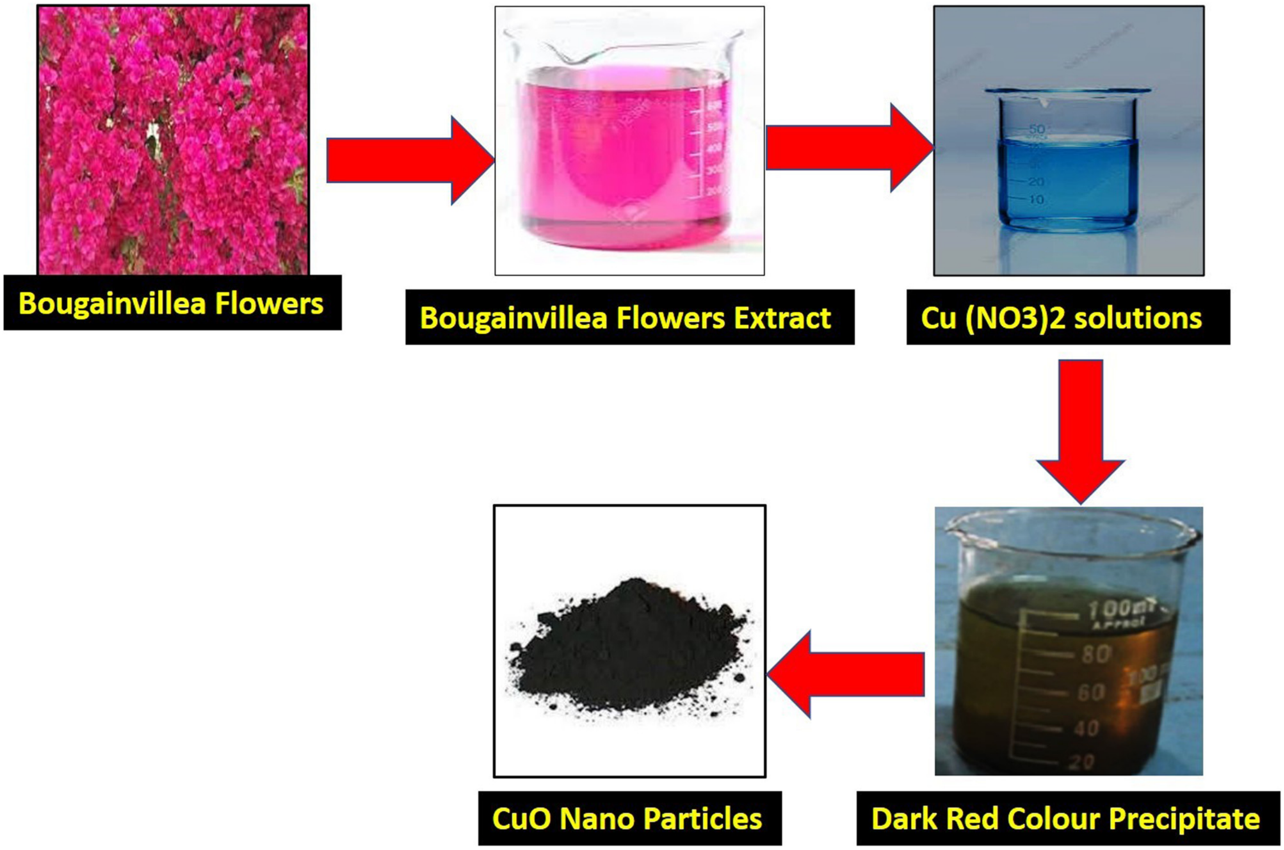

Figure 1: Biosynthesis process of CuO nanoparticles from veranera or bougainvillea flower extract.

between 300°C and 700°C to determine the weight reduction of CuO nanoparticles. At periodic times, the natural antioxidants' conversion of copper nitrate to copper nanomaterials was monitored using a double-stream UV spectrometer. To be more precise, approximately 300–700 nm wavelength regions were used to assess the changes in surface morphology. Transmission electron microscopy was used to evaluate the shape and particulate distribution of copper nanomaterials. A particle size analyzer was used to assess the particle size distribution and zeta potential of the biosynthesized CuO NPs (Malvern Instruments Ltd., Zetasizer Ver. 6.34) [24].

2.4 Catalytic activities of CuO nanoparticles

At an optimal level of 200 L, the efficiency of plant-derived produced oxidized copper nanomaterials for the breakdown of environmentally hazardous pigments was investigated. About 10^{-3} M 4-NP was mixed with 1 mL of 10^{-2} M sodium borohydride solutions with 1 mL of 10^{-4} M MB and CR. The optimizer rapid reduction process refers to the negative, which was measured using spectrophotometry. For the elimination of $NaBH_4$, nanomaterials were used as a control.

In the absence of an appropriate quantity of 10^{-2} M sodium borohydride solvent, oxidized copper nanomaterials have been used as both a heterogeneous and a homogeneous catalyst in the deterioration of synergistic effects of 10^{-4} M MB and CR reactive dyes at such an optimized amount of 200 L·10 mg^{-1}. The pigment breakdown was monitored using ultraviolet spectroscopy. Even the liquid immediately decolorized [25].

3 Result and discussions

3.1 Ultraviolet spectroscopy of CuO nanoparticles

The ultraviolet spectrum of a CuO nanoparticle catalytic reaction is shown in Figure 2. We found that the color progressively changed from mild yellowish to brickwork red owing to CuO nanoparticle stimulation by plasmon

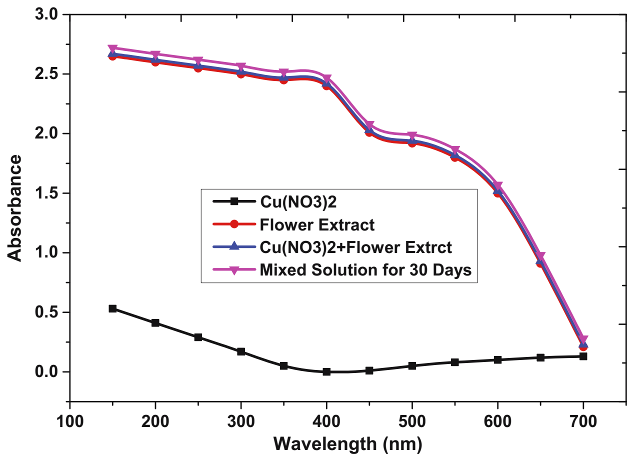

Figure 2: Ultraviolet spectroscopy of catalytic reactions of CuO nanoparticles.

oscillations. There was no additional increase after 30 h, indicating that the response had been completed. Its surface plasmon resonance (SPR) group altered in location during the catalytic reaction due to the amount of electrostatic interaction and interactions between the dimension and shape of CuO nanoparticles in an aqueous solution [26]. The specimen lacking floral extracts has a red shift in absorption that could be attributed to the increased particle diameter. Derivatives have photochromic characteristics because of particulate SPR range shifting to wavelengths. The production of CuO nanoparticles is indicated by a plasmonic absorbance peak with such a concentration at 270–390 nm [1]. The same endophyte CuO nanoparticles generated by this technique are all quite consistent, with no high variability in the form, dimensions, and evenness of a peak position after 30 days, which can be attributed to the presence of bioactive substances within the veranera blossoms, including the CuO nanoparticles [27].

3.2 XRD analysis

The transition and the degree of crystallinity of endophyte CuO nanoparticles were examined using XRD. Figure 3 depicts a typical XRD analysis of CuO nanoparticles. This figure contains 2θ reactions at 31.24°, 34.28°, 37.36°, 41.58°, 50.24°, 52.68°, and 62.20°, which correspond to 112, 123, 111, 203, 221, 211, and 223 intensities. Nanoparticles with such a phase transformation and dispersed phase are shown. The wave equation technique is used to determine the overall mean diameter of crystallographic nanostructures [28,29].

In the aforementioned equation, λ represents the X-ray wavelengths, α represents the average line widening around double its optimum in trigonometric functions, and $\ddot{\Theta}$ represents Bragg's inclination. We determined a spectrum of mean crystallite size of ca. 51.36 nm for CuO nanoparticles based on the distinct two maxima, which is compatible with both microscopic observations.

3.3 Thermal analysis

Figure 4a and b depicts a transmission electron microscopy (TEM) of CuO nanoparticles, which have been readily visible in size and cylindrical form. Their chemical compositions of

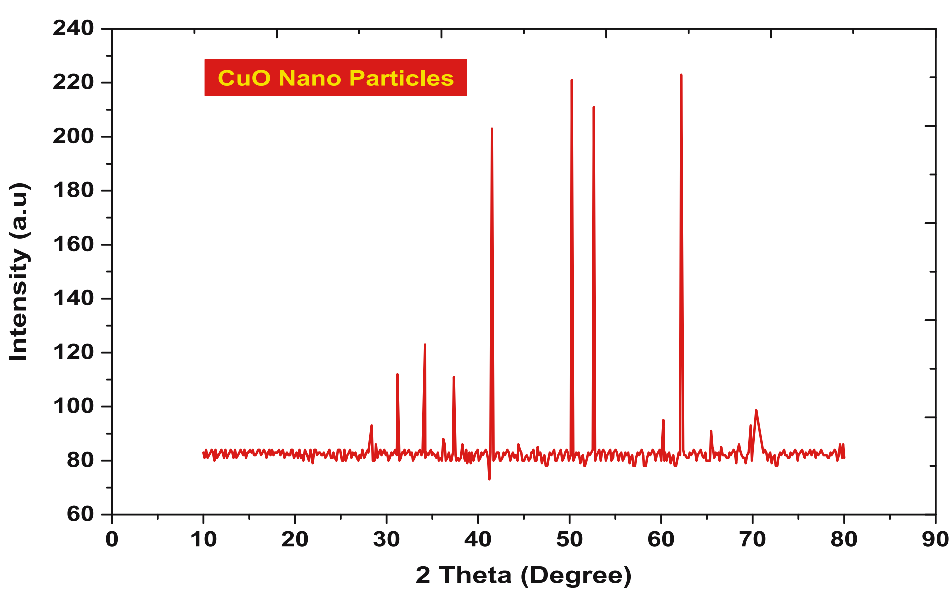

Figure 3: XRD patterns of biosynthesized CuO nanoparticles.

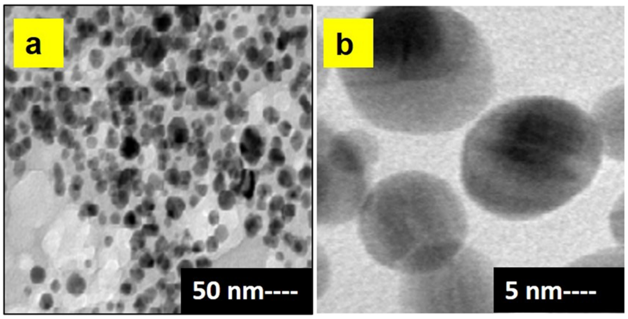

Figure 4: (a) Microstructural images of nanoparticle with 50 nm range. (b) Microstructural images of nanoparticle with 5 nm range.

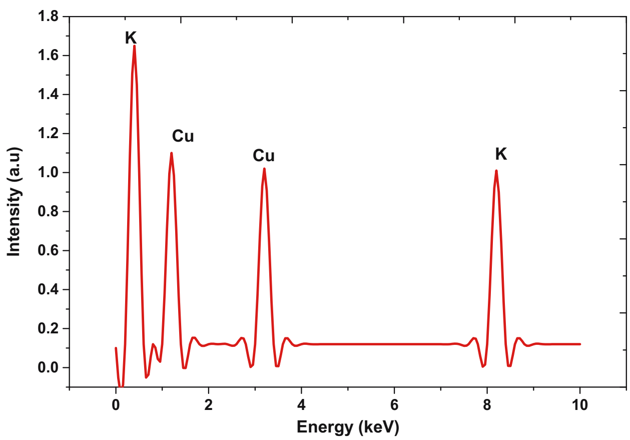

Figure 5: EDAX patterns of biosynthesized CuO nanoparticles.

the produced nanomaterials were validated using an EDAX analysis paired with a TEM, as shown in Figure 5. It displays the standard requirement of basic carbon molecules, suggesting ion concentration conversion. Its geometric dispersion of CuO nanoparticles produced from veranera flowers was validated again by TEM examination [30]. Figure 6 shows

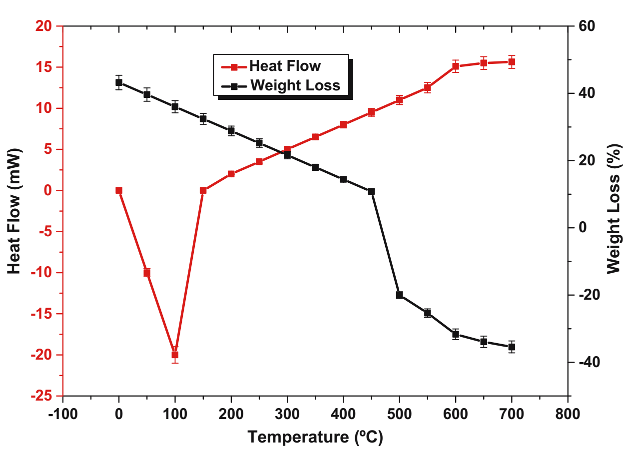

Figure 6: Thermogravity analysis of biosynthesized CuO nanoparticles.

an evaluation of the topping with crystallographic structure. The form and size of the generated nanoparticles were characterized using microscopy. These nanoparticles ranged in size from 36 to 54 nm. Thermogravimetric analysis (TGA) using DSC was used to assess the heat durability of CuO at a reaction temperature of 15°C·min^{-1} in the atmosphere throughout a temperature gradient of 25–700°C [31]. Figure 6 demonstrates the CuO TGA curves. The process of evaporation caused around 18% of the loss of weight between 25°C and 190°C, while soil organic breakdown caused almost 31% of the loss of weight around 300–700°C [32].

3.4 Zeta potential and DLS analysis

The sustainability of the biosynthesized CuO NPs was further investigated using zeta potential measurement. Figure 7a shows the zeta potential value of biosynthesized CuO NPs, which was determined to be −37.8 mV, indicating that the NPs have a negative surface charge and are highly stable. The particle size of the biosynthesized CuO NPs was also determined using the DLS technique. Figure 7b depicts the average size distribution of CuO NPs. As a result, the size distribution of NPs ranges from 30 to 80 nm, with the majority of NPs exhibiting in the 36–54 nm range, which extremely well matches with XRD investigations of biogenically generated CuO NPs [4,23].

4 Catalytic analysis of veranera flower-derived CuO NPs

The effectiveness of binary and ternary enzymatic actions of plant-sourced copper nanoparticles could be significantly influenced by particulate matter due to the chemical. The comprehensive enzymatic efficiency of CuO nanoparticles in removing MB, CR, and 4NP using sodium borohydride was assessed at room temperature [33]. They assessed 1 mL of 10^{-4} M MB and then added 1 mL of 10^{-2} M $NaBH_4$ through a spectrophotometric approach. This indicates that without a catalyst, the conversion rate remained notably slow even after introducing the corrosion inhibitor. Figure 8a and b demonstrates both the mixed and heterogeneous enzymatic effectiveness of CuO nanoparticles. Its MB distinctive ultra violet specification, maximum absorbance at 621 nm, and hump at 610 nm vanished immediately [34].

A similar approach was used to degrade CR, which had an emission peak of 471 nm. During milliseconds, CR is

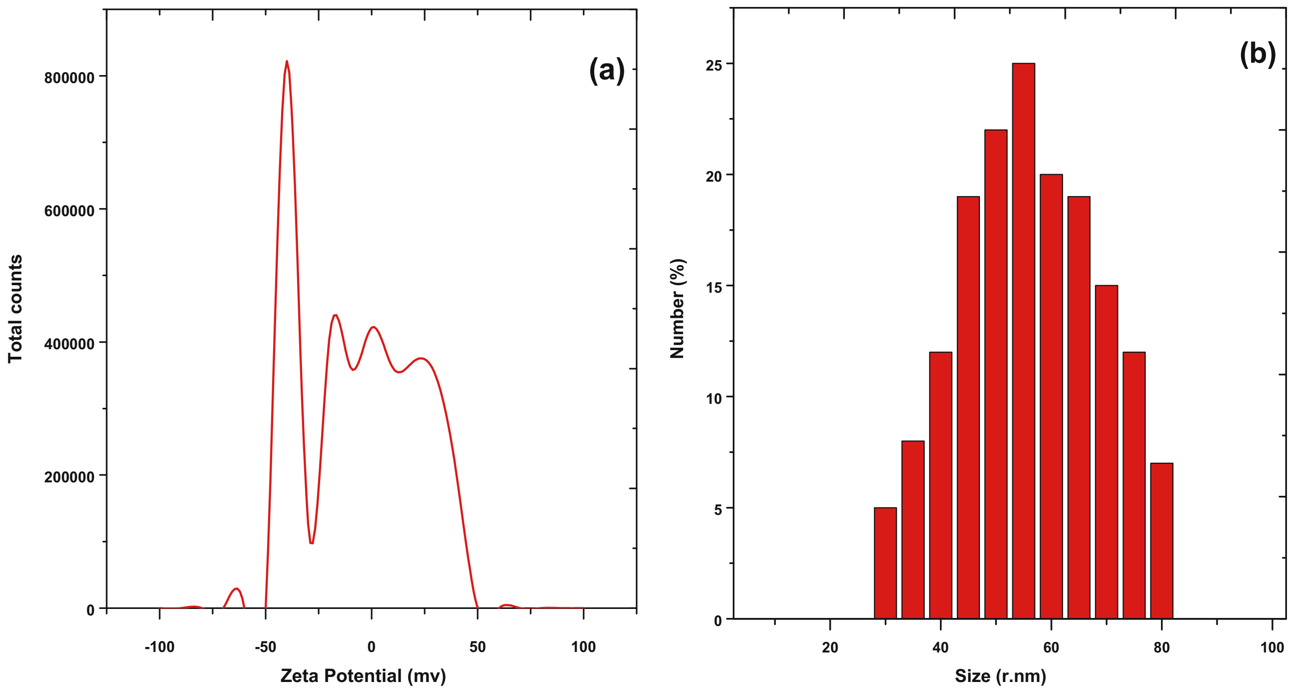

Figure 7: (a) Zeta potential and (b) DLS analysis of CuO nanoparticles synthesized from bougainvillea flower extract.

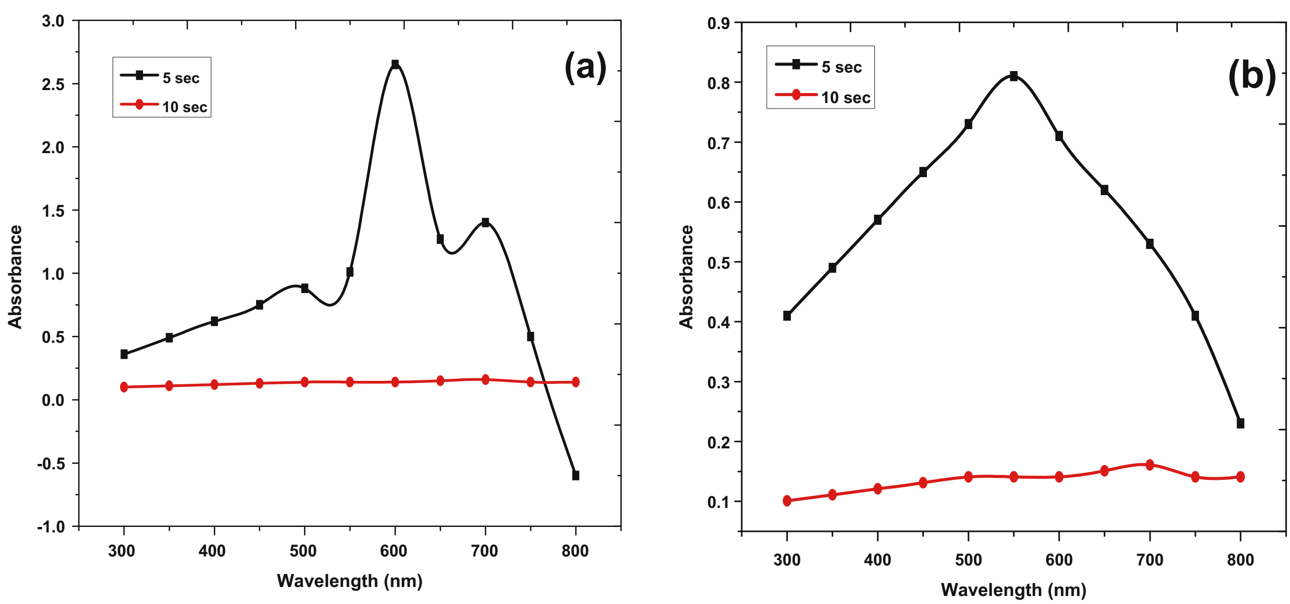

Figure 8: Catalytic reactions of MB: (a) homogeneous and (b) heterogeneous phases.

degraded by the enzymatic performance of CuO nanoparticles. Previous studies reported that the enzymatic breakdown of CR took a second. Spectrophotometrically, the relative percentage of MB and CR-blended dyestuff was determined by measuring the intensity shift of spikes at 621 nm vs 471 nm. In the absence of an enzyme, the deterioration of blended pigments was insignificant in the condition of sodium borohydride [35]. The image depicts a quick shift in the hue but also the strength of an absorption band including both pigments, with little to no additional spikes appearing. This means that now the MB-coupled proteins and CR pigments have deteriorated. The deterioration of combined pigments was likewise finished in a few minutes, as was the breakdown of individual pigments. As a result, this

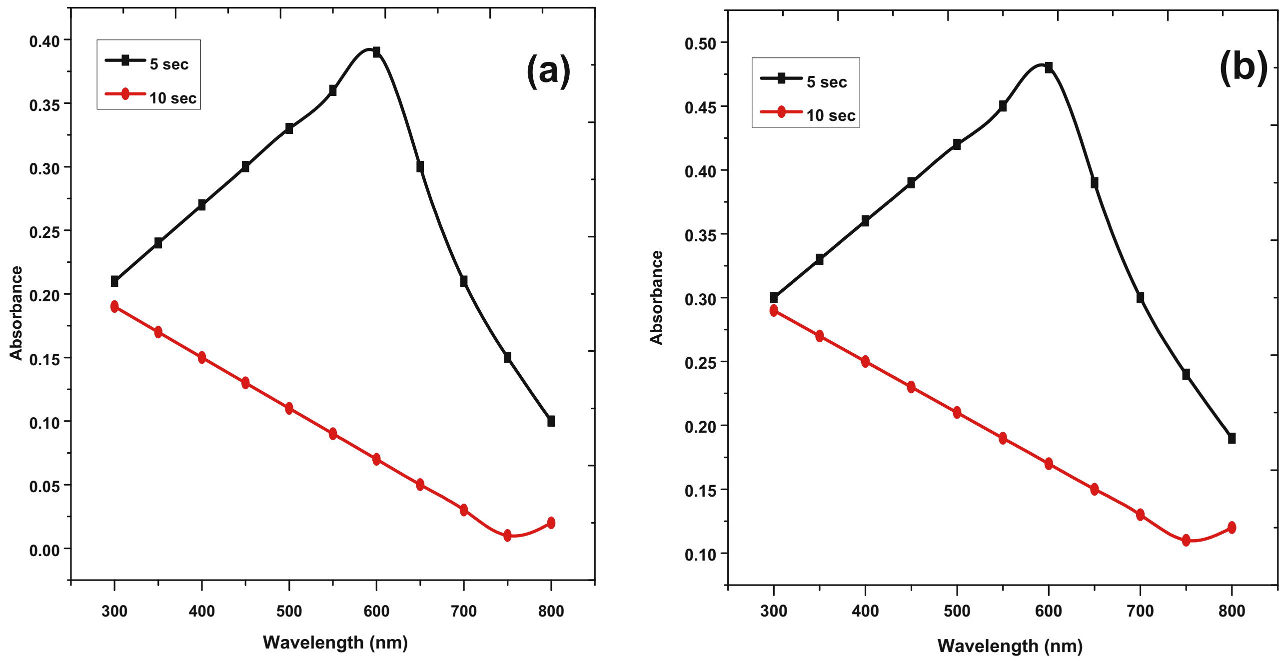

Figure 9: Catalytic reactions of CR: (a) homogeneous and (b) heterogeneous phases.

approach to preparing CuO catalysts could be appropriate for commercial processes. Figure 9 demonstrates the aforementioned findings [36].

4-NP is one of the most difficult contaminants to remove from polluted water, with the potential to harm people's and mammals' nervous systems, brains, kidneys, and circulation. The introduction of sodium borohydride to 4-NP resulted in a red shift of the absorption maximum to 450 nm. This demonstrates the production of 4-nitrophenolate protons using sodium borohydride in an acid condition. The decolorization remained unchanged after 30 days with the exclusion of the catalyst [37]. After the introduction of CuO nanoparticles, a fresh signal at around 323 nm appeared, indicating the synthesis of a balanced

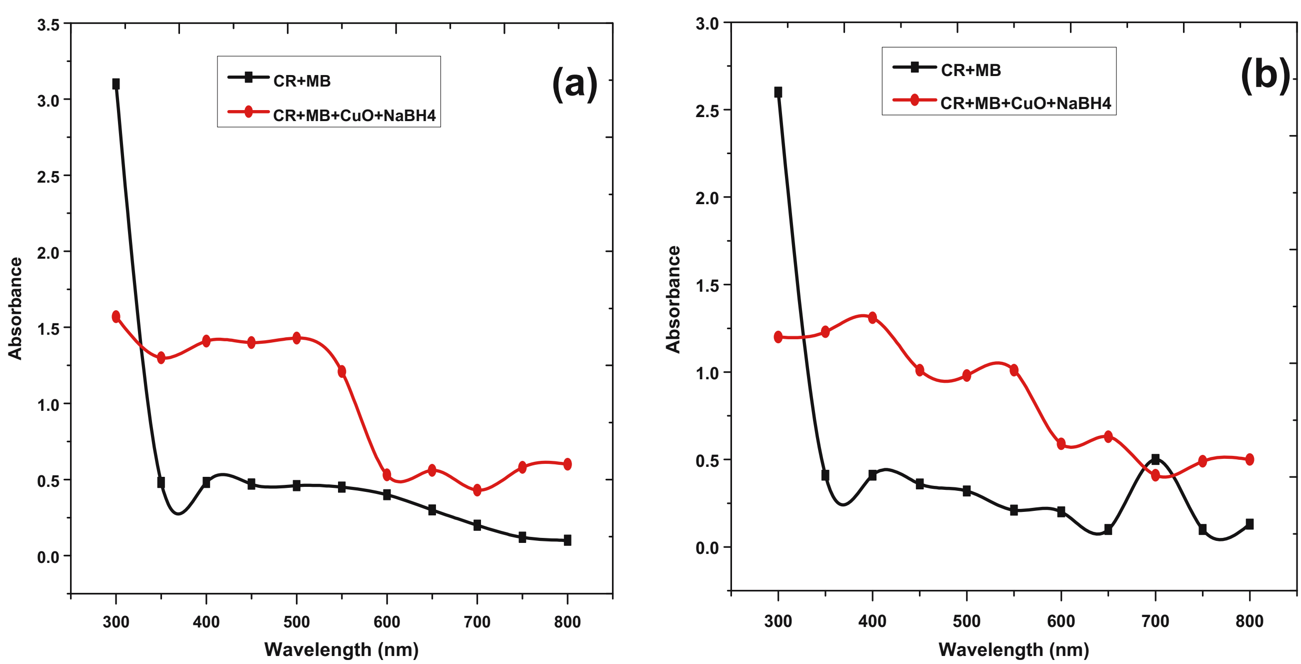

Figure 10: Mixed catalytic reactions: (a) homogeneous and (b) heterogeneous phases.

combination in a short amount of time over hours. 4-Aminophenol has several uses, including the production of antibacterial and analgesic medicines, as a heterogeneous catalyst, and many more. Copper nanoparticles facilitate electronic conductivity among 4-NP and $NaBH_4$. The content of sodium borohydride in the proposed chemical synthesis decomposition method is significantly higher compared to that of 4-NP, and it may remain static throughout the response time [17,31]. As a result, the reaction mechanism for 4-NP elimination might be calculated using the order model pharmacokinetics [38]. Both the homogeneous and heterogeneous reaction rates of CuO nanoparticles again for the breakdown of MB and CR, in addition to the catalyzed reductions of 4-NP, were completed so quickly that the ultraviolet absorbance spectrum was reduced in some few minutes. Figure 10 shows the mixed catalytic reactions of various pigments.

CuO nanoparticles had the greatest photocatalytic activity in the elimination of dangerous chemical pigments. Isolation and extraction of CuO nanoparticles are critical for effective catalytic reactions. Because after the experiment is completed, the nanoscale catalysts are subsequently collected using simple sedimentation. The reusability of enzymatic performance inside the deterioration but instead a significant decline of MB, CR, and 4-NP was evaluated, and thus, the effectiveness has been gradually reduced within a week of 3 consecutive periods, as shown in Figure 11 [39]. It demonstrates over 90% operation in the deterioration of four deleterious colorants up to the end of the process. Such nanostructures have been discovered to be very aggressive catalysts for reductive reactions outlined [40]. ICPAES (inductively coupled plasma atomic emission spectroscopy) investigated the dissolution of the

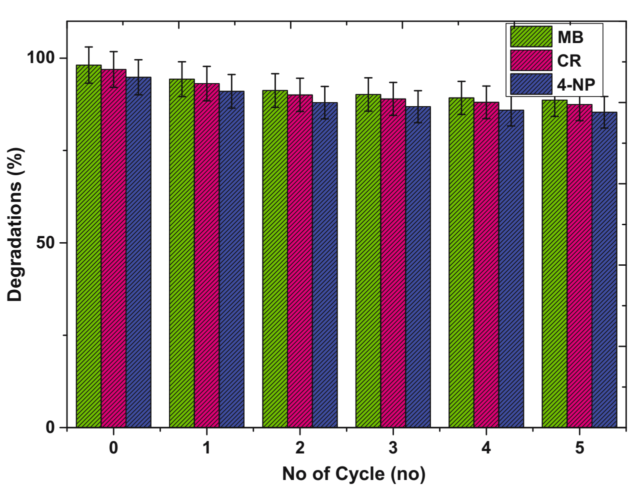

Figure 11: Recyclable and reuse of CuO nanoparticles for the degradation of pigments.

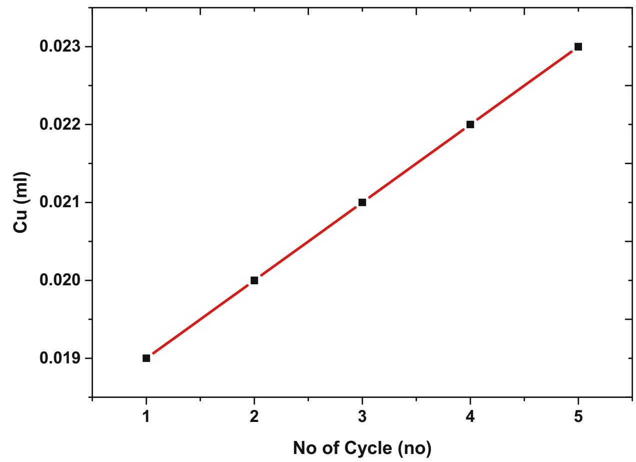

Figure 12: Copper ions at various cycles.

CuO nanocatalyst after equilibrium was reached. The little reduction in enzymatic effectiveness of the recoverable multilayer CuO substrate might be attributed to catalytic degradation throughout spinning and processing [41–46]. Figure 12 depicts the dissolving of catalysts.

5 Conclusion

To ensure a sustainable future, this work focuses on nanotechnology and a phytogenic technique for the production of CuO nanoparticles from ecologically friendly and renewable sources, eliminating the need for chemical-lowering and stabilizing agents. This study describes the green synthesis of CuO NPs using an aqueous extract of bougainvillea flowers as a lowering, capping, and stabilizing agent. The following conclusions were made:

- The shape and size of the generated nanoparticles were characterized using TEM. These nanoparticles ranged in size from 36 to 54 nm. TGA was used to assess the heat durability of CuO at a reaction temperature of 15°C·min^{-1} in the atmosphere throughout a temperature gradient of 25–700°C.
- CuO NPs in aqueous solutions are persistent even after 60 days of response. At room temperature, the CuO NPs demonstrated outstanding homogeneous and heterogeneous catalytic properties in the breakdown and elimination of hazardous organic contaminants.
- The phytogenically produced catalysts were reused and recovered six times with just a slight decrease in catalytic properties. As a result of its catalytic capabilities and other biomedical uses, this green approach might be used for the large-scale manufacturing of nanomaterials.

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Author contributions: L. Natrayan: writing – original draft, conceptualization, investigation, supervision; S. Kaliappan: methodology, writing – review and editing; Saravanan A.: investigation, software; Vickram A. S.: conceptualization, formal analysis; Pravin P.: resources, formal analysis; Mohamed Abbas: software, supervision; C. Ahamed Saleel: investigation, formal analysis; Mamdooh Alwetaishi: writing – review and editing, formal analysis; Mohamed Sadiq Mohamed Saleem: visualization, project administration.

Conflict of interest: The authors state no conflict of interest.

Data availability statement: The data used to support the findings of this study are included in the article. Should further data or information be required, these are available from the corresponding author upon request.

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