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Black Oil Sunflower Seeds in CuNP Synthesis

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Abstract

Black oil sunflower seeds (*Helianthus annuus* L) are the preferred feed for wild birds due to their high calorie content and their thin hulls. However, the oils can spoil easily in humid and hot climates resulting in wastage. Our hypothesis is that we can synthesize copper nanoparticles (CuNPs) using sunflower seeds as a reducing agent. The process used involved a solution of copper sulfate, an extract of black oil sunflower seeds, and starch as a capping agent. Visual observation showed a change in color from a bright blue to a light brown color and formation of reddish-brown precipitates on heating, indicating the formation of CuNPs. On testing part of the precipitate with Cuprotesmo test papers, the test papers turned pink, indicating the presence of metallic copper. Transmission Electron Microscope (TEM) images were analyzed using ImageJ software from the National Institute of Health (NIH) and showed a mean CuNP size of 58.55 nm. In shape, the synthesized CuNPs were mostly spherical. Energy dispersive spectroscopy (EDS) analysis showed multiple copper peaks, proving that CuNPs were synthesized. We conclude that an extract of black oil sunflower seeds acts as a strong reducing agent.

Subject Areas

Science, Nanotechnology, Nanoparticles, Green Chemistry, Biosynthesis

Keywords

Nanoparticles, Copper, Synthesis, Novel, Recyclable, Black Oil Sunflower Seeds, *Helianthus annuus* L

1. Introduction

Nanoparticles are particles with at least one dimension in the nanoscale (1 nm to 100 nm) [1]. In this scale range, particles have markedly different properties from those at larger scales. Melting point, conductivity, optical, magnetic, and chemical reactivity all change with the size of the particle [2]. Since copper is abundant in nature and is a required element in trace amounts for human health [3], copper nanoparticles (CuNPs) are a potential alternative to using more expensive metals [4].

CuNPs can be synthesized using chemical, physical, and biological methods. Chemical methods typically involve the reduction of a copper salt solution by adding a reducing agent and a capping/stabilizing agent. The reduction process results in the formation of nanoparticles. Another popular chemical method involves an electrochemical reaction where a current is passed between two electrodes separated by an electrolytic solution of copper sulfate and sulfuric acid [5]. Physical methods involve breaking down a large piece of material into nanoparticles by cutting and grinding [6]. Biological methods involve synthesizing nanoparticles using environmentally benign agents such as plants, microbes, and fungi [7]. This process does not result in toxic byproducts, and the resultant nanoparticles can be used in clinical settings. As a result, there has been growing interest in the green synthesis of nanoparticles [8].

Phytochemicals in plants act as antioxidants in the reduction of metal salts to nanoparticles. Green synthesis is an alternative to other methods, due to its reduced costs and toxicity [9]. As there are many different phytochemicals in a plant, it is not possible to measure each antioxidant separately. As a result, the ferric reducing/antioxidant power (FRAP) assay has been developed to measure the total antioxidant content in a plant or food [10].

Capping agents are used as a stabilizer in nanoparticle synthesis to prevent the overgrowth of nanoparticles and to prevent their reaction with oxygen. Since this experiment is being done in a home environment that cannot be controlled as well as a total lab environment, a capping agent must be used to control oxidation.

Several techniques have been created to study the size, composition, and structure of nanoparticles. A combination of techniques is used to reliably characterize them. Transmission electron microscopy (TEM) is used for characterizing shape, size, and dispersion [11]. Energy-dispersive X-ray spectroscopy (EDS) is used to further develop the characterization by providing chemical information [12].

The size and shape of the nanoparticles are dependent on the metal ion concentration, the reducing agent, and the capping/stabilizing agent.

Helianthus annuus L is a crop native to the United States, and its seeds are eaten by a variety of birds and mammals [13]. Black oil sunflower seeds are preferred by birds, as they have a high calorie content and are nutritionally dense due to their high oil content [14]. Also, the hulls are thinner and easier for birds to break open [15]. Sunflower seeds have a high level of sulfur-rich proteins, fatty acids, vitamin E and flavonoids which give them high antioxidant potential [16]. Black oil sunflower seeds are also used for making cooking oil. In 2020/2021, the world's production of sunflower oilseed was 49.60 million metric tons. Approximately 50% of the seeds are left after oil extraction [17], which present a significant opportunity for recycling.

Since black oil sunflower seeds are easy to procure, have a high antioxidant content, and have a large potential for recycling, the synthesis of CuNPs using its extract was studied (**Figure 1**). Furthermore, as black oil sunflower seeds have a high antioxidant value of 6.4 mmol/100g per the antioxidant food table [18], we hypothesized that it would be a good reducing agent. Our research purpose is to validate our hypothesis and demonstrate a novel, green pathway for the synthesis of CuNPs.

2. Materials and Methods

2.1. Materials

Reagent Grade Copper (II) Sulfate 5-Hydrate (Innovating Science®), BlackOil Sunflower Seeds (Publix®), Lab grade deionized water (Ecoxall LLC©), and Cuprotesmo (donated by CTL Scientific Supply Corp).

2.2. Preparation of Plant Extract

Black oil sunflower seeds were washed in deionized water to remove impurities. Seeds were then ground in a grinder. 5 g of the ground seeds were mixed with 100 mL water and boiled at 100˚C for 10 min. The resulting extract sat for 12 hours (**Figure 2(a)**) and was then filtered through Whatman No. 1 filter paper (**Figure 2(b)**).

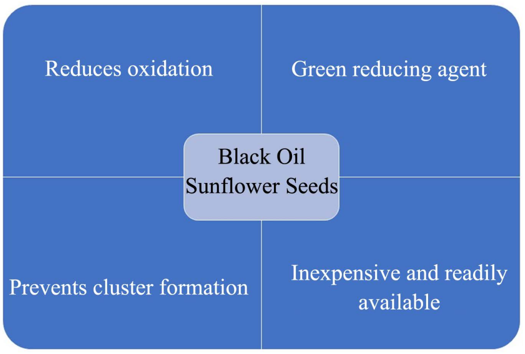

Figure 1. Advantages of using black oil sunflower seeds as a reducing agent in the synthesis of CuNPs.

(a) (b)

Figure 2. (a) Sunflower seed extract allowed to stand for 12 hours. (b) Sunflower seed extract undergoing filtration.

2.3. Reduction of Copper Sulfate

A solution of 5 g of copper sulfate in 80 mL of deionized water was made. 20 mL of the seed extract and 1 g of starch were added, and the contents were stirred. A second solution was prepared without the seed extract. Both flasks were placed in a boiling water bath for 1 hour. They were capped and placed in a dark cabinet to minimize oxidation and were allowed to stand for 36 hours. The flask with the seed extract formed precipitates and changed color. Part of the solution was transferred into amber glass bottles for TEM and EDS analysis. Visual and chemical tests were performed on the remainder of the solution. On the other hand, the flask without the seed extract did not form precipitates and did not change color. No further analysis was performed on this solution.

2.4. Characterization of CuNPs

TEM images were obtained using a Philips CM 120 Transmission Electron Microscope at an accelerating voltage of 100 kV and a point resolution of 0.34 nm. EDS analysis was done using an Oxford INCA EDS system featuring a 10 mm^2 detector with 140 eV resolution. TEM images were sized and characterized using ImageJ software from the National Institute of Health (NIH).

3. Results

3.1. Visual Analysis

When the seed extract was added to the copper sulfate solution, the mixture changed in color from a bright blue to a muddy brown. Upon heating, reddish precipitates formed, indicating CuNP synthesis (**Figure 3**). The CuNPs were observed to be stable in solution after 4 weeks and did not grow in size or change in color. No visual changes were observed in the sample solution without the seed extract.

3.2. Chemical Analysis

Furthermore, part of the precipitate was tested with Cuprotesmo test papers, after filtration through Whatman No. 1 Filter Paper. When used on the precipitate, the test papers turned pink, indicating that the precipitate indeed contained metallic copper (**Figure 4**).

Figure 3. Color change and precipitate formation when sunflower seed extract was added to copper sulfate solution.

Figure 4. Cuprotesmo test paper color changed from white to pink when tested on the precipitates formed. This indicated the presence of metallic copper.

3.3. TEM Analysis

TEM image (Figure 5) taken at a resolution of 0.34 nm shows that the nanoparticles are uniformly distributed in the solution and are predominantly spherical in shape. Analysis of the image with ImageJ software yielded an average size of 58.55 nm.

3.4. EDS Spectra Analysis

Energy dispersive spectroscopy (EDS) analysis (Figure 6) validated the presence of synthesized CuNPs in the solution with the seed extract. The carbon peak resulted from the carbon film used during the analysis procedures. Sunflower seeds have high phosphorus and potassium contents, which appeared in the EDS spectra. Trace amounts of oxygen and sulfur were found due to the copper sulfate initially used.

3.5. ImageJ Analysis

ImageJ software was used to improve the edges of the TEM images and analyze the sizes and morphologies of CuNPs (Figure 7). 20 nanoparticles were selected, and their diameters were analyzed and plotted on a chart.

4. Discussion

4.1. Overall

The presence of synthesized CuNPs was validated through visual and several analytical techniques. TEM image of CuNPs (Figure 5) shows that mainly spherical nanoparticles were synthesized. EDS analysis (Figure 6) shows peaks that match the characteristic EDS profile of copper. Therefore, the EDS Spectra results validate that CuNPs were generated. Twenty nanoparticles were sized from TEM images using ImageJ software. The average size of nanoparticles was

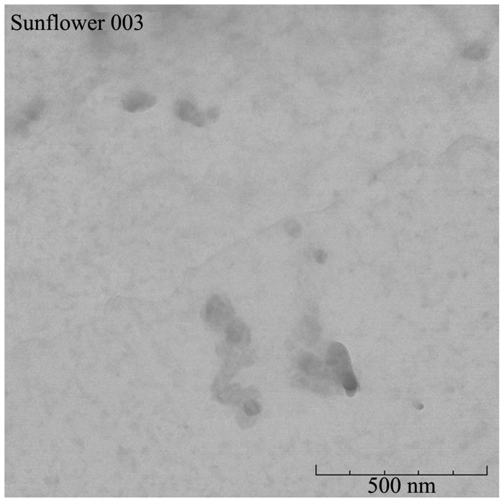

Figure 5. TEM image of CuNPs.

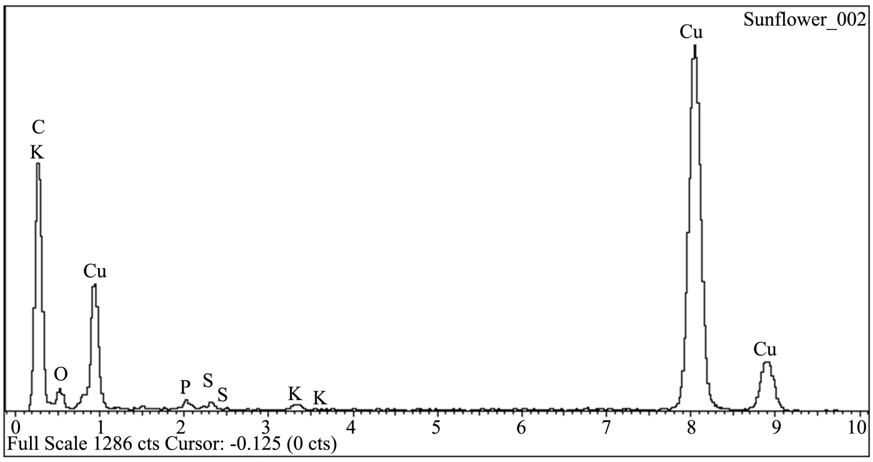

Figure 6. EDS Spectra of CuNPs.

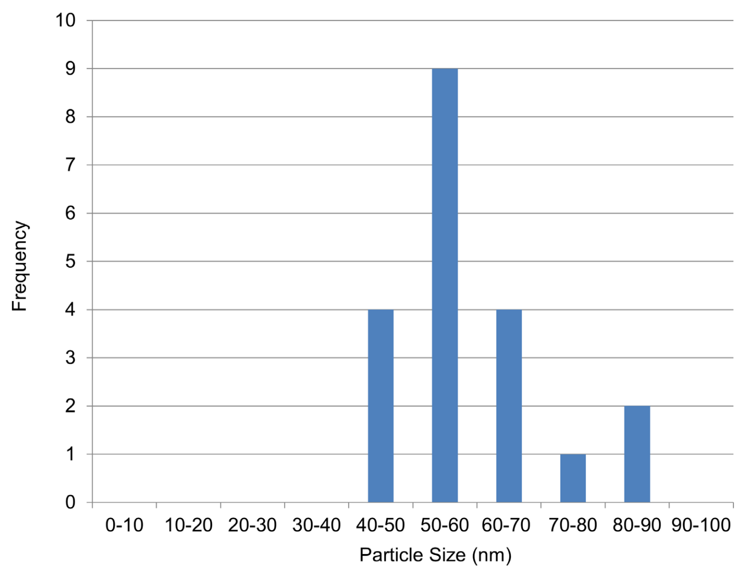

Figure 7. Nanoparticle size distribution based on ImageJ analysis.

58.55 nm. The majority of the nanoparticles were uniform in size with a few outliers (Figure 7).

4.2. Limitations

This experiment was conducted in a home environment, and there was no equipment available to centrifuge and wash the copper precipitates. The leftover oils in the supernatant made sample preparation for TEM imaging difficult. Additionally, there was not an inert atmosphere and there was potential for oxidation to occur. This was minimized by doing the experiment in a dark room and storing all materials in dark cabinets in amber bottles. The study used a smaller number of samples, as there was limited access to lab equipment. Despite these limitations, our study does prove the hypothesis that CuNPs can be synthesized using black oil sunflower seeds.

5. Conclusion

Black oil sunflower seeds are a common waste product of the bird feed industry. Due to its anti-oxidative properties, we hypothesized that sunflower seed extract would be successful as a reducing agent in the process of CuNP synthesis. To test this, we prepared a solution of copper (II) sulfate and seed extract. Precipitates of CuNPs were formed, and TEM and EDS analyses were performed. Thus, we can conclude that in this experiment, we were successful in demonstrating a new, environmentally friendly method to synthesize larger, spherical CuNPs using black oil sunflower seed extracts. Furthermore, through this method, waste products act as reducing agents, thus aiding recycling efforts. The technique is economical and contains no toxic substances.

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Conflicts of Interest

The author declares no conflicts of interest.

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