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Removal of perilous nitrocompound from aqueous phase using biogenic copper nanoparticles as a catalyst

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The present study mainly deals with the preparation of Cu nanoparticles utilizing *Cocinia grandis* flower extract. Here the flower extract acts as a reducing agent in the formation of Cu nanoparticles. The flower extract reduces the metal ion into metallic nanoparticles and help in the reduction process. A peak appears at 600 nm (UV spectra), establish the formation CuNPs. The synthesized NPs are analyzed using various techniques. As-synthesized CuNPs is utilized as a catalyst for the reduction of noxious nitrocompound.

Keywords: Green process, Nanoparticles, Reduction, Toxic nitrocompounds.

Cu NPs are believed to be cost-effective as compared to other noble metals, such as Ag, Au, and Pt. Hence, they are potentially applied in various fields, such as catalysis, cooling fluids and conductive inks [1-4]. Cu NPs exhibit enhanced nonlinear optical properties because of plasmon surface resonance, which allowed wide applications in optical devices and nonlinear optical materials, such as optical switches or photo chromic glasses[5,6].

Various methods have been reported for the synthesis of CuNPs using highly toxic expensive reagent[7-12]. CuNP has high thermal conductivity and also the production cost is very low as compared to noble metals like silver, gold and platinum. CuNPs preparation using chemical reduction method gives good results; however, utilization of hazardous and costly chemicals makes the process toxic. Biosynthesis is generally found to be better method for the preparation of Cu NPs because it avoids the utilization of toxic substances. In biosynthesis, naturally occurring compounds present in biomass serves as reducing and capping agents for the synthesis of nanoparticles.

Coccinia grandis is a type plant belonging to the Cucurbitaceae (commonly known as ivy gourd). This plant has also medicinal value in curing eczema, tongue sores and cerebral oxidative stress[1]. *Coccinia grandis* contain important raw materials for drug production.

Keeping in view the shortcoming of previous studies, in this article, we report a green method for the synthesis of CuNPs without using any toxic reagents. In this method, CuNPs were synthesized using *Cocinnia grandis* flower extract. The novelty of the method is that flower extract served the reducing agent for the formation of CuNPs. Form the literature, the phytochemical flavanoid present in the flower extract acts as a reducing agent for the formation in the CuNPs. Further it was confirmed by FT-IR spectra also. The synthesized CuNPs showed an excellent catalytic activity for the reduction toxic nitrocompound.

Experimental Section

Material

AR grade of Copper sulphate ($CuSO_4.5H_2O$), 4-nitroaniline (4-NA) and sodium borohydride ($NaBH_4$) were obtained from Merck India Limited and used without any further purification. The stock solution of 4-NA was prepared with ultrapure water.

Preparation of *Coccinia grandis* flower extract

Locally available freshly flower of *Coccinia grandis* was taken from Silchar Assam (India) and washed thoroughly with distilled water to remove dust particles. After washing, flowers were boiled and refluxed in a round bottomed flask with a requisite amount of distilled water. The flower extract was collected and filtered through a Whatmann filter paper no. 41 to remove any small fibers of flower extract.

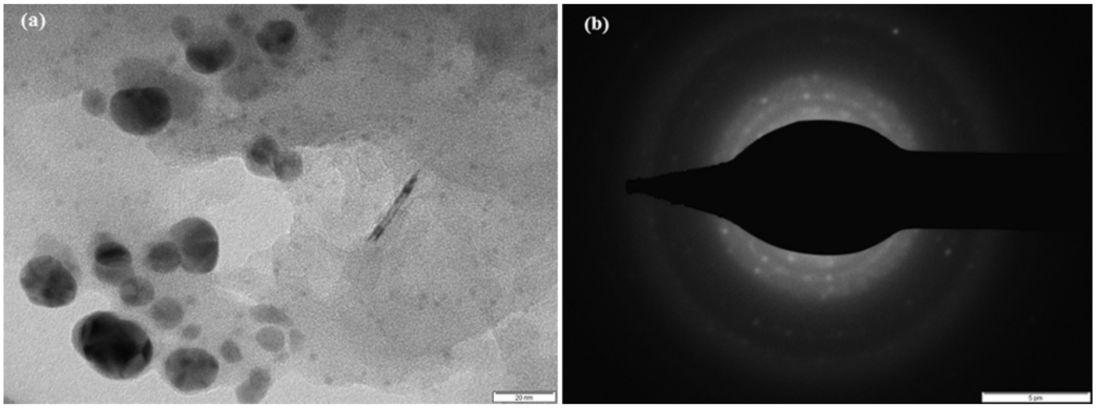


Fig. 1— (a-b) TEM and SAED pattern of the synthesized CuNPs.

Synthesis of copper nanoparticles using *Coccinia grandis* flower extract

Flower extract (10 mL) and $CuSO_4.5H_2O$ (0.01M, 10 mL) solution were mixed together in a 100 mL beaker and stirred at room temperature for 6 h. After 6 h, the reaction mixture was heated at 60°C for 10 min. The green colour of the reaction mixture was changed into brown colour indicates the formation of copper nanoparticles.

Catalytic activity of as-synthesized copper nanoparticle

In a standard quartz cuvette, having 1 cm path length, 2 mL of water and 60 µL of (6.07×10^{-3} M) nitro compound, 4-nitroaniline was taken separately and the cuvette was then placed in a UV–Visible spectrometer and absorbance was recorded. A total of 350 µL of aqueous $NaBH_4$ (0.1 M) was added into nitrocompound solution and absorbance was recorded. Thereafter, 150 µL of 10% CuNPs solution was added to that mixture and absorbance was recorded till the peak of the nitrocompound was completely vanished.

Characterization of copper nanoparticles

As-synthesised Cu NPs were characterized by P-XRD method using Phillips X'Pert PRO diffractometer with CuK radiation of wavelength 1.5418. For the morphology study, FT-IR spectroscopy and elemental study, JEM-2100 Transmission Electron Microscope, Bruker Hyperion 3000 spectrometer, FEG-SEM, Model: JSM-7600F, Magnification: x25 to 1,000,000a techniques have been used.

Results and Discussion

Morphology study

TEM studies showed the morphology and size of NPs**.** Figure 1(a-b) displays TEM and SAED patterns of as-synthesized CuNPs. The calculated average particle size (obtained from TEM image) of synthesised NPs was found to be 18-20 nm. As-synthesized Cu NP is polycrystalline in nature as evidenced from SAED pattern and supports the unit cell structure of CuNPs.

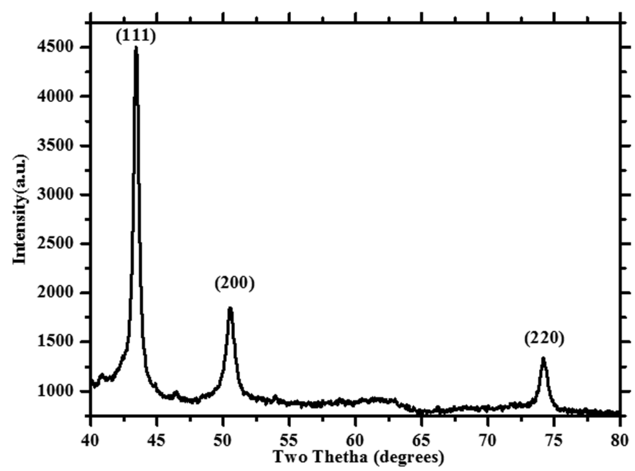


Fig. 2 — XRD peaks of the synthesized CuNPs.

UV-Visible spectroscopy

Noble metal nanoparticles have a unique property like surface Plasmon resonance (SPR). In copper nanoparticles, a spectrum had seen at around 550-650 nm due to the SPR property of Cu NPs.

Powder X-Ray Diffraction (P-XRD) studies

The appearance of peaks at 44.5, 50, and 74^0 (Fig. 2) corresponded to the lattice planes of (111), (200), (220) reflected face centered cubic (fcc) structure of Cu NPs (JCPDS file: 71-4610). The average crystallite particle sizes of as-synthesized nanoparticles was determined using Scherrer equation ($d = K\lambda/\beta\ \cos\theta$); where d is the average crystalline particle size; K is a dimensionless shape factor, with a value close to unity (0.9); λ is the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM); θ is the Bragg angle of the crystal plane. The calculated average crystallite particle size of Cu NPs was found to be 22.8 nm.

FT-IR spectroscopy

Figure 3 (a-b) presents the FT-IR spectra of flower extract and CuNPs. FT-IR spectra of flower extract showed sharp absorption peaks located at 3300, 2360 and 1640 cm^{-1}. The appearance of an intense absorption band around 3300 cm^{-1} corresponds to hydrogen bonded O-H stretching vibrations of alcohols and phenols and also to the presence of amines N-H group in flower extract. The peaks at 2360 and 1641 cm^{-1} were attributed to O-CH_3 and >C=O stretching. The peak 3300 cm^{-1} shifted to 3315 cm^{-1} after the formation of NPs, which may indicate the –OH group involved in the formation of nanoparticles.

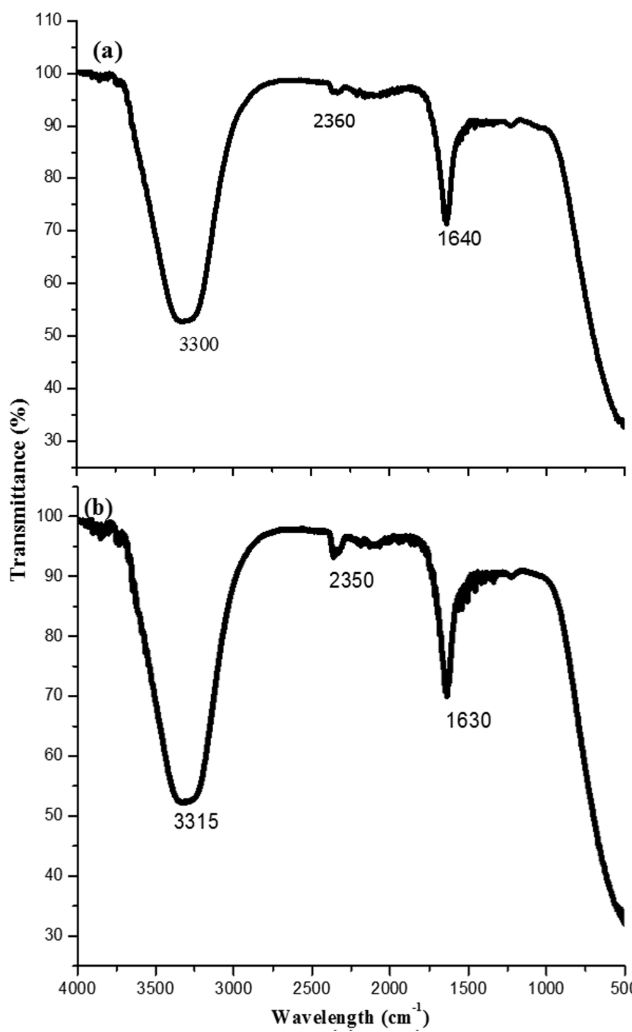


Fig. 3 — (a-b) FT-IR spectra of *Coccinia grandis* flower extract and synthesized Cu nanoparticles.

Catalytic study of Cu NPs for reduction of 4-NP

The catalytic property of Cu NPs were studied by carrying out reduction of 4-nitroaniline (4-NA) into amino compound in aqueous medium using $NaBH_4$ as a reducing agent.

When 4-NA was treated with $NaBH_4$ aqueous solution in presence CuNPs as a catalyst, a new peak was appeared at 300 nm. The appearance of new peak is due to the formation of 4-phenylenediamine. The characteristic peak for 4-NA was decreased with increase in time and simultaneously a new peak was appeared at 300 nm. Figure 4 (a) represents the absorption spectra of the reduction of 4-aminoanilne using copper nanoparticles. Approximately, 97.9%

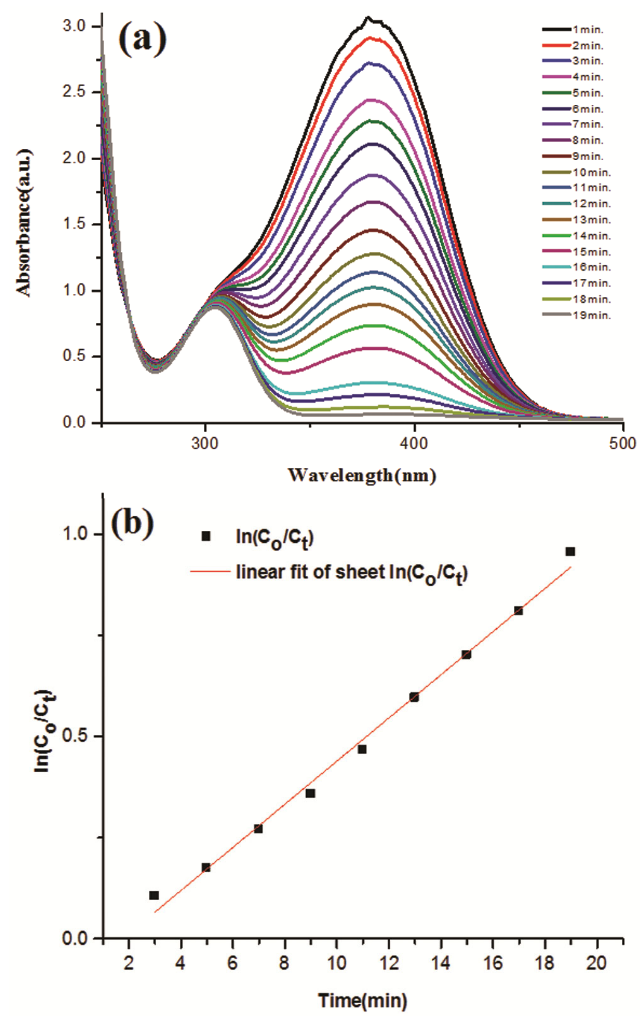
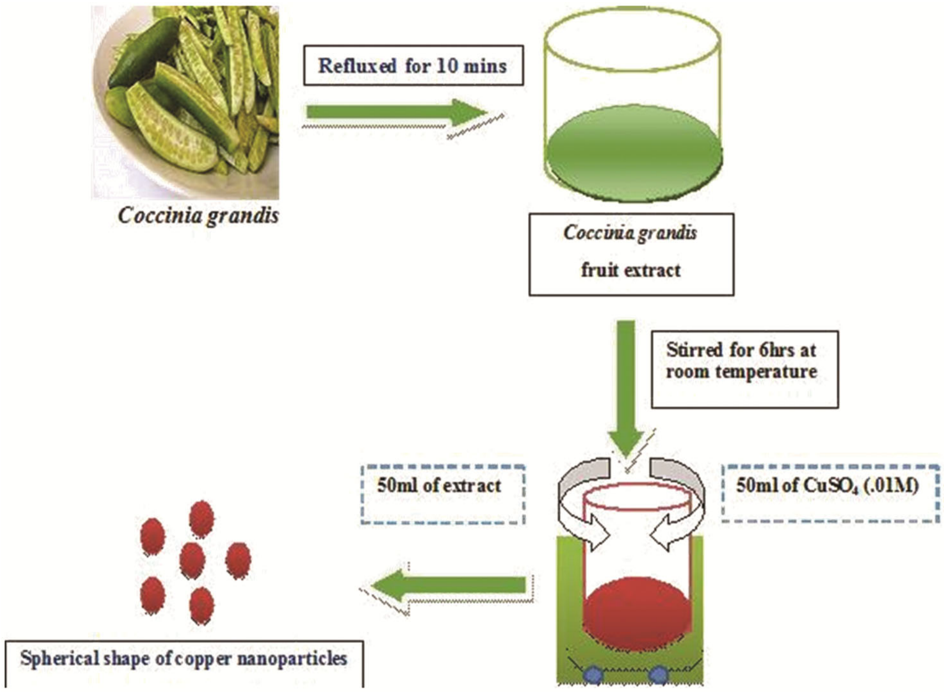


Fig. 4 — (a-b) Absorption spectra of reduction of para-nitroaniline using CuNPs as a catalyst in presence of $NaBH_4$ in aqueous medium and plot of ln [C_0/C] versus reduction time.



Scheme 1— Schematic representation of mechanism for the reduction of 4-NA using CuNPs as a catalyst.

reduction of 4-NA was reduced within 19 min. using Cu nanoparticles. The reduction also followed the pseudo first order kinetics (Fig. 4b) and rate constant was found to be 3.1×10^{-2} min^{-1}.

Mechanism of nitrocompounds reduction using Cu NPs as a catalyst

The reduction process consists of the following steps.

In the first step, an adsorption process was occurred between reactants and surface of the nanoparticles. Here, BH_4^- gets adsorbed on the surface of the as-synthesised Cu NPs and transfer surface hydrogen to the nanoparticles surface. Desorption takes place in second step and forms product on the surface of the nanoparticles. As soon as the final products (amino compounds) undergoes desorption, metal surface is set free for catalytic cycle. The probable mechanism for the reduction of 4-nitroaniline using Cu NPs as a catalyst was shown in Scheme 1[13-14].

Conclusion

In this article, a green process was developed for the synthesis of Cu nanoparticles using *Coccinia grandis* flower extract. The as-synthesized CuNPs were used as a catalyst for the reduction of para-nitroaniline. The result showed an exceptional catalytic activity of CuNPs (as a catalyst) for reduction process.

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