Green synthesis of copper nanoparticles using leaf extract of Ageratum houstonianum Mill. and study of their photocatalytic and antibacterial activities

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Abstract
The novel copper nanoparticles (CuNPs) were synthesized using aqueous leaf extract of Ageratum houstonianum Mill. (AHLE). The green synthesized AH-CuNPs have a useful dye degradation property in the existence of daylight. The photocatalytic activity of AH-CuNPs was evaluated against an azo dye congo red (CR), whereas, same NPs displayed no effect on other dyes. The CR was completely degraded within 2 h, and the reaction rate was followed by pseudo-first-order kinetics, and the rate constant was recorded $3.1 \times 10^{-4} \text{s}^{-1}$, ($R^2 = 0.9359$). Antibacterial activity of green synthesized AH-CuNPs was studied against gram-negative bacterium Escherichia coli (MTCC no. 40), and a significant growth inhibition was recorded with 12.43 ± 0.233 mm zone of inhibition. The AH-CuNPs were characterized through UV-visible spectroscopy, XRD, SEM, FT-IR, TEM, and zeta particle size analyzer. Ageratum houstonianum mediated green synthesized copper nanoparticles (AH-CuNPs) were cubic, hexagonal, and rectangular in shape, with average size of ~80 nm. The optical band gap was 4.5 eV, which was investigated using UV-visible spectroscopy, and the band gap value revealed that AH-CuNPs were semiconductor materials.

Abbreviations
Cu  Copper
CuNPs  Copper nanoparticles
CuCl₂  Copper chloride
AH  Ageratum houstonianum
AHLE  Ageratum houstonianum leaf extract
AgNPs  Silver nanoparticles
AH-AgNPs  Ageratum houstonianum mediated bio-fabricated silver nanoparticles
UV- vis  UV-visible spectrophotometer
FTIR  Fourier transform infrared spectrum
SEM  Scanning electron microscopy
TEM  Transmission electron microscopy
XRD  X-ray diffraction
Min.  Minutes

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1. Introduction

In recent years, metallic nanoparticles (NPs) have drawn the attention of researchers due to their significant applications in the field of material science, life science, agriculture, and pharmaceutics [1–3]. The amalgamation of biological technique with metal NPs has generated a new area of nanomedicine [4]. The unique characters of NPs like, high yield strength, high surface-to-volume ratio, rigidity, flexibility, specific magnetization, and quantum size are remarkable and contrary to bulk materials with the same chemical composition [5].

Among the metal NPs, copper nanoparticles (CuNPs) have maintained to attain public interest due to its high electrical conductivity, low electrochemical migration, magnificient and contrary to bulk materials with the same chemical composition [6], optical, and catalytic properties [7], being used in sensors [8], solar cells [9], information storage [10], heat transfer systems [11], textiles [12], water treatment [13], and antimicrobial coating material in surgical tools [14]. In addition, the synthesis of CuNPs is cheaper when compared to other noble metal NPs of platinum (Pt), silver (Ag), and gold (Au).

Various physicochemical methods are used for the synthesis of NPs, which include thermal decomposition [15], electrochemical reduction [16], vapor deposition [17], microwave irradiation [18], solvothermal [19], laser ablation [20] and chemical reduction of metal salts [21]. However, use of expensive reagents, lengthy and tedious process, and environmental toxicity are prime concern with these approaches [21]. Conversely, green synthesis of metal NPs follows biological routes involving bacteria, yeasts, moulds, enzymes, agricultural wastes, essential oils and plant extracts [22]. The plant-mediated green syntheses of NPs is a facile, rapid, reliable, cost-effective, eco-friendly and onestep method, and, have a considerable benefit over microbial synthesis due to prolonged process of microbial isolation and their pure culture maintenance. Some earlier reports have also recommended green synthesis approach for copper and copper oxide NPs using Syzygium aromaticum bud extract [25], Ziziphus spinosa-christi fruit extract [26], Azadirachta indica leaf extract [27], Henna leaf extract [28], and Tragacanth gel [29].

Azo dyes are synthetic colouring agents being utilized in a wide range of paper, plastic, tannery, food processing, and cosmetics industries [30]. These dyes were ultimately found their way into water bodies, thereby affecting human health, and causing the death of water ecosystems. The dye contaminants cause skin irritations, allergies, damage to the kidneys, liver, and severe effect on mammalian central nervous system [30]. The non-degradable congo red (CR) dye has mutagenic and carcinogenic properties because of having amine groups [31, 32]. During last few years, scientists have employed several techniques viz. adsorption [31], photocatalytic [1], organic drugs [34], sediments [35], coagulation/floculation [36], and Fenton framework [37], etc to remove these pollutants from fresh water bodies. Degradation of azo dyes in the presence of sunlight by using the specific catalyst for their oxidation or reduction has been gaining attention nowadays [38–41]. Studies on photocatalytic degradation of azo dyes and chemical pollutants by NPs are the primary concern, however, only few reports are available on photocatalytic degradation of CR by biosynthesized CuNPs [42].

Ageratum houstonianum Mill. (Family: Asteraceae) is an annual herb and commonly known as 'Floss flower' or 'blue mink' due to their blue inflorescence and thread like florets. It grows luxuriantly as a weed in Tropical and Sub-Tropical countries. The literature is almost silent on biological properties of A. houstonianum, and very few reports are available only on antioxidant and antibacterial activity of the plant [43, 44]. Synthesis of any metal-NP from this plant has not reported till date.

The present research was undertaken with the objective to synthesize CuNPs from the leaf extract of Ageratum houstonianum (AH) for the first time, characterization of phytosynthesized AH-CuNPs through spectroscopic and microscopic techniques, and further investigations on photocatalytic degradation of synthetic dyes and antibacterial response against Escherichia coli (MTCC No. 40).

2. Materials and methods

2.1. Materials
Copper chloride (CuCl₂), nutrient agar and nutrient broth media were purchased from Himedia (Mumbai, India). Congo red (CR), Methylene blue (MB), Methyl orange (MO), Rhodamine B (Rhb), and reagents/solvents for
phytochemical analyses were purchased from CDH (Mumbai, India). All the chemicals procured were AR grade and used as received. Double distilled water (DDW) was used for the experiments. All the apparatus were washed properly with DDW and dried in the hot air oven. *Ageratum houstonianum* leaf extract (AHLE) was used as a reducing agent for the formation of CuNPs.

2.2. Preparation of leaf extract
The fresh leaves of *A. houstonianum* (figure 1) were washed repeatedly with DDW to expel the residue impurities present on the leaf surface. About 20 g of the leaves were weighed through the digital balance and cut in equal pieces. Chopped leaves were taken into the 500 ml beaker containing 200 ml DDW, boiled at 60 °C for 20 min, and filtered twice through Whatman No. 42. The filtrate was stored at 4 °C for further use [45].

2.3. Phytochemical analysis
The major phytochemicals present in the leaves of *A. houstonianum* were identified following standard protocol with slight modification [46, 47].

**Test for Alkaloids:**
- 1 ml AHLE + 6–8 drops Mayer’s reagent — green precipitate.
- 1 ml AHLE + 1 ml Wagner’s reagent — reddish-brown precipitate.
- 1 ml AHLE + 2 ml Dragendorff’s reagent + 2 ml dil. HCl — orange precipitate.

**Test for Flavanoids**
- 1–2 ml AHLE + few drops neutral ferric chloride solution — blackish-red precipitate.
- 1–2 ml AHLE + few drops basic lead acetate solution — reddish-brown precipitate.

**Tests for Tannins:**
- 1 ml AHLE + 2 ml 5% ferric chloride — greenish-black/dark blue color.

**Test for Phlobatannins:**
- 10 ml AHLE + 2–3 ml 10 % HCl — boiling for 5 min — red precipitate.

**Test for Triterpenes:**
- Equal volume of Chloroform and AHLE shaken with few drops of conc. H₂SO₄ — lower layer turns yellow (Salkowski test).
Equal volume of Chloroform and AHLE + Few drops CH₃COOH + 1 ml conc. H₂SO₄ — deep red at the junction of two layers (Liberman test).

Test for Diterpenes:
• Equal volume of Copper acetate solution and AHLE gives green color on shaking.

Test for Steroids:
• 1–2 ml AHLE + 5 ml chloroform — 1 ml conc. H₂SO₄ added — mixed — reddish lower layer (Salkowski test).

Test for Saponins:
• 5 ml AHLE shaken vigorously to obtain a stable froth — 5–6 drops olive oil was added — formation of an emulsion.

Test for Cardiac glycoside:
• 1 ml AHLE + 1 ml glacial acetic acid — cooled — 2–3 drops ferric chloride + 2 ml of conc. H₂SO₄ along the wall of the test tube — bluish-brown ring at the junction of two layers (Keller Killani test).

Test for Glycosides:
• 1 ml AHLE + 2–3 drops Molisch’s reagent — added few drops conc. H₂SO₄ — formation of reddish-purple ring on junction.

2.4. Green synthesis of AH-CuNPs
Eighty milliliter CuCl₂ (3 mM) was stirred in Erlenmeyer flask for 2 h, and 20 ml of AHLE was added therein. The flask was further stirred for another 24 h at room temperature until the reaction mixture turned in greenish-brown solution. The resultant solution was centrifuged at 10 000–11 000 rpm for 10 min and the pellet was separated as AH-CuNPs.

2.5. Characterization
UV–vis analysis was performed by using a Shimadzu UV-1800 spectrophotometer with 1 nm between 200 to 600 nm of resolution. The FTIR spectra were obtained in the range of 500–4500 cm⁻¹ with Vertex 70 model, Bruker, Germany. The size and morphology of NPs were determined by using SEM (Model: EVO 18; Carl Zeiss, Germany) and TEM (Technai G20FEI). The hydrodynamic size of NPs was determined via dynamic light scattering using Zetasizer Nano ZS (Malvern Panalytical, UK). The examination of the samples was set up through covering the aqueous solution of AH-CuNPs on covered Cu lattices by moderate vanishing and afterward permitted to dry in vacuum at 25 °C for medium-term. XRD studies were conducted using Bruker D8 advanced x-ray diffractometer using Cu Kα (I = 1.54 A).

2.6. Photocatalytic activity
The photocatalytic activity of green synthesized AH-CuNPs was investigated against various dyes like MB, MO, Rh-B, and CR. The dye solutions were made by dissolving 1 mg powder of each dye in 100 ml DDW, and the absorption of dyes was measured through UV-visible spectrophotometer. Approximately, 10 mg of AH-CuNPs powder was added to 50 ml of each dye solution, and exposed to sunlight. A control set of experiment was also designed for the comparative study to determine the changes in color of the dye solutions in absence of AH-CuNPs. The absorption of the dye solutions was recorded at constant time intervals (every 20 min) [45]. The Langmuir- Hinshelwood kinetic model was used to determine the rate of photocatalytic reactions [48, 49]. The rate of reaction was described as follows:

\[ r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \]

The apparent pseudo-first order reaction rate constant, k is given as:

\[ k = \frac{\ln \frac{C_0}{C_i}}{t} \]

A plot of ln \( \frac{C_0}{C_i} \) versus time results in a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k.
2.7. Antibacterial activity
The disc diffusion method was used to investigate the antibacterial activity of the AH-CuNPs. As a test specimen, a gram-negative bacterium *E. coli* (MTCC no. 40) was used. On the disc A, 50 μg ml\(^{-1}\) concentration of AH-CuNPs was soaked, whereas, on disk B 50 μl reference antibacterial agent ciprofloxacin was used as control. The plates were incubated at 37 °C for 24 h and the zone of inhibition was measured [50].

3. Results and discussion

3.1. Phytochemical analysis
The presence of alkaloids, flavonoids, tannins, triterpene, steroids, and saponins was found through the phytochemical analysis of AHEL (table 1). These compounds are supposed to act as stabilizing and capping agents for green synthesis of AH-CuNPs, and also responsible for the reduction of Cu\(^{+}\) to Cu\(^0\). The plant is aromatic in nature and its essential oil was also reported to contain fifty compounds when analysed through GC-MS [51]. In a similar investigation, Zeeshan et al separated bioactive compounds from crude methanol extract of AH [43].

3.2. Green synthesis of AH-CuNPs
*A. houstonianum* leaves were examined to contain the phytochemicals like flavonoids, alkaloids, tannins, terpenes, steroid, and saponins, etc, which are responsible for reducing, capping and stabilization of synthesized AH-CuNPs (figure 2). The mixed solution was stirred for 24 h, and the change in colour of CuCl\(_2\) solution from blue to gleaming greenish due to precipitation of ions confirmed the successful reduction of Cu particles into CuNPs. AH-CuNPs indicate greenish-darker shades, which is due to the surface plasmon vibrations. Color change of reacting solution from bluish brown to dark green using seed extracts of *Punica granatum* and leaf extract of *Ocimum sanctum* was also confirmed by Nazar et al and Heera et al respectively [52, 53].

3.3. Characterization of AH-CuNPs
3.3.1. UV-Vis analysis
After the addition of 20 ml *A. houstonianum* leaf extract in 80 ml of 3 mM CuCl\(_2\) (2:8 ratio) at room temperature, the solution was continuously stirred for 24 h. The CuCl\(_2\) dissolves in water to give rise Cu\(^{2+}\) and 2Cl\(^{-}\). The Cu\(^{2+}\) further dissociates to give zero-valent ions (Cu\(^0\)) with reaction time by the activity of AHLE phyto-compounds, which aggregates to form CuNPs from Cu nuclei [54]. The reaction mixture changed into gleaming greenish color due to precipitation of ions confirmed the successful reduction of Cu particles into CuNPs. AH-CuNPs indicate greenish-darker shades, which is due to the surface plasmon vibrations. Color change of reacting solution from bluish brown to dark green using seed extracts of *Punica granatum* and leaf extract of *Ocimum sanctum* was also confirmed by Nazar et al and Heera et al respectively [52, 53].

![Table 1. Phytochemical analysis of *A. houstonianum* leaf extract.](image)

| S. No. | Phytochemicals | Test | Result |
|-------|----------------|------|--------|
| 1.    | Alkaloids      | Mayer’s test, Wagner test | +ve |
| 2.    |               | Drangendorff test | +ve |
| 3.    | Flavonoids    | Ferric chloride test | +ve |
| 4.    | Tannins       | HCL test | -ve |
| 5.    | Triterpenes   | Salkowski test, Liberman test | +ve |
| 6.    | Diterpenes    | Copper acetate test | +ve |
| 7.    | Steroids      | Salkowski test | +ve |
| 8.    | Saponins      | Foam test | +ve |
| 9.    | Cardiac glycoside | Keller Killani test | -ve |
| 10.   | Glycosides    | Molisch test | -ve |

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3.3.2. XRD analysis

The powdered sample of AH-CuNPs was also characterized by x-ray Diffraction analysis. The diffracted intensities were recorded from 10 to 70 at 2 theta angles. Four different and important characteristic peaks were observed at 2 theta of 16.17, 32.18, 39.79, and 49.78 which corresponding h, k, l, values to the reflection from (020), (002), (130), and (151), respectively (figure 3(b)). The unassigned peaks (*) appeared, are supposed to be associated with the capping agent stabilizing the nanoparticles. The crystalline nature of AH-CuNPs was
suggested by XRD and identical to simple cubic structure. The peak positions of present report are in agreement with literature standards [57].

3.3.3. FT-IR analysis

Figure 4 showed comparative Fourier Transform Infra-red (FT-IR) spectroscopic analysis of AHLE and AH-CuNPs. It was carried out to study the functional groups of phytochemicals present on NPs as adsorbent. The main peaks of the IR spectra, their wave-number and elucidation of probable functional groups are shown in Table 2. It is also apparent from the relative FTIR data that peaks of functional groups are almost similar in both the spectra. Hence, AHLE or their functional groups might be responsible for the reduction of Cu$^{+}$ to Cu$^{0}$ and further stabilization of AH-CuNPs.

| S. no. | AHLE Wave number | Probable functional group | AH-CuNPs Wave number | Probable functional group |
|-------|------------------|----------------------------|-----------------------|---------------------------|
| 1     | 3264.96          | O–H stretch                | 3236.34               | O–H stretch               |
| 2     | 2916.19          | N$^{+}$–H stretch          | 2918.71               | N$^{+}$–H stretch         |
| 3     | 2848.35          | C–H stretching             | 2849.20               | C–H stretching            |
| 4     | 2359.91          | C–O stretching             | 2359.93               | C–O stretch               |
| 5     | 1733.61          | C=O stretching             | 1595.13               | N–H bond                 |
| 6     | 1418.78          | C=C stretch                | 1377.76               | O–H bond                 |
| 7     | 1242.92          | C–O stretch                | 1260.17               | C–O stretch               |
| 8     | 1010.39          | O–C stretching             | 1074.64               | O–C stretching            |
| 9     | 667.88           | Aromatic H bending         | 667.81                | Aromatic H bending        |
| 10    | 517.60           |                             | 597.86                |                           |

Figure 4. FTIR spectra of AHLE and green synthesized AH-CuNPs.

3.3.4. SEM analysis

Morphology and shape of AH-CuNPs were determined by scanning electron microscopic measurements. Green synthesized AH-CuNPs were found in the maximum range of ~200 nm, and their structures were observed in different shapes as shown in figures 5(a)–(d) at 0.5, 1, 2 and 5 μm scales, respectively. These figures interpret that AH-CuNPs are found to be highly scattered with a cubic, hexagonal, and rectangular shape in nature. Among them, few NPs are very much isolated from each other while the majority were in the agglomerated form.
3.3.5. TEM and DLS analysis

To determine the nanoparticle sizes, the AH-CuNPs were characterized by transmission electron microscopy under various magnifications. Figures 5(e)–(f) indicates that AH-CuNPs are agglomerated and the particles have no specific shape. The average particle size of AH-CuNPs was found to be ~80 nm. The size of dispersed AH-CuNPs was also confirmed by DLS analysis (figure 6) with average size in same range. In similar investigations, the extract of Aspergillus sps. synthesized larger CuNPs of 500 nm [58], whereas, a bacterial strain Pseudomonas stutzeri provided CuNPs (50–150 nm) from electroplating waste water [59]. Leaf extract of Artabotrys odoratissimus was also reported to synthesize CuNPs within 115–135 nm [60].

3.3.6. Optical band gap

Figure 3(a) displays the UV visible spectrum of AH-CuNPs and band gap energy was calculated using UV-spectrum following the equation of Tauc’s relation [61].

\[(ahv)^n = A(hv - Eg)\]

Where \(\alpha\) represents the absorption coefficient, \(A\) is constant, \(E_g\) shows the optical band gap energy. \(n\) is the exponent that depends on transition, and \(h\) symbolizes the Planck’s constant. Figure 6(e) shows the optical band
gap which was calculated using Tauc relation by plotting \((ahv)^2\) versus \(hv\), and extrapolating the linear portion of the curve to \((ahv)^2 = 0\). Hence, the optical energy band gap of AH-CuNPs was 4.5 eV and it behaves as semiconductor materials and used as a photocatalyst.

3.3.7. Photocatalytic activity of AH-CuNPs
Since the band gap of AH-CuNPs indicates that these are semiconductor materials, it is therefore investigated the photocatalytic behaviour of AH-CuNPs in presence of different types of organic dyes (MO, MB, CR, and RB) and daylight. In this photocatalytic experiment, CR was more effectively degraded by AH-CuNPs as compared to other dyes (figure 7(d)). The dye degradation reaction by the AH-CuNPs was performed at room temperature and observed through the UV–Visible spectrophotometer at a constant time interval. In the absence of AH-CuNPs, aqueous solutions of dyes were kept into the sunlight and after more than two hours, the color of the dyes was found unchanged. However, on the addition of the catalytic amount of AH-CuNPs to the aqueous solutions of dyes in the presence of sunlight, the color of only CR was changed from red to colorless within two hours (figures 7(a), (b)), whereas, original colour of MO, MB and RB solutions retained unchanged. The efficiency of catalyst was not changed on two fold increase of CuNPs concentration. However, CR degradation decreased by 60% on doubling the initial dye concentration. When, the solutions of CuCl2 and AHLE were mixed separately to CR solution under sunlight, no decolourization was observed. Similarly, the reacting solution of AH-CuNPs and CR did not show any color change in dark. In similar reports, the decolorization efficiencies of CR were found to be 40% and 70%–75% respectively, for ZnO and Aloe baradensis mediated CuO nanoparticles after 2 h [62, 63].

The UV-Vis spectroscopy has shown that the absorption peak was decreased from 1 to 0.15 at 498 nm, the absorption maxima of CR (figure 7(b)). The photocatalytic activity of AH-CuNPs against CR dye followed the pseudo-first-order kinetics. Figure 7(c) showed a good linear graph between \(\ln C_0/C\) versus time. The rate constant of CR is \(3.1 \times 10^{-3}\, \text{s}^{-1}\) and the regression coefficient \(R^2 = 0.9359\) (slope = 0.042) confirmed that the photocatalytic degradation of CR followed the Langmuir–Hinshelwood kinetic model. Therefore, the biosynthesized AH-CuNPs may act as a stable and efficient green catalyst for the degradation of CR under sunlight. The electrons of AH-CuNPs were easily transitioned from Valence Band \((VB)\) to Conduction Band \((CV)\) in presence of sunlight, and degrade the CR with the degradation product as shown in figure 8(a) [64]. ESI-I indicates the possible mechanism for dye degradation by AH-CuNPs against CR.

3.3.8. Antibacterial activity
The significant bactericidal effect of several metallic nanoparticles has been reported, and used for various therapeutic purposes [65, 66]. Antibacterial activity of AH-AgNPs was investigated by the disc diffusion method. AH-AgNPs showed effective antibacterial activity against the gram-negative bacteria \(E.\, coli\). Figure 8(b) showed the zone of inhibition (mm) for disks A and B, corresponding to AH-CuNPs and ciprofloxacin, respectively. Results showed that AH-CuNPs have significant antibacterial activity against \(E.\, coli\) with 12.43 ± 0.233 zone of inhibition (mm ± SE). However, as a positive control, ciprofloxacin showed an inhibition zone of 32.00 ± 0.13 mm. The literature suggests different mechanisms for the antimicrobial activity of metallic NPs. Cytoplasmic membrane disturbance and the leakage of various cytoplasmic biomolecules such as protein, amino acids, and carbohydrates are the main reason for bacterial cell death due to exposure of NPs [67]. Bogdanovic et al suggested that Bacterial cell wall activity induces oxidation of CuNPs to release \(Cu^{++}\) ions,
further reduced to Cu$^+$ following electrostatic attraction with plasma membrane-based reductases. The Cu$^+$ ions easily move across the lipid bilayer into cytosol, producing ROS which leads to lipid peroxidation and oxidation of proteins [68]. Raja et al also reported that antibacterial activity of NPs was due to the high conductivity of treated cells and the release of cellular components [69].

4. Conclusions

Using the advantage of the natural reducing and capping properties of plant extract, the present studies showed an easy and environment-friendly, green synthesis of AHLE-based CuNPs. The synthesis was demonstrated to be successful for the reaction time as well as stability of the synthesized NPs, which exclude external reducing agents. The absorption peak at 326 nm was confirming the formation of stable CuNPs in the reaction mixture. The shape of the NPs with average size of ~80 nm was confirmed by SEM, DLS, and TEM. The AH-CuNPs has effective photocatalytic activity against carcinogenic azo dye CR. The antibacterial activity of AH-CuNPs was studied against gram-negative bacteria E. coli with a remarkable zone of inhibition.
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Conflicts of interest

The authors declare no competing financial interest.

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Figure 8. Schematic of proposed photocatalytic mechanism of AH-CuNPs (a), and antibacterial activity of green synthesized AH-CuNPs (A), and ciprofloxacin (B) against E. coli. (b).
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