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Research Article

Optimizing Green Synthesis of Copper Nanoparticles Using Neem Leaf Extract: Influence of Reaction Parameters On Size And Morphology

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ABSTRACT

This current study builds on the synthesis of CuNPs through green chemistry methods employing neem leaf extract as the reducing and stabilizing agent. Flavonoids, terpenoids, and glycosides present in Neem leaves can reduce and stabilize the copper ions under mild conditions. In this work, the concentration of the precursors, temperature, pH, and the ratio of neem extract to copper sulfate solution has been optimized to achieve the desired size and shape of CuNPs. The experimental design of the synthesis process involved the extraction of neem leaf, then adding varying concentrations of copper sulfate to the extract, and then varying reaction parameters. Identification of synthesized CuNPs was performed with UV-Vis spectroscopy, TEM, XRD, FTIR, and DLS. The results revealed that the reaction parameters affected the size, morphology, and stability of the developed nanoparticles. Thus, the CuNPs with the desired characteristics and high dispersion stability were achieved because of the growth of the synthesis conditions. These CuNPs have properties such as high electrical and thermal conductivity, high catalytic activity, and good antibacterial properties and so have uses in electronics, catalysis, and medical fields. The work under discussion is focused on the biosynthesis of CuNPs with the help of neem leaf extract and states that it is crucial to control the reaction conditions to achieve the desired properties of CuNPs. Future work should be devoted to the scale-up of the synthesis process and the investigation of new applications in modern state-of-the-art devices.

Keywords: Green synthesis, Copper nanoparticles, Neem leaf extract, Reaction parameters, Nanoparticle characterization

Introduction

Nanotechnology is an interdisciplinary domain that covers the utilization of material structures that are between one and one hundred nanometers in size. On this scale, substances have characteristics that are different from their mass counterparts, primarily because of quantum effects and high surface-to-volume ratio. These size-specific features are important in defining the uses and capabilities of nanomaterials that are applied in numerous fields. The size of the nanometer scale is crucial in describing nanomaterials since it is at this scale that quantum confinement occurs. This is evidenced by the changes in the electronic and optical properties of the materials including colour control and improvement of catalytic activity of nanoparticles. Nanomaterials have a large surface area to volume ratio, which enables them to have good interaction with the environment and hence be useful in many applications (Fatta-Kassinos& Michael-Kordatou, 2020).

Unique Properties of Nanomaterials

Nanomaterials are described by the miniaturization in electronics, the enhancement of renewable energy technologies, and environmental cleanup. For example, in electronics, nanomaterials can help to create miniaturized devices and improve the devices' performance. Integrated circuits such as the transistors and memory storage devices that are at the nanoscale benefit from the properties of nanomaterials. In renewable energy, nanomaterials are essential in the fabrication of solar cells and batteries owing to their high charge transport properties and catalytic activity. In environmental technology, nanomaterials have a great ability to adsorb contaminants and enhance the catalytic degradation of pollutants in water treatment and pollution control.

Table 1: Properties of nanoparticles compared to bulk materials

PROPERTY	NANOPARTICLES	BULK MATERIALS
Optical Properties	Tunable colors	Limited color range
	Enhanced absorption	
	Scattering	
Electronic Properties	Quantum confinement effects	Continuous bandstructure
	Enhanced catalytic activity	
	High surface-to-volume ratio	
Mechanical Properties	Increased strength	Bulk-like mechanical behavior
	Flexibility	
	Enhanced hardness	
Chemical Properties	High reactivity	Reactivity dependent on scale
	Surface functionalization	
	Tailored surface chemistry	

Green Synthesis of Nanoparticles
Nanoparticles can be synthesized using physical, chemical, as well as biological techniques. Among these methods, green synthesis has been widely researched for its sustainability and cheapness. Biogenic synthesis uses plant extracts, microorganisms and enzymes for the preparation of nanoparticles. This method also minimizes the utilization of toxic chemicals and also improves the biocompatibility of the synthesized nanoparticles. Plant extracts, especially, contain bioactive molecules that can perform reducing and stabilizing roles in the synthesis of nanoparticles under relatively moderate conditions (Kumar et al., 2015).

Neem Leaf Extract in Nanoparticle Synthesis
Neem (Azadirachta indica) is a multipurpose medicinal plant, which has got numerous uses in the field of medicine. Neem leaves contain flavonoids, terpenoids, and glycosides which can act as a reducing and stabilizing agent for the synthesis of nanoparticles. The preparation of copper nanoparticles using neem leaf extract is advantageous due to its inherent features such as simplicity, cheapness, and green synthesis. The bioactive compounds in neem extract enable the enhancement of the reduction of copper ions to copper nanoparticles and the stabilization of the formed nanoparticles without agglomeration (Mendoza & Jonkers, 2017).

Importance of Reaction Parameter
The preparation of CuNPs through neem leaf extract depends on several reaction conditions such as the concentration of the precursor, temperature, pH, and quantity of the reducing agent. These parameters are very important when it comes to defining the size, shape, and stability of the produced nanomaterials. The conditions for such reactions have to be fine-tuned to obtain the appropriate nanoparticle properties for a given application. For instance, the concentration of the copper precursor influences the nucleation and growth rates of the nanoparticles and temperature influences the reaction rate. Likewise, the pH of the reaction mixture affects the charge and stability of the nanoparticles; the volume of neem extract affects the extent of reduction and stabilization of copper ions (UN Water, 2020).

1. Precursor Concentration
The concentration of the copper precursor is one of the most important factors when synthesizing CuNPs. The concentration of precursors can be attributed to the increase in nucleation sites and growth rates thus resulting in the formation of larger nanoparticles. On the other hand, low precursor concentrations can lead to the formation of small nanoparticles with a relatively small distribution range. Thus, the concentration of the precursor should be adjusted to achieve the desired size and uniformity of the nanoparticles (UNESCO, 2018).

2. Temperature
Temperature is also another important factor that affects the synthesis of CuNPs. Higher temperatures also favor the reaction kinetics, which means that the reduction of copper ions and the formation of nanoparticles will be faster. However, very high temperatures can lead to the coalescence of the nanoparticles and hence larger particle sizes. On the other hand, the lower temperatures may reduce the rate of the reaction and result

in the formation of smaller and more monodisperse nanoparticles. Therefore, the reaction temperature should be strictly regulated to obtain the necessary characteristics of nanoparticles (UNICEF, 2021).

3. pH

The synthesis of CuNPs strongly depends on the pH of the reaction mixture. The pH affects the charge and stability of the nanoparticles and the activity of the reducing agents in neem extract. The formation of stable nanoparticles is commonly enhanced at high pH because the surface of the nanoparticles acquires a negative charge, which hinders agglomeration. On the other hand, acidic conditions may cause the nanoparticles to come together through the process of neutralization of charges on their surface. Hence, the pH of the medium should be controlled to obtain stable and well-dispersed CuNPs (Manickum& John, 2019).

4. Reducing Agent

The quantity of neem leaf extract involved in the synthesis of CuNPs plays the role of the reductant that reduces copper ions to CuNPs. As the concentration of neem extract is increased, the reduction rate is increased which results in the formation of nanoparticles of smaller size and better size distribution. However, if the neem extract concentration is too high, it leads to the formation of more nanoparticles because of the presence of other bioactive compounds. Therefore, the amount of reducing agent used has to be optimized to regulate the size and shape of the synthesized CuNPs (UNESCO, 2021).

5. Applications of Copper Nanoparticles

Copper nanoparticles are used in various fields because of their special features such as electrical and thermal conductivity, catalytic properties, and bactericidal action. CuNPs are applied in conductive inks and pastes for printed circuit boards and flexible electronics in the field of electronics. In catalysis, CuNPs act as efficient catalysts for various chemical reactions such as hydrogenation and oxidation. Moreover, CuNPs possess remarkable antibacterial properties and therefore can be applied in antimicrobial films, bandages, and water purification (Fatta-Kassinos& Michael-Kordatou, 2020).

Electronics: CuNPs are used in electronics to prepare conductive inks and pastes for PCBs and flexible electronics applications. Copper is highly conductive of electricity making it suitable for use in these applications. CuNPs in conductive inks make it possible to deposit thin lines of conductive material, which is crucial in the development of smaller electronics. Also, CuNPs can be sintered at low temperatures and this is suitable for flexible substrates (Tchobanoglous et al., 2014).

Catalysis: CuNPs are also used in the catalysis of chemical reactions because they possess a large surface area and great catalytic properties. They are most useful in hydrogenation and oxidation reactions where they help in the transformation of reactants to products efficiently. The catalytic activity of CuNPs can be further improved by the size and morphology of CuNPs and thus, they are useful in industrial applications (Kumar et al., 2015).

Antimicrobial Applications: Due to the antimicrobial properties of CuNPs, they can be effectively used in medical and environmental fields. CuNPs can be used in antibacterial coatings for medical instruments, bandages, and surfaces to avoid bacterial and other microbial growth. Also, CuNPs have their application in water treatment processes since they can eliminate microorganisms that are dangerous to human health. Due to the large surface area, CuNPs can effectively interact with the contaminants and therefore can be used for environmental applications (Qu et al., 2013).

Challenges and Future Directions

However, the green synthesis of CuNPs using neem leaf extract has its limitations and constraints which are as follows: Among them, the major issue is the scale-up of the synthesis process since the large-scale production of CuNPs may be associated with the need to optimize reaction conditions and purification procedures. Also, to apply the synthesized CuNPs in the various fields in the long run, the stability of CuNPs must be established. Future studies should aim at establishing standard procedures for the green synthesis of CuNPs and discovering new areas of application in the upcoming fields like nanoelectronics, nanophotonics, and nanorobotics (Mendoza & Jonkers, 2017).

Material and Methods

Preparation of Neem Leaf Extract

New neem leaves were bought, washed with distilled water to ensure that they were free from any surface dirt, and then left to dry at room temperature for 48 hours. To further process the leaves, they were dried and then ground into a fine powder using a mechanical grinder. The neem leaf powder was then mixed with distilled water at a ratio of 1:10 (w/v) and incubated at 80°C for 30 min. The mixture was left to cool to room temperature and the neem leaf extract was then filtered using Whatman No. 1 filter paper to get a clear solution. This extract was kept at 4°C until the next step was to be carried out.

Synthesis of Copper Nanoparticles

In preparation of copper nanoparticles, copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was used as the source of copper. Copper sulfate stock solution (0. 1 M) was prepared in distilled water and different dilutions were made to obtain the following concentrations; 0. 001 M, 0. 01 M, 0. 1 M. In each synthesis, 50 mL of the neem leaf extract was added to 50 mL of copper sulfate solution in a 250 mL conical flask. The mixture was stirred at room temperature for 30 min with a magnetic stirrer bar.

Optimization of Reaction Parameters

To understand the effect of the synthesis parameters on the size and morphology of CuNPs, the concentration of copper sulfate, the volume ratio of neem extract to copper sulfate solution, pH of the reaction mixture, temperature, and reaction time were systematically changed.

1. Concentration of Copper Sulfate: The impact of $CuSO_4$ concentration on CuNP formation was investigated by changing the concentration from 0. 001M to 0. 1M while maintaining other factors constant.
2. Volume Ratio of Neem Extract to Copper Sulfate Solution: The volume ratios of neem extract to copper sulfate solution were varied to 1:1, 1:2, and 2:1 to find out the most suitable ratio for the formation of nanoparticles.
3. pH of the Reaction Mixture: The pH of the reaction mixture was then adjusted with 0. 1 M NaOH and 0. 1 M HCl solutions. The tested pH values included 2, 4, 6, 8, and 10.
4. Temperature: The reaction was performed at different temperatures of 25°C, 50°C, 75°C and 100°C to analyze the impact of temperature on the formation of CuNPs.
5. Reaction Time: The impact of reaction time on nanoparticle synthesis was studied by permitting the reaction to go on for various time durations (30 minutes, 1 hour, 2 hours, and 4 hours).

Characterization of Copper Nanoparticles

Different techniques were used for the characterization of the synthesized CuNPs to achieve complete knowledge of their physical, structural, and chemical properties. The absorbance of the reaction mixtures at different time intervals was recorded using *UV–visible spectroscopy* to monitor the synthesis and stability of the CuNPs. The *TEM* images were used to analyze the size and shape of the CuNPs. The samples for measurement were prepared by drop-casting one drop of the nanoparticle solution onto a carbon-coated copper grid and allowing it to dry. *XRD* characterized the crystalline structure of the CuNPs with measurements taken in the 2θ range from 20° to 80°. *Fourier Transform Infrared Spectroscopy (FTIR)* determined the surface functional groups of CuNPs and the possible interactions between neem extract and copper ions. *Dynamic Light Scattering* measured hydrodynamic size distribution and zeta potential of the prepared CuNPs, whereby the stability and dispersion of the nanosystem in solution could be identified.

Data Analysis

The characterization techniques were used to gather data that was used to deduce the conditions that favor the synthesis of CuNPs with the required size and morphology. The effect of different reaction parameters was analyzed statistically using the relevant software to determine the p-values.

Result and Discussion

Synthesis of Metal Nanoparticles

Preparation of Leaf Broth: Neem (Azadirachta indica) leaves were used for the synthesis of metal nanoparticles. The leaves were cleaned, and 20 grams were boiled with 100 ml of deionized water at 80°C for 20 minutes. The resulting extract was filtered and stored at 4°C for further experiments.

Chemical Equations for Synthesis: The possible reactions involved in the synthesis of metal nanoparticles using neem leaf broth are:

$$M^{+n}_{(aq)} + A.indica\ leaf\ broth\ \rightarrow^{Stirring}{}_{at\ optimal\ temperature}\ [Ag/\ A.indica\ leaf\ broth\ ]^{tn}$$

$$[M/\ A.indica\ leaf\ broth\ ]^{+tn}\ \rightarrow^{Stirring}{}_{at\ optimal\ temperature}\ [M/\ A.indica\ leaf\ broth$$

When A. indica leaf broth was added to a metal salt solution, the leaf broth reacted with $M^{+n}_{(aq)}$ and formed $[M/\ A.indica\ leaf\ broth\ ]^{+n}$ a complex (Equation 1). Further complex bioreduced into metal nanoparticles capped by biomolecules of leaf broth (Equation 2).

Copper Nanoparticle Synthesis: Similarly, the reduction of copper ions (Cu2+) by components present in the neem leaf broth leads to the formation of copper nanoparticles (CuNPs). The overall reaction can be represented as follows:

$$Cu^{2+} + 2e^{-} + 2H_2O \rightarrow Cu + 4OH^{-}$$

This reaction depicts the reduction of copper ions by two electrons and two water molecules to form elemental copper (Cu) and hydroxide ions (OH^{-}).

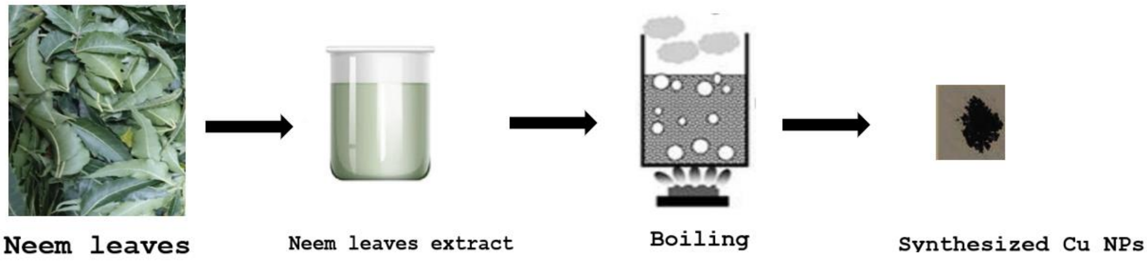

Figure 1: Steps involved in the preparation of Neem broth from leaves.

Characterization of the synthesized Copper Nanoparticles

Using neem leaf broth as the reducing and stabilizing agent, copper nanoparticles (CuNPs) were produced in this synthetic process by a green reduction method. First, an aqueous solution containing 7.5 x 10^-3 M of copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) was made. To guarantee even heating, this solution was heated to 85 °C in an oil bath while being continuously stirred by magnets. The heated copper salt solution was then mixed with neem leaf broth, which made up 20% of the total solution volume, added dropwise. The dispersion changed color several times because of this addition, signifying the reduction process and the creation of CuNPs. The solution's color changed over time, going from green to yellow, orange, radish brown, brown, and eventually dark brown, with multiple intermediate phases visible. These color changes show how Cu^2+ ions are gradually reduced to copper nanoparticles. The dark brown solution that was left over from the reduction procedure was centrifuged for 15 minutes at 6000 rpm to extract the nanoparticles from the supernatant. For a duration of two months, the produced supernatant was kept at 4 °C to provide additional stability and possible improvement of the nanoparticle characteristics.

1. TEM and SEM

The morphological and structural characteristics of the produced CuNPs were assessed by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). According to the SEM scans, the particles were around 2 µm in size and had a spherical form, as seen in Figure 2-a. The electrostatic interaction between the freshly generated nanoparticles may have contributed to the modest agglomeration of the nanoparticles that was noticed. In the process of creating nanoparticles, this agglomeration frequently occurs and can affect the functional characteristics and stability of the dispersion. Additional TEM investigation revealed more details about the form and surface properties of the CuNPs, as shown in Figure 2-b. The majority of the nanoparticles' shape was confirmed to be cubic by the TEM pictures. Furthermore, a thin layer of organic material made from the broth made from neem leaves encased the produced nanoparticles, according to the TEM data. The capping agent-like properties of this organic layer probably stabilize the nanoparticles and stop them from further agglomerating. This capping layer is essential because it improves the CuNPs' biocompatibility and functional qualities, enabling a range of biomedical and environmental remediation applications.

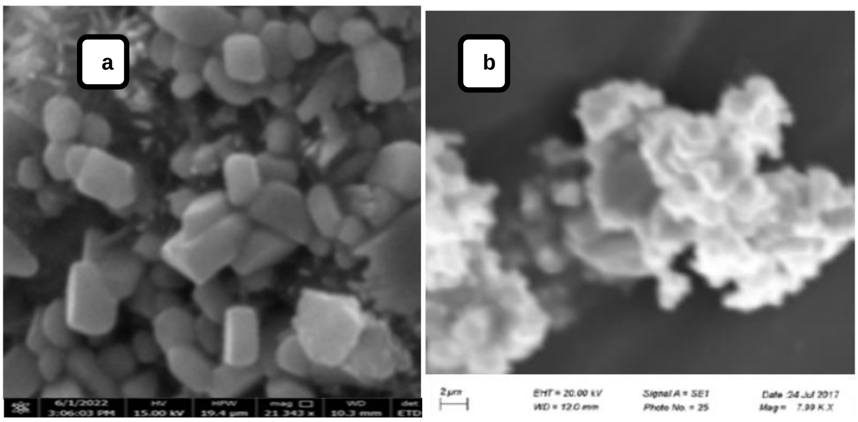

Figure 2: (a) SEM micrograph of synthesized CuNPs (b) TEM micrograph of synthesized CuNPs

The size distribution analysis indicates that most of the nanoparticles fall within the 3.0-3.5 nm diameter range, which corresponds to the highest frequency observed in the histogram. This peak suggests that the synthesis process predominantly produces nanoparticles of this size. The presence of a normal distribution curve suggests that most particles clustered around the mean size of approximately 3.0-3.5 nm (Figure 3).

Smaller peaks are also noted at other diameter ranges, such as 2.5-3.0 nm and 3.5-4.0 nm, though their frequencies are significantly lower.

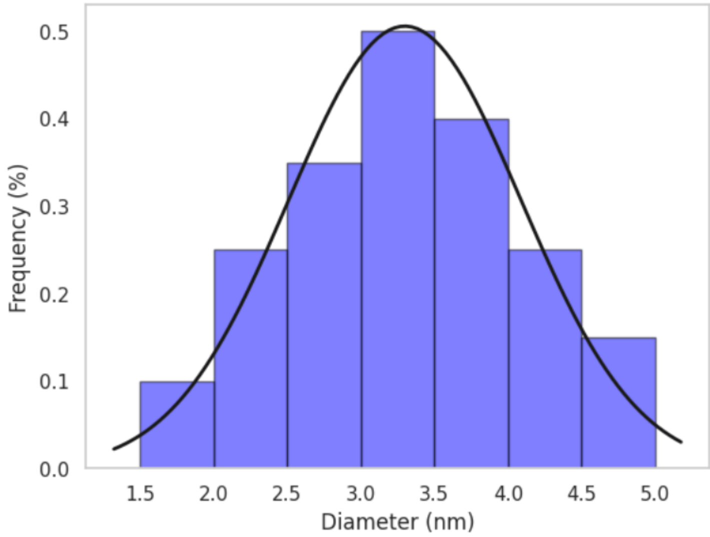

Figure 3: Size distribution of synthesized Copper nanoparticles

2. EDS

The components of CuNPs can be readily determined by the EDS spectra of the produced NPs. The spectra display a strong signal for copper atoms, confirming that the copper nanoparticles (CuNPs) are composed of pure copper, as illustrated in Figure 4. Additionally, the spectra show the presence of carbon and oxygen elements, which appear as contaminants around the copper peaks. These contaminants are attributed to phytochemicals from the plant extract used in the synthesis process. The detection of these elements indicates the presence of organic substances attached to the CuNPs, signifying successful capping by the phytochemicals. Notably, the EDS profile does not reveal any other impurities, indicating a high purity level of the synthesized CuNPs.

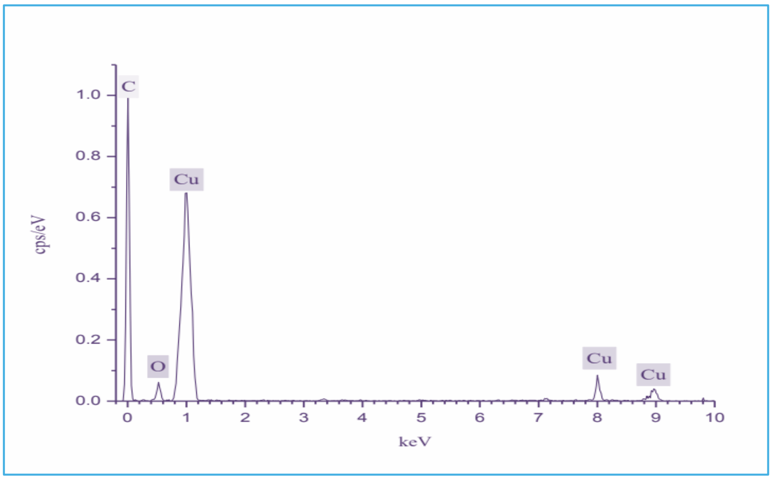

Figure 4: EDS spectrum of synthesized copper nanoparticles

3. XRD

The X-ray diffraction (XRD) pattern for copper nanoparticles (CuNPs) that were dried at room temperature shows the presence of capping biomolecules, yet it fails to clearly reveal the crystalline structure of the CuNPs. On the other hand, CuNPs that underwent vacuum drying at 70 °C for 12 hours exhibited sharp XRD peaks at 2θ values of 43.5°, 49.9°, and 74.01°. These peaks are associated with the (111), (200), and (220) planes, respectively, which confirm the "face-centered cubic (FCC)" crystal structure of copper, as demonstrated in Figure 5.

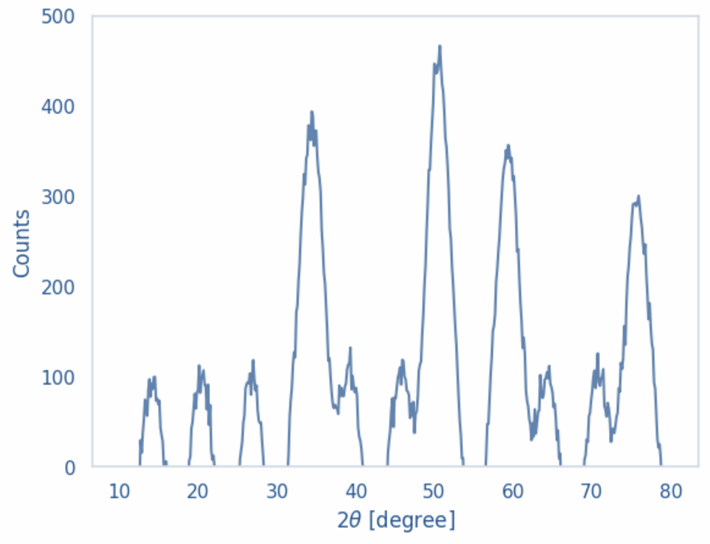

Figure 5: XRD pattern of synthesized CuNPs

Discussion

The method of preparation and the properties of the copper (Cu) nanoparticles are very crucial in defining their uses. Future improvements in synthesis and characterization methodologies will enable the enhancement of nanoparticles' applications and the creation of environmentally friendly and effective nanotechnologies. There are several approaches to synthesise nanoparticles and every technique has its pros and cons. Of all these methods, green synthesis techniques have been considered because of the friendly approach that the method uses natural materials. Biogenic synthesis methods employ plant extracts, microorganisms, and enzymes to synthesize nanoparticles. This method also minimizes the application of toxic chemicals and increases the biocompatibility of the synthesized nanoparticles. For instance, Mishra et al. (2021) showed that egg ovalbumin can be used to synthesize gold nanoparticles; hence, similar biological materials may be used to synthesize copper nanoparticles. Similarly, Primo JD. O. et al. (2020) used Aloe vera extract to synthesize zinc oxide nanoparticles with an emphasis on the green synthesis process. These studies stress the importance of the synthesis of new compounds with minimal adverse effects on the environment and with the utilization of renewable feedstocks. The structure and morphology of the nanoparticles are important to be determined because these aspects influence the nanoparticles' properties and their functioning in various applications. Some of the methods used to characterize nanoparticles are XRD, TEM, SEM, and UV-visible spectroscopy. Gupta et al. (2022) have employed SEM and XRD analysis to study the crystalline structure and morphology of the nanostructured titanium nitride. In the same manner, Patel et al. (2023) used XRD, SEM, and UV-visible spectroscopy techniques to analyze ZnO nanorods for their structure and optical properties. These characterization techniques enable the researchers to know the size, shape, composition, and surface properties of the nanoparticles to optimize them nanoparticles for specific uses. Thus, the preparation and analysis of copper nanoparticles are crucial for understanding their characteristics and possible uses. Green synthesis methods can be considered a promising strategy for the synthesis of nanoparticles with the characteristics of biocompatibility and environmental friendliness. Techniques like XRD, TEM, SEM, and UV-visible spectroscopy are very useful for the characterization of copper nanoparticles and their enhanced properties for potential applications in industry and the environment.

Conclusion

This work explains a green synthesis of CuNPs using the neem leaves extract, which is considered an eco-friendly method because the bioactive compounds of neem leaves are employed for the reduction as well as stabilization of CuNPs. It lowers the usage of toxic substances and enhances biocompatibility, which is ideal for various fields. Therefore, the size and shape of CuNPs can be controlled by varying the concentration of precursor, temperature, pH, and amount of neem extract. UV-Vis, TEM, XRD, FTIR, and DLS analysis of the synthesized nanoparticles provides structural and functional information about the nanoparticles. Some of these CuNPs have the following desirable properties; high electrical and thermal conductivity, catalytic activity, and antibacterial properties, which makes them suitable for use in electronic devices, catalysts, and medical sectors. Future research should be focused on the enhancement of the method of CuNP preparation, enhancement of the stability of CuNPs, and application of CuNPs in new fields including nanoelectronics and nanorobotics. The green synthesis of CuNPs using neem leaf extract offers environmental advantages as well as opens up new approaches for the synthesis of advanced nanomaterials.

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