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Eco-Friendly Fabrication of Copper Nanoparticles using Citrus sinensis Peel Extract; Comparative Insights and Characterization

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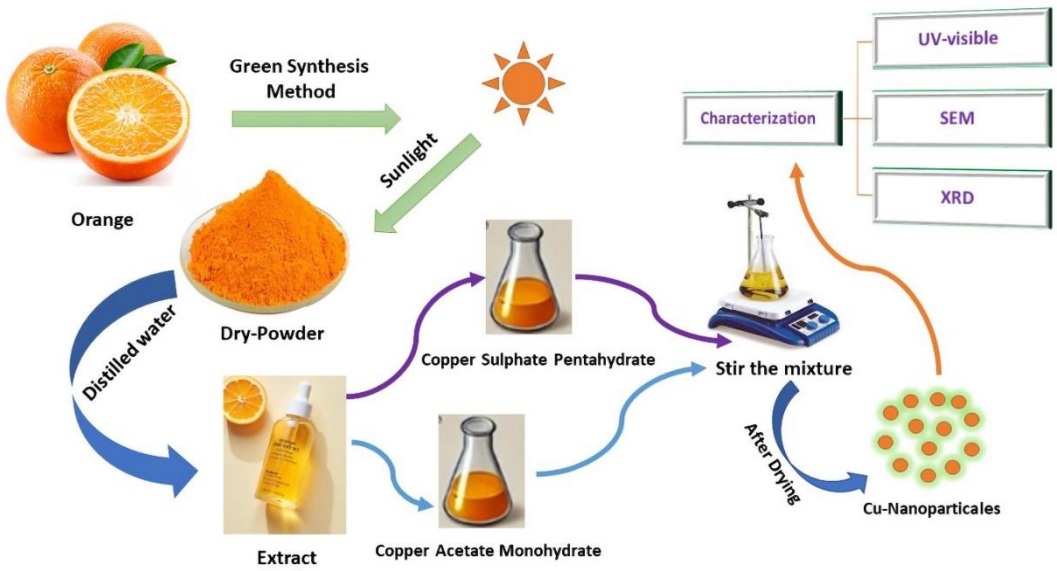
Abstract

Copper nanoparticles (CuNPs) were synthesized via green methods using orange peel extracts as reducing agents. Orange peels collected from Jhang, Pakistan, were washed, sun-dried, and powdered for extraction. Two different copper salts, copper sulfate pentahydrate and copper acetate monohydrate, were used as precursors. The resulting nanoparticles were characterized using UV-Vis spectroscopy, SEM, and XRD techniques. UV-Vis analysis revealed distinct peaks at 566-580 nm, indicating successful nanoparticle formation. SEM analysis showed varying particle sizes, with copper sulfate-derived nanoparticles averaging 26 nm and copper acetate-derived nanoparticles around 44 nm. XRD results confirmed high crystallinity in both nanoparticle types. The study demonstrates that orange peel extracts effectively reduce copper ions, offering a sustainable approach to CuNPs synthesis with potential for future applications. Further optimization is needed to improve particle uniformity and reduce aggregation.

Graphical Abstract



Key words: Citrus Sinensis, copper nanoparticles, green synthesis, peel extract

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1. Introduction

In the last few years, there has been an ever-increasing interest in nanotechnology because of its apparent ability to transform many domains, such as medicine and electronics[1-2], as well as environmental applications [3]. Among many nanoparticles, copper nanoparticles (CuNPs) have received a lot of attention due to their exceptional characteristics [4], such as electrical conductivity, antimicrobial properties and high catalytic activities [5]. Nevertheless, the common ways of producing CuNPs tend to use harmful chemicals and high energy-consuming reactions [6], which may lead to carbon footprints [7]. Therefore, green synthesis approaches have been explored, which utilize eco-friendly and renewable resources to fabricate nanoparticles [8]. Citrus fruits, especially oranges, contain many of these compounds [9], and their peel extracts are useful in the synthesis of green nanoparticles as reducing and stabilizing agents [10]. Other investigations have similarly shown that plant extracts can be employed for synthesizing metal nanoparticles [11]. Still, relatively more effort has yet to be invested in synthesizing nanoparticles from peels of Citrus sinensis through further exploration of the radical mechanisms involved [12]. Also, though there are few attempts made to synthesize CuNPs with different fruit extracts, systematic studies and the synthesis of CuNPs from Citrus sinensis peel extract [13-14]. The peel extract of Citrus sinensis was used to develop an eco-friendly method for fabricating copper nanoparticles (CuNPs) [15]. The nanocrystals were shaped and sized into CuNPs utilizing the bioactive agents encapsulated in the orange peel [16], and an extensive comparative study of their size, shape, and geometric surface was achieved [17]. The analysis of CuNPs produced by this eco-friendly strategy is currently lacking in the existing literature [18], research seeks to address by comparing their structural and chemical properties with those of copper nanoparticles produced by conventional chemical methods [19-20]. This effort produced nanoparticles of copper (Citrus sinensis) and an aqueous extract using powdered orange peel and two different copper salts, copper sulphate and copper acetate. Techniques such as UV-Vis, X-ray diffraction (XRD), and SEM (scanning electron microscopy) have been employed to validate the structural characteristics of the synthesised CuNPs.

CuNPs synthesized from Citrus sinensis peel extract not only meet the goal of being environmentally friendly but also exhibit superior stability, uniformity, and surface characteristics. These promising results open up exciting possibilities for the mass production of CuNPs, which can be used in a wide range of applications, including catalysis, antimicrobial treatments, and energy storage. This work paves the way for further development of green nanotechnology, offering a hopeful outlook for the future.

2. Experimental

2.1 Sample collection

Orange peels, were gathered from Jhang, Punjab, Pakistan's local fruit market. After giving them a thorough wash in distilled water, they were powdered and put away in a container that was airtight.

2.2 Preparation of the extract

First, fresh oranges were chopped into smaller pieces, had their peels removed, and were sun-dried. The peel was dried and ground into a fine powder. Five grams of finely crushed orange peel were combined with 250 ml of distilled water and protected with aluminium foil. It was then cooked for 20 minutes at 70 °C on a hot plate. After being combined, the liquid was cooled to room temperature and filtered using filter paper.

2.3 Preparation of copper salt solutions

The crystalline solid copper sulphate pentahydrate has a vivid blue colour. By dissolving 6.45 grams of $CuSO_4.5H_2O$ in 250 millilitres of distilled water, a 0.1 molar solution was achieved. The salt of copper acetate monohydrate has a stronger bluish-green hue. 250 millilitres of distilled water were used to dissolve 5 grams of salt to create a 0.1 molar solution.

2.4 Green synthesis of copper nanoparticles (Cu-NPs)

Numerous trial and error experiments were conducted to determine the best way to synthesise the nanoparticles. Thirty millilitres of peel from an orange aqueous extract were combined with ten millilitres of 0.1 M $CuSO_4.5H_2O$ solution to synthesis CuPs utilise copper sulphate and peel extract. At 700C, the mixture was stirred for 20 minutes. The reaction liquid was gradually mixed with 0.1 M NaOH until pH 11 was reached after it had cooled to room temperature. After another ten minutes of stirring, the mixture was left alone for twenty-four hours. Copper nanoparticles with an orange-brown colour were obtained the very following day. After multiple redispersions in deionized water to purify the precipitate, it was centrifuged for 15 minutes at 1000 rpm. The final product was dried for the full night at 80°C in an oven. The dried, powdered nanoparticles were collected and stored. The process was carried out as previously described utilising 20 mL of orange peel powdered water-soluble extract as well as 10 millilitres of 0.1 M $Cu(OOCCH_3)_2.H_2O$ salt solution in the green production of nanoparticles of copper using copper acetate monohydrate. Brick-red-colored copper nanoparticles were isolated and stored.

2.5 Characterization Techniques

Numerous methods were employed to characterise the synthesised nanoparticles. One milliliter (mL) of the combination from the filtered sample was taken for the UV-Vis analysis. The range of 300–700 nm was covered by the UV–Vis spectra. The dimensions and form of the particles were observed using the SEM technique. Using an X-ray diffractometer, the phase structure and material identity of CuNPs were investigated.

3. Result and Discussion

The unique optical properties of nanoscale materials are attracting a lot of attention. The hues of the nanoparticles varied greatly while they were being made. The reaction mixture turned greenish yellow after two hours, which was the main sign that a plant extract could combine with copper sulphate as well as copper acetate to form copper nanoparticles. The creation of nanoparticles was completed when precipitation seen and the colour change stopped after a 24-hour reaction as shown in Figure 1. On the other hand, by mixing 20 millilitres of peel of an orange extract with 10 millilitres of a copper acetate salt solution, fine nanoparticles from copper acetate can be produced at a ratio of 10:20. But still, there was a difference in the ratio of the formation of copper sulphate to copper acetate nanoparticles. At 10:30, 30

millilitres of orange peel extract and 10 millilitres of a copper sulphate solution of salt were combined to form copper sulphate nanoparticles.

3.1 UV–Visible spectroscopy

Figures 2 illustrate the copper acetate and copper sulphate nanoparticles that were produced via green synthesis along with their UV-visible absorption spectra. Because of their extraordinarily high excitation binding energies at ambient temperature, copper sulphate and copper acetate both show separate peaks. The UV-Vis spectral analysis of CuNPs shows a unique absorption peak at 565 to 580 nm, which after nine minutes exhibits an SPR behaviour. The bands show the existence of metallic copper, indicating the formation of CuNPs. The UV-visible spectra of copper sulfate pentahydrate and copper acetate monohydrate nanoparticles exhibit characteristic absorption peaks in the range of 577 nm, attributed to the ligand-to-metal charge transfer (LMCT) transition between the oxygen atoms of their respective ligands and copper ions. The prominent absorption peaks in both spectra confirm the successful formation of the nanoparticles. The absence of significant secondary peaks indicates high purity, with minimal impurities present. The slightly broader peak shapes suggest a degree of size heterogeneity within the nanoparticle populations, likely due to variations in nanoparticle size distribution. Overall, these spectral observations confirm the formation and purity of copper sulfate pentahydrate and copper acetate monohydrate nanoparticles. In addition, data from both experiments prove that it is possible to obtain copper nanoparticles using Citrus sinensis peel extract. At the same time, UV-Visible results suggest the nature of obtained nanoparticles depends on the salt precursor used.

3.2 Scanning electron microscopy (SEM)

Copper molecules grow gradually to form tiny spherical shapes when employing Cu sulphate as a precursor. The artificial nanoparticles, which were made using a copper sulphate salt solution of a 0.1 molar concentration, were examined for size and shape using a microscope equipped with scanning electrons. Green synthetic nanoparticles were visible at 500 nm, according to SEM data. The synthesised Cu-NPs were found to have irregular shapes, aggregating in smaller clusters having a size of +/-100 nm. These shaped particles were mainly square, polygon, sometimes spherical particles in clusters, according to the SEM images. It was discovered that there were no contaminants in the highly pure nanoparticles. The reduction of copper ions was discovered to exhibit spherical particles with smooth surfaces. Conversely, Cu nanoparticles were produced and accumulated to create a hexagonal shape with a size of +/-250 nm using copper acetate monohydrate as a precursor. The polarity as well as electrostatic attraction of the nanoparticles are the cause of this agglomeration. This study explores the synthesis and characterization of copper nanoparticles (CuNPs) produced using copper sulfate pentahydrate. Scanning Electron Microscopy (SEM) was employed to analyze the particle size, shape, and surface morphology of the nanoparticles. The SEM result in Figure 3 reveal that the CuNPs have an average size approximately 26 nm, with a wide distribution indicating significant variability in particle dimensions. The nanoparticles exhibit an array of shapes, from spherical to elongated, and demonstrate notable aggregation, resulting in clusters of particles. Despite this, the surface morphology of the nanoparticles appears relatively smooth, although fine surface features are not visible at the given magnification. The observed size distribution and aggregation suggest that further refinement of the synthesis parameters may be necessary to achieve more uniform nanoparticles and reduce clustering. SEM image of copper nanoparticles synthesized from copper acetate monohydrate reveals a diverse array of particle shapes, ranging from spherical to irregular and angular. The particles exhibit noticeable aggregation, forming small clusters, and their surfaces are relatively rough, characterized by visible bumps and protrusions. The scale bar, which represents 500 nm, indicates that the average particle size in Figure 4 is approximately 43 nm. However, there is considerable variation in particle size, with some particles being significantly smaller or larger than this average range. This SEM image offers valuable insights into the morphology and size distribution of the copper nanoparticles, helping to visualize their physical characteristics and potential applications.

3.3 X-ray diffraction (XRD)

X-ray diffraction (XRD) pattern of copper sulfate pentahydrate nanoparticles exhibits distinct peaks within the 5° to 70° range, indicating a well-ordered crystalline structure. Key diffraction peaks at approximately 15°, 20°, 30°, 40°, and 50° correspond to specific crystallographic planes of copper sulfate pentahydrate, confirming the formation of the expected phase. The sharp and intense peaks in Figure 5 particularly between 10° and 35°, suggest high crystallinity. Broader peaks may indicate smaller nanoparticle sizes, while sharper peaks suggest larger particle sizes or enhanced crystallinity. Utilizing the Scherrer equation on the most intense peak, typically near 20°, allows for the estimation of nanoparticle size. The absence of broad, poorly defined peaks further supports the successful synthesis of highly crystalline copper sulfate pentahydrate nanoparticles. For definitive phase confirmation, the observed peaks can be compared with standard JCPDS data for $CuSO_4 \cdot 5H_2O$, verifying both the crystal structure and the purity of the nanoparticles. X-ray diffraction (XRD) pattern of copper acetate monohydrate nanoparticles reveals characteristic peaks within the 5° to 70° range, indicating a well-defined crystalline structure. The most prominent peak is observed around 15°, with additional significant peaks appearing at approximately 10°, 25°, 30°, 35°, and 40°. These reflections correspond to specific crystallographic planes of copper acetate monohydrate, confirming the formation of the desired crystalline phase. The sharpness of the peaks, particularly the intense peak around 15°, highlights the high crystallinity of the nanoparticles in Figure . Broader peaks would indicate smaller particle sizes or amorphous regions; however, the narrow peaks observed here suggest a uniform particle size distribution and well-crystallized nanoparticles. These results confirm the successful synthesis of copper acetate monohydrate nanoparticles with a high degree of crystallinity and structural integrity.

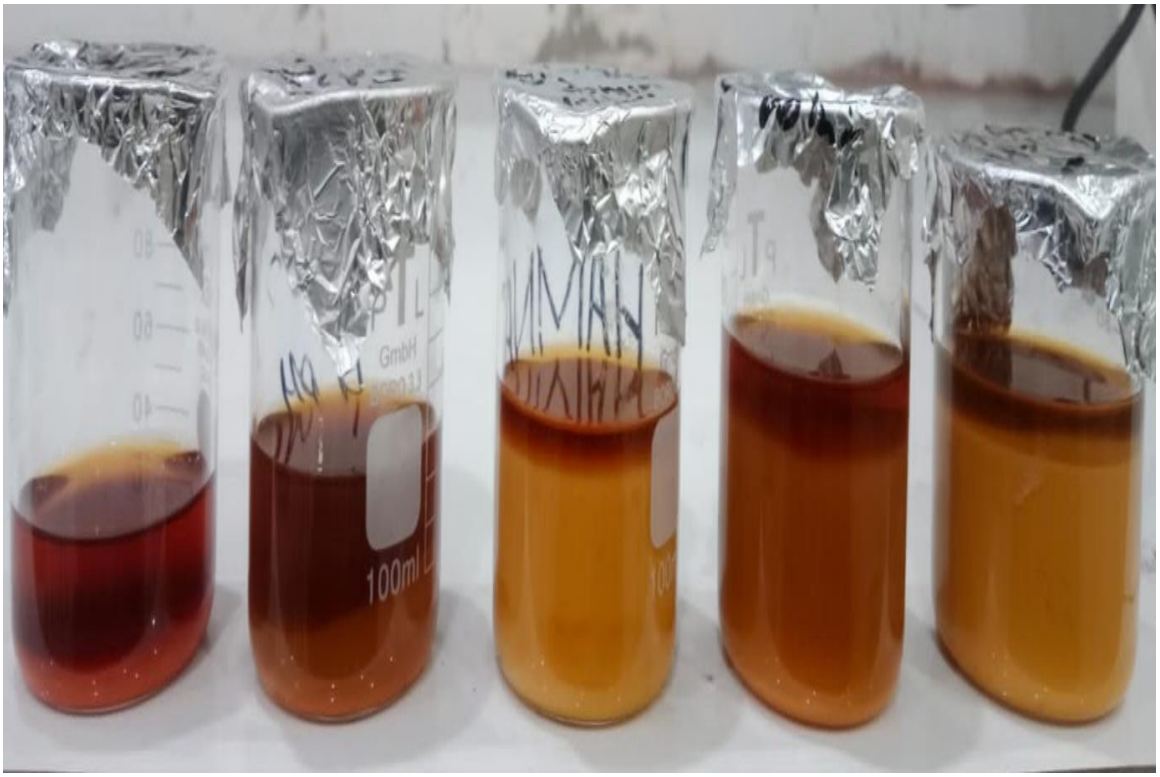

Fig. 1. After 24 hours, copper nanoparticles generated

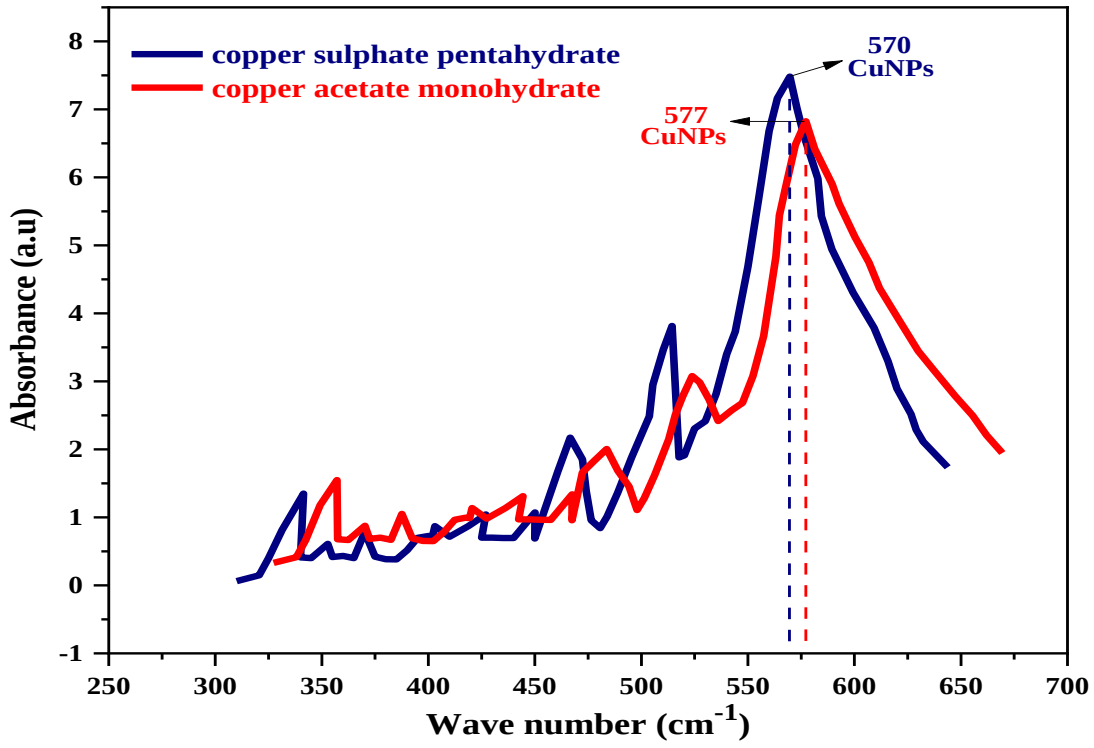

Fig. 2. UV-visible spectrum of copper sulphate pentahydrate and copper acetate monohydrate nanoparticles

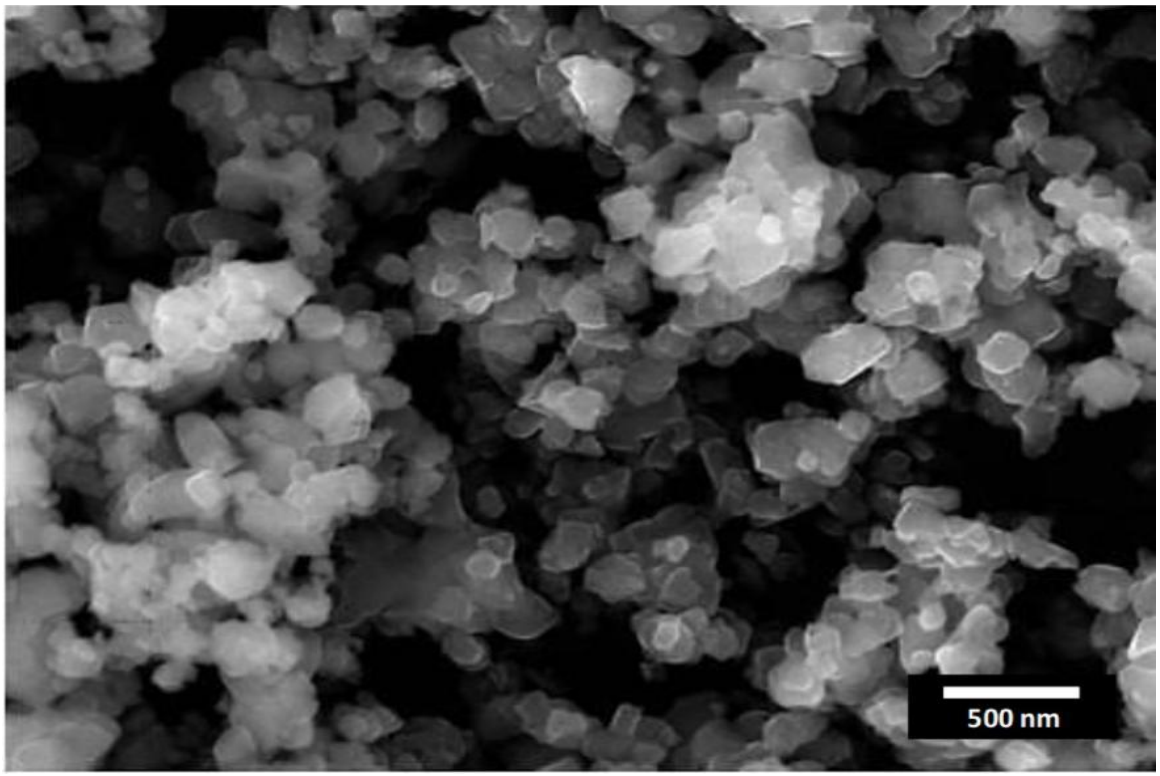

Fig. 3. SEM micrographs of nanoparticles of copper created using copper sulphate pentahydrate

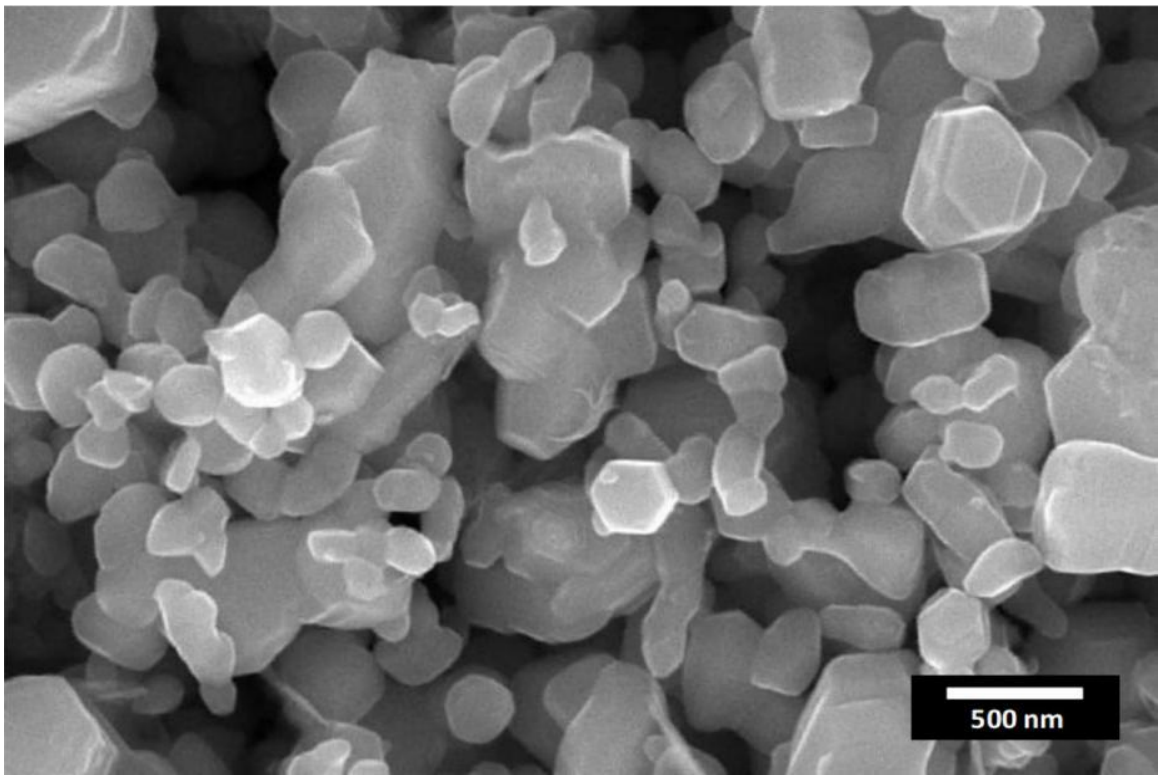

Fig. 4. SEM micrographs of copper nanoparticles derived from copper acetate monohydrate

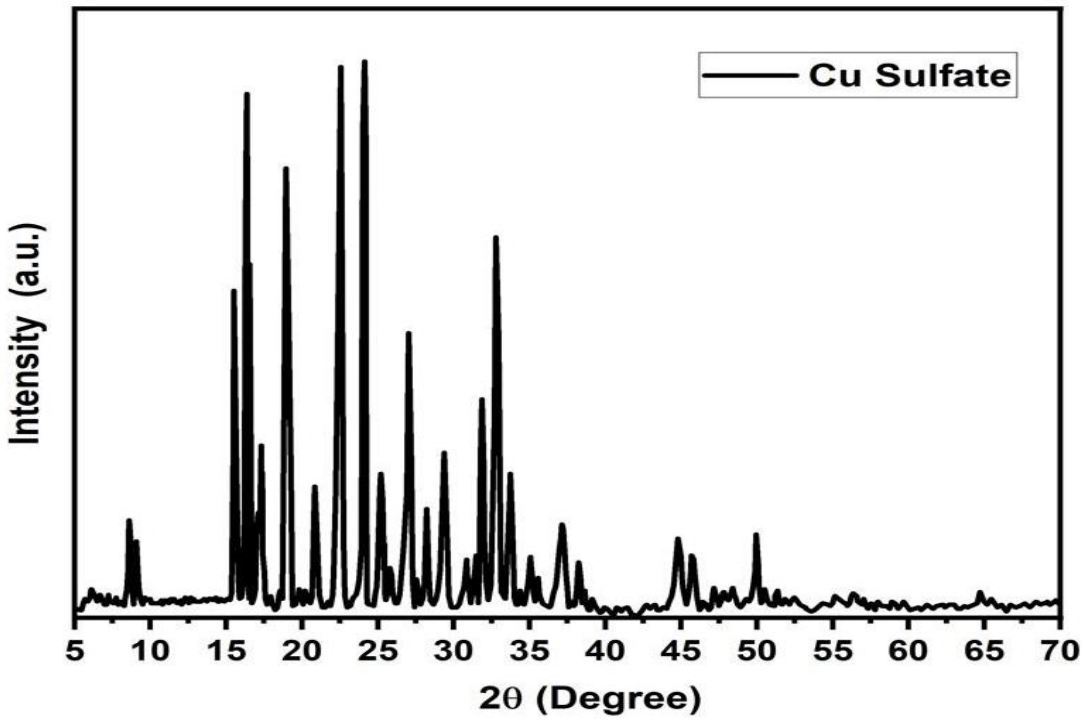

Fig. 5. XRD analysis of Copper sulphate pentahydrate nanoparticle

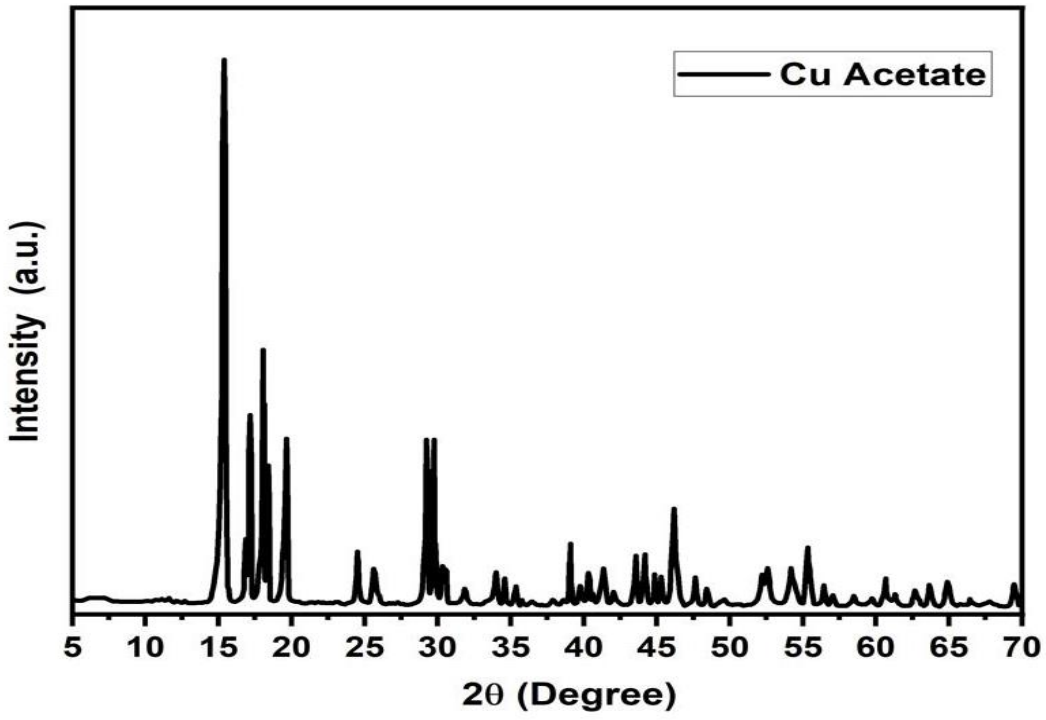

Fig. 6. XRD analysis of Copper acetate monohydrate nanoparticles

4. Conclusions

The present study conclusively revealed the environmentally friendly green synthesis of copper nanoparticles (CuNPs) using the peel extract of Citrus sinensis as a reducing agent, employing copper sulfate pentahydrate and copper acetate monohydrate as precursors. In this regard, and in a set of controlled experiments CuNPs were produced with variations on the precursor, which imparted different properties. The UV-Visible spectroscopy studies confirmed the synthesis of nanoparticles, and the intensity of particular peaks showed the degree of purity. SEM images of nanoparticles from cupric sulfate showed more rounded and smaller particles with noticeable agglomeration while those from copper acetate formed hexagon shaped larger nanoparticles. The structure and crystalline integrity of both nanoparticle types were confirmed by X-ray diffraction (XRD). This environmentally friendly synthesis route proves that plant extracts could be utilized in the formation of nanoparticles of the desired properties and there is room for improvement and use in many other applications including catalysis, electronics and biomedicine. In the following studies, it is suggested to pay more attention to checking the reproducibility and uniformity of the obtained particles as well as their dispersion degree.

Acknowledgement

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Conflicts of interest

There are no conflicts to declare

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