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RESEARCH

Biomimetic Synthesis of Copper Nanoparticles Using Tinospora Cordifolia Plant Leaf Extract for Photocatalytic Activity Applications

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Abstract

The copper nanoparticles (Cu-NPs), through a novel green synthesis method utilizing Tinospora Cordifolia (TC) aqueous leaf extract as a reducing and stabilizing agent, were synthesized, and investigated for their dye degradation potential. The bio-synthesis process, which is operationally simple, non-toxic, and cost-effective, involves using cupric oxide (CuO) as precursor material. The degradation of dyes in water bodies is challenging research due to their stable nature; therefore, it is essential to develop potential catalyst materials with desirable properties to degrade dyes in water bodies. The CuNPs were characterized using X-ray diffraction (XRD), UV–Vis spectrometer, scanning electron microscopy (SEM), and a Fourier transformed infrared spectrometer (FTIR). The FTIR results confirmed the presence of phytochemicals involved in the reduction, capping, and stabilization of CuNPs, which was corroborated by the XRD data. The photo-catalytic activity of biosynthetic CuNPs was studied using methylene blue (MB) dye upon exposure to visible light source irradiation. The results showed that bio-synthesized CuNPs exhibited a high potential for dye degradation for the methylene blue dye in the presence of a visible light source and a dye degradation rate of 81% was achieved. The green-synthesized CuNPs have proven to be a potential candidate for efficiently removing dyes from water bodies and provide a sustainable, environmentally friendly method for producing metal nanoparticles with excellent photo-catalytic properties.

Keywords Green synthesis · Copper nanoparticles · Photo-catalysis · Methylene blue dye · Dye degradation

Introduction

Technological modernization and industrialization discharged a bulk number of industrial effluents and different organic dyes into the water bodies. Organic dyes have been used as colorants in various industries, such as painting, textiles, leather, paper, cosmetics, hair dye, plastic, and pharmaceuticals, which cause harmful effects on aquatic animals and plants [1–4]. These organic dye materials can seriously threaten water bodies; they can cause serious health problems such as skin diseases, cancer, and allergic reactions in human beings [5, 6]. To degrade dyes in water bodies, researchers have developed different methods to degrade dyes in water bodies, such as ion exchange, chemical oxidation, and photocatalytic degradation techniques [7–11]. However, photo-catalytic degradation using a photo-catalyst made of metal nanoparticles has been identified as a potential green approach to degrading dyes [12, 13].

Metal nanomaterials with large surface area to volume artio are needed to degrade organic dyes in water bodies [14,

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15]. Metal nanoparticles (MNPs) such as CuNPs, ZnNPs, and AgNPs are active potential photo-catalysts under sunlight due to their small band gap [16–19]. Cuo is a p-type semiconductor with a narrow band gap of 2.0 to 2.7 eV [20]. CuNPs effectively respond to optical and photo-catalytic applications [20–22].

Biosynthesis of metal nanoparticles using plant leaf extract is considered the best green approach [23–25]. Tinospora Cordifolia (TC) is a well-known plant in the Indian medicinal plant system, and it is gaining more attention for its functionality in a wide spectrum of industrial applications [23]. It has already been used as a tonic for anti-cancer, anti-allergenic, and anti-diabetic patients [25–27]. This plant has the ability to protect against gastric mucosal damage, and can scavenge free radicals. It can also be used as the best capping and stabilizing agent to synthesize CuNPs, which can be used as the best photo-catalyst material to degrade dyes in water bodies.

The catalysis process plays a vital role in dye degradation and water purification. It has been estimated that the catalysis-based industries may produce commodities worth several trillion dollars annually, highlighting the importance of catalysis to our community [28–31] which clearly suggests that such catalysts are in global demand. But chemical industries mainly use only heterogeneous catalysis for several reasons, such as simple catalyst separation, durability, and suitability for continuous operations. However, designing catalyst materials is not a straightforward process due to their complex structure and poor understanding of active centers. Therefore, a significant amount of research focuses on designing catalysts, which indicates the tremendous efforts that go into understanding the different synthesis methods of active and stable catalysts [32, 33]. This idea is crucial for the consistent mass production of solid catalysts [34–36]. Designing an optimal and stable catalyst is a bit challenging, and metal nanoparticles are a potential candidate to fulfill the quality and quantity of the global demand.

Hence, in continuation of our previous work on metal oxide nanoparticles [28, 29], in this present study, we used a single-step green synthesis approach to synthesize CuNPs using TC leaf extract. We also examined the degradation efficiency of synthesized CuNPs to degrade MB dye under sunlight. Further, the scope of this paper is based on the environment-friendly green synthesis of CuNP nanoparticles and their applications on water pollutants (different dyes) for understanding the environmental photocatalytic properties of so-synthesized samples.

Materials and Methods

Materials

Cupric oxide (Copper (II) Oxide), acetone, toluene, and methylene blue (MB) dye were procured from Sigma-Aldrich, Bangalore, India. Tinospora Cordifolia plant leaves were collected from medicinal garden, Hyderabad, India.

Synthesis of Copper Nanoparticles (CuNPs)

Tinospora Cordifolia (TC) leaves were thoroughly washed with deionized water to remove any impurities. Afterward, the surface moisture of the leaves was dried at room temperature of 27 °C, and they were ground into a fine powder. Subsequently, 2 g of TC powder was mixed with 75 ml of deionized water and stirred at 70 °C for 20 min. The resulting TC extract was filtered using Whatman filter paper and then centrifuged for approximately 20 min.

To synthesize copper nanoparticles (CuNPs), 50 ml of the TC leaf extract was filled in a burrett and added dropwise (one drop per second) to 200 ml of CuO solution in a beaker. The solutions were prepared at a temperature of 90 °C and mixed for 20 min at a speed of 600 rpm. The rate of adding leaf extract to the CuO solution from the burette was carefully controlled, while the resulting mixture was continuously stirred at 600 rpm. The final solution was heated on a hot plate at a temperature of 90 °C until a noticeable change in the color of the reaction mixture occurred. Finally, the solution was centrifuged at 5000 rpm for 20 min and the residue was dried in an oven in order to collect the solid nanoparticle powder. The complete synthesis procedure of CuNPs is shown in Fig. 1.

Characterization of Synthesized CuNPs

The formation of Cu-metallic nanoparticles (CuNPs) was confirmed using UV–visible spectroscopy, which allowed for the surface plasmon resonance (SPR). UV–Vis spectra

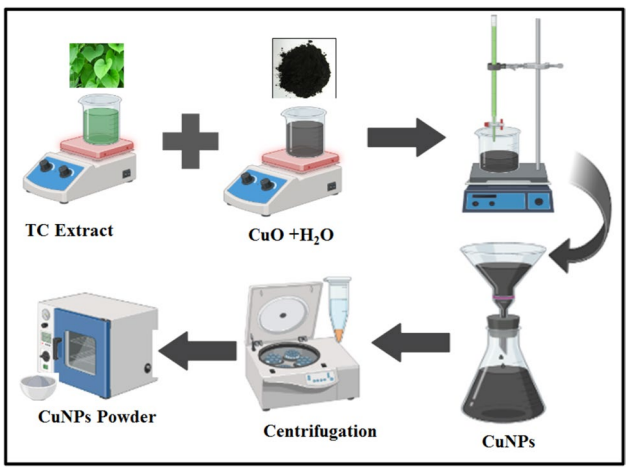

Fig. 1 Biogenic synthesis process of TC leaf extract mediated CuNPs

were obtained using a UV JACO V-750 spectrometer, scanning the nanoparticle solution over a 200–800 nm wavelength range. This analysis identified synthesized CuNPs based on their characteristic absorption peaks.

Fourier transform infrared spectroscopy (FTIR) was employed to identify the specific phytochemical groups responsible for forming these metallic nanoparticles (MNPs). The samples were analyzed using an IR-Thermo Fisher Nicolet iS5 spectrometer, which recorded 400 to 4000 cm^{-1} spectra. The FTIR analysis provided valuable insights into the functional groups and chemical bonds involved in the stabilization and capping of the CuNPs.

The surface morphology and size of the synthesized CuNPs were investigated using scanning electron microscopy (SEM). Thin films of the nanoparticles were prepared on carbon-coated copper grids and examined using a ZEISS Merlin Compact instrument operating at an accelerated voltage of 20 kV. The SEM analysis allowed for the visualization of the nanoparticles and the determination of their size distribution and morphology.

The crystal structure of the CuNPs was analyzed using X-ray diffraction (XRD) with a Bruker D8 Advance Instrument. This technique provided information about the synthesized nanoparticle's crystalline phases and crystallographic structure. The XRD patterns were obtained using Cu-Kα radiation.

Overall, the combination of UV–visible spectroscopy, FTIR, SEM, and XRD measurements facilitated a comprehensive characterization of the synthesized CuNPs, including their photo-catalytic, optical properties, chemical composition, morphology, and crystal structure.

Photocatalytic Activity

The photo-catalytic activity of the synthesized Cu-metallic nanoparticles (CuNPs) was assessed in the degradation of methylene blue (MB) dye. In the photo-catalysis process, a visible light source was used as an alternative to sunlight. The reaction was initiated by adding a 5 ml solution of CuNPs with density 10 mg/ml and was added it to 40 ml dye solution with density 15 mg/ml. The mixture solution was stirred for 20 min in the darkroom to establish the adsorption process. The samples were collected every 30 min to see the absorption peak with the help of UV–Vis spectroscopy. The UV–Vis spectra were collected for pristine MB dye, which showed bands at 630 nm and 430 nm wavelengths. The solution was stirred under sunlight irradiation, and 3 ml of suspension was withdrawn at intervals of 30 min up to 3 h to observe the dye absorption peak. The absorption peaks were analyzed for different periods, and the dye degradation was analyzed with UV–Vis spectrum data. The following equation was used to measure the dye degradation [37].

$$Degradation(\%) = \left(\frac{A_0 - A}{A_0}\right) \times 100$$

where A_0 is the absorption at time = 0 and A_t is the absorption at time = t.

Results

UV–Vis Spectroscopy Analysis

The formation of CuNPs was confirmed using UV–Vis spectroscopy. The location of the absorption band peak of CuNPs is characterized by factors such as surface morphology, size, reaction time, temperature, pre-cursor salt concentration, and aqueous leaf extract. Bio-phytochemicals found in plant leaf extract play a vital role in stabilizing and forming CuNPs. Figure 2 shows the UV-Vs absorption spectrum of CuNPs from a wavelength range of 200 to 600 nm. The absorption peak was observed as characteristic peak of CuNPs at wavelengths 282 and 330 nm, which is possibly due to the electron transition from the valency band to the conduction band (inter-band transition) [38]. The band gap of the CuNPs was calculated from the absorption spectrum using Tauc equation[39].

$$ahv = D(hv - E_g)^2$$

where hν is the energy of the photon, E_g is the band gap of nanomaterial, and D is constant.

For $n = 1/2$; the band gap was calculated to be 4.1 and 2.8 eV which is much greater than that of bulk CuO which might be due to the size effect of the CuNPs. The band gap calculation is calculated at lower energy side [39]. The

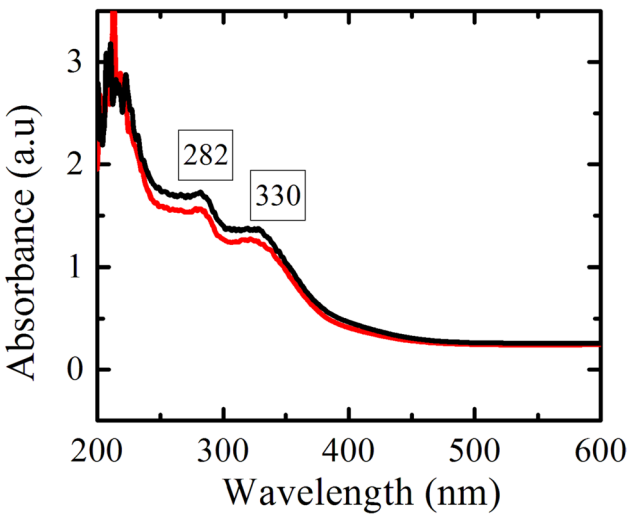

Fig. 2 UV–Vis absorption spectrum of biogenic CuNPs

absorption peak indicates that the particles are in nano size with a narrow size distribution.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR analysis data was carried out to understand the probable functional groups, or bio-phytochemicals, which are responsible for the formation of CuNPs. Figure 3 represents the IR spectrum of CuNPs that was recorded in the range of 400 to 4000 cm^{-1}. The observed peaks indicate the identification of the surface functional groups, or bio-phytochemicals which are responsible for bio-reducing and stabilizing the CuNPs. The high-intensity band at 652 cm^{-1} represents the stretching vibration of Cu–O linkage bands, which confirms the formation of pure CuNPs [40]. This indicates that biological functional groups in the Tinospora Cordifolia (TC) plant leaf extract have the dual role of reducer and stabilizer for the formation of pure CuNPs. These functional groups (aromatic, phenolic, amino groups, and hydroxyl) help to reduce copper ions into copper nanoparticles, which was only possible under the effect of hydroxyl and carbonyl linkages in the plant leaf extract.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to examine the surface morphology and structural features of the synthesized CuNPs. The observed images at different magnifications are depicted in Fig. 4. The micrograph images of the as-synthesized CuNPs reveal an accumulation of CuNPs in the form of aggregates. The CuNPs tend to form aggregates to minimize their surface energy, possibly due to van-der Waal forces acting between the CuNPs. The initial mechanism of Cu atoms favors isotropic growth in the early stages might be due to primarily atoms favoring relatively poor thermal energy. The lower thermal energy favors relatively large numbers of CuNPs which might be due to having more active sites for deposited Cu-nanoparticles. When reaction time increases, Cu atoms acquire high thermal energy and deposite the CuNPs cluster to minimize surface energy. The shape of CuNPs was observed as irregular-shaped structures with sizes ranging from 0.5 to 1.5 µm. The agglomerated clusters were formed, which might be due to the varying crystallization growth of CuNPs.

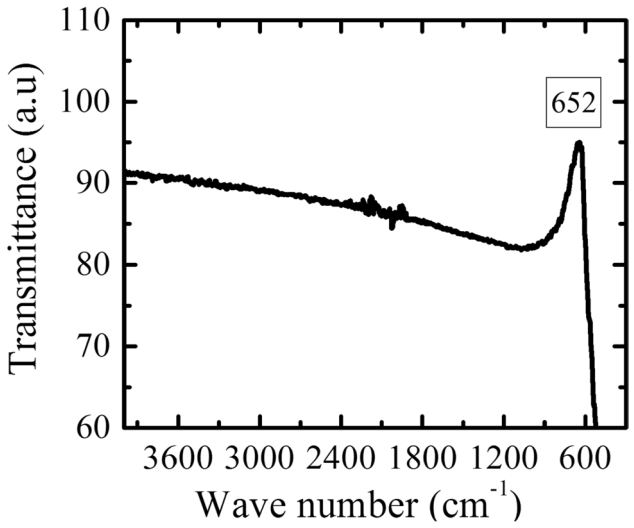

Fig. 3 FTIR spectrum of biogenic CuNPs

X-Ray Diffraction (XRD) Analysis

The XRD analysis was used to study and identify the crystalline structure of CuNP materials. The XRD patterns reveal that the as-synthesized CuNPs had crystalline structures and were free of impurities. The CuNPs were identified on three high-intensity diffraction peaks $2\theta = 38.5^0$, 35.8^0, and 47^0 corresponding with their crystal planes {200}, {002}, {202} of CuNPs with the monoclinic structure of CuNPs (Fig. 5). The most intense peak is observed at (200), and the lattice constant was calculated using the following equation:

$$\alpha = \lambda\left(\frac{\sqrt{h^2 + k^2 + l^2}}{2\sin\theta}\right)A^0$$

The crystalline size of the as-synthesized CuNP was measured using Debye-Scherr's formula ($D = 0.9\lambda/\beta\cos\theta$). Here, λ is the wavelength of X-ray radiation used in the XRD, β is the full width of half maximum, and 2θ is the diffraction angle. The crystalline size of the nanoparticle was measured to be around 15.5 nm. The XRD indicates several characteristic peaks of monoclinic structure for CuNPs as per the standard JCPDS data card-00–001-1117 [41].

Mechanism of Biogenic CuNPs

The reduction of the precursor CuO salt begins immediately after adding even a few drops of leaf extract, and the formation of CuNPs is demonstrated by the changing color of the solution. The bio-phytochemicals present in the Tinospora cordifolia (TC) plant leaf extracts play a vital role in reducing, capping, and stabilizing CuNPs [13]. In this process, releasing H atoms during the conversion process of enol into keto bio-flavonoids reduces Cu metal ions, resulting in the formation of CuNPs. The precise mechanism of CuNPs synthesis mediated by the plant leaf extract is still not understood. It is speculated that the color of the CuNPs in the environment after 30 to 40 min can be attributed to oxidation, which is responsible for the synthesis of CuNPs. Electrostatic attractions may also help to bind metal oxide ions together to form stabilized nanoparticles and prevent

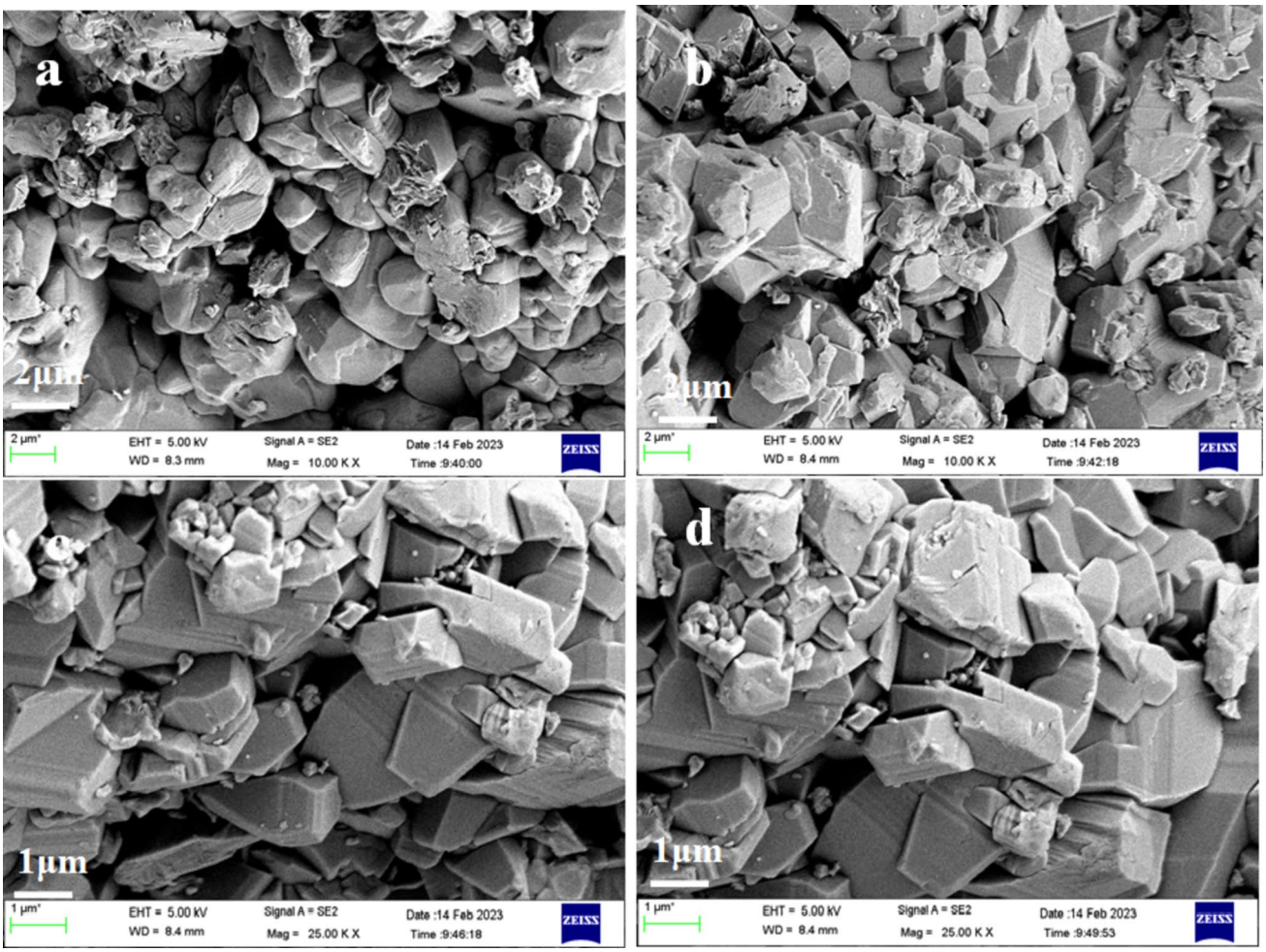

Fig. 4 SEM morphology image of the CuNPs at different magnifications (**a**, **b** 2 µm; **b**, **c** 1 µm)

CuNPs cluster formation. Despite the lack of a clear understanding of the metal nanoparticle synthesis mechanism, plant leaf extracts' play an important role in synthesizing CuNPs. The biogenic green synthesis approach is a potential pathway to synthesize metal nanoparticles due to its eco-friendly, non-toxic, and cost-effective features. The possible proposed mechanism of the formation of CuNPs is shown in Fig. 6.

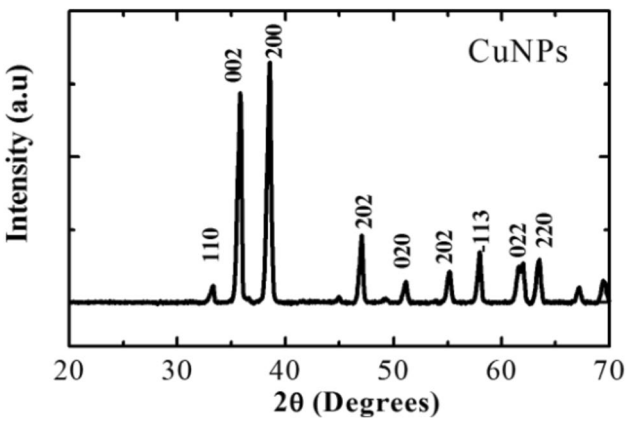

Fig. 5 XRD pattern of CuNPs, JCPDS data card-00–001-1117

Evaluation of Photo-catalytic Activity of Biogenic CuNPs

The photocatalytic activity of CuNPs in the degradation of MB dye is shown in Fig. 7. The degradation rate of dyes depends on various factors such as irradiation time, type of light source, concentration of dye, and catalyst. The degradation of dyes was characterized by using sunlight as the light source. The band gap and high surface area to volume ratio significantly influence the dye degradation activity. The samples were collected after irradiation with light and characterized the absorption spectra at regular intervals using UV–Vis spectroscopy. It was found that the intensity of the absorption band decreased as the illumination time under light increased. The magnitude of absorption of MB dye in the presence of CuNPs is shown in Fig. 8.

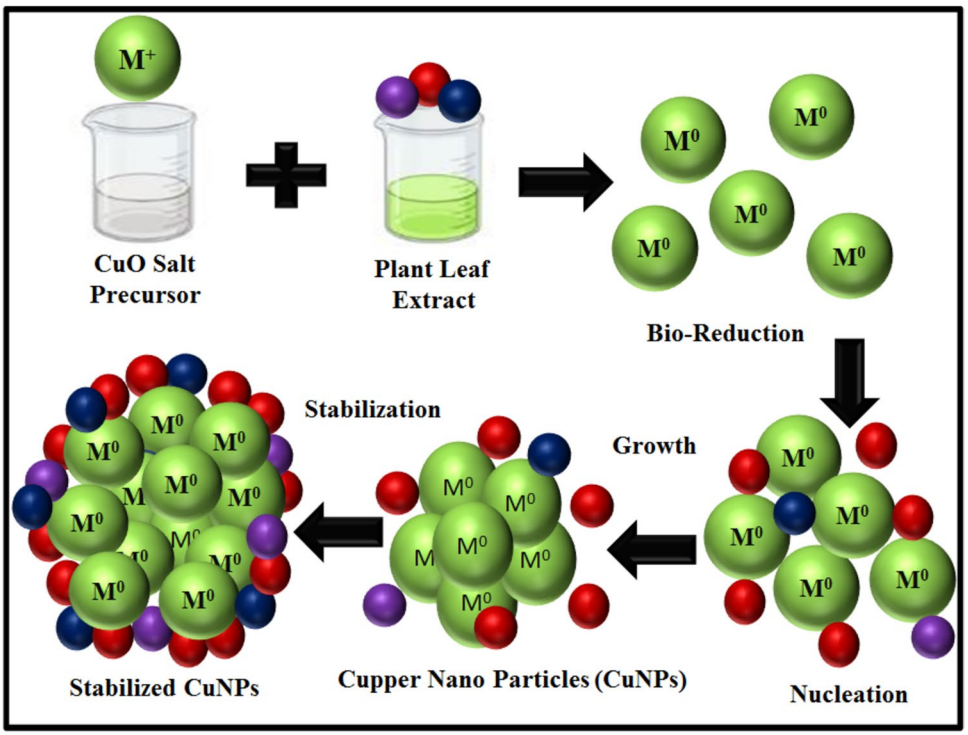

Fig. 6 Schematic mechanism of formation of CuNPs

The main factors that are responsible for the degradation or decolonization of dyes are oxygen radicals and hydroxyl, which degrade toxic contaminants in the dye. Further, the blue color of MB dye turns into a light blue color or colorless with time as the illumination time under light is increased. The degradation efficiency for MB dye was 81% after about 2 h of exposure to a light source in the presence of a photo-catalyst (CuNPs), as shown in Fig. 9. It was noted that the higher the degradation rate observed, for the faster the reaction rate of dyes with a catalyst.

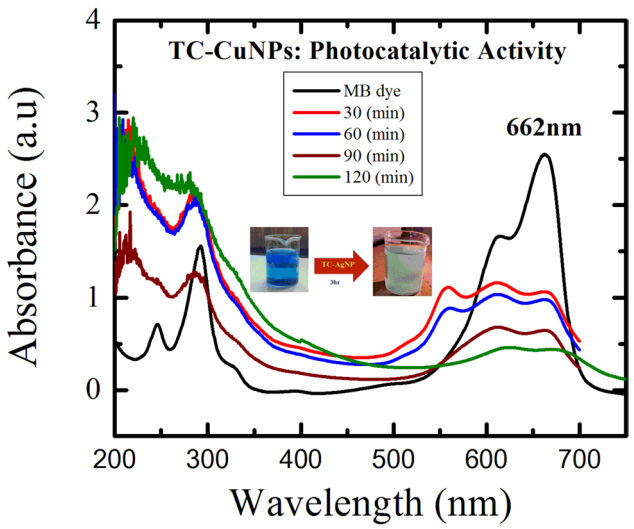

Fig. 7 Absorption spectra of MB dye at different time intervals

Kinetic Studies of Biogenic CuNPs

The photocatalytic performance of MB dye degradation kinetic behaviuor procedure of CuNPs catalyst examined by the first order kinetic theory model which can be expressed as

$$\ln\left(\frac{A_0}{A_t}\right) = kt \tag{1}$$

In the above equation, A_0 is the dye absorption at time $t = 0$, A_t is the dye absorption at time t, and k is the rate constant. The kinetic photo-degradation of MB dye by

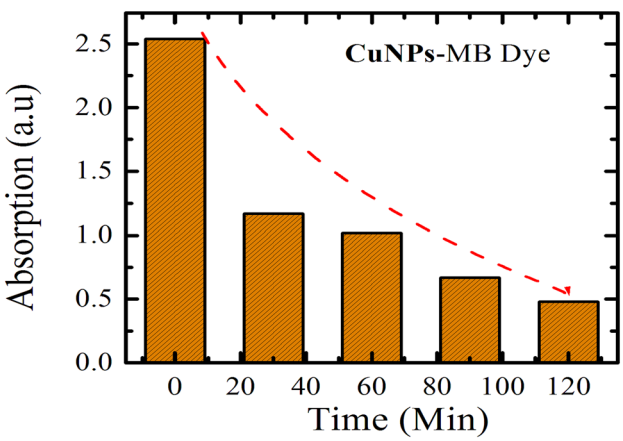

Fig. 8 Absorption of MB dye at different time intervals

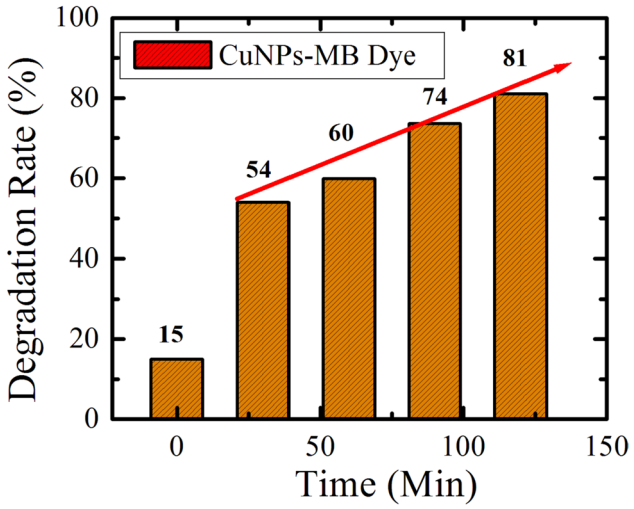

Fig. 9 Degradation rate of MB dye

CuNPs was investigated and results are depicted in Fig. 10 ($\frac{A_0}{A_t}$ versus time) and Fig. 11 ($\ln\left(\frac{A_0}{A_t}\right)$ versus time). Therefore, the rate constant of MB dye degradation by CuNPs measured using the first order of reaction (-pseudo-first-order kinetics) which is attributed to the degradation of dye [42]. The slope of the fitting line determines the rate constant for the biosynthesis of CuNPs. In the presence of visible a light source, the bio-phytochemicals present in the TC extract promoted the transfer of electrons from the valency band to the conduction band of CuNPs, which increases the superoxide radicals and leads to higher efficiency of photo-degradation of CuNPs catalyst.

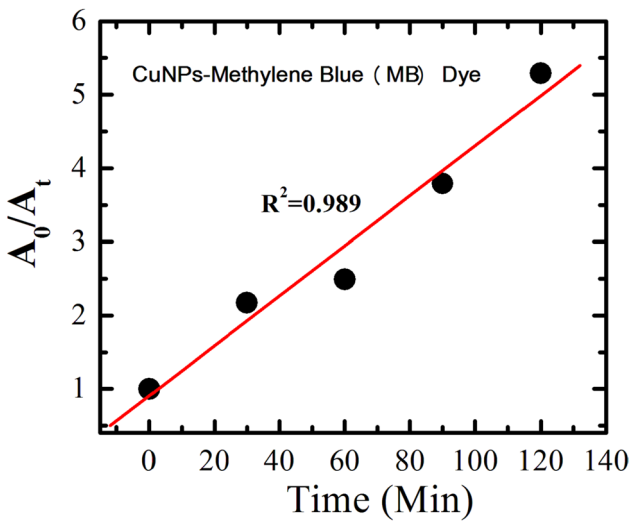

Fig. 10 Kinetic results for dye degradation: (A_t/A_0) vs time

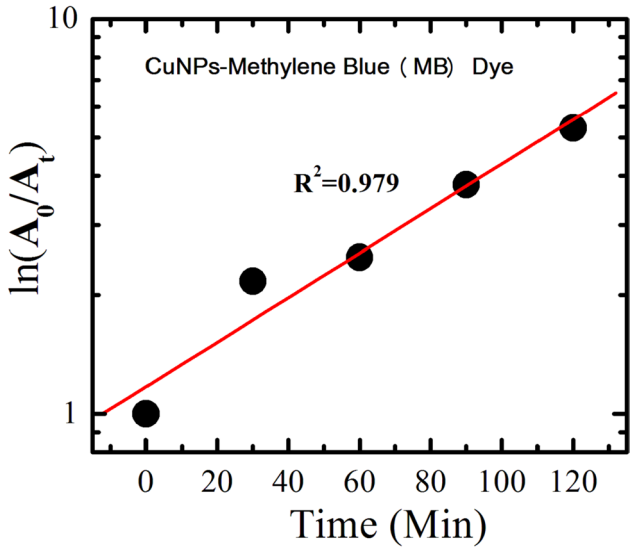

Fig. 11 Kinetic results for dye degradation: $\ln(A_t/A_0)$ vs time

Possible Mechanism of Biogenic CuNPs

The primary species involved in detoxifying dye molecules under light irradiation were identified via the photo-catalysis process. Figure 12 represents the proposed mechanism for the photocatalytic degradation of dye. Metal nanoparticles with a small band gap promote the creation of electron–hole pairs, as low absorption energy is required for electrons to move from the highest occupied molecular orbit state to the lowest unoccupied molecular orbit state. When a catalyst (CuNPs) absorbs light energy, the absorption intensity is equal to the band gap energy of the catalyst (CuNPs). The electron transition occurs from the ground state to the excited state, creating a gap, a valence band hole (h^+), a free electron, and a conduction band e^-. The hole is a promising candidate to accept an electron from pollutants to degrade them. Highly oxidizing species convert the water molecules into hydroxyl radicals (OH), degrading the organic contaminants. Oxygen molecules combine with an electron and convert into superoxide radicals (O_2) [43]. The process involved in the reduction of pollutants is given as follows:

$$\text{Photocatalyst CuO} + hv \rightarrow e^- + h^+$$

$$\text{Photocatalyst CuO}(e^-) + hv \rightarrow O_2^-$$
$$\text{Photocatalyst CuO}\left(h^+\right) + h_2O \rightarrow OH^-$$
$$O_2^-(or)OH^- + Dye \rightarrow \text{Degraded material}$$

The surface of the CuNPs was anchored by the phenols and bio-flavonoids of TC extract. These phytochemicals can enhance the conversion of oxygen to superoxide

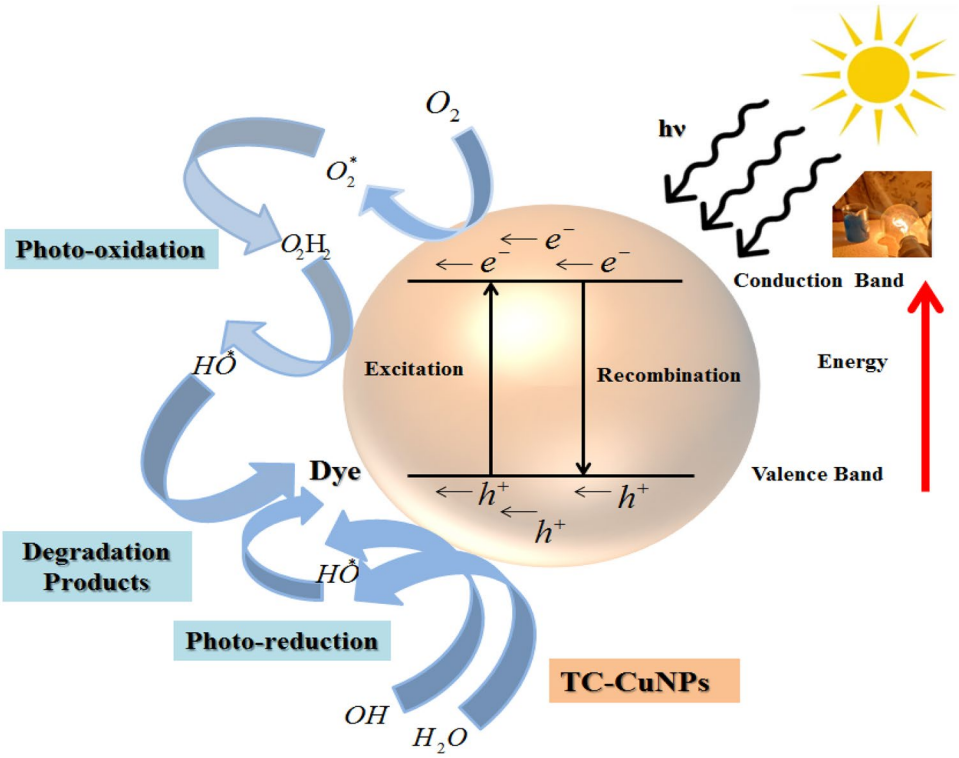

Fig. 12 Schematic representation of photo-catalytic degradation of dye

radicals, which improves the photocatalytic activity. It is observed that oxide and hydroxyl radicals are the main reactive species during photo-catalysis dye degradation of water-soluble dyes.

Factors Affecting Photocatalytic Degradation of Biogenic CuNPs

In order to achieve potential photo-catalytic activity, some features must be considered, such as the concentration of dye, the concentration of the photo-catalyst, the structure and morphology of the catalyst, the irradiation time, and the light source. An inhibited reaction is observed when the concentration of dyes is increased, as there is no interaction with the catalyst's active sites. This is due to the dye's lack of absorption of light intensity by the dye molecules and the difficulty of electrons to migrate to the photo-catalyst, resulting in insufficient hydroxyl radicals for dye degradation and reducing the efficiency of dye degradation. We noted that MB dye solutions with a 1 mg/lit concentration produced better results.

As the concentration of photo-catalyst is increased, many reaction sites become available, leading to an increased production of electron–hole pairs, which help to produce hydroxyl radicals for efficient detoxification of organic pollutants. The morphology and size of CuNPs play an important role in producing higher efficiency in dye degradation. Smaller-sized catalyst nanoparticles show higher efficiency for dye degradation, as they provide more active sites for the absorption of dyes. In our studies, a good result was obtained using 10 mg/ml CuNPs 95 ml solution and the dye degradation rate of 81% was achieved after a time duration of 120 min. Other methods of CuNPs catalyst fabrication showed degradation efficiency varying from 32 to 95%. Our CuNPs catalyst was prepared in a simple, single-step green synthesis process using TC leaf extract, and it showed dye degradation efficiency of 81% using MB under the visible light source. This value is within the reported literature using other preparation methods and extracts, but our synthesis method is much simpler, non-toxic, and eco-friendly.

Conclusion

In this study, we successfully synthesized copper nanoparticles (CuNPs) using a novel, one-step, eco-friendly, and cost-effective biogenic synthesis method. The bio-components present in Tinospora cordifolia (TC) leaf extract served as excellent reducing and stabilizing agents during the synthesis process. The UV–Vis and XRD analyses confirmed the high purity and monoclinic crystal structure of the CuNPs phase, with a crystalline size of 15.5 nm. The green-synthesized CuNPs reveal monoclinic crystal clusters with different diameters. Through the degradation of MB dye, the synthesized biogenic CuNPs effectively demonstrated photo-catalytic properties under visible light illumination. The photo-catalytic reduction followed pseudo-first-order kinetics, with a degradation rate of 81%

for MB dye. The biosynthesized route is more important than the chemically because it offers a new means for researchers to produce cost-effective, highly active sites with high purity, non-toxic, eco-friendly and have low energy consumption. It is concluded that biogenic CuNPs with TC extract are the best photo-catalyst candidates for dye degradation. Further studies should also focus on optimizing the concentrations of catalyst and dye, clearly understanding the photo-catalyst mechanisms, evaluating potential toxicity effects, assessing the long-term stability and performance of the CuNPs in real-world applications. These efforts will facilitate the translation of synthesis of CuNPs from the laboratory scale to large-scale industrial production, with the goal of benefiting human health and the environment.

Author Contribution Parvathalu K.: supervision, writing—original draft and editing, visualization. Rajitha K. and Chandrasekhar B.: designing experiment, and data collection. Pranay Bhaskar K., Sathvik K., and Bala Bhaskar P.: review of articles and data collection. All other authors were involved in various parts of discussion of the project.

Data Availability Data is provided with the request.

Declarations

Conflict of Interest The authors declare no conflict of interest.

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