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Research Article

Investigate the Potential Applications of Copper Nanoparticles Synthesized from Extracts of Brassica Juncea, Cuminum Cyminum, Cinnamomum Verum, Laurus Nobilis, As Photocatalysts, Antimicrobial Agents and Antioxidants

Nilam A Patil¹, Prof. Prakash D Patil^{2*}

¹Assistant Professor, Department of Chemistry, Fergusson College (Autonomous), Pune-411004.

^{2*}Principal, Department of Chemistry, Dr. Arvind Telang ACS college, Nigadi, Pune-411044

***Corresponding Author:** Prof. Prakash D Patil

***Email:** pdp1111@gmail.com

Abstract:

Due to its many applications, green production of copper nanoparticles is currently a popular area of study. Researchers have numerous options to investigate additional application areas due to the broad scope of nanoparticle research. Our current study uses widely accessible Indian spices like *Laurus nobilis*, *Cuminum cyminum*, *Cinnamomum verum*, and *Brassica juncea* to synthesize copper nanoparticles. Research was conducted on the stability of the produced copper nanoparticles and their characterization using a variety of methods, including UV-visible spectroscopy, FTIR, XRD, FESEM, and HRTEM. Copper nanoparticles breakdown of methyl orange dye showed their photocatalytic efficacy when exposed to sunlight, and as a result, they can be used as a tool in purifying processes along with antimicrobial and antioxidant properties.

Keywords: Nanoparticles, Copper nanoparticles, Green synthesis, Photocatalysis, Antioxidant, Antibacterial activity

***Author of Correspondence: Email:** pdp1111@gmail.com

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1. Introduction:

Copper nanoparticles (CuNPs) have gained significant attention in recent years due to their unique physical, chemical, and electronic properties, which are distinct from those of bulk copper. These properties make them ideal candidates for a variety of applications, including catalysis, sensors, electronics, and biomedical fields. The journey of copper nanoparticles begins with the fundamental understanding that materials often exhibit novel behaviors at the nanoscale. The concept of nanotechnology emerged in the 1950s, but it was not

until the 1980s that the synthesis and applications of nanoparticles, including those of copper, began to draw significant scientific interest. Early research focused on the preparation and characterization of nanoparticles, primarily through physical methods such as laser ablation and sputtering^{1,2,3}.

In the 1990s, the development of chemical synthesis techniques enabled more controlled fabrication of CuNPs, which led to a broader exploration of their properties and applications. Notably, the introduction of green chemistry methods in the 2000s provided more

sustainable and environmentally friendly alternatives to traditional chemical synthesis methods, further expanding the potential uses of CuNPs in industries ranging from electronics to medicine^{4,5,6}.

Today, copper nanoparticles are considered among the most promising materials due to their cost-effectiveness, abundance, and excellent catalytic activity, particularly in organic reactions and energy storage systems. Despite the progress in understanding their behavior and applications, challenges remain in optimizing their synthesis and stability for large-scale applications. This paper explores the synthesis, properties, and current trends in the utilization of copper nanoparticles, as well as their potential future in various technological advancements⁷.

2. Experimental

2.1 Materials and methods: All required chemicals were purchased from Sigma-Aldrich and Merck. All chemicals were used without purification.

The current study focuses on the synthesis of nanomaterials, outlining different methods such as precipitation, sol-gel, and solvothermal techniques are there but we more focused on green synthesis. It briefly introduces each synthesis route along with its underlying principles. The study also provides an overview of characterization techniques including UV-Visible, XRD, FTIR, particle size analysis, FESEM and HRTEM, explaining their fundamentals and applications for the physicochemical analysis of synthesized nanomaterials.

2.2 Plant materials: The spices of Brassica juncea, Cuminum cyminum, Cinnamomum verum, Laurus nobilis were collected from Savitribai Phule University, Pune, Maharashtra, India in January 2024 (Fig. 1).

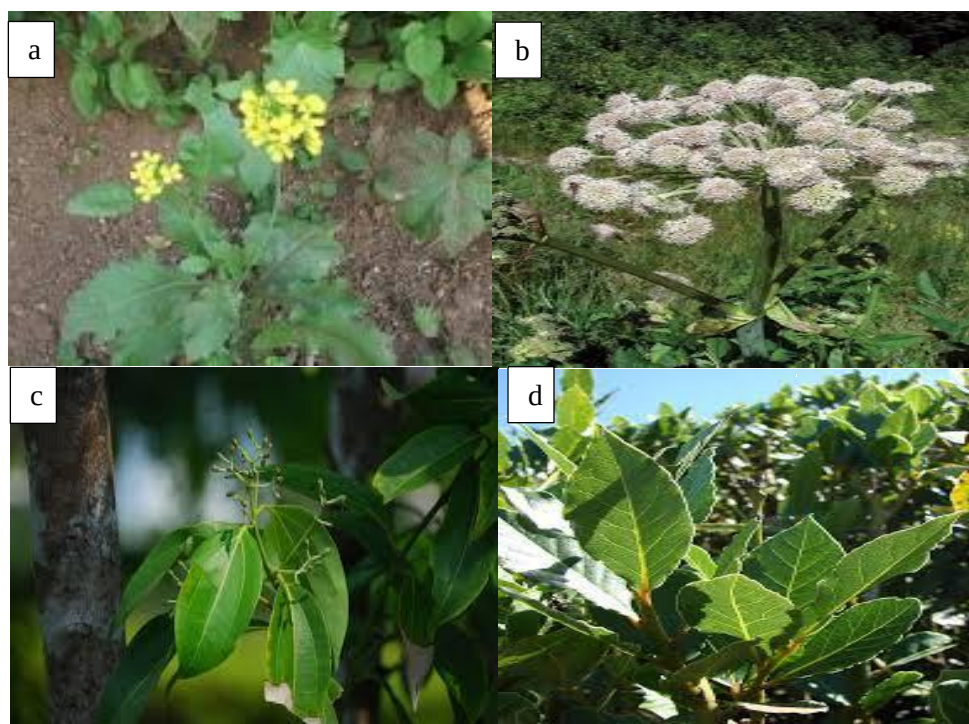


Fig.1 (a) Brassica juncea , (b) Cuminum cyminum (c) Cinnamomum verum, (d) Laurus nobilis

2.3 Extract preparation-

The extract of Brassica juncea, Cuminum cyminum, Cinnamomum verum, Laurus nobilis were used for green synthesis of CuNPs. To remove debris and related dust, fresh spices were washed with double distilled water (DDW) and cut into very fine pieces before being dried in the presence of sunlight. 5 g of the spices were immersed in 100 mL distilled water and the spices were stirred for 30 min at 50–60°C. Furthermore, the extract of the spices was kept at room temperature for cooling, filtered using Whatman (41) filter paper and used for the synthesis of the CuNPs. Then it was kept at 4°C for further uses.

2.4 Synthesis method-

The Copper Sulfate was dissolved in 1000 ml deionized water to obtain concentration of 1 mM CuSO₄.

2.4.1 Synthesis of Copper nanoparticles (CuNp's)-

In an Erlenmeyer flask, Copper Sulfate solution (CuSO₄) was stirred for 2 minutes, and then extract of spices was added to the mixture and the mixture was heated at 60–70° with constant stirring for 25–30 min. During the reaction, the colour of the solution mixture turned from yellow to brown, indicating the formation of the CuNPs, and this was also confirmed by UV-Vis spectroscopy measurements. Afterwards, the final mixture was centrifuged at 1000–1100 rpm and the CuNPs were separated from the mixture. Finally, the

solution was decanted and the blackish-brown powder of copper nanoparticles (CuNPs) were collected. (Fig.2)

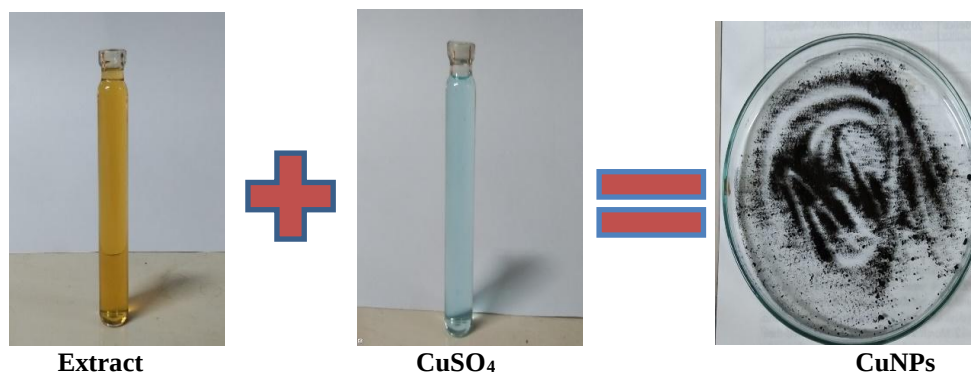


Fig.2 Synthesis of Cu Nanoparticles from Spices

3. Characterization:

The crystal structure of the CuNPs was measured by X-ray diffraction (XRD) at room temperature using a D8 Advance BRUKER diffractometer equipped with Cu K α (1.54060 $^{\circ}$ A) as the incident radiation. The Scherrer equation was used for the calculation of the crystal size. The Scherrer equation was $D = \frac{K}{b} \cos \theta$, where $K = 0.9$, D $\frac{1}{4}$ crystal size ($^{\circ}$ A), θ $\frac{1}{4}$ wavelength of the Cu-K α radiation, and b $\frac{1}{4}$ corrected half-width of the diffraction peak. The IR spectra were recorded on a SHIMADZU FTIR-8400S spectrometer at room temperature. The fine structure of the prepared samples was analysed by Field Emission Scanning Electronic Microscopy (FESEM) (Carl Zeiss Germany, Model Supra-40). Energy-dispersion X-ray spectroscopy (EDX) of the

nanoparticles was carried out on a Sigma ZEISS, Oxford Instruments Field Emission Scanning Electron Microscope. Size of prepared sample was analyzed by - Transmission Electron Microscope 200 kV (TEM 200 kV) (Make JEOL, Model JEM 2100F). The photocatalytic activities were investigated using a UV-visible spectrophotometer (UV-1800, Shimadzu).

3.1 UV-Visible spectroscopy of CuNPs from Spices

UV-Visible spectra of CuNPs for

- Brassica juncea (mustard) (CuNPS1)
- Cuminum cyminum, (Cumin) (CuNPS2)
- Cinnamomum verum (Cinnamon) (CuNPS3)
- Laurus nobilis (Bayleaves) (CuNPS4),

Table 1. Band gap energy from UV-Visible spectroscopy

Sample	Maximum wavelength(nm)	Band gap energy (eV)
CuNPS1	630	1.98
CuNPS2	630	1.98
CuNPS3	630	1.98
CuNPS4	630	1.98

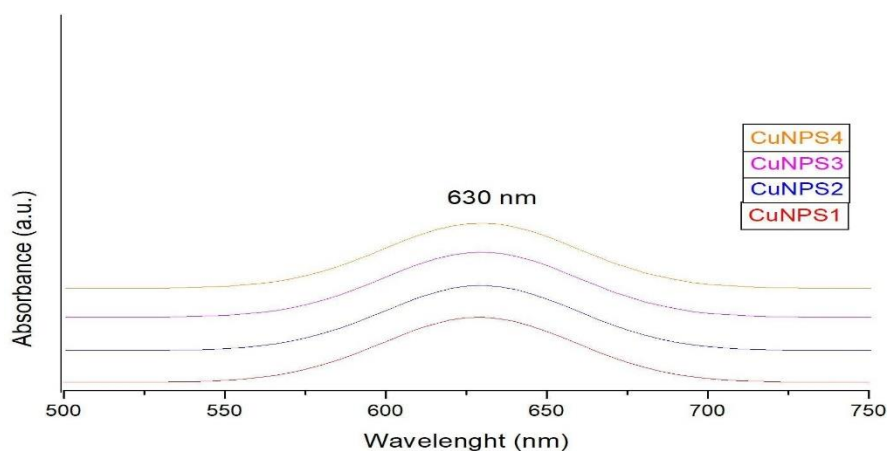


Fig. 3 UV-Visible spectra of CuNPs from Spices

The SPR peak in the visible range confirms the presence of CuNPs. As shown in Fig.3 the SPR band of the nanoparticles in aqueous solution showed peak absorbance at 630 nm for the spices extracts, with the

energy band gap of 1.98eV as shown in Table1.

The spectra showed the presence of primary amine stretching and aromatic amine groups in the capping agent of green synthesized nanoparticles^{6,7}.

3.2 FTIR spectra of CuNPs from Spices:

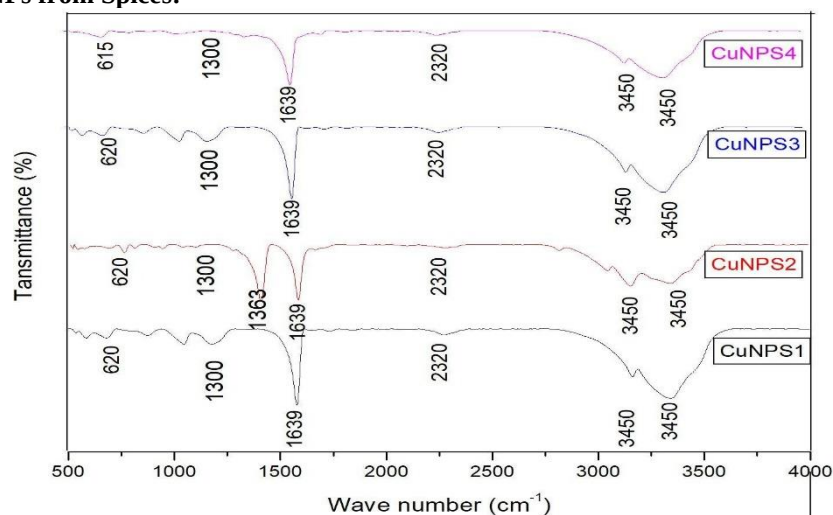


Fig. 4 FTIR spectra of CuNPs from Spices

Spices range of 4,000 to 500 cm^{-1} . It could be evident from the figure the presence of an amine vibration band at 3450 cm^{-1} representing a primary amine (N-H) stretching, in addition, the presence of bands at 1300 cm^{-1} in the FTIR spectra suggested the capping agent of green synthesized nanoparticles possesses an aromatic amine groups with specific signatures of amide linkages between amino acid residues in the proteins in the

infrared region of the electromagnetic spectrum, as reported by Shaligram et al. While the stretching frequency 1639 cm^{-1} belongs to aromatic carbonyl frequency which acts as stabilizing agent on the surface of NPs. The spectral data recorded revealed two types of vibrations (i.e., stretching and bending) in the wavelength^{8,9,10}.

3.3 XRD spectra of Spices AgNPs

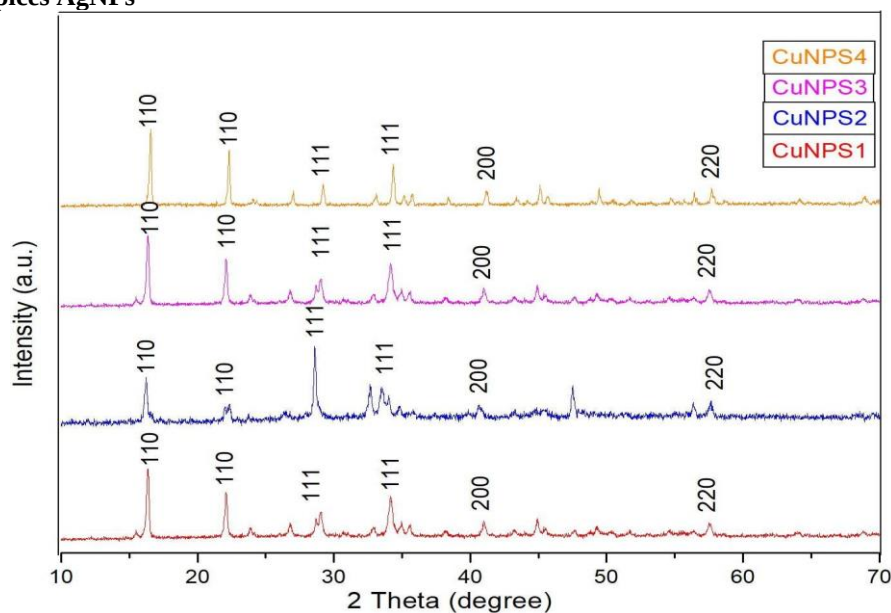


Fig 5 XRD spectra of CuNPs from Spices

The XRD pattern shows intense peaks in the whole spectrum of 2θ values ranging from 10 to 70. Intense peaks were observed at 2θ values (110) at 16°, (110) at 22°, (111) at 29°, (111) at 34°, (200) at 42.3°, (200) at 57.4° planes for copper nanoparticle, respectively which are in accordance with the crystal planes of the CuNPs

FCC with JCPDS no 04-0836. XRD confirmed the crystalline nature of CuNPs. The average crystallite size is estimated to be 15.01nm calculated using Debye Scherrer's formula. The sharp peaks suggest that Copper nanoparticles are good crystallized^{11,12,13,14}.

3.4 FESEM images of CuNPs from Spices:

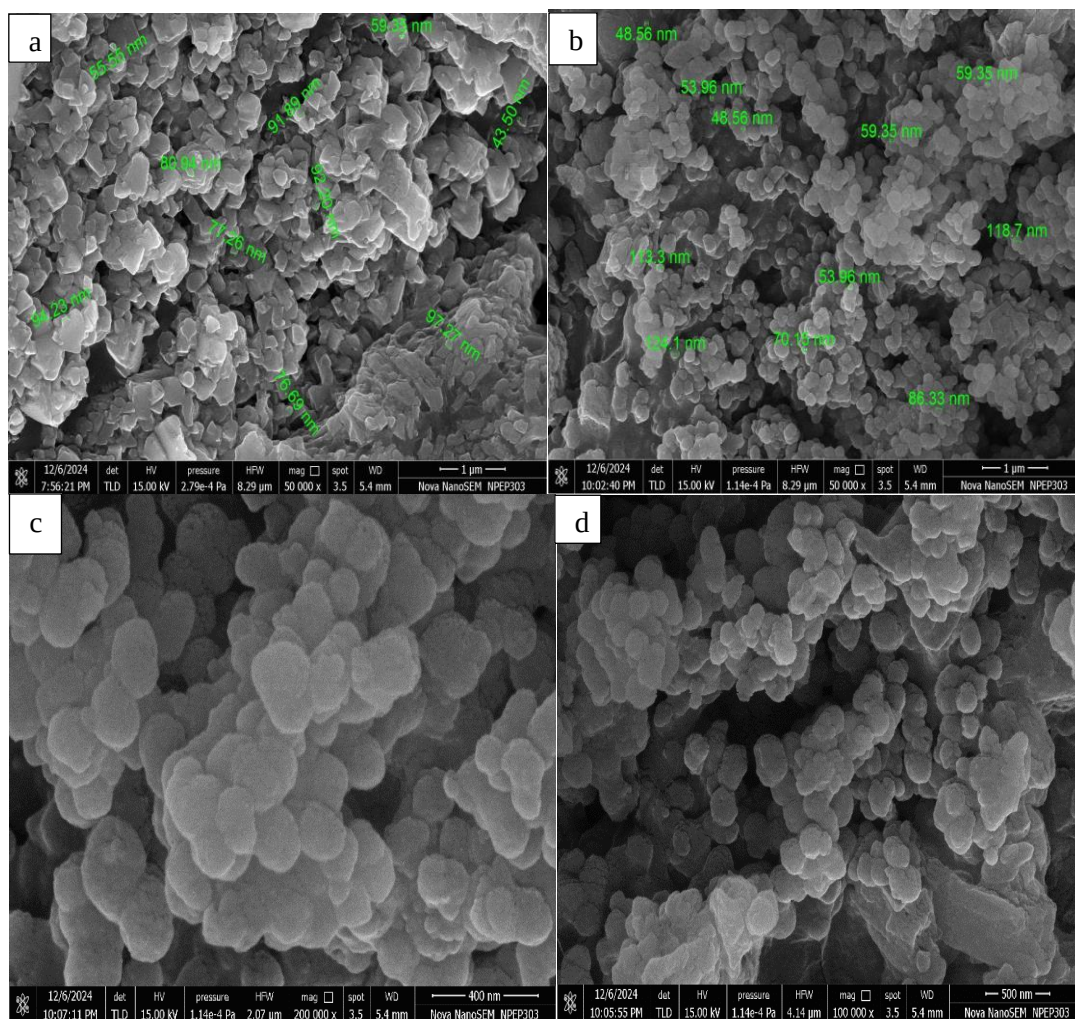
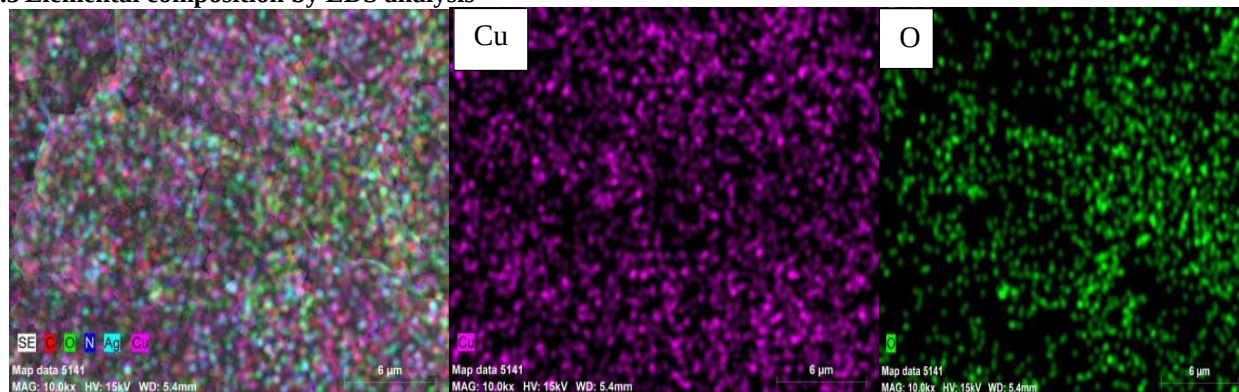


Fig- 6 (a), (b), (c), (d) FESEM image of copper nanoparticles (S1), (S2), (S3) and (S4).

Scanning electron microscopy pictures of the copper nanoparticles predominantly revealed spherical shaped particles measuring less than 100 nm. The size distribution of the biogenic CuNPs, determined by FESEM analysis, ranged from 50 to 100 nm (Figure 6). It is hypothesized that larger particles formed through agglomeration, possibly stabilized by smaller molecules acting as capping agents.

3.5 Elemental composition by EDS analysis



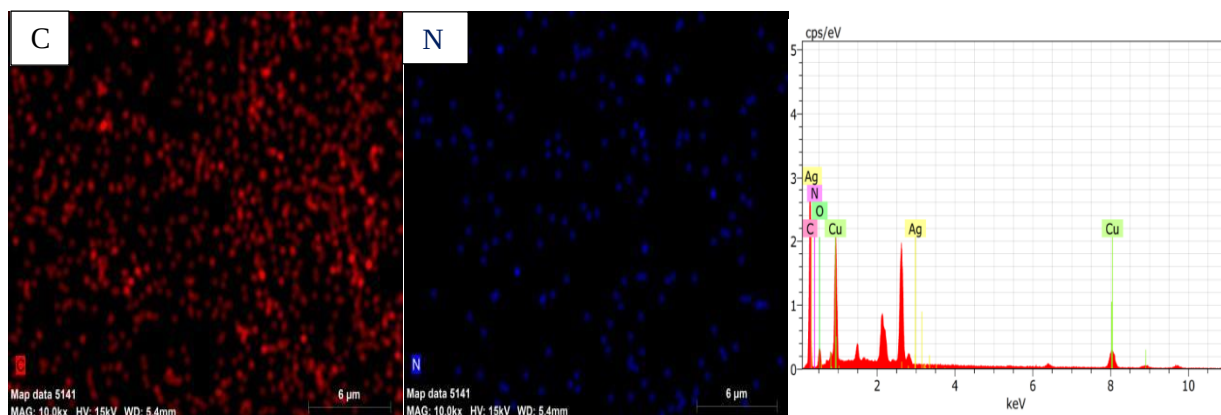


Fig.7 EDAX and Elemental mapping for CuNP's from Spices

The E-DAX study also provided information about the elemental composition of the CuNPs and their applications in physicochemical analysis. EDS data of

the CuNPs confirmed the presence of copper in the highest ratio of 70.89%, 66.49%, 69.95%, and 69.95% respectively among all other elements¹².

3.6 HRTEM images of CuNPs from Spices:

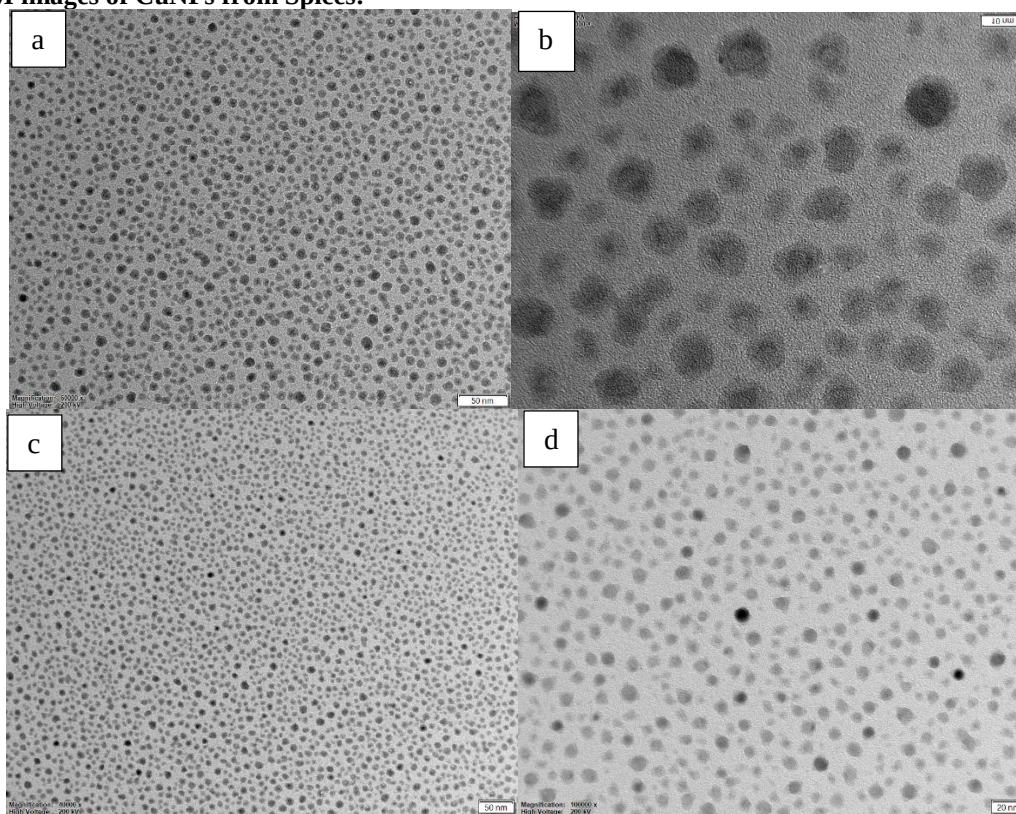


Fig. 8 (a), (b), (c) and (d) HRTEM images of copper nanoparticles from Spices S1, S2, S3, S4.

To elucidate the details of their shape and size, biosynthesized CuNPs were characterized using HRTEM (**Figure 8**). The resulting TEM profile showed that the nanoparticles were spherical morphology (Fig.8 a, b, c and d). Furthermore, diameter measurements of 100 randomly selected particles (Fig.8) from the TEM images with an average particle diameter of 20 nm.

4. Applications:

4.1 Photocatalytic Activity: (Photocatalytic degradation)

The photocatalytic activity of copper nanoparticle was analyzed by photo degradation of methyl Blue dye(MB) act as a model. An additional vital application of copper nanoparticle is in the domain of photocatalytic degradation, which has become an ever more effective,

ecofriendly with low cost by mean of eliminate toxic organic materials from the ecosystem. Methyl Blue is an anionic organic dye which has an azo (N=N) and diethyl amine group and therefore, it is risky for livelihood and has to be degraded from the nature. In this study, the degradation activity of synthesized nanomaterial was evaluated against methyl blue. The UV-vis absorbance peak of methyl orange dye at 649 nm is recorded. The

result of absorbance peak is gradually decreased with increasing for period of 15 min incubation. The degradation is initiated by photons of sunlight strike on the surface of copper nanoparticle, as it should be excitation of conduction electrons on surface of copper

nanoparticle as a result of SPR effect. Therefore, this article is designed for degradation of organic dyes under visible light irradiation in the presence of biogenic nanoparticles, which is very stable and efficient photocatalysts^{15,16,17,18}.

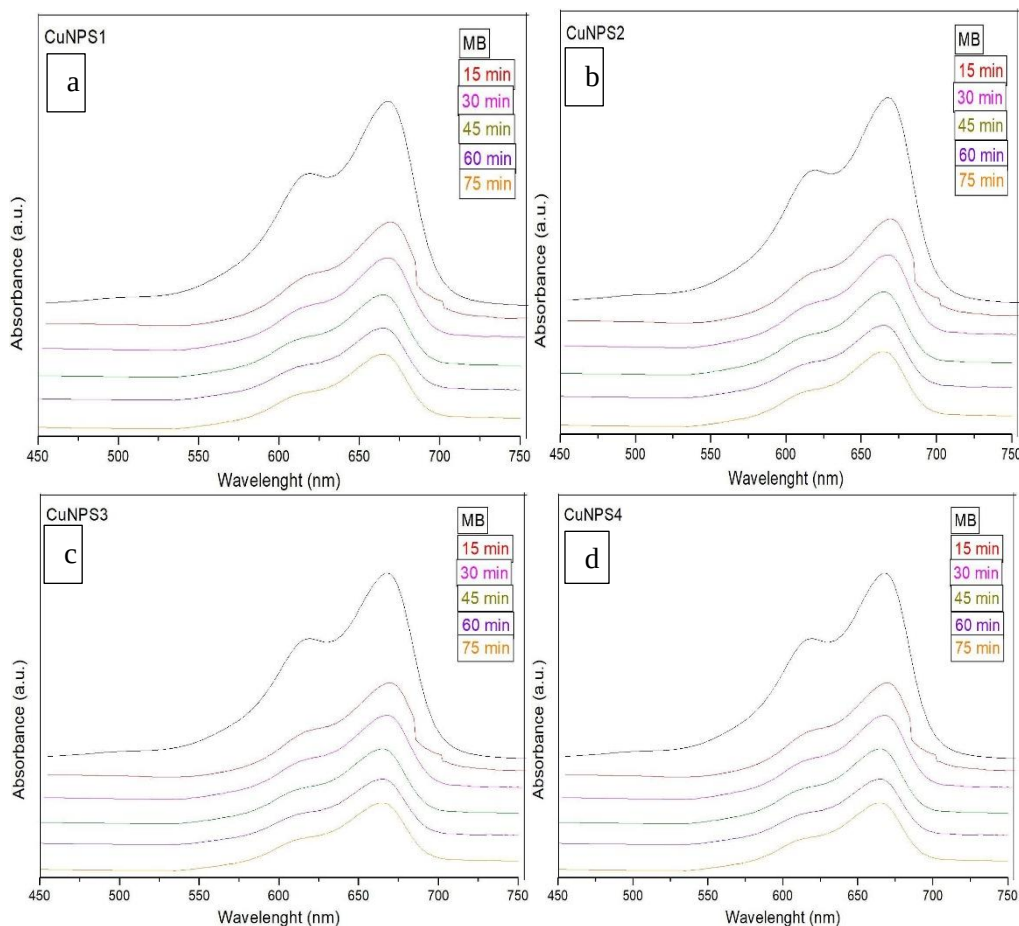


Fig.9 (a), (b), (c) & (d) Photocatalytic MB dye degradation UV-visible spectra for Spices samples

4.2 Antimicrobial Activity:

CuNPs can interact with bacterial cell membranes, causing structural damage. The high surface reactivity of CuNPs can lead to the formation of holes or lesions in the bacterial membrane, resulting in leakage of intracellular contents and disruption of cellular integrity. This membrane disruption is a key factor in the bactericidal activity of CuNPs. CuNPs release

copper ions (Cu^{2+}) into the surrounding environment, which can further contribute to antimicrobial activity. Cu^{2+} ions can bind to cellular components, including proteins, enzymes, and nucleic acids, disrupting their normal functions. The release of Cu^{2+} ions enhance the antimicrobial effects of CuNPs and is thought to be a significant factor in their bactericidal activity^{19,20,21}.

Table 2. Zone inhibition of CuNPs and standard against B. subtilis, S. aureus, E. coli and P. aeruginosa

Test (sample)	Concentration ($\mu\text{g/mL}$)	Zone of inhibition (mm)			
		B. subtilis	S. aureus	E.coli	P. aeruginosa
CuNPS1	0	-	-	-	-
	10	8	7	10	4
	30	10	8	12	6
	50	12	10	11	7
	70	14	17	16	8
	100	15	18	18	8
CuNPS2	0	-	-	-	-
	10	11	12	11	6
	30	11	10	12	7

	50	15	16	13	10
	70	12	18	15	11
	100	18	19	16	12
CuNPS3	0	-	-	-	-
	10	11	13	2	5
	30	11	14	5	6
	50	11	14	9	7
	70	12	16	11	10
	100	15	19	12	11
CuNPS4	0	-	-	-	-
	10	2	6	10	6
	30	4	9	13	7
	50	6	11	7	9
	70	7	14	9	10
	100	8	16	13	12

4.3 Antioxidant Property

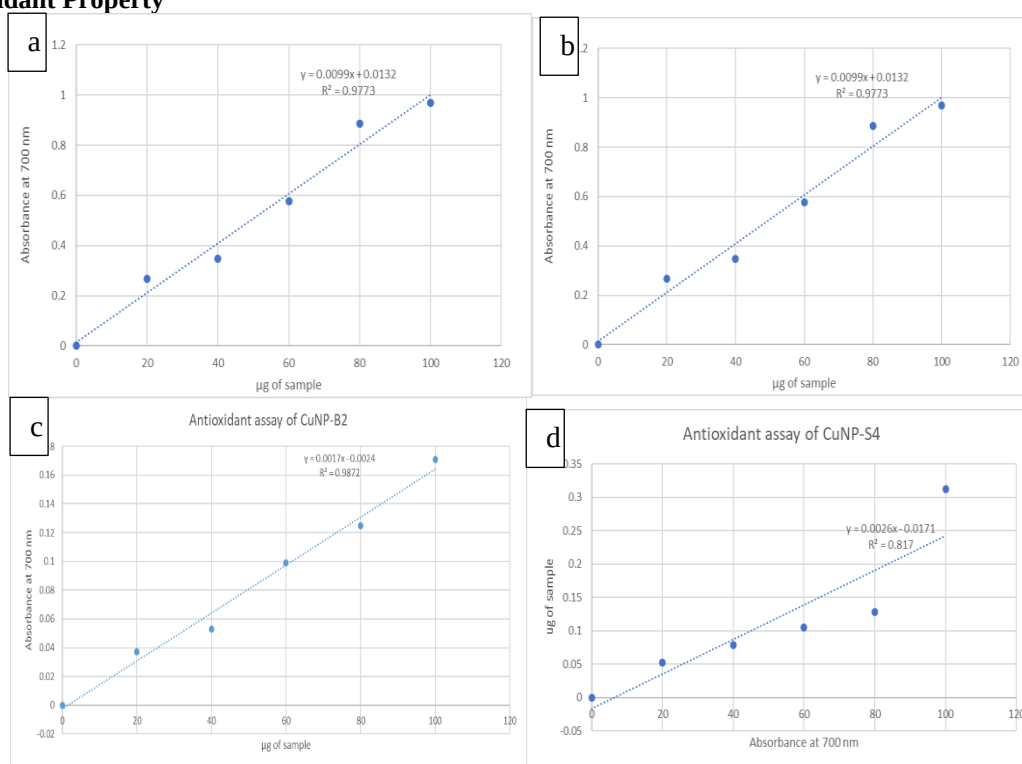


Fig. 10 (a), (b), (c), (d) Antioxidant activity of CuNPs for S1,S2,S2 and S4 sample

The potassium Ferricyanide Fe^{3+} gets reduced to potassium Ferrocyanide Fe^{2+} which then reacts with Ferric chloride to form Ferric- Ferrous complex that shows difference in absorbance. The graph in Fig 10(a,b,c,d) shows the increase in absorbance with increase in concentration of the sample and a regression value near to 1. These results correlates with the antioxidant property of nanoparticles extracted from spices ^{22,23}.

5. Conclusion:

The green production of copper nanoparticles from *Laurus nobilis*, *Cuminum cyminum*, *Cinnamomum verum*, and *Brassica juncea* has been studied for its antioxidant, antibacterial, and photocatalytic properties. The study used a variety of techniques, including UV-

Visible Spectroscopy, FTIR, XRD, FESEM, and HRTEM, to characterize the stability of synthesized copper nanoparticles. In the presence of biogenic nanoparticles, which are incredibly stable and effective photocatalysts, the study was created to examine how organic dyes degrade under exposure to visible light. The study offers insightful information about the possible uses of Copper nanoparticles in photocatalytic degradation and green synthesis. Strong antibacterial qualities were demonstrated by the produced copper nanoparticles, which may find application in disinfectants, medical equipment, and wound dressings. Copper nanoparticles' antioxidant properties can be investigated for potential applications in a range of medicinal formulations. This work offers a straightforward, secure, one-step method for creating

copper nanoparticles with spices extract. When creating nanoparticles, spices serve as a reducing agent, doing away with the requirement for surfactant templates or chemical reagents. Since there is no need for a chemical reagent or surfactant template, the bioprocess is environmentally benign. The results advance our knowledge of the potential of spices in the synthesis of nanoparticles for a range of uses.

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