



Article

In Situ Synthesis of Cu₂O Nanoparticles Using *Eucalyptus globulus* Extract to Remove a Dye via Advanced Oxidation

Pablo Salgado ¹, Olga Rubilar ^{2,3}, Claudio Salazar ⁴, Katherine Márquez ⁵ and Gladys Vidal ^{6,7,*}

¹ Departamento de Ingeniería Civil, Facultad de Ingeniería, Universidad Católica de la Santísima Concepción, Concepción 4090541, Chile; psalgado@ucsc.cl

² Centro de Excelencia en Investigación Biotecnológica Aplicada al Medio Ambiente (CIBAMA-BIOREN), Facultad de Ingeniería y Ciencias, Universidad de La Frontera, Temuco 4811230, Chile; olga.rubilar@ufrontera.cl

³ Departamento de Ingeniería Química, Universidad de La Frontera, Av. Francisco Salazar 01145, Casilla 54-D, Temuco 4811230, Chile

⁴ Centro de Investigación de Polímeros Avanzados (CIPA), Concepción 4051381, Chile; c.salazar@cipachile.cl

⁵ Centro de Estudios en Alimentos Procesados (CEAP), Campus Lircay, Talca 3460000, Chile; kmarquez@ceap.cl

⁶ Grupo de Ingeniería y Biotecnología Ambiental (GIBA-UDEC), Facultad de Ciencias Ambientales, Universidad de Concepción, Concepción 4070386, Chile

⁷ Water Research Center for Agriculture and Mining (CRHIAM), ANID Fondap Center, Victoria 1295, Concepción 4070411, Chile

* Correspondence: glvidal@udec.cl; Tel.: +56-41-2204067

Abstract: Water pollution, particularly from organic contaminants like dyes, is a pressing issue, prompting exploration into advanced oxidation processes (AOPs) as potential solutions. This study focuses on synthesizing Cu₂O on cellulose-based fabric using *Eucalyptus globulus* leaf extracts. The resulting catalysts effectively degraded methylene blue through photocatalysis under LED visible light and heterogeneous Fenton-like reactions with H₂O₂, demonstrating reusability. Mechanistic insights were gained through analyses of the extracts before and after Cu₂O synthesis, revealing the role of phenolic compounds and reducing sugars in nanoparticle formation. Cu₂O nanoparticles on cellulose-based fabric were characterized in terms of their morphology, structure, and bandgap via SEM-EDS, XRD, Raman, FTIR, UV–Vis DRS, and TGA. The degradation of methylene blue was pH-dependent; photocatalysis was more efficient at neutral pH due to hydroxyl and superoxide radical production, while Fenton-like reactions showed greater efficiency at acidic pH, primarily generating hydroxyl radicals. Cu₂O used in Fenton-like reactions exhibited lower reusability compared to photocatalysis, suggesting deterioration. This research not only advances understanding of catalytic processes but also holds promise for sustainable water treatment solutions, contributing to environmental protection and resource conservation.

Keywords: LED-assisted photocatalysis; Fenton-like heterogeneous; methylene blue; phenolic compounds; cellulose-based fabric



Citation: Salgado, P.; Rubilar, O.; Salazar, C.; Márquez, K.; Vidal, G. In Situ Synthesis of Cu₂O Nanoparticles Using *Eucalyptus globulus* Extract to Remove a Dye via Advanced Oxidation. *Nanomaterials* **2024**, *14*, 1087. <https://doi.org/10.3390/nano14131087>

Academic Editor: Vincenzo Vaiano

Received: 5 June 2024

Revised: 19 June 2024

Accepted: 20 June 2024

Published: 25 June 2024



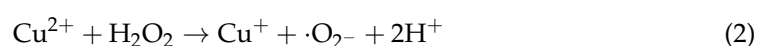
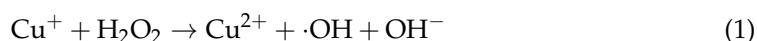
Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

With the rapid progress of society, the escalating prevalence of pesticides, dyes, antibiotics, and other organic pollutants in the environment has become increasingly alarming, posing significant risks to both human health and aquatic ecosystems [1]. Dyes find extensive application in diverse industries, including textiles, food, plastics, printing, leather, cosmetics, and pharmaceuticals, leading to the generation of substantial volumes of wastewater containing these colorants. The presence of such dyes in water and wastewater presents a formidable threat to human health and the environment given that most of them exhibit toxicity and mutagenicity [2]. Consequently, the development of effective and environmentally sustainable technology for treating water contaminated with dyes is imperative.

The treatment of wastewater typically involves a combination of various mechanical, biological, physical, and chemical processes. Depending on the specific needs of the wastewater in question, processes such as filtration, flocculation, sterilization, or chemical oxidation of organic pollutants are integrated in a customized manner to achieve the desired treatment outcomes [3]. Recent studies have emphasized advanced oxidation processes (AOPs) [4]. These methods facilitate the in situ generation of reactive oxygen species (ROS), including hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$), effectively enhancing the degradation efficiency. This enhancement holds the potential to achieve complete conversion of the targeted pollutant into harmless byproducts such as CO_2 , H_2O , and mineral acids [4]. Within the realm of AOPs, there is a notable focus on heterogeneous visible-light photocatalysis and certain Fenton processes that can function under mild conditions. The quest for effective catalysts is crucial for the practical application of these processes and has garnered significant attention [5].

The Fenton process utilizes Fe^{2+} as the catalyst and hydrogen peroxide (H_2O_2) as the oxidant. However, a drawback of this process is the substantial formation of iron sludge at pH levels ≥ 4 due to the precipitation of ferric hydroxide [2,6]. Consequently, the Fenton process is confined to a narrow pH range to mitigate the production of solid wastes [6]. In addressing the limitations of the Fenton process, extensive research has been directed towards alternative catalysts [2]. Copper, with its multiple valences (Cu^0 , Cu^+ , and Cu^{2+}), emerges as a promising catalyst for Fenton-like reactions owing to its favorable redox ability, higher solubility of Cu^+ and Cu^{2+} in water compared to Fe^{3+} , and reduced generation of metal solid wastes [2]. The Fenton-like redox chemistry involving copper catalysis has been extensively examined. In this mechanism, the $\text{Cu(I)}/\text{Cu(II)}$ half-cycle facilitates the reduction of H_2O_2 to $\cdot\text{OH}$ and OH^- (Equation (1)). Simultaneously, the $\text{Cu(II)}/\text{Cu(I)}$ half-cycle enables the oxidation of H_2O_2 to hydrogen peroxide radicals ($\text{HO}_2\cdot$) or $\cdot\text{O}_2^-$ depending on the pH of the system, constituting the speed-limiting step (Equation (2)) [7]. Notably, the kinetics difference observed in the copper Fenton-like process is approximately 50–100 times less than that of the ferrous Fenton process, rendering copper Fenton-like catalysis significantly more efficient [7].



Semiconductor photocatalysis, a prominent AOP, has gained popularity for decomposing organic pollutants into harmless compounds by generating ROS. Lopis et al. [8] describe the photocatalysis as a process that involves the illumination of semiconductor particles in water, leading to the creation of electron–hole pairs (e^-/h^+). These pairs induce oxidation and reduction reactions at the valence band (VB) and conduction band (CB), respectively, resulting in ROS generation. This technology holds promise for its ability to completely degrade pollutants without causing secondary pollution. However, the effectiveness of the process relies on the simultaneous reactivity of both h^+ and e^- with their respective reactants, determined by the oxidation/reduction potentials at the valence band (VB) and conduction band (CB) of the photocatalyst. If VB or CB lacks sufficient oxidation/reduction potentials, the photocatalyst remains inactive.

Metal oxide semiconductors, such as TiO_2 and ZnO , have been studied as photocatalysts [9]. However, the conventional method of achieving photocatalytic degradation of pollutants involves the use of ultraviolet lamps, primarily mercury vapor lamps. These lamps have drawbacks such as high energy consumption, hazardous mercury content, the need for cooling, short lifespan, and operational challenges [10]. Solar light, while an alternative, presents challenges such as the requirement of a large area, high installation costs, and limitation to daylight hours, hindering the development of photocatalytic reactors and processes [10]. To address the need for energy-efficient sources, the emergence of solid-state technology has led to the development of compact, cost-effective, and environmentally friendly light-emitting diodes (LEDs). LEDs enhance the flexibility of reactor

design, eliminating the constraints associated with the shape of mercury lamps, and offer versatility in emitting light of different wavelengths (visible or near-ultraviolet) based on the composition and condition of the semiconducting materials [3]; hence, identifying a visible-light-driven photocatalyst with high efficiency is a critical priority.

Cuprous oxide (Cu_2O), characterized by a direct bandgap ranging from 2.0 to 2.2 eV (visible light), is a p-type semiconductor with promising potential for applications in visible light-driven processes. These applications include solar energy conversion, hydrogen production, gas sensors, and the degradation of organic contaminants [11]. Utilizing Cu_2O as a photocatalyst offers various advantages. First, its intrinsic characteristics, including low toxicity, environmental friendliness, and affordability, position it as a promising candidate for photocatalytic applications [9]. Second, the band gap of Cu_2O can be adjusted for direct utilization of visible light [11]. Third, Cu_2O demonstrates effective molecular oxygen adsorption, facilitating the scavenging of photo-generated electrons. This process inhibits the recombination of electron-hole pairs, thereby enhancing the overall photocatalytic efficiency [9]. These characteristics make Cu_2O a promising green technology for wastewater treatment.

For Cu_2O synthesis, various methods, including electrodeposition, precipitation, hydrothermal synthesis, liquid phase reduction, solvothermal synthesis, thermal oxidation, and microwave-assisted heating, are employed [12]. However, traditional methods involve chemical reducing agents, such as hydrazine hydrate and sodium borohydride, which are costly and require special disposal procedures [13]. In response to these limitations, the green synthesis method of nanoparticles has gained prominence, offering advantages like waste prevention, pollutant removal, use of suitable solvents, and sustainable raw materials [14]. Plant and fruit extracts, rich in compounds like sugars, phenolic compounds, and proteins are harnessed as environmentally friendly reagents for reducing inorganic salts, presenting an alternative to conventional physical and chemical methods for nanoparticle synthesis. Eucalyptus extracts are extensively researched for nanoparticle synthesis due to their global abundance and a high concentration of phenolic compounds [14]. In these environmentally friendly synthesis processes, it has been identified that a high concentration of phenolic compounds in extracts favors the formation and stabilization of nanoparticles [14]. In this same sense, although there is abundant evidence of the use of plant extracts for the synthesis of Cu_2O [15–17], there does not seem to be evidence through which to understand the role of the phytochemicals involved in the formation and stabilization of Cu_2O . It was also not possible to find research works that address the use of Eucalyptus globulus extracts for the formation of Cu_2O nanoparticles.

Designing the reactor is a crucial aspect, and researchers are actively exploring two approaches: suspended particle (slurry) reactors and fixed-catalyst reactors. Although rapidly mixed slurry systems excel in contaminant-to-surface mass transfer, concerns arise about potential nanoparticle loss to the treated effluent, raising environmental issues. Nanoparticle separation through membrane filtration adds complexity and cost to the process. While gravity and magnetic separation strategies are under exploration, their practical feasibility remains uncertain. The attention paid to immobilizing a photocatalyst on a suitable substrate has grown because it allows for easy recovery, reusability from water without compromising efficiency, minimizing washout, and preventing aggregation [18]. Utilizing a resilient cellulose matrix is essential for preventing nanoparticle aggregation thanks to its intricate three-dimensional porous structure. Cellulose, the most abundant natural polymer, boasts commendable attributes like biodegradability and biocompatibility. Moreover, the cellulose's seamless compatibility with metal nanoparticles ensures minimal risk of secondary pollution [19]. However, this approach is constrained by mass transfer limitations, necessitating a maximized surface area for both nanoparticles and support material. Moreover, it introduces geometric challenges in light delivery, prompting the exploration of unconventional reactor designs.

There is a wealth of evidence supporting the use of Cu_2O nanoparticles for the effective degradation of dye pollutants through photoenergy-driven photocatalysis [9,11,13,15,17,19–21]

or chemical catalysis, specifically in heterogeneous Fenton-like reactions [2,20,22]. The scientific community generally agrees that immobilized nanomaterials are advantageous in these processes [2,9,18–20,23]. However, there has not been exploration of these activities using Cu₂O nanoparticles synthesized from *E. globulus* plant extracts and immobilized on cellulose supports. This lack of experimentation has resulted in a gap in knowledge regarding the impact of pH on these systems, the effectiveness of visible radiation from LEDs in photocatalytic processes, and the potential for novel reactor designs. Therefore, immobilizing Cu₂O nanoparticles on cellulose-based supports has the potential to expand their applications beyond enhancing photocatalytic activities to also improving Fenton-like reactions for the efficient degradation of organic pollutants, driven by both photoenergy and chemical potential. The objectives of this study were to develop Cu₂O nanoparticles using *E. globulus* extracts and immobilize them on cellulose-based supports, such as fabric. The study also aimed to investigate the role of the main phytochemicals in the extracts in the synthesis of Cu₂O and to characterize the nanoparticles. The immobilized Cu₂O nanoparticles were then tested for their photocatalytic activity under visible radiation from an LED source, as well for as their catalytic activity in the heterogeneous Fenton-like reaction at both acidic and neutral pH levels. The study also examined the reusability capacity of these systems and the type of ROS they generated.

2. Materials and Methods

2.1. Preparation of *E. globulus* Extracts and Synthesis of Cu₂O on Supports

In the summer, leaves of *E. globulus* were collected from Concepcion in southern Chile. The leaves were then washed with deionized water and dried at 50 °C for 24 h before being crushed. The crushed leaves were heated to 60 °C and refluxed for 20 min at a concentration of 60 g/L. After cooling, the extract was centrifuged at 7000 rpm for 20 min. The resulting supernatant was then vacuum filtered using 0.45 µm pore size filter paper and stored at 2 °C for future use. To synthesize Cu₂O nanoparticles using *E. globulus* extracts supported on cellulose-based support, the procedure was as follows: A 4 × 4 cm² piece of fabric was immersed in 50 mL of 0.5 mol/L CuCl₂ solution and stirred at 200 rpm at 60 °C for 30 min. The fabric was then removed from the solution. Next, 10 mL of 1 g/50 mL NaOH solution was added to the CuCl₂ solution via constant dripping and stirred at 500 rpm to form Cu(OH)₂. The fabric was immersed in this solution and stirred at 200 rpm for 30 min at 60 °C. After 30 min, the fabric was removed and placed in 25 mL of *E. globulus* extracts at 60 °C and 200 rpm for an additional 30 min. Finally, the fabric was rinsed with deionized water and dried in an oven at 60 °C. Hereafter, the Cu₂O nanoparticles synthesized on fabric are named F-CuNP.

The *E. globulus* extracts were analyzed using FTIR spectroscopy, employing the Spectrum Frontier/Spotlight 400 Microscopy System (Perkin Elmer, Inc., Waltham, MA, USA) with a linear array of mercury–cadmium–tellurium (MCT) detectors. Spectra were collected in transfer mode, with each extract solution (before and after nanoparticle synthesis) represented by a 0.5 µL drop on a MirrIR slide. After drying for 30 min at 70 °C in an oven, spectra were acquired using the following parameters: an aperture of 100 × 100 µm², a spectral range of 4000–500 cm^{−1}, a spectral resolution of 4 cm^{−1}, and 64 scans per spectrum. Background spectra were obtained from a low-emissivity area of the glass slide without the materials under analysis and were automatically subtracted from the material spectra. For the analysis of F-CuNP in ATR mode, a germanium crystal (refraction index 4.01) with a pixel size of 6.25 µm × 6.25 µm was used, with a spectral range from 4000 to 750 cm^{−1}, a spectral interval of 4 cm^{−1}, a spectral resolution of 8 cm^{−1}, 64 scans per spectrum, and an aperture of 400 × 400 µm². The spectra underwent atmospheric noise removal and baseline correction.

2.2. SEM Analysis

The nanoparticle distribution across the substrate was investigated through the acquisition of SEM images (SU3500, Hitachi, Tokyo, Japan). An X-ray energy-dispersive

spectroscopy (EDX)-based detector (QUANTAX 100, Bruker, Ettlingen, Germany) was utilized to observe the elemental distribution on the surface, operating at an acceleration voltage of 30.0 kV and a working distance of 10.8 mm. The calculation of particle size for nanoparticles and the creation of a histogram plot were performed using ImageJ software version 1.53t.

2.3. XRD Analysis

The X-ray diffraction (XRD) patterns of the samples were collected using a Bruker D4 ENDEAVOR X-ray diffractometer, with Cu K α radiation as the source. The operating voltage and current were set at 40 kV and 20 mA, respectively. Diffraction peak intensities were recorded within a 10–80° (2 θ) range, with increments of 0.02° and a count duration of 0.3 s per increment. To estimate the crystallite sizes of nanoparticles, the Debye–Scherrer formula (Equation (3)) was used, where D represents the mean crystallite size, K is a dimensionless shape factor (assumed to be 0.94 in this case), λ is the X-ray radiation wavelength (Cu K α = 0.154056 nm), β denotes the band broadening at half-maximum intensity, and θ is the diffraction angle.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

2.4. TGA Analysis

Thermogravimetric analysis (TGA) was performed on sample fragments using a Perkin-Elmer instrument STA 6000. The samples were heated at a rate of 15 °C/min under a nitrogen flow of 40 mL/min, spanning a temperature range of 25–600 °C.

2.5. Optical Analysis

The optical characteristics of the supported nanoparticles were evaluated using diffuse reflectance UV–vis spectra (DRS) on a Jasco V-750 UV-Visible spectrophotometer, which is outfitted with Jasco ISV-922 integrating sphere (Tokyo, Japan). The band gap of the copper oxide nanoparticles was ascertained from a Tauc plot derived from the UV–Vis diffuse reflectance spectra.

2.6. Phytochemical Analysis before and after Synthesis

The analysis of the *E. globulus* extracts, both before and after nanoparticles formation, included the quantification of phenolic compounds, reducing sugars, and proteins [24]. The Folin–Ciocalteu method was employed to measure the phenolic compounds, with the results expressed as gallic acid equivalents based on a calibration curve of standard gallic acid solutions. The DNS method was used to determine the concentration of reducing sugars, with the values calculated as glucose equivalents using a calibration curve of standard glucose solutions. The Bradford method was utilized to quantify the protein content of the extracts, using bovine albumin serum solutions as the standard. The ferric-reducing antioxidant power method (FRAP) and cupric reducing antioxidant capacity (CUPRAC) [25] were modified and applied to ascertain which phytochemicals in the *E. globulus* extract function as reducing agents in the formation of supported nanoparticles.

2.7. MB Degradation by Photocatalysis and Fenton-like Reaction

The experiment on photocatalytic and Fenton-like degradation of methylene blue (MB) at a concentration of 50 mg/L was conducted in a homemade reactor consisting of four borosilicate glass chambers, each with a volume of 20 mL, at room temperature (Figure 1).

The 4 × 4 cm² pieces of F-CuNP were placed onto 3D-printed supports. The solution was stirred continuously in the dark for 120 min to achieve adsorption and desorption equilibrium. After 120 min, the LED light strips were turned on for photocatalysis. For the Fenton-like experiments, 50 mM H₂O₂ was added after 120 min in darkness. All the Fenton experiments were conducted in the dark. Every 20 min, 0.5 mL of the solution was

sampled, and the absorbance was measured at 664 nm using a UV-vis spectrophotometer (Jasco, V-750). The impact of pH (3.0 and 7.0) on the photocatalytic and Fenton-like activity of F-CuNP was examined. The pH of the aqueous solution was regulated using HCl and NaOH.

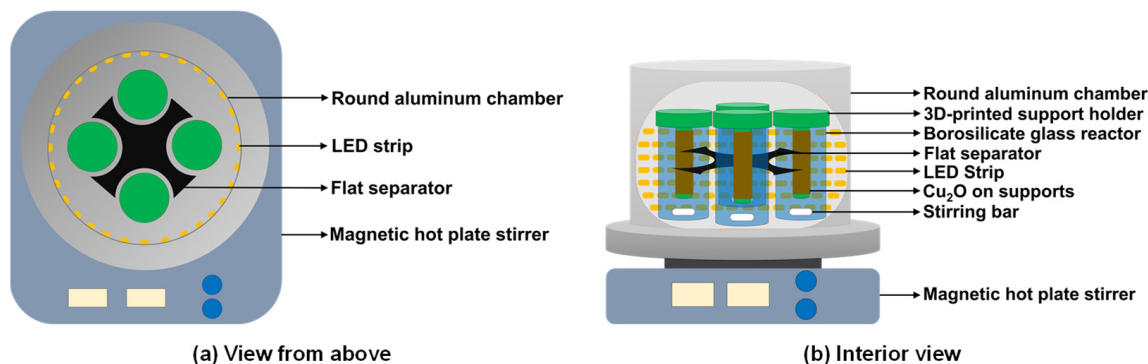


Figure 1. View from above and inside the reactor used for degradation of MB via photocatalysis and Fenton-like reaction.

The degradation percentage of the dye was calculated using Equation (4):

$$\text{MB degradation (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100, \quad (4)$$

where C_0 and C_t are the initial and final concentrations of MB, t is time (min), and k_{app} (min^{-1}) is the first-order apparent rate constant for MB degradation.

After a selection of the best performances obtained in previous studies, the recyclability and stability of F-CuNP samples were assessed after five cycles of degradation using photocatalysis and Fenton-like processes. After each cycle, the samples were rinsed with deionized water and dried in an oven at 50 °C before being used for another degradation reaction. To better understand the degradation mechanism of MB by F-CuNP, active species trapping experiments were conducted using scavengers such as CrO_3 , $\text{Na}_2\text{C}_2\text{O}_4$, p-benzoquinone (BQ), and isopropanol (IP) as the representative scavengers of e^- , h^+ , $\cdot\text{O}_2^-$, and $\cdot\text{OH}$, respectively.

3. Results

3.1. Synthesis of Nanoparticles Supported

To examine the appearance of cotton fabric and as support before and after the synthesis of Cu_2O , their digital photos were obtained (Figure 2). The evident change of color indicated on the surface of supports suggest the formation of nanoparticles.

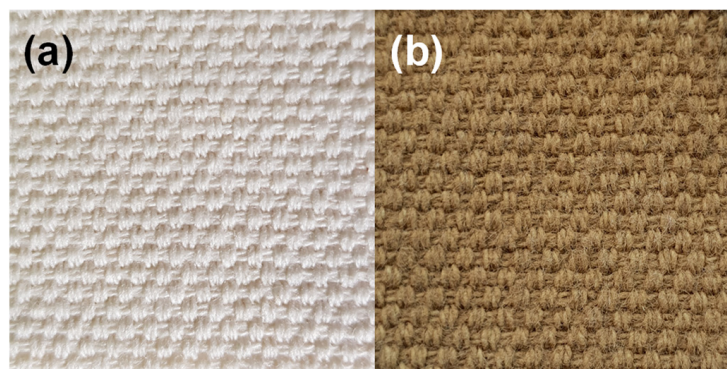


Figure 2. Photographic images of (a) pristine fabric and (b) F-CuNP.

3.2. Characterization of Nanoparticles

3.2.1. SEM-EDX Analysis

From SEM images (Figure 3), it can be seen that synthesized F-CuNP are spherical with uniform distribution on the support surface. The size of F-CuNP varied from 34.0 to 173.5 nm, with a mean diameter of 81.84 nm. EDX analyses indicate a concentration of 45.72% C, 50.55% O, and 3.73% Cu for F-CuNP.

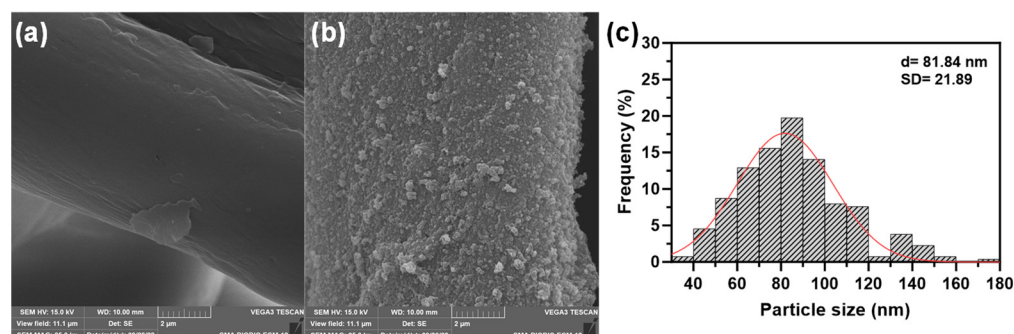


Figure 3. SEM analysis for (a) pristine fabric, (b) F-CuNP, and (c) histogram of particles size of F-CuNP.

3.2.2. XRD Analysis

Figure 4a shows that XRD analysis of F-CuNP reveals the diffraction peaks at 2θ values 29.51° , 36.38° , 42.34° , and 61.39° , corresponding to the lattice planes (110), (111), (200), and (220), respectively. These values agree with the monoclinic Cu_2O phase (JCPDS N° 05-0667 database) [26]. Through the Debye–Scherrer equation, the average crystalline size of F-CuNP from the four diffraction peaks was determined to be 97.21 nm. The other diffraction peaks close to 25° and 34° are typical of cellulose [27,28].

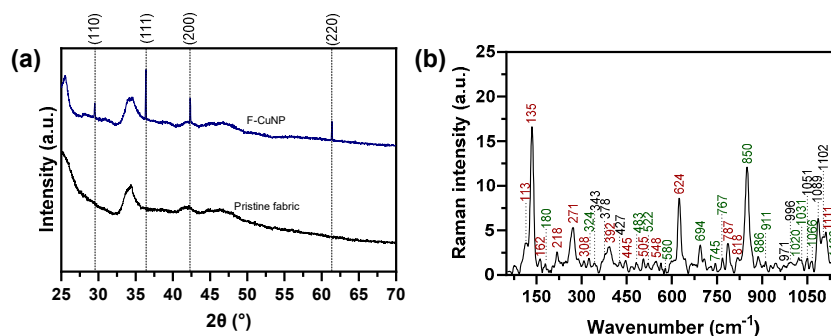


Figure 4. (a) XRD patterns of F-CuNP and pristine fabric; (b) Raman spectra for F-CuNP (red numbers for Cu_2O nanoparticles signals, green numbers for phenolic compounds signals, and black numbers for cellulose signals).

3.2.3. Raman Analysis

Raman spectra of F-CuNP as a function of wavenumbers ranging from 50 to 1160 cm^{-1} are illustrated in Figure 4b.

The F-CuNP exhibited distinct peaks in the spectra at 113, 135, 162, 218, 271, 308, 392, 445, 505, 548, 624, 787, 818, and 1111 cm^{-1} . These peaks confirm the successful preparation of Cu_2O nanoparticles [29–35]. These analyses are consistent with the findings from the XRD analyses. Other peaks in the spectra at 180, 324, 483, 522, 580, 694, 745, 767, 850, 886, 911, 1020, 1031, 1066, and 1136 cm^{-1} for F-CuNP confirm the presence of various phenolic compounds [36,37]. Signals related to cellulose cotton are exhibited at 343, 378, 427, 971, 996, 1051, 1089, and 1102 cm^{-1} for F-CuNP [38,39].

3.2.4. FTIR Analysis

The FTIR spectrum of pristine fabric and F-CuNP is shown in Figure 5.

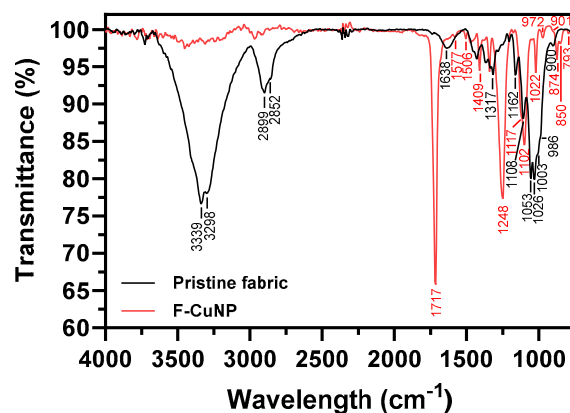


Figure 5. FTIR analyses for pristine fabric and F-CuNP.

The main bands observed in the FTIR analyses of the pristine fabric, as well as in F-CuNP, are summarized in Table 1.

Table 1. Main FTIR bands in pristine fabric and F-CuNP.

Wavenumber (cm ⁻¹)		Vibration	Reference
Pristine Fabric	F-CuNP		
3339	-	Intra-molecular hydrogen bonding C(3)OH...O(5) or C(6)O...O(1)H	[40]
3298	-	Inter-molecular hydrogen bonding C(3)OH...C(6)O	[40]
2899	-	Asymmetric stretching vibration of —CH ₂	[41]
2852	-	Symmetric stretching vibration of —CH ₂	[41]
-	1717	C=O stretching	[42]
1638	-	O—H bending of adsorbed water	[40]
-	1506	C=C—C aromatic stretching	[42]
-	1472	—CH ₂ bending of methylene chains in lipids	[43]
1458	1458	O—H in-plane deformation	[40]
1430	-	CH ₂ scissoring	[44]
-	1409	C—OH stretching of alcohol	[45]
1368	-	C—OH bending	[42]
1338	1339	C—O stretching	[42]
1317	-	C—N stretch of aromatic amines	[46]
1205	-	C—O stretching	[40]
-	1176	Phenolic alcohol OH stretching	[45]
1162	-	Anti-symmetrical bridge C—O—C stretching	[44]
-	1117	—CN stretching	[47]
1108	1102	C—OH bending	[45]
1053	-	Stretching vibration of C—O—C in the pyranose skeletal ring	[15]
1026	1022	C—OH groups of cellulose	[40]
1003	-	C—O—H stretching vibration	[48]
986	972	C—O and ring stretching modes	[40]
900	901	Glycosidic deformation —C ₁ —O—C ₄ characteristic of the β-glycosidic bond of cellulose	[44]
-	874	C—H out of plane glucose ring	[49]
-	850	Aromatic C—H out-of-plane deformation	[42]
-	793	C—H bending	[50]

In the FTIR analysis of pristine fabric, signals identified at approximately 3339, 3298, 2899, 2852, 1638, 1458, 1430, 1368, 1338, 1317, 1205, 1162, 1053, 1003, and 900 cm⁻¹, mainly attributed to cellulose in the fabric, exhibit a decrease in intensity. This phenomenon has been associated by Mussino et al. [51] with the interaction of cellulose groups with other

nanoparticles and by Sedighi et al. with the interaction of cellulose with Cu_2O -NP [27]. Additionally, it has been suggested that this decrease is linked to the interaction between the functional groups of cellulose and phytochemicals present in the *E. globulus* extract [52].

Conversely, in the FTIR analyses of F-CuNP, certain signals emerge that were not present in the pristine fabric samples. Bands indicating this behavior are observed at 1506, 1409, 1176, 850, and 793 cm^{-1} , characteristic of phenolic compounds, a band at 1117 cm^{-1} , characteristic of proteins, a band at 1472 cm^{-1} , characteristic of lipids, and a band at 874 cm^{-1} , attributed to the presence of glucose, possibly due to the interaction of these phytochemicals with the Cu_2O -NPs [53]. Another band close to 1717 cm^{-1} is attributed to the presence of C=O bonds, possibly arising from the oxidation of -OH groups to C=O during the reduction of Cu^{2+} ions to Cu^+ for the subsequent formation of Cu_2O [54].

Furthermore, characteristic cellulose signals around 1108, 1026, and 986 cm^{-1} are discernible, showing a slight shift when comparing the spectra of pristine supports with those incorporating Cu_2O -NPs. This shift could signify the interaction of these groups either with the Cu_2O -NPs or with the phytochemicals from the *E. globulus* extract [27,28].

3.2.5. TGA Analysis

The TGA was carried out to study the thermal behavior of pristine fabric and F-CuNP samples. To enhance comprehension of the results, derivative thermograms are graphically represented in conjunction with the thermograms. The results are shown in Figure 6.

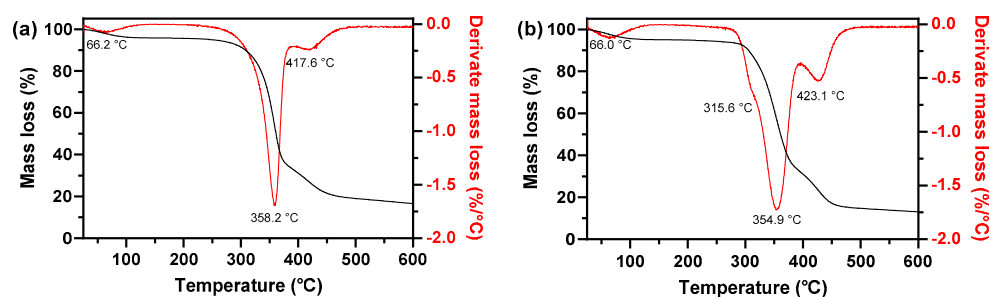


Figure 6. TGA curves of (a) pristine fabric and (b) F-CuNP.

The mass of samples decreased as the temperature increased from 250 to 600 °C, consistent with the chemical nature of cellulose [55]. The derivative thermograms distinctly reveal multiple degradation events in the samples. The first stage occurs at a temperature below 100 °C, due to the loss of water, which could be strongly bound to the cellulosic fibers due to its hydrophilic character [56]. Notably, the primary degradation of the cellulose matrix is evident between 350 and 370 °C, attributed to the decarboxylation, decomposition, and depolymerization of glycosyl units within cellulose during heating scans [56,57]. Low-intensity peaks were observed at 417.6 °C and 423.1 °C for samples with fabric, which can be attributed to the release of volatiles because of the decomposition of by-products at previous stage [56,57]. Intriguingly, the degradation temperature of cellulose decreases in the F-CuNP sample. This reduction could be attributed to the catalytic activity of Cu_2O -NP, accelerating the thermal degradation of cellulose [48]. Furthermore, the appearance of a mass loss stage at 315.6 °C for the F-CuNP sample has been attributed to the phase transition from Cu_2O to CuO [58]. In this same sense, Balik et al. [35] demonstrated through XRD, FTIR, and Raman analysis that Cu_2O nanoparticles begin a phase transition to CuO from 250 to 350 °C.

3.2.6. Optical Analysis

The direct optical bandgap values of F-CuNP were determined via Tauc plot [59]. The bandgap values (E_g) of F-CuNP are calculated as 2.64 eV (Figure 7a).

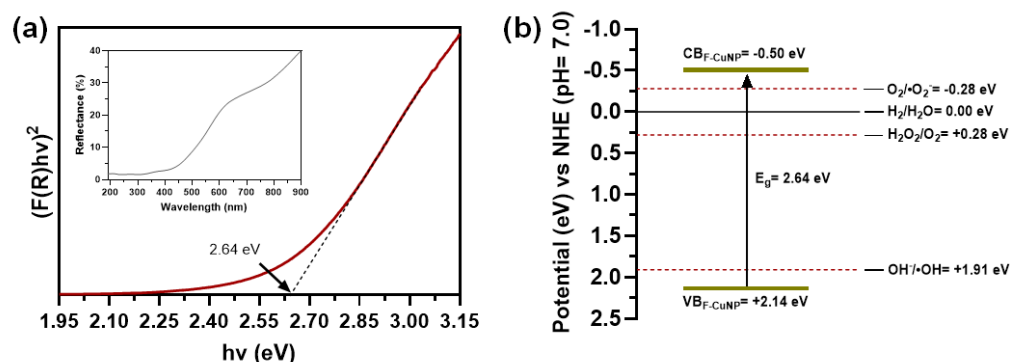


Figure 7. (a) Tauc plot and DRS spectra (inset graph) and (b) potential band diagram for F-CuNP.

The conduction and valence band positions of Cu_2O on F-CuNP can be determined using the following empirical relations (Equations (5) and (6)) [60]:

$$E_{CB} = \chi - E^e - 0.5E_g, \quad (5)$$

$$E_{VB} = E_{CB} + E_g, \quad (6)$$

where E_{CB} is the conduction band potential; E_{VB} is the valence band potential; E_g is the bandgap of the semiconductor; χ is the absolute electronegativity of the semiconductor, which is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy [61] (5.32 eV for Cu_2O [62]); and E^e is the energy of free electrons on the hydrogen scale (~ 4.5 eV) [60]. Therefore, the calculated values of E_{CB} and E_{VB} for F-CuNP are -0.50 and 2.14 eV, respectively (Figure 7b).

To maximize the utilization of electrons and holes in redox reactions, the conduction band (CB) of Cu_2O should be significantly higher than the reduction potential of $O_2/\cdot O_2^-$ and H_2O_2/O_2 , and the valence band (VB) should be substantially lower than the oxidation potential of $OH^-/\cdot OH$ [63]. The results in Figure 7b indicate that the e^- in the CB of the synthesized Cu_2O nanoparticles could be trapped by O_2 in the medium to produce $\cdot O_2^-$ and H_2O_2 , while the h^+ in the VB could react with OH^- to produce $\cdot OH$.

Cu_2O is a p-type semiconductor with direct bandgap energy of about 2.0–2.2 eV [19,23,64], which indicates an unusual increase in the bandgap energy detected in the Cu_2O samples synthesized on F-CuNP. It has been proposed that the shift in the bandgap energy of semiconductors could be related mainly to changes in the size of the particles [64–66], the effect of the exposed facets in the crystalline structure of the particles [65,67], the effect of ligands that interact with particles [68,69], and defects in the materials [70–72].

As already mentioned, there is abundant evidence regarding the effect of particle size and the exposed facets in the crystalline structure on the bandgap of semiconductors. However, Huang et al. [65] describe the effect of both factors together on the optical properties of Cu_2O nanoparticles. The authors confirm, after studying different sizes and structures of Cu_2O nanoparticles, that at smaller Cu_2O sizes, their bandgap increases for each of the exposed facets in the crystalline structure. Furthermore, it is notable that the authors found that Cu_2O nanoparticles with the exposed facet (111) and diameters of 85 and 117 nm exhibit a bandgap of 2.70 and 2.61 eV, respectively, similar to what was found in this investigation. Accordingly, these findings could indicate a strong influence of the particle size and the exposed facet on the bandgap of synthesized F-CuNP.

3.3. Identification of Biomolecules Involved in the Synthesis of Cu_2O Nanoparticles

3.3.1. Spectrophotometric Analysis of Extracts before and after Formation Cu_2O Nanoparticles

Figure 8 reveals the changes in the main phytochemicals contained in the *E. globulus* extract before and after the formation of F-CuNP.

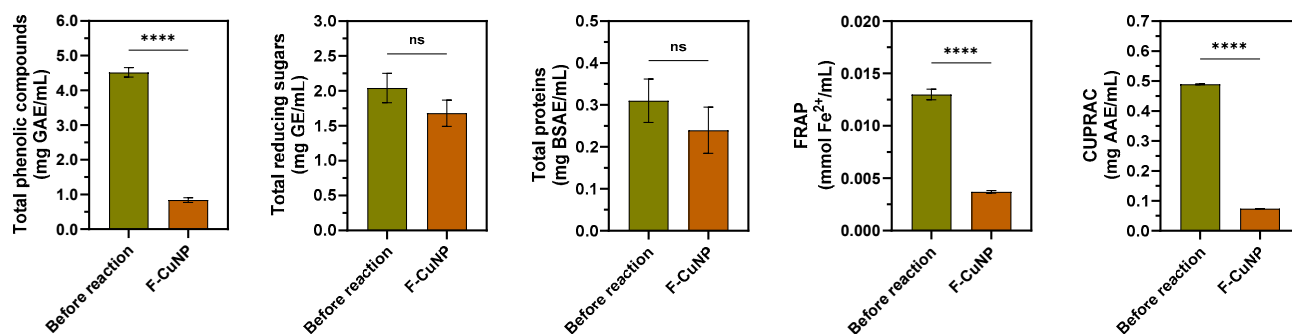


Figure 8. Spectrophotometric analysis of total phenolic compounds, total reducing sugars, total proteins, FRAP, and CUPRAC capacity in the extract of *E. globulus* before and after the synthesis of F-CuNP. The data obtained are presented as mean $\pm$ standard deviation. Differences among groups were compared via ANOVA with Tukey post hoc analysis. **** $p < 0.0001$, ns: no significant differences.

First, it is notable that no significant changes occur in the concentration of reducing sugars or in the concentration of proteins when comparing the initial and post-synthesis of Cu₂O nanoparticles. Several authors have carried out similar studies, concluding that these proteins do not seem to actively participate in the reduction of Cu²⁺ to form Cu₂O [73] or other nanoparticles [74,75]. Regarding the role of sugars in leaf extracts for the Cu₂O nanoparticle synthesis process, there are some authors who attribute an ion-reducing role to sugars [16,17], while others attribute more of a stabilizing role to these phytochemicals [73,76]. Otherwise, the changes in the concentrations of phenolic compounds before and after the formation of Cu₂O nanoparticles were significant. There is abundant evidence regarding the role that phenolic compounds play in the formation of Cu₂O nanoparticles, acting as reducers or stabilizers [45,73,76,77]. It is possible to observe a similar behavior when the results of FRAP and CUPRAC are analyzed since both methods used in the characterization of plant extracts attempt to quantify the antioxidant capacity based mainly on the presence of phenolic compounds [25]. Consequently, this result would again suggest the main role of phenolic compounds in the formation of Cu₂O nanoparticles.

3.3.2. FTIR Analysis of Extracts before and after Formation Cu₂O Nanoparticles

A comparative experiment was conducted to examine the formation of Cu₂O nanoparticles on fabric substrates using *E. globulus* extract. The objective of this experiment was to understand the role of different components of plant extracts in the synthesis process. FTIR measurements were performed to identify the primary functional groups involved in the formation of Cu₂O. Figure 9 shows the FTIR spectra of the *E. globulus* extract before and after the synthesis of Cu₂O on the fabric substrates. A considerable decrease is observed in the signals ~ 3375 cm^{−1}, indicating the presence of alcoholic and phenolic -OH groups [50]; ~ 2936 cm^{−1}, attributed to C-H asymmetric stretching [50]; ~ 1700 cm^{−1}, attributed to C=O stretching; the band ~ 1610 [50], correlated with C=C stretching; the signal at ~ 1350 cm^{−1}, attributed to C-H bending modes [54]; ~ 1450 cm^{−1}, associated with C=C aromatic ring stretching [45]; ~ 1400 cm^{−1}, attributed to C-OH stretching vibrations [45]; ~ 1250 cm^{−1}, attributed to C-O stretching (in aromatic esters) [50]; and 1060 cm^{−1}, attributed to C-O-C stretching asymmetric vibration [76]. All these signals are clearly attributed to different phenolic compounds in *E. globulus* extracts, and after the synthesis of nanoparticles, these phytochemicals decrease in concentration.

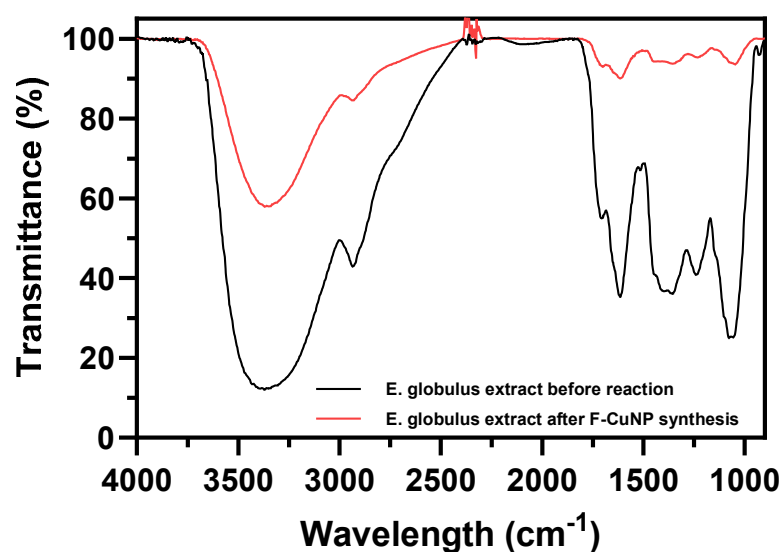


Figure 9. FTIR spectra of *E. globulus* extract before and after synthesis of F-CuNP.

3.4. Photocatalytic and Fenton-like Degradation of MB

A series of experiments were carried out to compare the performance of F-CuNP in the degradation of MB at pH 3.0 and 7.0 via photocatalysis and a heterogeneous Fenton-like reaction.

Figure 10a shows the photocatalytic degradation kinetics of MB catalyzed by F-CuNP at pH 3.0 and 7.0. It is clearly noticeable that F-CuNP at pH 7.0 exhibits photocatalytic capacity greater than at pH 3.0, with apparent rate constants (k_{app}) of 0.0233 and 0.00377 min^{-1} , respectively (Figure 10b). These results indicate a clear effect of the pH. Accordingly, the fact that the greatest degradation of MB is observed at basic pH could be related to the interactions between Cu_2O and MB. Akter et al. [78] found similar results when studying the effect of pH on MB removal using Cu_2O . These authors have postulated a greater influence of electrostatic interactions, compared to another interaction, between MB and Cu_2O at basic pH as the reason for greater removal. Specifically, it would be associated with a greater negative charge on the Cu_2O at higher pH and a greater cationic character of the MB at higher pH. These differences in the charges of the dye and the Cu_2O nanoparticles would favor the AM to be better adsorbed on the Cu_2O surface, causing a higher degradation rate. In this sense, making the same comparison but only in the dark adsorption process, it is possible to observe that for F-CuNP, a greater amount of AM is adsorbed at pH = 7.0 than at pH = 3.0, which would also agree with what was previously postulated. This pH effect was also found in systems with other adsorbents to remove MB [79,80] and with Cu_2O nanoparticles to remove other contaminants [81].

Figure 10c shows the degradation of MB using a heterogeneous Fenton-like process using F-CuNP at pH 3.0 and 7.0. Once again, it is possible to observe a clear effect of the pH in the MB removal. It is possible to indicate that in the system using F-CuNP at pH 3.0, the MB removal is greater than at pH 7.0 with k_{app} values of 0.0347 and 0.00722 min^{-1} , respectively (Figure 10d). Similar effects with respect to pH have been detected in systems that include the use of Cu_2O for Fenton-like reactions [2,20,82–85]. The reasons that have been attributed to the greater degradation of contaminants in Fenton-like systems using Cu_2O are varied: (i) at acidic pH, the dissolution of Cu_2O is favored, forming Cu(I) ions that react quickly with H_2O_2 to produce $\cdot\text{OH}$ according to Equation (1) [20,82–84]; (ii) H_2O_2 could decompose at high pH, preventing it from reacting and forming $\cdot\text{OH}$ [20,85]; and (iii) $\cdot\text{OH}$ could react with OH^- ions, decreasing the availability of $\cdot\text{OH}$ to degrade MB [86].

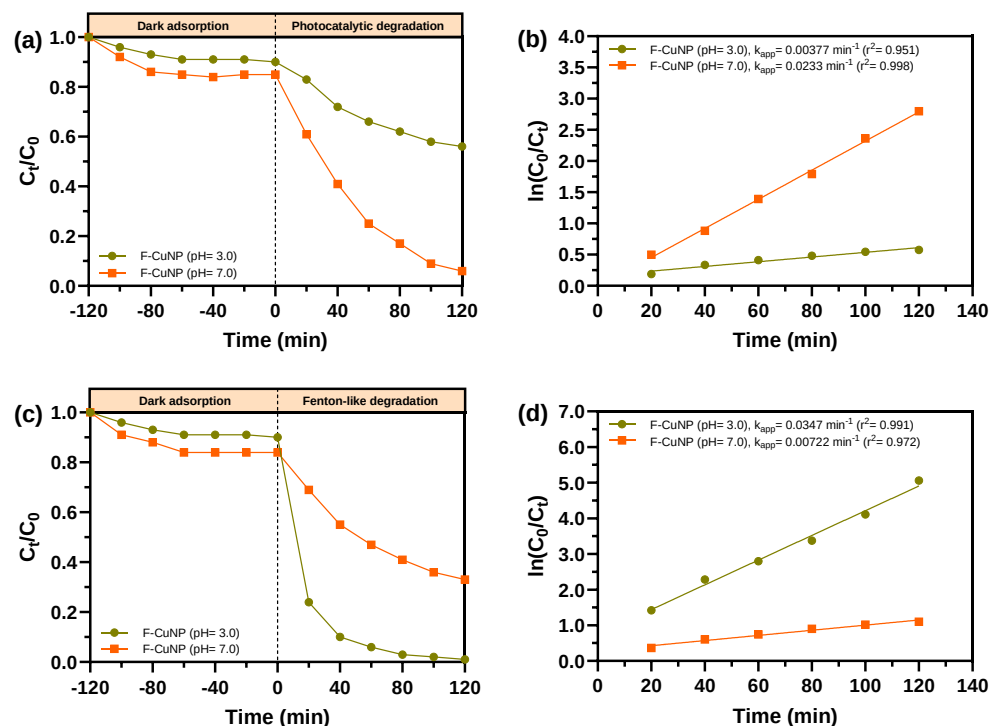


Figure 10. (a) Photocatalytic under LED visible light and (c) Fenton-like degradation efficiency of MB at different time intervals catalyzed by F-CuNP at pH 3.0 and 7.0 (inset: legend represents samples at different pH). (b) Photocatalytic and (d) Fenton-like calculated degradation rate constant k_{app} for F-CuNP at pH 3.0 and 7.0 (inset: legend represents samples at different pH, k_{app} value, and r^2 of pseudo-first-order model).

3.5. Reusability of Photocatalytic and Fenton-like Degradation of MB

The reusability studies were conducted to study the recyclability of F-CuNP in the removal of MB dye solution at pH 7.0 for photocatalysis and at pH 3.0 for Fenton-like reaction (Figure 11). The photocatalytic degradation efficiency for F-CuNP after five cycles of reuse (Figure 11a) decreased from 93.9% to 86.5%, while for the Fenton-like reaction (Figure 11b), the degradation efficiency after five cycles of reuse decreased from 99.36% to 77.38% at pH = 3.0. It is possible to indicate that the reusability efficiency is longer in photocatalytic systems, with a less abrupt decline in the efficiency of AM degradation than for AM degradation by Fenton-like systems. The lower performance of F-CuNP for Fenton-like systems throughout the reuse cycles could be associated with the greater dissolution of Cu₂O at acidic pH [22] or with the reaction of Cu⁺ on the Cu₂O surface with H₂O₂, causing a lower availability as Cu⁺ are consumed and converted into Cu²⁺ [5].

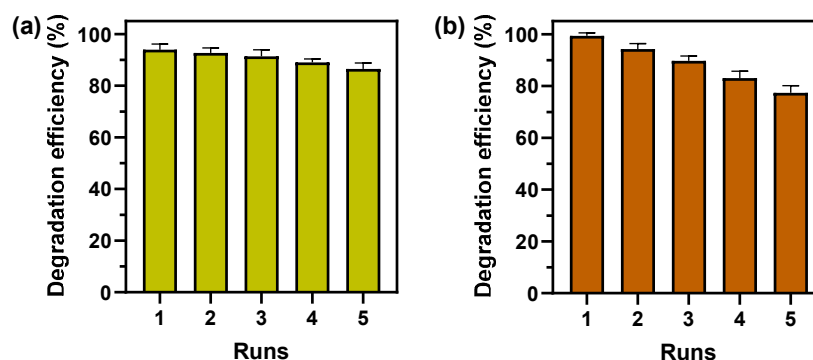


Figure 11. Reusability study of MB degradation using F-CuNP (a) via photocatalysis under LED visible light for F-CuNP at pH = 7.0 and (b) via Fenton-like reaction for F-CuNP at pH = 3.0 in darkness. The data obtained are presented as mean $\pm$ standard deviation.

3.6. Reactive Species in Photocatalytic and Fenton-like Degradation of MB

To propose a mechanism for the photocatalytic and Fenton-like degradation of MB, the reactive species in these processes were investigated (Figure 12). Instead of measuring the degradation efficiency in a solution containing MB and F-CuNP, it is possible to detect the first step of photocatalysis via the generation of e^- and h^+ using scavengers. Similarly, it is possible to detect the radicals $\cdot OH$ and $\cdot O_2^-$ generated in the photocatalytic system using scavengers. Thus, CrO_3 was used as an e^- scavenger, $Na_2C_2O_4$ was added as an h^+ scavenger, p-benzoquinone (BQ) as an $\cdot O_2^-$ scavenger, and isopropanol (IP) as an $\cdot OH$ scavenger.

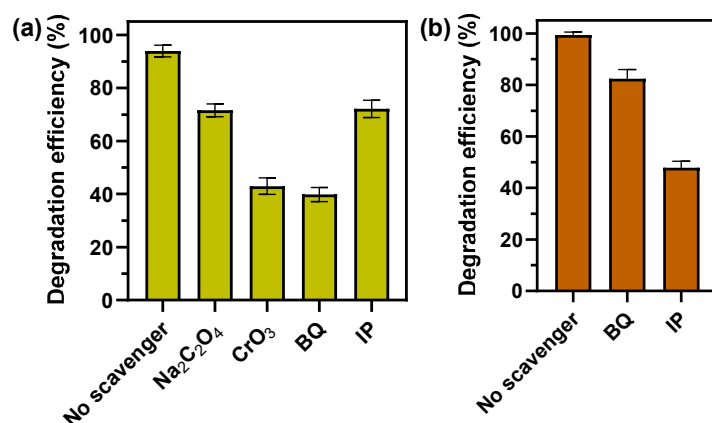


Figure 12. (a) Effect of $Na_2C_2O_4$, CrO_3 , BQ, and IP scavengers on photocatalytic degradation of MB over F-CuNP under LED visible light; (b) effect of BQ and IP scavenger on Fenton-like degradation of MB over F-CuNP in darkness. The data obtained are presented as mean $\pm$ standard deviation.

Regarding the effect of scavengers in Fenton-like systems at pH = 3.0 for F-CuNP, the effect of BQ as an $\cdot O_2^-$ scavenger causes a decrease in the MB degradation efficiency of 16.95% for F-CuNP, respectively, compared to the system without scavengers (Figure 12b). However, the use of IP as an $\cdot OH$ scavenger induces a more notable decrease in MB degradation efficiency of 71.58% for F-CuNP. This greater decrease in degradation efficiency when using IP indicates a greater influence of $\cdot OH$ on MB degradation than $\cdot O_2^-$, similar to what has been found in other works using Cu_2O/H_2O_2 at acidic pH [20,87]. There are several things that can explain this behavior: (i) $\cdot OH$ (1.5–2.8 V) [88] has a higher redox potential than $\cdot O_2^-$ ($\cdot O_2^-/H_2O_2 = +0.94$ V, $O_2/\cdot O_2^- = -0.35$ V) [89]; (ii) the reaction between Cu^+ and H_2O_2 (Equation (1); 1 in Figure 13) has a higher rate constant to produce $\cdot OH$ and Cu^{2+} ($k = 4 \times 10^5$ M $^{-1}$ s $^{-1}$ at pH 6–8) than the reaction between Cu^{2+} and H_2O_2 that produces $\cdot O_2^-$ and Cu^+ ($k \leq 1$ M $^{-1}$ s $^{-1}$ at pH 7) (Equation (2); 2 in Figure 13) [90]; and (iii) the interaction of H_2O_2 on the surface of Cu_2O causes the breaking of the O-O bond of H_2O_2 to generate $\cdot OH$ [20]. It is worth mentioning that the possible reaction pathways involving Cu^+ , Cu^{2+} , and H_2O_2 could occur with the copper ions bound to the surface of the Cu_2O nanoparticles ($=Cu^+$ and $=Cu^{2+}$) as well as with the dissolved ions.

Otherwise, for the effect of scavengers on photocatalytic processes at pH = 7.0 (Figure 12a), using $Na_2C_2O_4$ slightly affects the degradation efficiency of the MB, decreasing only 11.8% for F-CuNP with respect to the systems without scavengers. On the contrary, the use of CrO_3 significantly affects the MB degradation efficiency, decreasing by 60.94% for F-CuNP with respect to systems without scavenger. These results suggest an effective migration of the photoexcited e^- to the Cu_2O surface, causing CrO_3 to be effective in its inhibition. On the other hand, the effect of $Na_2C_2O_4$ does not seem relevant, which seems to indicate the low availability of h^+ on the Cu_2O surface to degrade MB or react with OH^- (7 and 8 in Figure 13). These results could indicate that reduction reactions would be more important than oxidation reactions. Regarding the effect of radical scavengers, the presence of BQ causes a decrease of 32.3% for F-CuNP in terms of the degradation efficiency of MB with respect to systems without scavengers. Otherwise, the use of IP

showed a significantly greater decrease in MB degradation of 81.08% for F-CuNP in relation to the system evaluated without scavengers. Because the action of IP is important, the production and subsequent action of $\cdot\text{OH}$ in the degradation of MB seems to be more relevant than the action of the $\cdot\text{O}_2^-$ produced. Similarly, Bayat and Sheibani [91], using a $\text{CuO}/\text{Cu}_2\text{O}$ heterostructure as a photocatalyst under visible radiation to degrade MB, also discovered that the main species responsible for the degradation of this dye are the $\cdot\text{OH}$ and e^- produced [91].

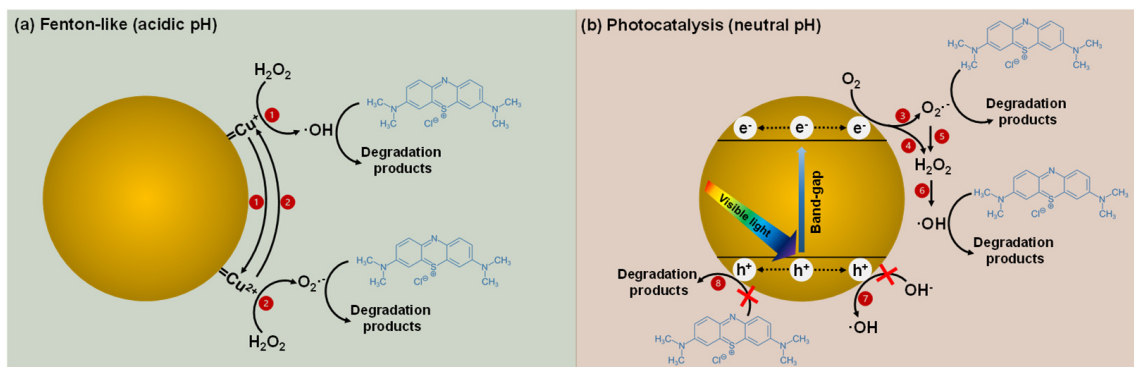
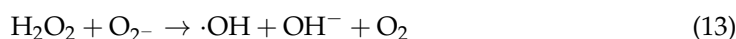
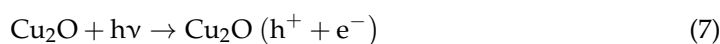


Figure 13. Schematic illustration of Fenton-like reaction at pH = 3.0 and photocatalysis at pH = 7.0 under visible light to generate reactive species and MB degradation process. Numbers in red circles are possible pathway reactions.

Based on what has already been mentioned, it is possible to suggest a low presence of h^+ on the Cu_2O surface, so the $\cdot\text{OH}$, the main reactive species that is responsible for degradation of MB would not be produced by the reaction of the h^+ and OH^- ions (7 and 8 in Figure 13). On the other hand, the high presence of e^- on the Cu_2O surface and the activity of $\cdot\text{O}_2^-$ with respect to the degradation of MB could support the assumption that $\cdot\text{OH}$ radicals are being produced by parallel reactions (Equations (7)–(13), 3, 4, 5, and 6 in Figure 13) and not because of the h^+ oxidizing OH^- [21,78,91].



Chu and Huang [92], in a study on facet-dependent photocatalytic properties of Cu_2O using scavengers, found results and trends similar to those of the present study for Cu_2O nanoparticles with a predominantly octahedral structure. The authors suggest that the photocatalytic activity of octahedral Cu_2O arises mainly from the migration of e^- to the catalyst surface to produce $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ and not from the weak migration of h^+ to the surface.

4. Conclusions

Cu_2O nanoparticles were synthesized in situ on cellulose-based fabric using *E. globulus* extracts, resulting in sizes below 100 nm. Raman and FTIR analyses demonstrate the interaction between phenolic compounds from the extracts and Cu_2O nanoparticles. Additionally, FTIR shows the formation of C=O bonds, indicating the oxidation of -OH

groups in phenolic compounds to produce Cu_2O . Furthermore, FTIR reveals potential interactions between the cellulose and Cu_2O or phenolic compounds. TGA studies confirm the presence of Cu_2O in F-CuNP, as well as the accelerated cellulose degradation in their presence. Optical properties analyses suggest the potential for generating $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ through photogenerated e^- and h^+ . The effect of size and facet exposure on the Cu_2O bandgap is also proposed. Phytochemical analyses imply the involvement of phenolic compounds in the reduction of Cu^{2+} to Cu^+ and the stabilization of nanoparticles. MB degradation is more significant via photocatalysis at $\text{pH} = 7.0$ and Fenton-like reaction at $\text{pH} = 3.0$ using F-CuNP. The reusability of these systems is high, but it declines faster in Fenton-like systems due to Cu_2O nanoparticle decomposition at acidic pH . Photocatalytic systems primarily degrade MB through $\cdot\text{OH}$ and e^- , while Fenton-like systems are influenced by $\cdot\text{OH}$ generation. This research highlights the feasibility of obtaining Cu_2O nanoparticles immobilized on cost-effective supports, functioning as both photocatalysts and Fenton-like reaction catalysts. These nanoparticles can be activated by visible light and synthesized in an eco-friendly manner.

Author Contributions: Conceptualization, P.S.; methodology, P.S.; software, K.M.; validation, K.M.; formal analysis, O.R., C.S. and K.M.; investigation, P.S.; resources, O.R. and P.S.; data curation, P.S.; writing—original draft preparation, P.S.; writing—review and editing, G.V.; visualization, P.S., C.S. and K.M.; supervision, G.V. and P.S.; project administration, P.S. and G.V.; funding acquisition, G.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Agencia Nacional de Investigación y Desarrollo, grant number ANID/FONDAP/1523A0001, and ANID Convocatoria Nacional Subvención a Instalación en la Academia convocatoria año 2019 Folio PAI77190082. The authors thank Centro de Microscopía Avanzada, CMA BIO-BIO, Proyecto PIA-ANID ECM-12.

Data Availability Statement: Data have been included in the present paper.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Yao, J.; Huang, L.; Li, Y.; Zhu, M.; Liu, S.; Shu, S.; Huang, L.; Wu, X. Enhanced photo-degradation of pollutants in three dimensions by $\text{rGO}/\text{Bi}_{12}\text{O}_{15}\text{C}_{16}/\text{InVO}_4$: LED-light photocatalytic performance and mechanism investigation. *Ceram. Int.* **2023**, *49 Pt B*, 19422–19433. [\[CrossRef\]](#)
2. Sun, B.; Li, H.; Li, X.; Liu, X.; Zhang, C.; Xu, H.; Zhao, X.S. Degradation of organic dyes over Fenton-like Cu_2O -Cu/C catalysts. *Ind. Eng. Chem. Res.* **2018**, *57*, 14011–14021. [\[CrossRef\]](#)
3. Jo, W.-K.; Tayade, R.J. New generation energy-efficient light source for photocatalysis: LEDs for environmental applications. *Ind. Eng. Chem. Res.* **2014**, *53*, 2073–2084. [\[CrossRef\]](#)
4. Ma, D.; Yi, H.; Lai, C.; Liu, X.; Huo, X.; An, Z.; Li, L.; Fu, Y.; Li, B.; Zhang, M.; et al. Critical review of advanced oxidation processes in organic wastewater treatment. *Chemosphere* **2021**, *275*, 130104. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Zhao, W.; Liang, C.; Wang, B.; Xing, S. Enhanced photocatalytic and Fenton-like performance of CuO_x -decorated ZnFe_2O_4 . *ACS Appl. Mater. Interfaces* **2017**, *9*, 41927–41936. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Salgado, P.; Melin, V.; Contreras, D.; Moreno, Y.; Mansilla, H.D. Fenton reaction driven by iron ligands. *J. Chil. Chem. Soc.* **2013**, *58*, 2096–2101. [\[CrossRef\]](#)
7. Zhou, M.; Ji, C.; Ji, F.; Chen, M.; Zhong, Z.; Xing, W. Micro-octahedron Cu_2O -based photocatalysis-fenton for organic pollutant degradation: Proposed coupling mechanism in a membrane reactor. *Ind. Eng. Chem. Res.* **2022**, *61*, 7255–7265. [\[CrossRef\]](#)
8. Lopis, A.D.; Choudhari, K.S.; Sai, R.; Kanakikodi, K.S.; Maradur, S.P.; Shivashankar, S.A.; Kulkarni, S.D. Laddered type-1 heterojunction: Harvesting full-solar-spectrum in scavenger free photocatalysis. *Sol. Energy* **2022**, *240*, 57–68. [\[CrossRef\]](#)
9. Dong, J.; Xu, H.; Zhang, F.; Chen, C.; Liu, L.; Wu, G. Synergistic effect over photocatalytic active Cu_2O thin films and their morphological and orientational transformation under visible light irradiation. *Appl. Catal. A Gen.* **2014**, *470*, 294–302. [\[CrossRef\]](#)
10. Akbal, F. Photocatalytic degradation of organic dyes in the presence of titanium dioxide under UV and solar light: Effect of operational parameters. *Environ. Prog.* **2005**, *24*, 317–322. [\[CrossRef\]](#)
11. Su, Y.; Nathan, A.; Ma, H.; Wang, H. Precise control of Cu_2O nanostructures and LED-assisted photocatalysis. *RSC Adv.* **2016**, *6*, 78181–78186. [\[CrossRef\]](#)
12. Becerra-Paniagua, D.K.; Torres-Arellano, S.; Martinez-Alonso, C.; Luévano-Hipólito, E.; Sebastian, P.J. Facile and green synthesis of Cu/ Cu_2O composite for photocatalytic H_2 generation. *Mater. Sci. Semicond. Process* **2023**, *162*, 107485. [\[CrossRef\]](#)
13. Zhu, H.; Li, Y.; Jiang, X. Room-temperature synthesis of cuprous oxide and its heterogeneous nanostructures for photocatalytic applications. *J. Alloys Compd.* **2019**, *772*, 447–459. [\[CrossRef\]](#)

14. Salgado, P.; Mártire, D.O.; Vidal, G. Eucalyptus extracts-mediated synthesis of metallic and metal oxide nanoparticles: Current status and perspectives. *Mater. Res. Express* **2019**, *6*, 082006. [[CrossRef](#)]
15. Kerour, A.; Boudjadar, S.; Bourzami, R.; Allouche, B. Eco-friendly synthesis of cuprous oxide (Cu₂O) nanoparticles and improvement of their solar photocatalytic activities. *J. Solid State Chem.* **2018**, *263*, 79–83. [[CrossRef](#)]
16. Amrani, M.A.; Srikanth, V.V.S.S.; Labhsetwar, N.K.; Al-Fatesh, A.S.; Shaikh, H. Phoenix dactylifera mediated green synthesis of Cu₂O particles for arsenite uptake from water. *Sci. Technol. Adv. Mater.* **2016**, *17*, 760–768. [[CrossRef](#)] [[PubMed](#)]
17. Muthukumaran, M.; Niranjani, S.; Barnabas, K.S.; Narayanan, V.; Raju, T.; Venkatachalam, K. Green route synthesis and characterization of cuprous oxide (Cu₂O): Visible light irradiation photocatalytic activity of MB dye. *Mater. Today Proceed.* **2019**, *14*, 563–568. [[CrossRef](#)]
18. Hodges, B.C.; Cates, E.L.; Kim, J.-H. Challenges and prospects of advanced oxidation water treatment processes using catalytic nanomaterials. *Nat. Nanotechnol.* **2018**, *13*, 642–650. [[CrossRef](#)]
19. Tu, K.; Wang, Q.; Lu, A.; Zhang, L. Portable visible-light photocatalysts constructed from Cu₂O nanoparticles and graphene oxide in cellulose matrix. *J. Phys. Chem. C* **2014**, *118*, 7202–7210. [[CrossRef](#)]
20. Zhou, H.; Kang, L.; Zhou, M.; Zhong, Z.; Xing, W. Membrane enhanced COD degradation of pulp wastewater using Cu₂O/H₂O₂ heterogeneous Fenton process. *Chin. J. Chem. Eng.* **2018**, *26*, 1896–1903. [[CrossRef](#)]
21. Su, X.; Chen, W.; Han, Y.; Wang, D.; Yao, J. In-situ synthesis of Cu₂O on cotton fibers with antibacterial properties and reusable photocatalytic degradation of dyes. *Appl. Surf. Sci.* **2021**, *536*, 147945. [[CrossRef](#)] [[PubMed](#)]
22. Zhang, L.; Li, J.; Chen, Z.; Tang, Y.; Yu, Y. Preparation of Fenton reagent with H₂O₂ generated by solar light-illuminated nano-Cu₂O/MWNTs composites. *Appl. Catal. A-Gen.* **2006**, *299*, 292–297. [[CrossRef](#)]
23. Sabbaghan, M.; Argyropoulos, D.S. Synthesis and characterization of nano fibrillated cellulose/Cu₂O films; micro and nano particle nucleation effects. *Carbohydr. Polym.* **2018**, *197*, 614–622. [[CrossRef](#)] [[PubMed](#)]
24. Salgado, P.; Bustamante, L.; Carmona, D.J.; Meléndrez, M.F.; Rubilar, O.; Salazar, C.; Pérez, A.J.; Vidal, G. Green synthesis of Ag/Ag₂O nanoparticles on cellulose paper and cotton fabric using Eucalyptus globulus leaf extracts: Toward the clarification of formation mechanism. *Surf. Interfaces* **2023**, *40*, 102928. [[CrossRef](#)]
25. Özyürek, M.; Güçlü, K.; Apak, R. The main and modified CUPRAC methods of antioxidant measurement. *Trac-Trends Anal. Chem.* **2011**, *30*, 652–664. [[CrossRef](#)]
26. Gupta, A.; Maruthapandi, M.; Das, P.; Saravanan, A.; Jacobi, G.; Natan, M.; Banin, E.; Luong, J.H.T.; Gedanken, A. Cuprous oxide nanoparticles decorated fabric materials with anti-biofilm Properties. *ACS Appl. Bio Mater.* **2022**, *5*, 4310–4320. [[CrossRef](#)] [[PubMed](#)]
27. Sedighi, A.; Montazer, M.; Samadi, N. Synthesis of nano Cu₂O on cotton: Morphological, physical, biological and optical sensing characterizations. *Carbohydr. Polym.* **2014**, *110*, 489–498. [[CrossRef](#)]
28. Mohammadi, F.; Montazer, M.; Mianehro, A.; Eslahi, N.; Mahmoudi Rad, M. Preparation of antibacterial cellulose fabric via copper (II) oxide and corn silk (*Stigma maydis*) nanocomposite. *Starch Stärke* **2023**, *75*, 2200156. [[CrossRef](#)]
29. Prabhakaran, G.; Murugan, R. Synthesis of Cu₂O nanospheres and cubes: Their structural, optical and magnetic properties. *Adv. Mater. Res.* **2014**, *938*, 114–117. [[CrossRef](#)]
30. Sahai, A.; Goswami, N.; Kaushik, S.D.; Tripathi, S. Cu/Cu₂O/CuO nanoparticles: Novel synthesis by exploding wire technique and extensive characterization. *Appl. Surf. Sci.* **2016**, *390*, 974–983. [[CrossRef](#)]
31. Yu, P.Y.; Shen, Y.R.; Petroff, Y. Resonance Raman scattering in Cu₂O at the blue and indigo excitons. *Solid State Commun.* **1973**, *12*, 973–975. [[CrossRef](#)]
32. Solache-Carranco, H.; Juárez-Díaz, G.; Galvan-Arellano, M.; Martínez-Juárez, J.; Romero-Paredes, R.G.; Pena-Sierra, R. Raman Scattering and Photoluminescence Studies on Cu₂O. In Proceedings of the 5th International Conference on Electrical Engineering, Computing Science and Automatic Control, Mexico City, Mexico, 12–14 November 2008.
33. Ansari, A.; Jha, A.K.; Akhtar, M.J. Preparation and characterization of oxidized electrolytic copper powder and its dielectric properties at microwave frequency. *Powder Technol.* **2015**, *286*, 459–467. [[CrossRef](#)]
34. Sander, T.; Reindl, C.T.; Klar, P.J. Breaking of Raman selection rules in Cu₂O by intrinsic point defects. *MRS Proc.* **2013**, *1633*, 81–86. [[CrossRef](#)]
35. Balık, M.; Bulut, V.; Erdogan, I.Y. Optical, structural and phase transition properties of Cu₂O, CuO and Cu₂O/CuO: Their photoelectrochemical sensor applications. *Int. J. Hydrogen Energy* **2019**, *44*, 18744–18755. [[CrossRef](#)]
36. Krysa, M.; Szymańska-Chargot, M.; Zdunek, A. FT-IR and FT-Raman fingerprints of flavonoids—A review. *Food Chem.* **2022**, *393*, 133430. [[CrossRef](#)] [[PubMed](#)]
37. Espina, A.; Sanchez-Cortes, S.; Jurašeková, Z. Vibrational study (Raman, SERS, and IR) of plant gallnut polyphenols related to the fabrication of iron gall inks. *Molecules* **2022**, *27*, 279. [[CrossRef](#)] [[PubMed](#)]
38. Edwards, H.G.M.; Farwell, D.W.; Williams, A.C. FT-Raman spectrum of cotton: A polymeric biomolecular analysis. *Spectrosc. Acta Part A Mol. Biomol. Spectr.* **1994**, *50*, 807–811. [[CrossRef](#)]
39. Agarwal, U.P.; Ralph, S.A.; Baez, C.; Reiner, R.S. Detection and quantitation of cellulose II by Raman spectroscopy. *Cellulose* **2021**, *28*, 9069–9079. [[CrossRef](#)]
40. Abidi, N.; Cabrales, L.; Haigler, C.H. Changes in the cell wall and cellulose content of developing cotton fibers investigated by FTIR spectroscopy. *Carbohydr. Polym.* **2014**, *100*, 9–16. [[CrossRef](#)]

41. Yang, A.-L.; Li, S.-P.; Wang, Y.-J.; Wang, L.-L.; Bao, X.-C.; Yang, R.-Q. Fabrication of Cu₂O@Cu₂O core-shell nanoparticles and conversion to Cu₂O@Cu core-shell nanoparticles in solution. *Trans. Nonferrous Met. Soc. China* **2015**, *25*, 3643–3650. [\[CrossRef\]](#)
42. Grasel, F.d.S.; Ferrão, M.F.; Wolf, C.R. Development of methodology for identification the nature of the polyphenolic extracts by FTIR associated with multivariate analysis. *Spectroc. Acta Part A Mol. Biomol. Spectr.* **2016**, *153*, 94–101. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Hu, Y.; Pan, Z.J.; Liao, W.; Li, J.; Gruget, P.; Kitts, D.D.; Lu, X. Determination of antioxidant capacity and phenolic content of chocolate by attenuated total reflectance-Fourier transformed-infrared spectroscopy. *Food Chem.* **2016**, *202*, 254–261. [\[CrossRef\]](#)
44. Ventura-Cruz, S.; Tecante, A. Extraction and characterization of cellulose nanofibers from *Rose stems* (*Rosa* spp.). *Carbohydr. Polym.* **2019**, *220*, 53–59. [\[CrossRef\]](#)
45. Mohamed, E.A. Green synthesis of copper & copper oxide nanoparticles using the extract of seedless dates. *Heliyon* **2020**, *6*, e03123. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Chinnaiyah, K.; Maik, V.; Kannan, K.; Potemkin, V.; Grishina, M.; Gohulkumar, M.; Tiwari, R.; Gurushankar, K. Experimental and theoretical studies of green synthesized Cu₂O nanoparticles using *Datura metel* L. *J. Fluoresc.* **2022**, *32*, 559–568. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Khoshraftar, Z.; Safekordi, A.A.; Shamel, A.; Zaeifzadeh, M. Synthesis of natural nanopesticides with the origin of *Eucalyptus globulus* extract for pest control. *Green Chem. Lett. Rev.* **2019**, *12*, 286–298. [\[CrossRef\]](#)
48. Muthulakshmi, L.; Varada Rajalu, A.; Kaliaraj, G.S.; Siengchin, S.; Parameswaranpillai, J.; Saraswathi, R. Preparation of cellulose/copper nanoparticles bionanocomposite films using a bioflocculant polymer as reducing agent for antibacterial and anticorrosion applications. *Compos. Part B Eng.* **2019**, *175*, 107177. [\[CrossRef\]](#)
49. Brangule, A.; Šukele, R.; Bandere, D. Herbal medicine characterization perspectives using advanced ftir sample techniques—Diffuse reflectance (DRIFT) and photoacoustic spectroscopy (PAS). *Front. Plant Sci.* **2020**, *11*, 356. [\[CrossRef\]](#)
50. Dhara, M.; Kisku, K.; Naik, U.C. Biofunctionalized cuprous oxide nanoparticles synthesized using root extract of *Withania somnifera* for antibacterial activity. *Appl. Nanosci.* **2022**, *12*, 3555–3571. [\[CrossRef\]](#)
51. Musino, D.; Rivard, C.; Landrot, G.; Novales, B.; Rabilloud, T.; Capron, I. Hydroxyl groups on cellulose nanocrystal surfaces form nucleation points for silver nanoparticles of varying shapes and sizes. *J. Colloid Interface Sci.* **2021**, *584*, 360–371. [\[CrossRef\]](#)
52. Phan, A.D.T.; D'Arcy, B.R.; Gidley, M.J. Polyphenol-cellulose interactions: Effects of pH, temperature and salt. *Int. J. Food Sci. Technol.* **2016**, *51*, 203–211. [\[CrossRef\]](#)
53. Mannarmannan, M.; Biswas, K. Phytochemical-Assisted Synthesis of Cuprous Oxide Nanoparticles and Their Antimicrobial Studies. *ChemistrySelect* **2021**, *6*, 3534–3539. [\[CrossRef\]](#)
54. Taherzadeh Soureshjani, P.; Shadi, A.; Mohammadsaleh, F. Algae-mediated route to biogenic cuprous oxide nanoparticles and spindle-like CaCO₃: A comparative study, facile synthesis, and biological properties. *RSC Adv.* **2021**, *11*, 10599–10609. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Seon, J.; Hwang, Y. Cu/Cu₂O-immobilized cellulosic filter for enhanced iodide removal from water. *J. Hazard. Mater.* **2021**, *409*, 124415. [\[CrossRef\]](#) [\[PubMed\]](#)
56. da Silva, C.G.; Benaducci, D.; Frollini, E. Lyocell and cotton fibers as reinforcements for a thermoset polymer. *BioResources* **2012**, *7*, 0078–0098. [\[CrossRef\]](#)
57. Gong, X.; Xiong, Z.; Chen, X.; Meng, F.; Wang, H. Multifunctional superamphiphobic cotton fabrics with highly efficient flame retardancy, self-cleaning, and electromagnetic interference shielding. *ACS Appl. Mater. Interfaces* **2023**, *15*, 3395–3408. [\[CrossRef\]](#) [\[PubMed\]](#)
58. Gupta, D.; Meher, S.R.; Illyaskutty, N.; Alex, Z.C. Facile synthesis of Cu₂O and CuO nanoparticles and study of their structural, optical and electronic properties. *J. Alloys Compd.* **2018**, *743*, 737–745. [\[CrossRef\]](#)
59. Tauc, J.; Grigorovici, R.; Vancu, A. Optical properties and electronic structure of amorphous germanium. *Phys. Status Solidi B Basic Res.* **1966**, *15*, 627–637. [\[CrossRef\]](#)
60. Alp, E. The Facile Synthesis of Cu₂O-Cu hybrid cubes as efficient visible-light-driven photocatalysts for water remediation processes. *Powder Technol.* **2021**, *394*, 1111–1120. [\[CrossRef\]](#)
61. Jiang, H.-Q.; Endo, H.; Natori, H.; Nagai, M.; Kobayashi, K. Fabrication and efficient photocatalytic degradation of methylene blue over CuO/BiVO₄ composite under visible-light irradiation. *Mater. Res. Bull.* **2009**, *44*, 700–706. [\[CrossRef\]](#)
62. Xu, Y.; Schoonen, M.A.A. The absolute energy positions of conduction and valence bands of selected semiconducting minerals. *Am. Miner.* **2000**, *85*, 543–556. [\[CrossRef\]](#)
63. Das, S.; Deka, T.; Ningthoukhangjam, P.; Chowdhury, A.; Nair, R.G. A critical review on prospects and challenges of metal-oxide embedded g-C₃N₄-based direct Z-scheme photocatalysts for water splitting and environmental remediation. *Appl. Surf. Sci. Adv.* **2022**, *11*, 100273. [\[CrossRef\]](#)
64. da Costa, W.V.; Pereira, B.d.S.; Montanha, M.C.; Kimura, E.; Hechenleitner, A.A.W.; de Oliveira, D.M.F.; Pineda, E.A.G. Hybrid materials based on cotton fabric-Cu₂O nanoparticles with antibacterial properties against *S. aureus*. *Mater. Chem. Phys.* **2017**, *201*, 339–343. [\[CrossRef\]](#)
65. Huang, J.-Y.; Madasu, M.; Huang, M.H. Modified semiconductor band diagrams constructed from optical characterization of size-tunable Cu₂O cubes, octahedra, and rhombic dodecahedra. *J. Phys. Chem. C* **2018**, *122*, 13027–13033. [\[CrossRef\]](#)
66. Singh, M.; Goyal, M.; Devlal, K. Size and shape effects on the band gap of semiconductor compound nanomaterials. *J. Taibah Univ. Sci.* **2018**, *12*, 470–475. [\[CrossRef\]](#)

67. Chen, T.-N.; Kao, J.-C.; Zhong, X.-Y.; Chan, S.-J.; Patra, A.S.; Lo, Y.-C.; Huang, M.H. Facet-specific photocatalytic activity enhancement of Cu₂O polyhedra functionalized with 4-ethynylaniline resulting from band structure tuning. *ACS Central Sci.* **2020**, *6*, 984–994. [\[CrossRef\]](#) [\[PubMed\]](#)
68. Higashimoto, S.; Nishi, T.; Yasukawa, M.; Azuma, M.; Sakata, Y.; Kobayashi, H. Photocatalysis of titanium dioxide modified by catechol-type interfacial surface complexes (ISC) with different substituted groups. *J. Catal.* **2015**, *329*, 286–290. [\[CrossRef\]](#)
69. Gao, C.; Wang, J.; Xu, H.; Xiong, Y. Coordination chemistry in the design of heterogeneous photocatalysts. *Chem. Soc. Rev.* **2017**, *46*, 2799–2823. [\[CrossRef\]](#) [\[PubMed\]](#)
70. Wang, Y.; Miska, P.; Pilloud, D.; Horwat, D.; Mücklich, F.; Pierson, J.F. Transmittance enhancement and optical band gap widening of Cu₂O thin films after air annealing. *J. Appl. Phys.* **2014**, *115*, 073505. [\[CrossRef\]](#)
71. Kumar, A.; Kumar, R.; Verma, N.; Anupama, A.V.; Choudhary, H.K.; Philip, R.; Sahoo, B. Effect of the band gap and the defect states present within band gap on the non-linear optical absorption behaviour of yttrium aluminium iron garnets. *Opt. Mater.* **2020**, *108*, 110163. [\[CrossRef\]](#)
72. Norouzzadeh, P.; Mabhouti, K.; Golzan, M.M.; Naderali, R. Investigation of structural, morphological and optical characteristics of Mn substituted Al-doped ZnO NPs: A Urbach energy and Kramers-Kronig study. *Optik* **2020**, *204*, 164227. [\[CrossRef\]](#)
73. Yadav, S.; Jain, A.; Malhotra, P. A review on the sustainable routes for the synthesis and applications of cuprous oxide nanoparticles and their nanocomposites. *Green Chem.* **2019**, *21*, 937–955. [\[CrossRef\]](#)
74. Santos, S.A.O.; Pinto, R.J.B.; Rocha, S.M.; Marques, P.A.A.P.; Neto, C.P.; Silvestre, A.J.D.; Freire, C.S.R. Unveiling the chemistry behind the green synthesis of metal nanoparticles. *ChemSusChem* **2014**, *7*, 2704–2711. [\[CrossRef\]](#)
75. Waris, A.; Din, M.; Ali, A.; Ali, M.; Afridi, S.; Baset, A.; Ullah Khan, A. A comprehensive review of green synthesis of copper oxide nanoparticles and their diverse biomedical applications. *Inorg. Chem. Commun.* **2021**, *123*, 108369. [\[CrossRef\]](#)
76. Djamila, B.; Eddine, L.S.; Abderrhmane, B.; Nassiba, A.; Barhoum, A. In vitro antioxidant activities of copper mixed oxide (CuO/Cu₂O) nanoparticles produced from the leaves of *Phoenix dactylifera* L. *Biomass Convers. Biorefinery* **2022**, *14*, 6567–6580. [\[CrossRef\]](#)
77. Atri, A.; Echabaane, M.; Bouzidi, A.; Harabi, I.; Soucase, B.M.; Ben Chaâbane, R. Green synthesis of copper oxide nanoparticles using *Ephedra Alata* plant extract and a study of their antifungal, antibacterial activity and photocatalytic performance under sunlight. *Heliyon* **2023**, *9*, e13484. [\[CrossRef\]](#) [\[PubMed\]](#)
78. Akter, J.; Sapkota, K.P.; Hanif, M.A.; Islam, M.A.; Abbas, H.G.; Hahn, J.R. Kinetically controlled selective synthesis of Cu₂O and CuO nanoparticles toward enhanced degradation of methylene blue using ultraviolet and sun light. *Mater. Sci. Semicond. Process* **2021**, *123*, 105570. [\[CrossRef\]](#)
79. Bayomie, O.S.; Kandeel, H.; Shoeib, T.; Yang, H.; Youssef, N.; El-Sayed, M.M.H. Novel approach for effective removal of methylene blue dye from water using fava bean peel waste. *Sci. Rep.* **2020**, *10*, 7824. [\[CrossRef\]](#)
80. Salazar-Rabago, J.J.; Leyva-Ramos, R.; Rivera-Utrilla, J.; Ocampo-Perez, R.; Cerino-Cordova, F.J. Biosorption mechanism of methylene blue from aqueous solution onto white Pine (*Pinus durangensis*) sawdust: Effect of operating conditions. *Sustain. Environ. Res.* **2017**, *27*, 32–40. [\[CrossRef\]](#)
81. Messaadia, L.; Kiamouche, S.; Lahmar, H.; Masmoudi, R.; Boulahbel, H.; Trari, M.; Benamira, M. Solar photodegradation of rhodamine B dye by Cu₂O/TiO₂ heterostructure: Experimental and computational studies of degradation and toxicity. *J. Mol. Model.* **2023**, *29*, 38. [\[CrossRef\]](#)
82. Qin, H.; Wang, Z.; Yang, S.; Jiang, W.; Gu, Y.; Chen, J.; Yang, G. High efficiency degradation of 2,4-dichlorophenol using Cu₂S/Cu₂O decorated nanoscale zerovalent iron via adsorption and photocatalytic performances. *J. Clean. Prod.* **2022**, *378*, 134587. [\[CrossRef\]](#)
83. Ai, Z.; Xiao, H.; Mei, T.; Liu, J.; Zhang, L.; Deng, K.; Qiu, J. Electro-fenton degradation of rhodamine b based on a composite cathode of Cu₂O nanocubes and carbon nanotubes. *J. Phys. Chem. C* **2008**, *112*, 11929–11935. [\[CrossRef\]](#)
84. Xia, H.; Zhang, Y.; Zhou, P.; Li, C.; Yang, D. Oxidative degradation of organic pollutants using cuprous oxide in acidic solution: Hydroxyl radical generation. *Desalin. Water Treat.* **2019**, *171*, 262–269. [\[CrossRef\]](#)
85. Zayed, M.F.; Eisa, W.H.; Anis, B. Gallic acid-assisted growth of cuprous oxide within polyvinyl alcohol; a separable catalyst for oxidative and reductive degradation of water pollutants. *J. Clean. Prod.* **2021**, *279*, 123826. [\[CrossRef\]](#)
86. Wu, M.; He, S.; Ha, E.; Hu, J.; Ruan, S. A facile synthesis of PEGylated Cu₂O@SiO₂/MnO₂ nanocomposite as efficient photo–Fenton–like catalysts for methylene blue treatment. *Front. Bioeng. Biotechnol.* **2022**, *10*, 1023090. [\[CrossRef\]](#)
87. Cheng, Y.; Lin, Y.; Xu, J.; He, J.; Wang, T.; Yu, G.; Shao, D.; Wang, W.-H.; Lu, F.; Li, L.; et al. Surface plasmon resonance enhanced visible-light-driven photocatalytic activity in Cu nanoparticles covered Cu₂O microspheres for degrading organic pollutants. *Appl. Surf. Sci.* **2016**, *366*, 120–128. [\[CrossRef\]](#)
88. Li, Y.; Dong, H.; Xiao, J.; Li, L.; Chu, D.; Hou, X.; Xiang, S.; Dong, Q.; Zhang, H. Advanced oxidation processes for water purification using percarbonate: Insights into oxidation mechanisms, challenges, and enhancing strategies. *J. Hazard. Mater.* **2023**, *442*, 130014. [\[CrossRef\]](#)
89. Winterbourn, C.C. Biological chemistry of superoxide radicals. *ChemTexts* **2020**, *6*, 7. [\[CrossRef\]](#)
90. Liu, Y.; Tan, N.; Guo, J.; Wang, J. Catalytic activation of O₂ by AlO-CNTs-Cu₂O composite for Fenton-like degradation of sulfamerazine antibiotic at wide pH range. *J. Hazard. Mater.* **2020**, *396*, 122751. [\[CrossRef\]](#)

91. Bayat, F.; Sheibani, S. Enhancement of photocatalytic activity of CuO-Cu₂O heterostructures through the controlled content of Cu₂O. *Mater. Res. Bull.* **2022**, *145*, 111561. [[CrossRef](#)]
92. Chu, C.-Y.; Huang, M.H. Facet-dependent photocatalytic properties of Cu₂O crystals probed by using electron, hole and radical scavengers. *J. Mater. Chem. A* **2017**, *5*, 15116–15123. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.