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Green Synthesis of Manganese Oxide and Copper Oxide Nanoparticles Using Piper dravidii leaves Extract and Evaluation of their Antimicrobial Activity

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Abstract- Manganese oxide nanoparticles (MnO_2-NPs) and copper oxide nanoparticles (CuO-NPs) have a wide range of advantageous features that make them ideal for a variety of biological applications when their surface chemistry is properly matched. These include targeted drug delivery, tissue regeneration, cell separation, hyperthermia therapy, and enhancing contrast in magnetic resonance imaging (MRI). The study successfully demonstrated an eco-friendly approach to synthesizing CuO-NPs and MnO_2-NPs using a previously unidentified extract derived from the Piper dravidii leaves. To characterize the synthesized nanoparticles, a comprehensive suite of analytical techniques was employed, including UV-visible spectrophotometry, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). Structural analysis revealed that the obtained MnO_2-NPs and CuO-NPs possessed a cubic morphology, were inherently stabilized without additional chemical modifications, and had particle sizes ranging between 26.98 nm and 65.20 nm. The phytochemicals present in the leaves extract functioned as natural reducing agents, playing a crucial role in the green synthesis of these nanoparticles. This environmentally sustainable process also contributed to their enhanced antibacterial properties. FT-IR analysis confirmed that the nanoparticles predominantly contained hydroxyl (-OH) and carboxyl (-COOH) functional groups, rendering them hydrophilic. Due to their innate surface chemistry, additional functionalization was unnecessary for their intended applications. To assess their antibacterial efficacy, the synthesized MnO_2-NPs and CuO-NPs were tested against both Gram-positive (Staphylococcus aureus and Bacillus subtilis) and Gram-negative (Escherichia coli and Pseudomonas aeruginosa) bacterial strains. The results demonstrated notable antibacterial activity, with a zone of inhibition measuring 17 mm against E. coli and 15 mm against S. aureus. Given their natural stabilization, herbal attributes, and potent antimicrobial properties, these nanoparticles hold significant potential for diverse biomedical and biotechnological applications.

Keywords- MnO2-NPs, CuO-NPs; Green synthesis; Piper dravidii leaves; Antimicrobial activity.

I. INTRODUCTION

Plant floral extracts provide environmentally safe and appropriate substitutes for medicinal and biological applications in the manufacture of manganese and copper oxide nanoparticles1-2 since they do not require dangerous chemicals. Hazardous chemicals that may have detrimental impacts on medicinal applications can be introduced by chemical production procedures. Currently, researchers are employing plant extracts to produce nanoparticles biologically3,4. Numerous physical, chemical, biological, and hybrid methods exist for preparing different kinds of nanoparticles5. Each method yields unique nanoparticle characteristics. There are currently efforts underway to produce metal nanoparticles using plant-mediated means 6-7. The field of green nanotechnology, which has attracted a lot of attention, includes a variety of techniques meant to reduce or eliminate hazardous substances to benefit the environment. A modern technique is the production of metal nanoparticles from inert plant tissue, plant extracts, exudates, and other live plant materials. Safe, non-toxic, and ecologically friendly compounds are used in the green production of nanoparticles8–12.

Inorganic materials, which are usually found at nanoscale scales, are produced by microorganisms and plants. Nanoparticles with different sizes and chemical compositions can be created from cellular extracts of different biological entities13–15. Green synthesis is an effective and economical technique for extracting metal nanoparticles from a variety of plant parts, primarily leaves. The synthesis process involves the bio-reduction of metal ions. Iron ions are decreased by the plant extract components, and the nanoparticles are stabilized by water-soluble heterocyclic components. An appropriate precursor for reducing plant extracts is metal salts. The field of green nanotechnology, which has attracted a lot of attention, includes a variety of techniques meant to reduce or eliminate hazardous substances to enhance the environment.

Piper dravidii leaves are a large, spherical, gently hairy shrub that grows in India and other places16. Traditional medical systems recognize the therapeutic qualities of the entire plant. In addition to being delicious, the fruit has antiperiodic, diuretic, antipyretic, antibilious, tonic, and vulnerary qualities. It can be used to treat dry cough, muscle discomfort, and blood problems. They have amino, carboxyl, and hydroxyl functional groups in their phytochemicals. In a single step, these groups can form a robust coating on metal nanoparticles by acting as effective metal-reducing and capping agents. One modern technique17 is the production of metal nanoparticles from deactivated plant tissue, plant extracts, exudates, and other parts of live plants.

Green synthesis of nanoparticles guarantees the use of safe, non-toxic, and ecologically friendly substances. CuO-NPs and MnO2-NPs nanoparticles have a variety of biomedical uses, such as acting as magnetic beads to capture bacteria, developing sensors to identify various biological danger agents, and being essential in the medical industry. We have investigated the green chemistry production of Mn and Cu nanoparticles.

In this study, dried powder from Phaseolus lunatus flowers was used to create iron nanoparticles. Because of its importance in both industry and the environment, the manufacturing of MnO2 and CuO nanoparticles is summarized. The pharmacological benefits of Phaseolus lunatus (PL), which are recorded in Ayurvedic scriptures, have been verified by scientific research18–19. According to studies, the plant has potent depressive, analgesic, diuretic, antihyperglycemic, anticancer, and antioxidant qualities. This study assesses the antibacterial effectiveness of iron nanoparticles and looks at their characterization and manufacturing processes. Potassium permanganate and copper chloride were used as manganese and copper sources, while Piper dravidii leaves extract was used as a stabilizing agent and reducing agent in the synthesis of the MnO2-NPs and CuO-NPs nanoparticles.

II. EXPERIMENTAL METHOD

Collection of Plant Material and Preparation of Extract

Piper dravidii leaves were collected from nearby farmers in the Indian state of Maharashtra. Every test technique was conducted using fresh flowers.

Chemicals

Potassium permanganate ($KMnO_4$), copper chloride hexahydrate ($CuCl_2 \cdot 6H_2O$, 98%), and an analytical-grade solvent of the highest purity were employed in the study. S. D. Fine Chem supplied the solvent.

Extraction Preparation

The components of the Piper dravidii leaves were washed and stored at -4 °C. About 5 g of ground, air-dried Piper dravidii leaves samples were cooked with 100 ml of double-distilled water in an Erlenmeyer flask with steady stirring for 15 minutes to create the extract. After cooling to room temperature and filtering, the extract was kept for further use at -4°C.

Preparation of MnO2-NPs

A modified process based on previous research studies20–25 was used to manufacture manganese oxide nanoparticles. Just combine the Piper dravidii leaves extract and a 0.01 M $KMnO_4$ solution in a 1:1 volume ratio. Rapid preparation of MnO_2-NP nanoparticles was achieved by the reduction process. To create a colloidal suspension, the liquid was shaken for 60 minutes and then allowed to sit at room temperature for another 30 minutes. To create the MnO_2-NPs, the mixture was centrifuged, repeatedly cleaned with ethanol, and then vacuum-dried at 40 °C. Piper dravidii leaves exhibit greater reduction capability against $KMnO_4$, as demonstrated by the color change on the outside. Flowers that fit the requirements were selected for further procedures. The same procedure was used to produce the MnO_2-NPs for further characterisation after the confirmation test.

Preparation of CuO-NPs

To prepare copper oxide nanoparticles, a modified procedure based on earlier studies was employed26–28. Simply mix the Piper dravidii leaves extract with a 0.01 M solution of $CuCl_2 \cdot 6H_2O$ in a 1:1 volume ratio to get started. Through the reduction process, CuO nanoparticles were produced quickly. After 60 minutes of stirring, the liquid was left to stand at room temperature for an additional half hour to create a colloidal suspension. CuO nanoparticles were prepared by centrifuging the mixture, cleaning it with ethanol several times, and vacuum-drying it at 40°C. Compared to other plant parts (fruit and seeds), Piper dravidii leaves have a greater reduction capability against copper chloride, as evidenced by the exterior color shift. leaves that met the criteria were chosen to proceed to the following stages. Following the confirmation test, the same process was used to create the CuO-NPs for additional characterisation.

Characterisation

Characterization methods offer trustworthy insights into the measured values and help to quickly and precisely comprehend the special characteristics of the materials or nanocrystals under study. Numerous characterisation investigations were conducted on the produced MnO_2 and CuO nanoparticles to examine their structural, morphological, elemental, particle size, and functional group characteristics. Advanced techniques as UV-VIS spectroscopy (JASCO V650 UV-Vis model), XRD (PANalytical X'Pert Pro instrument with Cu Kα1 radiation of wavelength (λ) of 1.5406 (°A)), SEM (FEI Nova Nano SEM 450), EDS (Bruker XFlash 6I30), and FT-IR (BRUCKER) were used to carefully analyze these properties. The tactics helped to validate that our approach is well-optimized and satisfies the specifications.

Antimicrobial Activity Test

To learn more about the herbal usefulness of nanoparticles, the antibacterial properties of produced MnO_2 and CuO nanoparticles were investigated. According to a prior study29–30, the disc diffusion method was used to measure antimicrobial activity. Gram-positive and Gram-negative bacteria, including E. coli, were used in the antibacterial test. Aureus Staphylococcus Streptomycin at a concentration of 20 µg/ml is the standard medication reference.

III. RESULT & DISCUSSION

Metal nanoparticles are coated in a single step, changing their hue from yellowish brown to brownish black. The production of MnO2-NPs and CuO-NPs was validated by the color change. In comparison to the plant's seeds and fruits, the PL plant's flowers have a higher capacity to produce MnO2 and CuO nanoparticles. The UV-visible absorption peak at 510 and 715 nm is compared in the preface test, revealing plant debris and protein-bound MnO2-NPs and CuO-NPs, respectively31. Chloride interference in the plant extract32 could be the cause of the observed disparity.

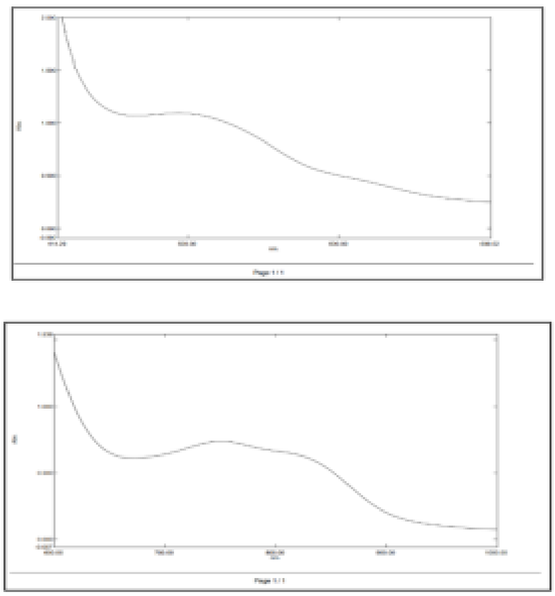


Figure 1. UV-vis spectra of MnO2-NPs and CuO-NPs

Along with Mn and Cu nanoparticles, the EDX spectrum in Figure 2 shows the presence of molecules like potassium, calcium, and chloride in the reaction mixture, indicating the formation of a complex with the plant extract. According to the analysis, the Piper dravidii leaves extract possesses 19.73% copper and 34.44% oxygen in the total weight of CuO-NPs and 30.15% manganese and 34.13% oxygen in the total weight of MnO2-NPs.
This is based on the energy-related bremsstrahlung X-ray intensity. The physical structure of the enzyme molecule is changed by carbon, exposing the appropriate chemically active regions for reaction. The pH is stabilized between 7 and 8, which is optimal for enzyme function, by carbon neutralizing organic anions and other substances in the plant. The number of enzymes that can be activated and the rate at which chemical reactions can take place are determined by the amount of carbon (C) present in the cell.

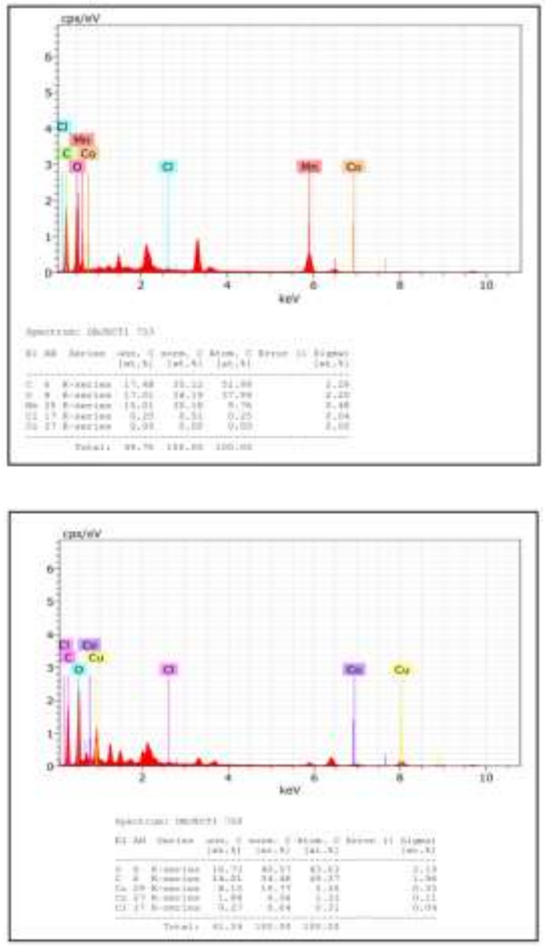


Figure 2: EDAX spectrum for MnO2-NPs and CuO-NPs

SEM analysis was performed on the sample to measure its size and examine its morphology. The morphological dimensions and production of MnO2-NPs and CuO-NPs were investigated using the SEM. According to the study, the average size of the nanoparticles was between 26.93 and 65.18 nm, which is consistent with results from other investigations. Figures 3 and 4 also show the creation of cube-shaped copper and manganese nanoparticles. Chloride and plant enzymes are responsible for the formation of cube-shaped nanoparticles. The shape of the nanoparticles is influenced by the presence of carbon compounds in the sample. SEM micrographs' narrow electron beam and large depth of field give them a unique three-dimensional appearance that is useful for examining a material's surface structure.

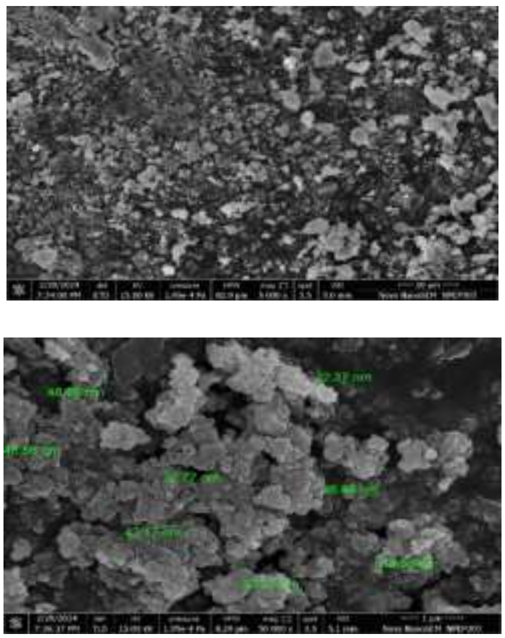


Figure 3: FE-SEM images of MnO2-NPs with a magnification (10µm and 1µm)

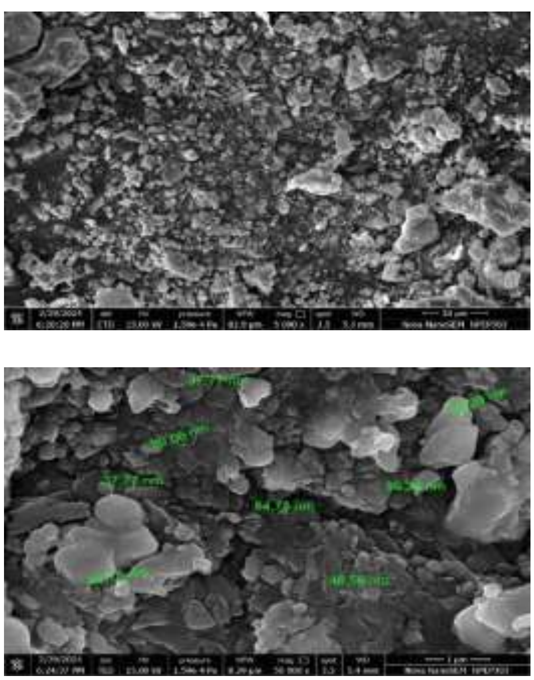


Figure 4: FE-SEM images of CuO-NPs with a magnification (10µm and 1µm)

Figure 5 shows the MnO2-NPs and CuO-NPs' X-ray diffraction patterns after they were synthesized using Piper dravidii leaves extract. The crystalline phase of MnO2-NPs and CuO-NPs nanoparticles matching JCPDS cards No. 39-1346 and 89-4319 was shown by the X-ray diffraction study, which showed prominent diffraction peaks at 2θ values of 28.40° and 35.62°, which corresponded to the hkl values of 220 and 222. The Debye-Scherrer equation was used to calculate the grain size, establishing a correlation between particle size and peak broadening in XRD. The average crystallite diameters of the MnO2-NPs and CuO-NPs were found to be between 16 and 19 nm using the Scherrer equation. The findings demonstrated that every nanoparticle has a face-centered cubic phase and a spinel structure.

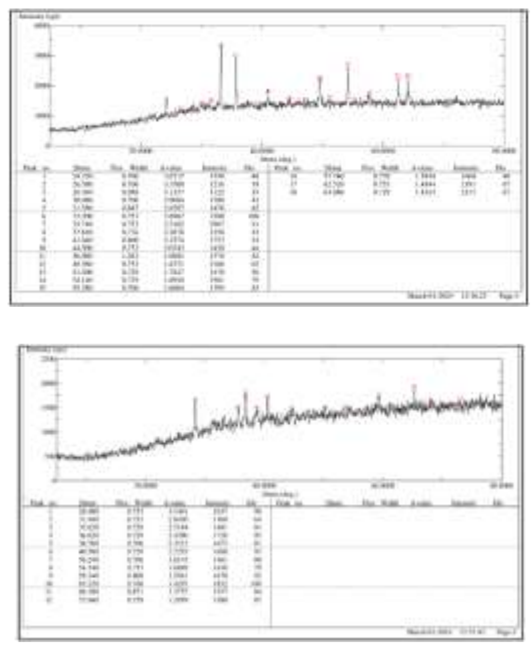
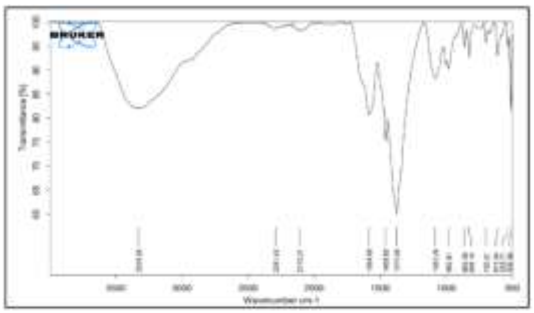


Figure 5: XRD spectra of Fe2O3 and CoO NPs

Within the 500–4000 cm-1 region, stretching vibrations were detected by FT-IR analysis at 3320–3630 cm-1, 1582–1583 cm-1, and 615-618 cm-1 (Figure 6). The peaks show that the sample's bonding confirms the reducing agent's involvement in the formation of MnO2-NPs and CuO-NPs. The stretching of -OH bonds in the aqueous phase and the reduction of metal salts are represented by the peak at 3325–3640 cm-1. The presence of phytochemicals and amino acids that stabilize and serve as capping agents in the plant extract is shown by the peak at 1583–1588 cm-1, which corresponds to the stretching of the C=O bond.

The few organic acids that contribute to the sample's low pH and aid in the synthesis of MnO2-NPs and CuO-NPs are indicated by the remaining unexplained peaks. The inorganic stretching of CuO-NPs and MnO2-NPs is represented by the strong peak at 612-619 cm-1. Because of the substantial negative surface charge, the zeta potential of MnO2-NPs and CuO-NPs was measured at -50 mV, showing excellent stability.



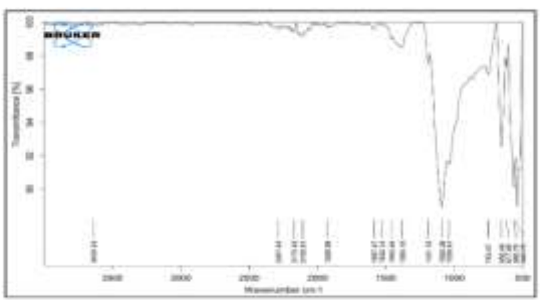


Figure 6: FT-IR spectra of Fe2O3 and CoO NPs

In comparison to the reference medication, the produced MnO2-NPs and CuO-NPs show moderate antibacterial activity. Their antibacterial activity is moderate against S. aureus and higher against E. coli. In culture conditions, the MnO2-NPs and CuO-NPs have inhibitory effects that are similar to those of the common antibiotic ampicillin. When compared to the genuine plant extract, synthesized nanoparticles show comparable antibacterial effectiveness. Functional groups based on the plant's herbal properties that coat the NPs' surface activate their antibacterial properties. Cell death results from increased NP penetration into the cell wall caused by reduced NP size. Following moderate activity, it was found that S. aureus was the more resistant bacterium and E. coli was the more susceptible. Both CuO-NPs and MnO2-NPs have a larger surface area and are naturally stabilized, making them appropriate for a variety of uses. To avoid the existence of plant pollutants that could alter the NPs' characteristics, the ingredients used to produce MnO2-NPs and CuO-NPs must be separated and purified.

IV. CONCLUSION

The NPs were spontaneously stabilized by the phytochemicals in the sample, which served as capping and reducing agents. This method is favored because of its non-toxic green synthesis and natural functionalization with herbal features, even if it produces less nanoparticles than other chemical and physical procedures. The plant's mild antibacterial efficacy against the chosen pathogen demonstrates its herbal qualities. Few NPs can efficiently synthesize NPs by using the plant extract as a reducing agent. Validating the superparamagnetic for use in cancer treatment will be the main goal of future studies.

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