

PHOTOCATALYTIC DEGRADATION OF SAFRANINE DYE BY USING COPPER NANOPARTICLES (CUNPS)

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ABSTRACT

Copper nanoparticles (CuNPs) are one of the most widely used nanomaterials nowadays. Plant extract mediated biosynthesis of CuNPs and their potential application gained enormous attention in recent world due to ever-increasing demand of safe, cost-effective and environmentally friendly process for synthesizing metal nanoparticles in a sustainable manner. The current investigation carried out green synthesis of copper nanoparticles (CuNPs) using *Psidium guajava* leaf extract as capping and stabilizing agent, and copper sulphate as metal precursor. The biosynthesized CuNPs were characterized using wide variety of techniques i.e. Visual observation, UV-Vis spectroscopy and FTIR. Signatory colors changed confirm the synthesis of CuNPs. The data obtained by FTIR spectroscopy revealed that copper nanoparticles were surrounded by different organic molecules such as alcohols, ketones, aldehydes and carboxylic acid. Being semiconductor, phytofabricated CuNPs exhibited an excellent photocatalytic activity to degrade of hazardous dyes (16% to 56%), which was reconfirmed by UV-Vis spectroscopy. The results revealed that guava leaf extract mediated CuNPs synthesis may be the cost effective, time saving, renewable, green and sustainable route and its application for photodegradation of organic dyes may open a new avenue of wastewater treatment and keep our environment clean.

INTRODUCTION

The widespread use of synthetic dye has led to significant environmental pollution. At production stages, many textile, printing, pharmaceutical, and food industries use dyes, which is noxious, persistent, and carcinogenic (Mullerova *et al.*, 2019; Kaur *et al.*, 2018; Zhu and Tian, 2017). These pollutants adversely affect the quality of water, and a serious threat to aquatic ecosystems and public health (Chang *et al.*, 2015). Safranine, an azine dye, commonly used in pharmaceutical and biochemical industries, especially for staining gram-negative bacteria and for detecting cartilage, mucin, mast cell granules and lignified tissues in plant (Moawed and Abulkibash, 2016). Moreover, the food grade of safranine is used in food products such as flavoring and coloring of candies and cookies. Besides these, in the process of coloring and treatment of tannins, cotton, fibers, wool, silk, leather, and paper Safranine-O (SO) is widely used (Asfaram *et al.*, 2015).

According to most scientific information, approximately 70% of the Earth's surface is covered by water. But rapid increase of organic pollutants such as pesticides, personal care products, and pharmaceuticals, water resources are subjected to pollution, which directly or indirectly affect the harmonious ecosystems (Wu *et al.*, 2018, Moreno-Castilla *et al.*, 2019, Chen *et al.*, 2019). So eradication of the venomous and persistent organic compounds from the wastewater is absolutely crucial (Xu *et al.*, 2017). In this context, the complete removal of the pollutants by the development of simple, efficient, and low-cost technologies is required (Asfaram *et al.*, 2015). Scientists proposed many scientific methods for dye removal, such as membrane filtration (Shao *et al.*, 2013, Jalilvand *et al.*, 2020), precipitation (Park *et al.*, 2021); ion exchange (Sharma *et al.*, 2016), electrocoagulation (Khemila *et al.*, 2018), advanced oxidation processes, like photocatalysis (Calza *et al.*, 2006; Rizzo *et al.*, 2009), photo electro-Fenton (Pérez-Estrada *et al.*, 2005), photo-Fenton, ozonation (Vogna *et al.*, 2004), and UV/H₂O₂ treatment (Klavarioti *et al.*, 2009; Kim *et al.*, 2009). Among these methods, photocatalysis is widely used by the scientific community because of its eco-friendly nature, cost-effectiveness, and ability to completely mineralize the organic matter (Kansal *et al.*, 2013; Zhang *et al.*, 2017). As global

warming is another talk of the town caused by various industrial pollutants, photocatalysis using visible light or solar light (including UV) get popularity (Zhang *et al.*, 2012; Xiang *et al.*, 2012; Woan *et al.*, 2009). Though photocatalysis using visible-light-active semiconductors has shown remarkable progress due to its ease of operation, feasibility, reproducibility, reliability, and commercialization, UV active semiconductor use is quite difficult due to its limited use of the solar spectrum. Therefore, copper oxide (CuO) is one of the potential semiconductors with excellent optical, electrical, physical, and magnetic properties (Xiang *et al.*, 2015; Chauhan *et al.*, 2020, Yang *et al.*, 2016).

Excess elemental copper is harmful to humans, the environment, and aquatic life; but copper and its complexes have been utilized over the years by humans in water purification, pesticides as antibacterial and anti-fouling agents (Padil and Černík, 2013, Nagajyothi *et al.*, 2017). Recently, nanoparticles are using for the removal of dyes from contaminated water, Copper oxide nanoparticles (CuO-NP) are noteworthy in such case because of its low cost and high availability (Dhananasekaran *et al.*, 2016; Mazaheri *et al.*, 2016; Kumar and Upadhyay, 2016; Rohaizad *et al.*, 2020). However, synthesis of conventional metal nanoparticles is not cost-effective and also can cause environmental problem (Sharma *et al.*, 2019). However, green synthesis of nano-particles using plant extracts as reducing and stabilizing agents is simple, cost-effective, and eco-friendly (de Lima Barizão *et al.*, 2020; Chauhan *et al.*, 2020; Mondal *et al.*, 2020). This green synthesis of CuO NPs was done using plants such as *Calotropis procera* leaf extract (Reddy, 2017), and *Punica granatum* leaf extract (Vidovix *et al.*, 2019). In Bangladesh, *Psidium guajava* is abundantly available. This medicinal plant leaves contains phytochemicals which can be use in green synthesis of CuNPs (Varughese *et al.*, 2020; Patil and Rane 2020). Therefore, the aim of this study is to synthesize and characterize the CuNPs using *Psidium guajava* leaf extract and evaluate the photocatalytic activity of biogenic CuNPs to degrade safranine dye.

MATERIALS AND METHODS

Plant materials

Fresh Guava (*Psidium guajava*) leaves were collected from the Germplasm center at Bangladesh Agricultural University, Mymensingh and it was used for phytofabrication of copper nanoparticles.

Chemicals

High purity copper sulfate pentahydrate (CuSO₄·5H₂O), HOOC-COOH, FeCl₃, AlCl₃, DPPH, H₂SO₄, KI, NH₄OH, HCl, NaOH, KBr, Methanol, safranine dye were purchased from Sigma-Aldrich Co. delivered by Z.H. Scientific and Chemicals Mart Company, Bangladesh and used without further purification. The purity was at least 99.5%. The solutions for the metal salts were prepared using de-ionized water.

Methods

Details of experimentation

The experiment was conducted at plant Physiology Laboratory in the Crop Botany Department by following the standard method. Guava leaf was used for Nanoparticles synthesis as described by Juthee *et al.*, (2022). Accordingly, guava leaf extract was selected for phytoconstituent screening and analyzed for antioxidant (DPPH). In addition, guava leaf extract mediated synthesized CuNPs was characterized by FTIR technique and it was applied in photodegradation of safranine dye.

Preparation of the leaf extract

The fresh leaves were washed thoroughly and air dried at room temperature (~25°C). Then, 10 g finely chopped leaves was heated taking in 100 mL of deionized water in a 1000 mL Borosil flask at 80°C for 2 min, before cooling down to room temperature. The yellowish extract was filtered through a Whatman filter paper with a pore size of 0.2 µm and then stored in a refrigerator at 4°C as a stock for the synthesis of CuO nanostructures. The same extract was also used for reduction.

Experiment on Phytoconstituent screening content in guava leaf extract

The analysis of phytochemical constituents in the aqueous leaf extract of *Psidium guajava* was conducted with slight modifications. Phytochemical compounds such as phenolics, tannins, flavonoids, alkaloids, saponins, and anthocyanins were screened using methods described by Mir *et al.* (2013) and others.

Test for Alkaloids

Wagner's reagent was used to detect alkaloids. Three milliliters (3 mL) of the extract were placed into a test tube, followed by the addition of 3 mL of concentrated H₂SO₄. Wagner's reagent, prepared as

2.5 g of iodine (I₂) in 250 mL of 5% potassium iodide (KI) solution, was added dropwise to the acidified extract. The presence of alkaloids was confirmed by the formation of a red-brown precipitate.

Test for Saponins

The frothing test was performed to qualitatively analyze saponins. Five milliliters (5 mL) of the extract were placed into a test tube and shaken vigorously for several minutes. The appearance of stable foam persisting for more than 10 minutes confirmed the presence of saponins.

Test for Phenols

Fifty milligrams (50 mg) of *Psidium guajava* leaf extract were dissolved in 5 mL of alcohol (50 mg/mL) and treated with a few drops of neutral FeCl₃ solution (prepared with NH₄OH and FeCl₃). The sudden appearance of a blue-green or black coloration confirmed the presence of phenols (Obouayeba et al., 2015).

Test for Tannins

To test for tannins, 1 mL of plant extract was placed in a test tube, and 2 drops of 5% FeCl₃ solution were added. The formation of a dirty green precipitate indicated the presence of tannins.

Flavanoid Confirmatory Test

Flavonoids were confirmed using the following tests:

(a) FeCl₃ Test: One milliliter (1 mL) of the *Psidium guajava* leaf extract was mixed with FeCl₃, and observations were recorded.

(b) AlCl₃ Test: One milliliter (1 mL) of the *Psidium guajava* leaf extract was mixed with 5% AlCl₃ solution.

In the FeCl₃ test, the acidified methanol extract turned brown, while the AlCl₃ test produced a blue color, confirming the presence of flavonoids (Harborne, 1998).

Test for Anthocyanin:

Anthocyanins were tested as follows:

(a) Using 2M HCl: One milliliter (1 mL) of the *Psidium guajava* leaf extract was mixed with 2 mL of 2M HCl and heated at 100°C for 5 minutes. Any color changes were recorded.

(b) Using 2M NaOH: One milliliter (1 mL) of the sample extract was mixed with 2 mL of 2M NaOH, and any color changes were observed.

DPPH radical scavenging assay

For the determination of antioxidant activity, DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical scavenging assay was performed according to the modified protocol of (MacDonald-Wicks *et al.* 2006). The reaction mixture was prepared by adding 100µL of different concentrations of the plant solvents extract and synthesized CuNPs with 300µL of methanol and subsequently, 400µL of 0.2 mM concentration of DPPH solution was added. The mixture was then vortexed for 10s and further incubated for 30 min at room temperature. Absorbance was then recorded at 517 nm using DR 6000 UV-Vis spectrophotometer. Ascorbic acid (Vitamin C) was taken as the standard antioxidant and lineared between 10 and 50µg/mL (R² = 0.95). The experiment was done in triplicates. The antioxidant potential of the leaf extracts prepared in different solvents and CuNPs was calculated as the percentage inhibition of DPPH discoloration using the equation below:

$$\text{Per cent Inhibition} = 100 \times \left(1 - \frac{\text{Abs (sample)}}{\text{Abs (blank)}}\right) \dots \dots \dots (1)$$

where, A_{blank} is absorbance of the solution when nothing was added,

A_{sample} is absorbance of the solution when plant extract or CuNPs was added.

Synthesis of copper nanoparticles (CuNPs)

Leaf Extract

A solution of 0.02 M copper sulfate was prepared by weighing 0.499 g of anhydrous copper sulfate using an electric balance and dissolving it in 100 mL of distilled water. To synthesize copper oxide nanoparticles, 30 mL of the prepared copper sulfate solution was mixed with 10 mL of leaf extract. The mixture was stirred using an electric stirrer at 100°C for 10 minutes. During the stirring process, the pH of the solution was adjusted using 0.1 M NaOH solution. As the reaction progressed, the solution's color changed from dark greenish to brownish-black. This color change indicates the formation of copper oxide nanoparticles, consistent with the observations reported by Baur et al. (1996).

Ascorbic acid

Ascorbic acid 1g was dissolved in 20ml double distilled water taking in a beaker. Then 0.05M copper sulphate solution was prepared. Fifty (50) mL copper sulphate anhydrous was added to 15 mL of

ascorbic acid and stirred using electric stirrer for 20 minutes at 70°C temperature. During the stirring process the pH was adjusted by using of 0.2 M NaOH solution drop by drop. Then the yellow color turned to maroon color solution which indicate the formation of copper oxide nanoparticles.

Characterization

Visual observation: The primary detection was carried out by visual observation. The change in colour of solution from blue color to bright brown/red-brown indicated the formation of CuNPs and control (1 mM CuSO₄ solution) remained blue after keeping in bright sunlight for 10 min.

UV-Vis Spectrometer: The optical property of prepared Cu nanoparticles was analyzed via UV-visible (UV-Vis, Perkin Elmer, Lambda 35) absorption double beam spectrophotometer with a deuterium and tungsten iodine lamp in the range from 200–800 nm at room temperature as described by Hossain *et al.*, 2020.

Fourier Transform Infrared (FTIR) Spectroscopy: To investigate the possible reducing and stabilizing agents, FTIR analysis was performed. The functional group of the biosynthesized CuNPs was planned by FTIR as described by Singh *et al.* 2018. Briefly, 1 mg of CuNPs were blended with KBr (300 mg) and the FTIR were measured with an AVATAR 370 FTIR spectrometer (Thermo Nicolet, MA, USA) at a spectral range of 400–4000 cm⁻¹ at BCSIR, Dhaka.

Application of biogenic CuNPs for keeping environment clean

Greenly synthesized copper nanoparticles were evaluated for catalytic degradation ability against safranin dye. A stock solution of 50 µg mL⁻¹ concentration was prepared for safranin dye. Different dilutions of synthesized copper nanoparticles were mixed with constant concentration of dye solution. 1ml of synthesized copper nanoparticles added with 5ml of safranin dye and it was kept for incubation of 40 min at 35°C temperature. Then the solution was centrifuged at 7000 rpm and supernatant was collected in a beaker and the degradation rate of sample was measured by scanning in UV Visible spectrophotometer (Fayaz *et al.* 2010).

Photocatalytic activity of CuO-NPs

The photocatalytic dye reduction ability of CuNPs was performed against safranin under visible light irradiations as described by Divya *et al.* 2018 with slight modifications. Briefly, about 25 mg of CuNPs were added to 100 mL of safranin solution (0.1 mg/100 mL). Control was maintained without adding of CuNPs to the safranin dye. Before to irradiation, the dye was stirred for 30 min in dark conditions to achieve adsorption/desorption equilibrium between the dye and catalyst. After that, the suspension was subjected to irradiations. At every 1h time intervals, 5 mL of safranin dye solution was taken out and centrifuged at 8000 rpm for 5 min, and then the absorbance was measured using UV-Visible spectroscopy. The percentage of activity was calculated from the formula,

$$E (\%) = \frac{C_0 - C_t}{C_0} \times 100 \dots \dots (2)$$

Where E is the degradation percentage, C₀ is the absorbance of dye at before irradiation and C_t is the absorbance of dye after irradiation at different time.

Statistical analysis:

The collected data were statistically analyzed by using Minitab 17 statistical Computer Package Programmer in accordance with the principles of Completely Randomized Design with 3 replications.

RESULT AND DISCUSSION

Qualitative Phytochemical Screening of *Psidium guajava* leaf extract

The qualitative estimation of *Psidium guajava* leaf extract was performed and the results showed the availability of various phyto-chemicals, which are presented in Table 1. Phytochemical analysis exhibits positive result for phenolic, alkaloids, tannins & flavonoids content in the leaf extract inferring its significant properties and shows negative results for saponins and anthocyanins.

Table 1. qualitative phytochemical screening of fresh *Psidium guajava*

Serial No.	Phytochemical	Results
1	Flavonoids	+
2	Alkaloids	+
3	Tannins	+

4	Saponins	-
5	Phenols	+
6	Anthocyanin	-

Antioxidant activity of biogenic synthesis of CuNPs

The antioxidant activity of biogenic synthesis of CuNPs was assessed using DPPH scavenging method, which showed that a compound's reducing power is directly proportional to its antioxidant activity. CuNPs is found to have antioxidant properties and it was $IC_{50} = 65.4 \text{ mg.mL}^{-1}$ by DPPH (Figure1). For the DPPH assays, Ascorbic acid was used as a norm, where IC_{50} value was 31.24 mg.mL^{-1} . The study reveals that *Psidium guajava* mediated CuNPs are effective enough for scavenging free radicals and can be used as a major antioxidant source in donating electron for bioreduction of Cu^{2+} ions. The CuNPs' scavenging behaviour increases as the sample concentrations increase. In compared to other green synthesized nanoparticles, the presence of proteins and amino acids, as well as carbohydrates, flavonoids, glycosides, phenolic compounds, saponins and tannins, results in higher operation. Lower the IC_{50} value, greater is the hydrogen donating potential of the free radical scavengers and thus their antioxidant activity.

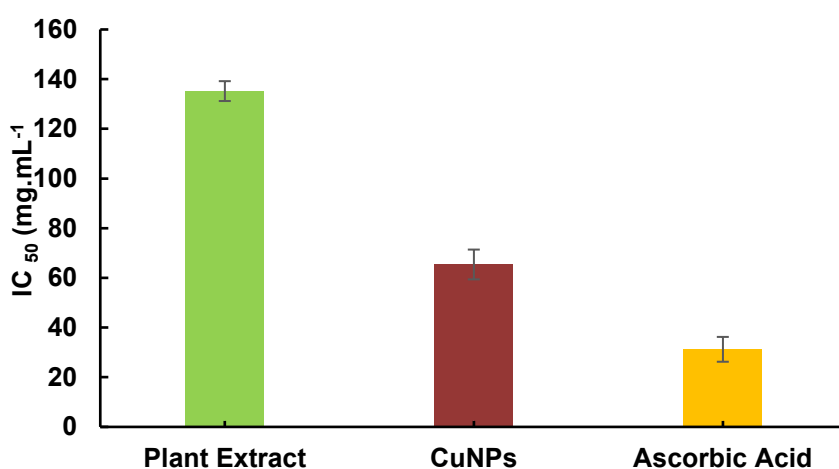


Figure 1 Efficiency of reducing power of plant extract, CuNPs and Ascorbic acid.

Preparation of copper nanoparticles

The reducing power of oxalic acid and ascorbic acid depends both on the concentration of the reducing agents and the reaction temperature. As seen from the Table 2, it is clear that among two reducing agents, ascorbic acid induces slower reduction (20 min). In addition, the amount of ascorbic acid is also less. On adding oxalic acid to the colloid at 70°C , the colour of the colloid changes to maroon within 10 min which indicates the significant reduction.

Table 2 Amount of reducing agent in the formation of stable Cu at different temperature and time

Amount of reducing agent	Temperature & time	Colour of colloid	Possible phase formed/stability
Ascorbic acid (g)			
0.01	$70^{\circ}\text{C}/100^{\circ}\text{C}$ (20 min)	Maroon colloid	Cu, Cu_2O , CuO
0.02	70°C (20 min)	Yellowish brown	Cu_2O
0.05	$70^{\circ}\text{C}/100^{\circ}\text{C}$ (20 min)	Maroon colloid stable	Cu (stable)
Oxalic acid (ml) 70°C (10 min)			
10		Maroon colloid stable	Cu (unstable after one day)
15		Maroon colloid stable	Cu (unstable after one day)
20		Maroon colloid stable	Cu (stable)

Visual Observation of copper nanoparticles

Pure CuSO_4 solution is blue in color and guava leaf extract is light yellow. The color change was noted by visual observation in the test tubes which contains CuSO_4 solution with guava leaf extract.

After adding blue color CuSO_4 solution into the solution that containing colorful plant extract, showed CuNPs signatory color (Figure 2). The color change primarily indicated the formation of CuNps in the solution.

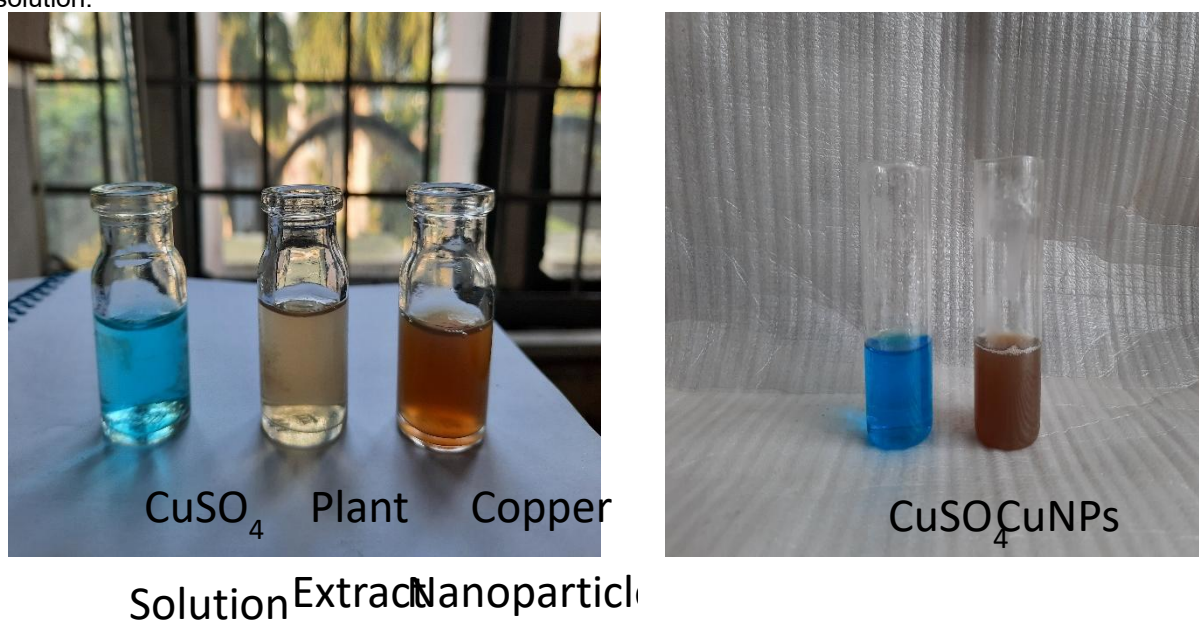


Figure 2 Signatory color of CuNPs after adding colorful leaf extract into blue color CuSO_4 solution.

UV-Vis spectrophotometry

The synthesized copper nanoparticles were characterized by using UV-Vis spectrophotometer and showed maximum absorbance at 650 nm by using guava leaf extract as reducing agent (Figure 3). The change in color of reaction mixture was due to the reduction of copper ions (Cu^{2+}) by aqueous extract of plant materials used in the experiment and it was reconfirmed by a UV-Vis spectrophotometer. As shown in the Table 3, the formation of phytofabricated CuNPs confirmed by presence of the peak ranging from 260 nm to 650 nm. UV-Vis spectrum of guava leaf extracts phytofabricated CuNPs showed the peak at 650 nm (Figure 3). UV-Vis spectrum showed absorption peak at 650 nm which has been taken as an evidence for the formation of CuNPs. Blue CuSO_4 solution turned reddish brown due to the formation of Cu_2SO_4 after the addition of guava leaf extract. It is suggested that the UV-Vis spectra of the resulting colloids on reduction of CuO by reducing agents, a red shift is observed compiled in Figure 3.

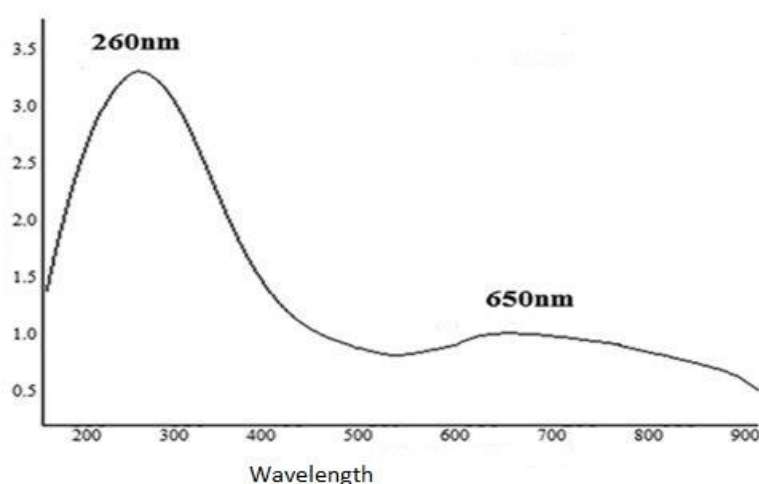


Figure 3. The UV-visible spectrum for green synthesized CuNPs.

Table 3. Guava leaf extracts mediated CuNPs and their λ max values

Materials in cuvette	UV- Absorption(λ max)
<i>Psidium guajava</i>	Flat (without peak)
CuSO ₄	260
CuNPs	650

Fourier Transform Infra Red Spectroscopy (FTIR)

The FTIR spectroscopy was operated to identify the organic functional groups on the surface of CuNPs. The FTIR spectrum provides information to confirm the formation of Cu nanoparticles as shown in Figure 4 in the range of 400–4000 cm^{-1} . The peaks 783, 624 and 530 cm^{-1} denote the different species Cu metal ions. The absorption peak at 1108 cm^{-1} corresponds to the C-O stretching of phenol and alcoholic compounds. The peak 1627 cm^{-1} represents ketone (C=O) functional group in *Psidium guajava* extract indicates the formation of CuNPs. The peak 3437 cm^{-1} denoted to a-OH group present water molecules in the sample, since the nano crystalline materials possess high surface area to volume ratio leading to the absorption of moisture in the lattice.

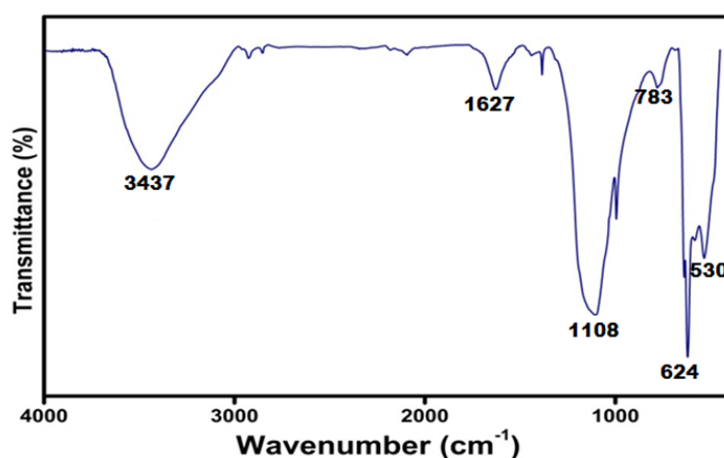


Figure 4 FT-IR analysis of copper nanoparticles synthesized from *Psidium guajava* leaf Photocatalytic degradation.

Application of biogenic CuNPs for keeping environment clean

Control experiments were carried out in the dark (both with and without CuNPs) to rule out any possibility of dye self-degradation, dye adsorption, or NP catalytic activity in the dark. In the absence of Cu nanoparticles, negligible dye degradation was noticed after completion the experiment (Figure 5).

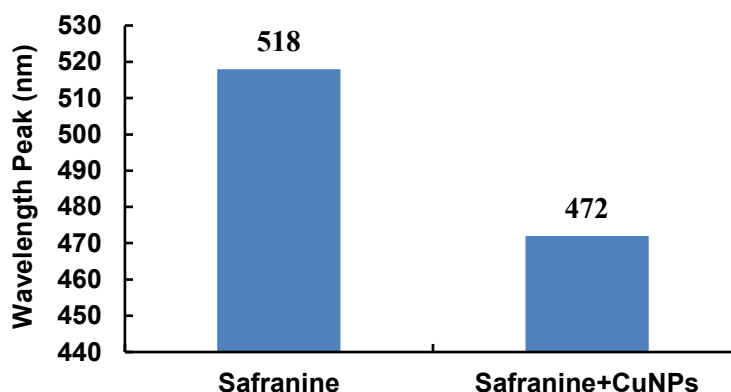


Figure 5 Photocatalytic degradation before and after exposing to sunlight of the reaction mixture consisting of dye and CuNPs.

Photocatalytic activity of CuNPs

Figure 6 depicts the dye degradation of 20 ppm guava leaf extract mediated CuNPs. The removal rate of 97% was attained at 10 mgL⁻¹ dye concentration. The degradation rates were diminished to 69% and 50% for 20 and 30 mgL⁻¹ dye concentrations, respectively. The results clearly expressed that the maximum decomposition of safranine was accomplished when the catalyst amount was of 20 ppm and substrate concentration of 10 mg L⁻¹. It was also found that the absorbance maximum (λ_{\max} = 518 nm) of safranine dye mixture before exposing to solar light but with the increase in illumination time, there was a significant reduction in the absorbance maximum (λ_{\max} = 472 nm instead of λ_{\max} = 518 nm) of the mixture was accomplished in 2h. The result revealed that photocatalytic degradation of safranine dye was successfully done by guava leaf extract mediated biogenic CuNPs.

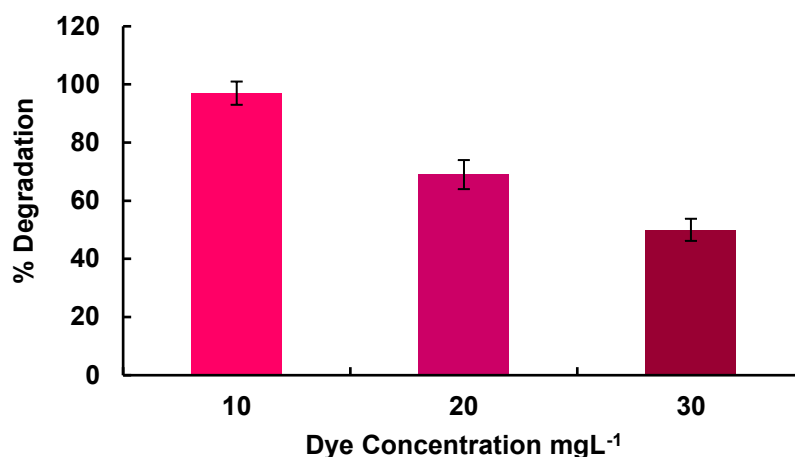


Figure 6 Photocatalytic degradation at different concentration of dye.

CONCLUSION

The green synthesis of CuNPs is a safe alternative to physical and chemical methods. The present study reports for the first time about the plant mediated biosynthesis of CuNPs by using *Psidium guajava* leaf extracts. The formation of biogenic CuNPs was confirmed through visual observation (color change), reconfirmed by UV-Vis spectrophotometry and characterized capping and stabilizing molecules by FTIR spectroscopy. In addition, the biosynthesized CuNPs exhibited strong photocatalytic activity against organic dye (safranine) in the wastewater. Overall, these results revealed that biogenic CuNPs have the potential to photodegrade organic dyes/pollutants by generation ROS or OH radicals. Hence, more research investment and an interdisciplinary team work are therefore required to elevate the plant-mediated biosynthesis method successfully to compete with chemical and physical syntheses of nanoparticles.

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