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GREEN SYNTHESIS OF COPPER OXIDE NANOPARTICLES USING COFFEE, *Piper Nigrum,* AND *Coriandrum Sativum* AND ITS APPLICATION IN PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE DYE

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ABSTRACT

This study focuses on the green synthesis of nanoparticles and its utilization in the development of nanotechnology for promoting environmental sustainability. Copper Oxide nanoparticles are synthesized using plant extracts of Coffee, *Piper Nigrum*, and *Coriandrum Sativum* containing bio-components acting as reducing agents to reduce 1M Copper Sulphate ($CuSO_4.5H_2O$) solution., for further formation of Copper Oxide nanoparticles. Instrumental techniques were adopted to characterize the synthesized Copper Oxide nanoparticles, Viz. UV-visible spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). These biosynthesized Copper Oxide nanoparticles were employed as catalysts for the photocatalytic degradation of Methylene blue dye, resulting in a very effective and feasible photocatalyst.

Keywords: Copper Oxide Nanoparticles, Green Synthesis, Plant Extract, Photocatalytic Dye Degradation, Methylene Blue.

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INTRODUCTION

Nanoparticle research has gained increasing interest due to its unique properties such as electrical conductivity, toughness, and ductility, increased hardness and strength of metals and alloys, and luminescent efficiency of semiconductors.[1] Metal oxides such as Copper Oxides (CuO) have attracted attention mostly because of antimicrobial[2,3], and biocide properties which can be used in many biomedical applications. Apart from the earlier mentioned applications Copper-based nanoparticles also showed advantageous usage in cancer detection[4], as nanofluids in heat transfer systems[5], and as catalyst[6], photocatalysts.[7,8] Mainly, Copper based nanoparticles are less expensive as compared to other widely studied nanoparticles like Silver and Gold. The synthesis of nanoparticles using plant extract comes with great advantages due to the availability of materials, eco-friendly approach[9], safer alternative[10], simple methodology, and low cost.[11] The principal mechanism in such a synthesis method is the role of phytochemicals present in the plant extracts, which act as reducing agents to reduce aqueous metal ions.[12] It can be noted that various water pollutants like dyes are of major concern as far as water safety is concerned. Among the various applications and advantages of metallic nanoparticles, photocatalytic degradation of numerous pollutants like dyes can be achieved using nanoparticles as photocatalysts.[13,14] In this research work, the green synthesis of Copper Oxide nanoparticles was reported using plant extracts of coffee, *Piper Nigrum,* and *Coriandrum Sativum* which are easily available in our day-to-day life and household. Methylene blue dye is used as a model for the water-contaminant dye. Using sunlight and synthesized Copper Oxide nanoparticles as a catalyst, the degradation of Methylene blue dye was studied.

EXPERIMENTAL

Chemicals

Copper Sulphate ($CuSO_4.5H_2O$), Double distilled water.

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Preparation of 1M Copper Sulphate $CuSO_4.5H_2O$) Solution: Weighed accurately 62.42g of Copper Sulphate ($CuSO_4.5H_2O$) in a 250 ml volumetric flask dissolved in double distilled water and diluted up to the mark with double distilled water.

Plants Used

Coffee: Finely grounded coffee powder (Nescafe classic manufactured by Nestle India Limited).
Piper Nigrum: Seeds of *Piper Nigrum* were washed and dried thoroughly followed by grinding into a fine powder using a mortar and pestle.
Coriandrum Sativum: Seeds of *Coriandrum Sativum* were washed and dried thoroughly followed by grinding into a fine powder using mortar and pestle.

Preparation of Plant Extracts

Three extracts were used to produce Copper oxide nanoparticles. 20g fine grounded powders of coffee, *Piper Nigrum,* and *Coriandrum Sativum* each were weighed, separately added to 200 ml of double distilled water, and heated at around 80°C for 30 minutes in a water bath. Each of these mixtures was filtered separately. The filtrates were stored for further use in a refrigerator (in a cold condition).

Synthesis of Copper Oxide Nanoparticles using Coffee extract, *Piper Nigrum* extract, *and Coriandrum Sativum* Extract

In 200 ml of each, coffee extract, *Piper Nigrum* extract, *and Coriandrum Sativum* extract were taken separately. 50 ml of 1M Copper Sulphate ($CuSO_4.5H_2O$) solution was added dropwise to each extract while stirring on the magnetic stirrer. During the addition of the Copper Sulphate solution, the gradual change in the color of the solution was observed from brown to dark green visually indicating the formation of nanoparticles. The solutions were stirred for about 1 hour for completion of the reduction reaction and were kept aside for 24 hours. These solutions were then centrifuged at 4000 rpm with washings of double distilled water. The solid precipitate obtained was collected and oven dried for 2 hours at 50°C to 60°C. The dried powder was obtained from three different extracts and used for further analysis.

Characterization of Copper Oxide Nanoparticles and Photocatalytic Dye Degradation

UV- Visible Spectroscopy Analysis

The synthesized Copper Oxide nanoparticles were characterized by thermo scientific evolution 201 UV-visible spectrophotometers, to determine the absorption.

Fourier Transform Infra-Red Spectroscopy Analysis (FTIR)

Fourier Transform Infra-Red Spectroscopy (FTIR) analysis was used to determine the find entities along with functional groups which are associated with the synthesized nanoparticles. Here Thermo Scientific Nicolet iS5 instrument was used using the KBr pellet method.

Scanning Electron Microscopy Analysis (SEM)

To determine the shape and size of the synthesized nanoparticles Scanning Electron Microscopy imaging was used with ZEISS EVO 18 special edition instrument, at the voltage of 20.00 kV.

Photocatalytic Degradation of Methylene Blue Dye

Methylene blue dye was used as a model system for the photocatalytic degradation experiment. 5mg of synthesized Copper Oxide nanoparticles were added to 250 ml of 5 ppm Methylene blue solution. This solution mixture was exposed to direct sunlight for the process of photocatalytic degradation to occur. The absorption of this solution mixture was measured at the time interval of 20 minutes using Thermo scientific evolution 201 UV-Visible spectrophotometers. The absorbance of Methylene blue dye before and after the addition of nanoparticles was compared. This experiment was carried out using green synthesized Copper Oxide nanoparticles from all three plant extracts.

RESULTS AND DISCUSSION

UV- Visible Spectroscopy Analysis

Nanoparticles in the reaction mixture were excited by light absorption at different wavelengths due to surface plasmon resonance (SPR) to give respective peaks. in the wavelength range from 200 nm to 600 nm to determine the absorption. The synthesized nanoparticles from coffee, *Piper Nigrum,* and *Coriandrum*

Sativum plant extracts showed broads peaks at 286.20 nm, 279.79 nm, and 260.77 nm respectively as shown in Fig.-1(a), Fig.-1(b), Fig.-1(c); which corresponds to Copper Oxide. Thus, it was confirmed that the Copper Oxide nanoparticles were formed using the three plant extracts.[15]

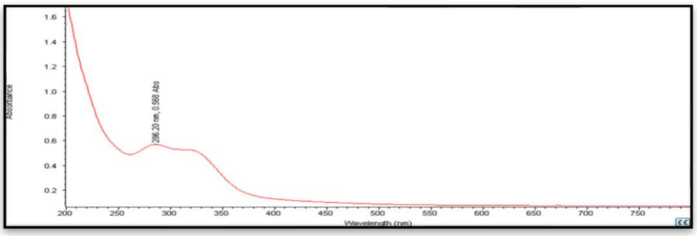

Fig.-1: (a) UV-Visible Spectra of synthesized Copper Oxide Nanoparticles from Coffee extract

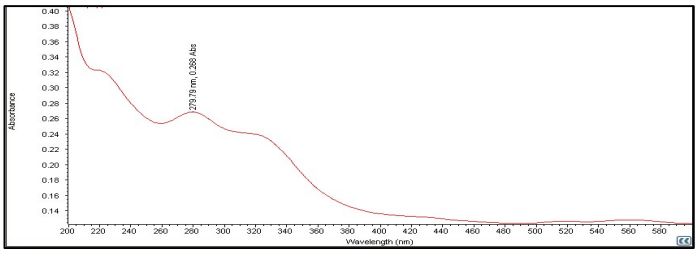

Fig.-1: (b) UV-Visible Spectra of synthesized Copper Oxide Nanoparticles from *Piper Nigrum* extract

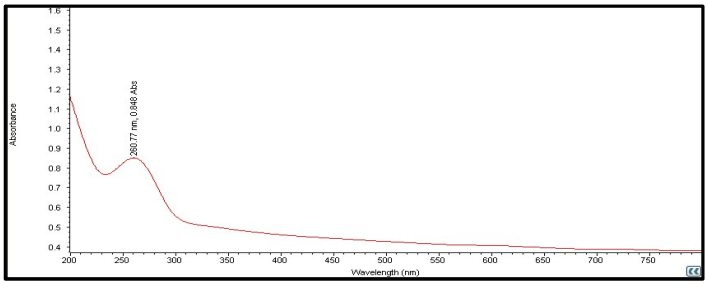

Fig.-1: (c) UV-Visible Spectra of Synthesized Copper Oxide Nanoparticles from *Coriandrum Sativum* extract

Fourier Transform Infra-Red Spectroscopy Analysis

Copper Oxide Nanoparticles from Coffee Extract

The FTIR spectrum of synthesized nanoparticles showed bands at 3417.83 cm^{-1}, 2928.92 cm^{-1}, 1638.21 cm^{-1}, 1126.95 cm^{-1}, 439.69 cm^{-1} (Fig.-2(a). The band observed at 3417.83 cm^{-1} indicates the –OH group. The band at 2928.92 cm^{-1} corresponds to C-H stretching in alkanes and aldehydes, whereas the band at 1638.21 cm^{-1} was assigned to carbonyl and carboxylic (C-O) stretching. The band at 1126.95 cm^{-1} presence of amine groups due to the plant origin of the sample. The absorption peak obtained at 439.69 cm^{-1} in the spectra corresponds to Cu-O stretching.[16,17,18]

Copper Oxide Nanoparticles from *Piper Nigrum* Extract

The FTIR spectrum of synthesized nanoparticles showed bands at 3409.45 cm^{-1}, 2920.54 cm^{-1}, 1638.21 cm^{-1}, 1146.51 cm^{-1}, 435.74 cm^{-1} (Fig.-2(b1) and Fig.-2(b2). The band observed at 3409.45 cm^{-1} indicates the –OH group. The band at 2928.92 cm-1 corresponds to C-H stretching in alkanes and aldehydes, whereas the band at 1638.21 cm^{-1} was assigned to carbonyl and carboxylic (C-O) stretching. The band at 1146.51 cm^{-1} presence of amine groups due to the plant origin of the sample. The absorption peak obtained at 435.74 cm^{-1} in the spectra corresponds to Cu-O stretching.[16,17,18]

Copper Oxide Nanoparticles from *Coriander Sativum* Extract

The FTIR spectrum of synthesized nanoparticles showed bands at 3431.80cm^{-1}, 2912.16cm^{-1},1627.03cm^{-1}, 1110.09 cm^{-1}, and 431.77 cm^{-1} (Fig.-2c). The band observed at 3431.80 cm^{-1} indicates the –OH group. The

band at 2912.16 cm^{-1} corresponds to C-H stretching in alkanes and aldehydes, whereas the band at 1627.03 cm-1 was assigned to carbonyl and carboxylic (C-O) stretching. The band at 1110.09 cm^{-1}presence of amine groups due to the plant origin of the sample. The absorption peak obtained at 431.77 cm^{-1} in the spectra corresponds to Cu-O stretching.[16,17,18] The presence of these functional groups as shown in the spectra (Fig.-2(a), Fig.-2(b1) and Fig.-2(b2), Fig.-2(c)) play a very important role in the synthesis of Copper Oxide nanoparticles.

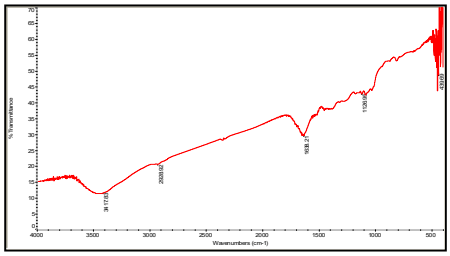

Fig.-2: (a) FTIR Spectra of Synthesized Copper Oxide Nanoparticles from Coffee Extract

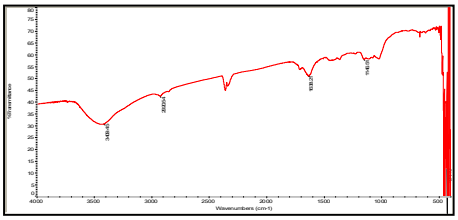

Fig.-2: (b1) FTIR Spectra of Synthesized Copper Oxide Nanoparticles from *Piper Nigrum* Extract

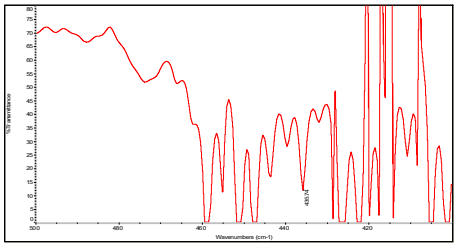

Fig.-2: (b2) FTIR Spectra of Synthesized Copper Oxide Nanoparticles from *Piper Nigrum* Extract

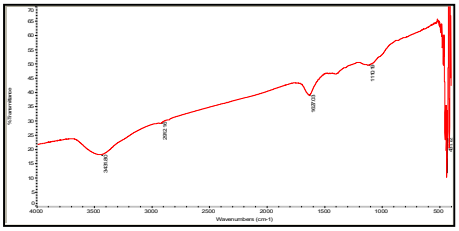

Fig.-2:(c) FTIR Spectra of Synthesized Copper Oxide Nanoparticles from *Coriandrum Sativum* Extract

Scanning Electron Microscopy Analysis

The synthesized nanoparticles were subjected to Scanning Electron Microscopy (SEM) which showed the formation of nanoparticles within the nanometer range below 100 nm. It was observed that Copper Oxide nanoparticles prepared by Coffee extract (Fig.-3(a) were in the agglomerated state. The SEM images of Copper Oxide nanoparticles synthesized by *Piper Nigrum* extract (Fig.-3(b)) and *Coriandrum Sativum* extract (Fig.-3(c)) indicated the formation of spherical-shaped Copper Oxide nanoparticles.[16,19,20]

Photocatalytic Degradation of Methylene Blue Dye

The photocatalytic degradation of Methylene blue dye on the addition of green synthesized Copper Oxide nanoparticles from Coffee extract (Fig.-4. (a)), *Piper Nigrum* extract (Fig.-4.(b)), *Coriandrum Sativum* extract (Fig.-4.(c)), was obtained using UV-visible spectra. These spectra showed a gradual decrease in the absorption of the Methylene blue dye with an increase in time, thus decreasing the peak intensity of spectra. The numerical data for the decrease in the absorption of the Methylene blue dye are shown in Table-1,

Table-2, and Table-3. This decrease in absorption confirmed the effectiveness of the synthesized nanoparticles in terms of the successful degradation of the Methylene blue dye.

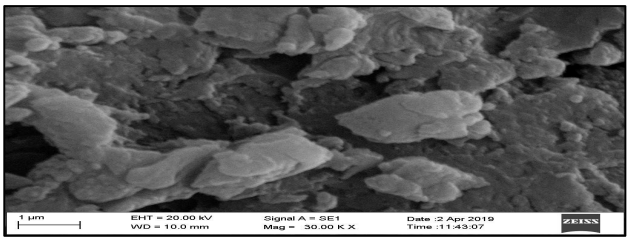

Fig.-3: (a) SEM Image of Synthesized Copper Oxide Nanoparticles from Coffee Extract

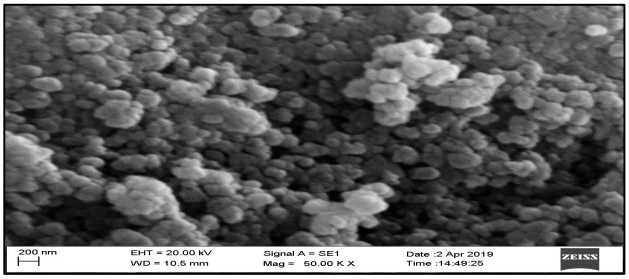

Fig.-3: (b) SEM Image of Synthesized Copper Oxide Nanoparticles from *Piper Nigrum* Extract

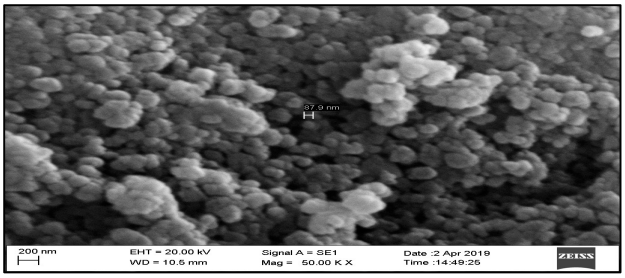

Fig.-3: (c) SEM Image of Synthesized Copper Oxide Nanoparticles from *Coriandrum Sativum* Extract

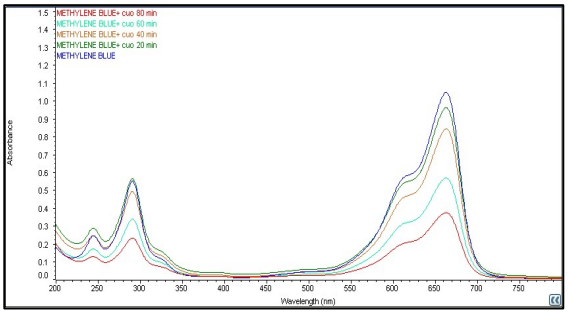

Fig.-4 :(a) UV-Visible Absorption Spectra of for Photocatalytic Degradation of Methylene Blue Dye Using Synthesized Copper Oxide Nanoparticles from Coffee Extract

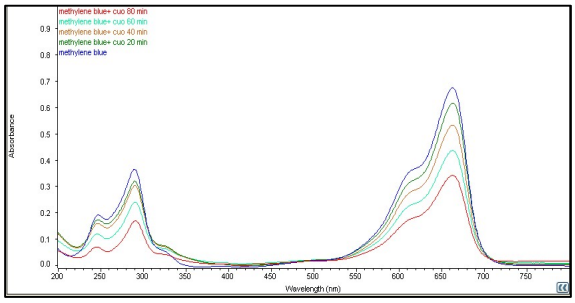

Fig.-4: (b) UV-Visible Absorption Spectra of for Photocatalytic Degradation of Methylene Blue Dye Using Synthesized Copper Oxide Nanoparticles from *Piper Nigrum* Extract

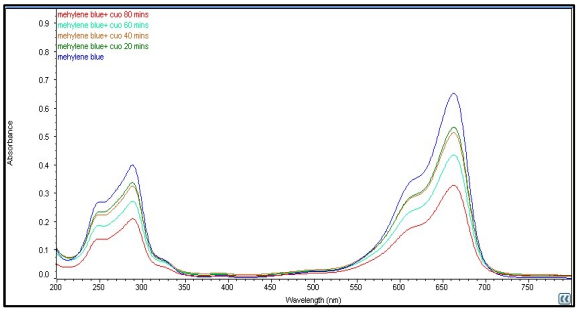

Fig.-4: (c) UV-Visible Absorption Spectra of for Photocatalytic Degradation of Methylene Blue Dye Using Synthesized Copper Oxide Nanoparticles from *Coriandrum Sativum* Extract

Table-1: The Numerical Data for Decrease in the Absorption of the Methylene Blue Dye using Synthesized Copper Oxide Nanoparticles from Coffee Extract

Solutions	Time(Min.)	Absorbance(nm)
Methylene blue dye	0	1.389
Methylene blue dye + CuO np's	15	1.167
Methylene blue dye + CuO np's	30	1.134
Methylene blue dye + CuO np's	45	0.941
Methylene blue dye + CuO np's	60	0.693

Table-2: The Numerical Data for the Decrease in the Absorption of the Methylene Blue Dye Using Synthesized Copper Oxide Nanoparticles from *Piper Nigrum* Extract

Solutions	Time(Min.)	Absorbance(nm)
Methylene blue dye	0	1.375
Methylene blue dye + CuO np's	15	1.322
Methylene blue dye + CuO np's	30	1.022
Methylene blue dye + CuO np's	45	0.830
Methylene blue dye + CuO np's	60	0.677

Table-3: The Numerical Data for the Decrease in the Absorption of the Methylene Blue Dye Using Synthesized Copper Oxide Nanoparticles from *Coriandrum Sativum* Extract

Solutions	Time(Min.)	Absorbance(nm)
Methylene blue dye	0	1.372
Methylene blue dye + CuO np's	15	1.176
Methylene blue dye + CuO np's	30	1.097
Methylene blue dye + CuO np's	45	0,879
Methylene blue dye + CuO np's	60	0.682

CONCLUSION

Eco-friendly, green synthesis of Nanoparticles is the desired process of synthesis in the field of Nanoscience and Nanotechnology due to being a low-cost process, less toxic, and environment-friendly method. This study for green synthesis of Copper Oxide Nanoparticles using Coffee, *Piper Nigrum,* and *Coriandrum Sativum* extracts showed all these aspects and can be adapted for bulk production of Copper Oxide nanoparticles providing cost convenience. The Copper Oxide nanoparticles synthesized using the three extracts were analyzed and characterized using UV-Visible spectroscopy, Fourier Transform Infra-Red spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). The reduction of Copper Sulphate to Copper Oxide nanoparticles was confirmed by UV-visible spectroscopy. The confirmation stretching bonds and presence of functional group was obtained using Fourier Transform Infra-Red spectroscopy (FTIR). Scanning Electron Microscopy (SEM) images determined the size and morphology of the synthesized Copper Oxide nanoparticles. In the study of photocatalytic degradation of Methylene blue dye where synthesized Copper Oxide nanoparticles were used as a catalyst in presence of sunlight effectively degraded the dye with a periodic increase in time, proving that Copper Oxide nanoparticles could be used as an

efficient photocatalyst and can be used in the future application towards the pollution control and water purification.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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