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Green Synthesis and Characterization of Copper Nanoparticles and Their Applications

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ABSTRACT

In the present work, copper nanoparticles have been synthesized by green method, using *Syzygium cumini* plant leaf extract as reducing agent. The biosynthesized CuNPs were characterized using UV-Vis analysis, X-ray diffraction analysis (XRD) and Transmission Electron Microscopy (TEM) analysis. TEM image shows that the synthesized CuNPs were spherical in shape with a mean diameter of 4.68 nm. The electrochemical activity of copper nanoparticles was studied by cyclic voltammetry. The CuNPs showed excellent catalytic activity in the reductive degradation of indigo carmine and methyl red dye.

1. Introduction

Nanotechnology is one of the powerful technologies and it is being applied in all fields, because of their small size (10^{-9} m) and large surface area. Nanoparticles offer a larger surface-to-volume ratio than the corresponding bulk materials. The unique physical and chemical properties of nanoparticles as compared to that of bulk material [1] are due to a strong interplay between elastic, geometric, and electronic parameters. Nanoparticles are prepared in many ways such as physical, chemical and green method. Green synthesis method was found to be the best method when compared to the other methods such as chemical reduction, photochemical reduction, electrochemical reduction, heat evaporation etc.,[2]. Biological synthesis is one of the bottom up approach for synthesis of metal nanoparticles. In this approach the microorganism, plants and animal source are used as reducing agent [3-6].

The advantages of green synthesis over other methods are low cost, simplicity, use of less temperature, the usage of less toxic materials, moreover it is compatible for medical and food applications [7]. Many researchers used green synthesis methods for different metal nanoparticles due to their growing need of eco-friendly processes. Copper nanoparticle is one of the commonly used material for their electrical, optical, catalytic, biomedical and antibacterial applications among various metal particles such as gold, silver, iron, palladium, zinc and quantum dots [8]. It can give more yields in mild reaction conditions when compared to other traditional catalysts.

Green synthesis of CuNPs using nontoxic and inexpensive materials like curd, milk, and herbal extracts such as tamarind and lemon juice as capping agents was reported by Sastry et al., [9]. CuNPs have attracted much attention of researchers due to its application in wound dressings and biocidal properties [10]. Due to these properties CuNPs are used in processes such as gas sensors, catalytic process, high temperature superconductors and solar cells [11]. In this study CuNPs have been synthesized using leaves extract of *Syzygium cumini* as a reducing agent.

2. Experimental Methods

2.1 Materials

In the present work all the chemicals used are of analytical grade and were obtained from E-Merck chemicals. Whatman no.1 filter papers are used for filtration purpose. Double distilled water was used for dilution purpose. All glassware were washed well, rinsed with double distilled water and dried in hot air oven before starting the experiment.

2.2 Preparation of Syzygium cumini Leaves Extract

The leaves of *Syzygium cumini* was collected and the fresh leaves were washed well with double distilled water and cut into small pieces. About 5 grams of cut leaves were weighed and transferred into 250 mL beaker containing 100 mL of water. This was boiled for about 20 minutes and the extract was filtered through whatman filter paper. The filtrate was collected and stored in refrigerator for further purpose.

2.3 Biosynthesis of Copper Nanoparticle

5 mL of *Syzygium cumini* leaves extract and 10 mL of 1 mM $CuSO_4$ solution were taken in a 100 mL beaker and the total volume was made upto 25 mL using double distilled water. The solution was kept in a heating magnetic stirrer heated at 70 °C for 20 minutes. After 20 minutes the colour changed from light colour to dark brown colour which indicated the formation of CuNPs.

2.4 Characterization

UV–Vis spectral studies of CuNPs was monitored on a JASCO V-600 spectrophotometer. TEM analysis was performed by using a PHILIPS CM 200 instrument operated at operating voltages 200 kV, resolution 2.4 Å. Shimadzu (IR Tracer-100) instrument was used for recording FT-IR spectra. Electro-catalytic activity was studied in the electrochemical analyzer, CH Instruments, Electrochemical workstation model 660C.

3. Results and Discussion

3.1 UV-Vis Spectra

UV-Vis spectrum of CuNPs is shown in Fig. 1. The peak observed at 301 nm indicates the formation of CuNPs [12, 13]. The peak is also intense which shows that the particles are small in size and are easily dispersed in the solvent.

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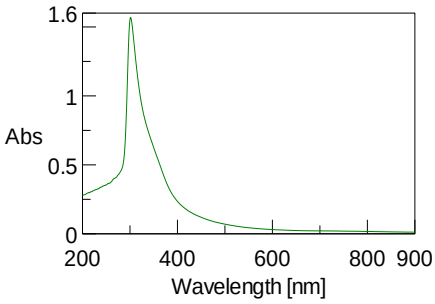

Fig. 1 UV-Vis spectra of CuNPs synthesized from the extract of *Syzygium cumini leaves*

3.2 FTIR Analysis

Fourier transform infrared spectroscopy gives data of functional groups present in compounds in the extract that interact with metal ions.

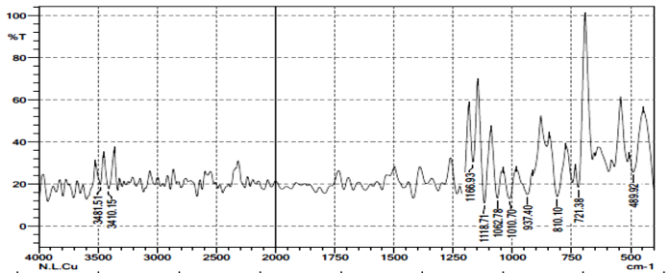

Fig. 2 FTIR spectrum of CuNPs synthesized using *Syzygium cumini* leaves extract

The FTIR spectrum of CuNPs synthesized using *Syzygium cumini* leaves extract is shown in Fig. 2. Peak 3410, 3481 cm^{-1} corresponds to O-H or N-H stretching. The peak at 1633 cm^{-1} is due to presence of C=O stretching [14]. The peak at 1166 cm^{-1} shows C-O stretching of phenol and alcoholic compounds. The peak at 810 cm^{-1} is due to aromatic C-H bending the peak at 721 cm^{-1} is due to O-H out of plane deformation in aromatic phenol. The peak at 663 cm^{-1} is due to aromatic C-H bending. The peak at 489 $cm^{-1}$is due to metal- carbon stretch. The FTIR analysis suggests that the CuNPs might be surrounded by organic molecules such as polyphenols, alkaloids and terpenoids, as already reported [15]. The phenolic constituents present in plant leaves extract are responsible for the reduction of copper ions to copper nanoparticle.

3.3 Transmission Electron Microscopy Analysis

TEM image of copper nanoparticles synthesized using *Syzygium cumini* leaves at different magnifications are shown in Fig. 3. The CuNPs are spherical in shape with particles in size range 2.75 – 6.58 nm with a mean diameter of 4.68 nm. A faint thin layer around the surface of copper nanoparticles may be due to the presence of polyphenolic compounds from *Syzygium cumini* leaves extract, which act as capping agent.

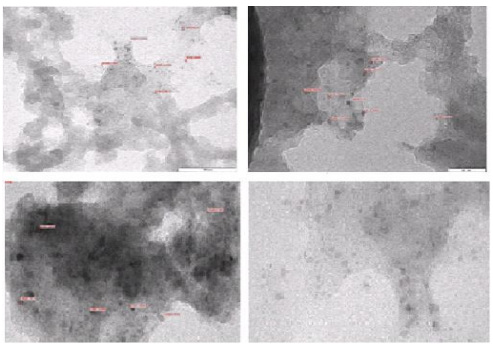

Fig. 3 TEM images of CuNPs synthesized using *Syzygium cumini* leaves

3.4 Cyclic Voltammetry

The cyclic voltammogram was run between the potential range of –1.0 and 1.0 V at the scan rate 75 mVs^{-1} to study the electrochemical behaviour of CuNPs on Glassy Carbon Electrode. The cyclic voltammogram of CuNPs at pH 1 is shown in Fig. 4. Anodic peaks at -0.15 V, 0.45 V and a cathodic peak at -0.35 V shows there is oxidation and reduction, and the reaction is found to be reversible. The high value suggests that the CuNPs can be used as a redox catalyst.

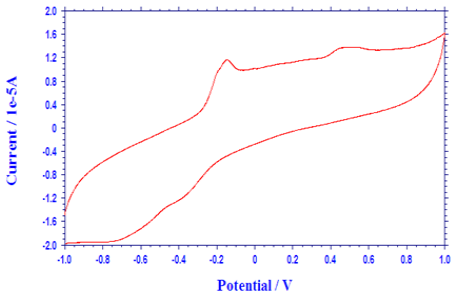

Fig. 4 Cyclic Voltammogram of CuNPs synthesized using *Syzygium cumini* leaves extract

3.5 Applications

3.5.1 Degradation of Indigo Carmine

The catalytic activity of synthesized CuNPs was monitored by using Indigo Carmine (IC) dye as a test compound. The progression of the catalytic degradation of indigo carmine dye can easily be examined by decrease in optical density at 610 nm, as shown in Fig. 5a UV-Vis spectra of IC (100 µM) and $NaBH_4$ (10 mM) mixtures in the absence of CuNPs showed only a small increase of degradation with time, as shown in Fig. 5a. The degradation of dyes by other metal nanoparticles have also been reported in literature [16]. However, the reductive degradation observed after addition of CuNPs catalyst in the same sample solutions were highly enhanced. The process of degradation of IC dyes as shown in Fig. 5b. It was also observed that the reaction rate of IC degradation with CuNPs enhanced the degradation efficiency when compared with the results of the control test.

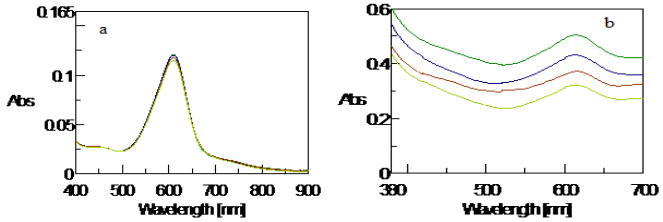

Fig. 5 UV spectra for IC degradation a) in absence and b) in presence of CuNPs

3.5.2 Degradation of Methyl Red

The catalytic degradation of Methyl Red (MR) dye can easily be examined by decrease in absorbance at 520 nm, as shown in Fig. 6. UV-Vis spectra of methyl red (100 µM) and $NaBH_4$ (10 mM) mixtures in the absence of CuNPs showed only a small increase of reductive degradation with time, as shown in Fig. 6a. However, the reductive degradation after addition of CuNPs in the same sample solutions was complete within 3 mins, as shown in Fig. 6b. It was also observed that the reaction rate of MR degradation with CuNPs enhanced the degradation efficiency when compared with the results of the control.

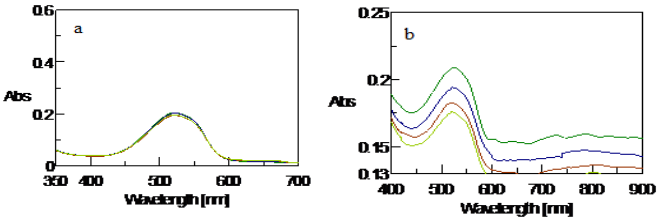

Fig. 6 UV spectra for MR degradation a) in absence and b) in presence of CuNPs

4. Conclusion

The copper nanoparticles were successfully synthesized by using *Syzygium cumini* leaves extract as reducing agent which provides cost effective method for synthesis of CuNPs. The copper nanoparticles were characterized using UV-spectrophotometer, FTIR, TEM and CV. From the FTIR analysis the functional groups in the leaf extract which are responsible for the reduction of copper ions into metallic CuNPs were identified. The synthesized CuNPs were spherical in shape as seen in TEM images. From CV, the redox property of CuNPs was proved. The catalytic activity of synthesized CuNPs was studied by degradation of indigo carmine and methyl red dye.

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