Indonesian Journal of Chemical Research

http://ojs3.unpatti.ac.id/index.php/ijcr Indo. J. Chem. Res., 11(3), 212-217, 2024

Synthesis of Copper Nanoparticles Using Dragon Fruit (*Hylocereus polyrhizus*) Extract as a Bio-Reductor and Their Analysis Using a UV-Visible Spectrophotometer

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Received: August 2023
Received in revised: September 2023
Accepted: December 2023
Available online: January 2024

Abstract

Nanotechnology is a branch of science that investigates materials on a scale of 1-100 nanometers. One method that is often used to create copper nanoparticles is biosynthesis using plant extracts because it is more environmentally friendly, does not use toxic reagents and solvents and the process is simpler. Dragon fruit extract (*Hylocereus polyrhizus*) has potential as a reducing agent for metal compounds because it contains phenolic and carboxylic groups. This study aimed to synthesize copper nanoparticles (Cu-NPs) using a bio-reductor in the form of dragon fruit extract with various volume variations of $CuSO_4$, pH variations, and stirring time variations. Red dragon fruit extraction was carried out by the maceration method to obtain extracts from dragon fruit, which were then used as a Cu metal-reducing agent. The resulting Cu nanoparticles were characterized using a UV-Visible Spectrophotometer. Based on the data, the highest absorbance value was obtained from the most volume of $CuSO_4$, namely 2 mL with an absorbance peak at a wavelength of 700-750 nm. The optimum pH was obtained at pH 6 with a peak absorbance at a wavelength of 750 nm. The most effective time to obtain the absorbance peak at a wavelength of 700 nm was 15 min.

Keywords: Bio-reductor, Copper, Dragon fruit, Nanoparticles, UV-Visible Spectrophotometer.

INTRODUCTION

Nanotechnology is a field of science that studies materials on a scale of 1-100 nanometers which has developed rapidly in recent years and has attracted a lot of interest from researchers (Anu Mary Ealia & Saravanakumar, 2017). The word nano is taken from the Greek word "nanos" which means small (Putri et.al., 2023). One of the most developed nanotechnology studies involves the use of copper nanoparticles (Parningotan & Hamzah, 2020). Copper nanoparticles (Cu-NPs) have better oxidizing properties than other metals and are non-toxic to mammals (Fatiha et.al, 2022). According to research conducted by Parningotan and Hamzah (2020), copper has antibacterial and antiviral properties. They also reported that copper can efficiently inactivate influenza A viruses and Q bacteriophages.

Copper nanoparticles (Cu-NPs) are commonly manufactured by scientists owning to their economic cost. One method that is often used is bottom-up biosynthesis using bacteria, fungi, or plant extracts (Rusly & Rahman, 2023). Biosynthesis is a more environmentally friendly method because it does not use toxic reagents and solvents, the process is simpler, and it is inexpensive to utilize bio-reductors in the form of plant extracts. This method can produce nanoparticles with better stability and morphology and have various therapeutic benefits (Haruna et.al., 2020).

The synthesis of copper nanoparticles (Cu-NPs) using a biosynthesis method with bio-reductors in the form of plant extracts was carried out by Rusly and Rahman (2023). The peak measurements of the Cu-NPs were obtained in the range of 269 nm. These results are consistent with the characterization of Cu-NPs formed through absorbance spectrum analysis using a UV-Visible Spectrophotometer at wavelengths of 200-650 nm (Putri et al., 2023). Then the synthesis of copper nanoparticles with Aloe vera leaves produced a size of 20 nm (Aini et al., 2022), *Cissus vitinea* leaves produced a size of 10-20 nm (Fitra et.al, 2021), and using black soybean extract produced copper nanoparticles with an average size 26 nm (Avilia & Hilda, 2022). In addition, dragon fruit (*Hylocereus polyrhizus*) also has the potential as a reducing agent for metal compounds because it contains phenolic and carboxylic groups (Noviyanty et.al, 2019; Qomariyah et al., 2022.; Shofinita et.al, 2020).

Dragon fruit is a living plant found in almost all parts of Indonesia (Lestari & Santoso, 2018; Noor & Yufita, 2016). Banyuwangi Regency is one of the regencies in East Java Province which has a superior product from the agricultural sector, namely dragon fruit. Based on the data for 2020, the total production of dragon fruit has reached 82,544 tons. The dragon fruit farming center areas in Banyuwangi district consist of the sub-districts of Siliragung, Pesanggaran, Cluring, Tegaldlimo, Purwoharjo, Bangorejo, Sempu, and Srono (Ministry of Agriculture, 2022).

According to Noor and Yufita (2016), dragon fruit contains phenolic compounds that are useful as antioxidants that can capture free radicals because they contain hydroxyl groups, which are reducing agents and can act as hydrogen donors against free radicals. Based on the results of phytochemical and Fourier Transform Infra-Red (FTIR) tests, the antioxidant compounds in dragon fruit are tannins, flavonoids, alkaloids, steroids, and saponins (Rohim, 2016). Several other molecules were also identified, including betanin, isobetanin, phyllocactin, isophyllocactin, hylocerenin, and isohylocerenin. These compounds contribute to the red color of the fruit. All these compounds contain phenolic and carboxylic groups in their molecular structure (Nuryono et al., 2019; Qomariyah et.al, 2021). This content is found in the flesh, skin, roots, stems, and leaves of dragon fruit with different concentrations (Anggraheni et.al, 2020).

This provides an opportunity to exploit the potential of dragon fruit as a bio-reductor in the synthesis of copper nanoparticles. This study aimed to synthesize copper nanoparticles (Cu-NPs) using a bio-reductor in the form of dragon fruit extract with various volume variations of $CuSO_4$, pH variations, and variations in stirring time. Because variations in pH and variations in stirring time will affect the performance of the nanoparticles (Anu & Saravanakumar, 2017), it is necessary to investigate this in this study. The results of the synthesis of Cu-NPs will be observed qualitatively by looking at the color change and analyzed using a UV-visible spectrophotometry instrument.

METHODOLOGY

Materials and Instrumentals

The equipment used in this study was a UV-Visible Genesys 10S spectrophotometer, cuvette, mortar and pestle, pH Universal paper, Whatman filter paper, plastic basin, and laboratory glassware including 100 mL of beaker glass (Pyrex), 100 mL of volumetric flask (IWAKI), measuring cups 5 mL, 10 mL, 50 mL (Pyrex), Erlenmeyer 100 mL (Pyrex), stir bar, pipette, and funnel. The materials used in this study were 4 mL of dragon fruit extract taken from Pesanggaran Village, Banyuwangi Regency, 0.03 M $CuSO_4$ solution (Merck), 1 M NaOH (Merck), ice cubes, and distilled water.

Dragon fruit extraction

Red dragon fruit was extracted using the maceration method. The dragon fruit used in this study was fresh red dragon fruit. The red dragon fruit was washed, cut into small pieces, and mashed using a mortar until smooth. It was then filtered to remove the filtrate. Distilled water was used at a ratio of 1:4 (ingredient: solvent). The dragon fruit extract was taken as much as 1 mL and diluted in a 100 mL volumetric flask, then homogenized.

Cu-NPs synthesis with $CuSO_4$ volume variation

The volume of $CuSO_4$ was varied to 0.5, 1, and 2 mL. It was prepared with 3 beakers, then 38 mL of distilled water, 0.5 mL, 1 mL, and 2 mL of 0.03 M $CuSO_4$ were added, and the mixture was homogenized. Subsequently, a dragon fruit reducer was added to each beaker to a volume of 4 mL. The pH was then measured at an initial pH of 4.5. Subsequently, 20 drops of NaOH were added to achieve pH of 12. The mixture was stirred in an ice bath and analyzed using a UV-Visible spectrophotometer.

Cu-NPs synthesis with pH variation

In this study, three solutions were prepared, each containing 38 mL distilled water and 2 mL 0.03 M $CuSO_4$. Then, the mixture was stirred until it was evenly distributed. Next, 4 mL of red dragon fruit extract was added to the solution as a reducing agent. Each solution was conditioned at varying pH values (6, 9, and 12) with the addition of 1 M NaOH. At pH 6, three drops of 1 M NaOH were added, five drops at pH 9, and 20 drops at pH 12. The mixture was stirred for 15 min in a container containing ice cubes. The absorbance was then measured using a UV-visible spectrophotometer with a wavelength of 400-800 nm. The highest absorbance was used to determine the maximum pH.

Synthesis of Cu-NPs with a variation of stirring time

In this study, variations in stirring were performed with stirring durations of 5, 15, and 25 min. Then, 38 mL of distilled water was added to 2 mL of 0.03 M $CuSO_4$ in three beaker glasses and homogenized. Subsequently, the beaker glass was labeled with a specified time variation. A dragon fruit reducer was added to each beaker to a volume of 4 mL. Next, the pH was measured at an initial pH of 4.5. Approximately 20 drops of NaOH were added so that the pH was 12. The mixture was stirred in an ice bath for various durations and analyzed using a UV-Visible Spectrophotometer.

Data Analysis

The maximum value of each variation determined the success of the optimal $CuSO_4$ reduction. Of all the variations that have been carried out, the absorbance was analyzed to determine the maximum value of each variation. The absorbance was measured using a UV-Visible Spectrophotometer at a wavelength of 400-800 nm.

RESULTS AND DISCUSSION

Based on the results of the synthesis of copper nanoparticles (Cu-NPs) with dragon fruit extract, the presence of secondary metabolites such as phenolics acted as electron donors to Cu metal. During the copper nanoparticle (Cu-NPs) synthesis process, a color change occurred when the extract solution was mixed with the $CuSO_4$ solution. This color change is a strong indication of the formation of Cu-NPs. The reduction of Cu metal by dragon fruit extract was possible in the presence of phenolic compounds, resulting in the reduction of Cu^{2+} to Cu^0. This is illustrated in Figure 1. These phenolic compounds contain hydroxyl groups that can bind to metals. The ability to chelate metals from phenolic compounds is due to the highly nucleophilic character of the aromatic rings. Flavonoids are a large group of polyphenolic compounds that actively chelate and reduce metal ions into nanoparticles (Avilia & Hilda, 2022).

Wavelength absorbance measurements were performed using a UV-visible spectrophotometer to prove that the reduction reaction occurred. The formation of copper nanoparticles was indicated by the formation of absorbance peaks at a wavelength of 200-650 nm (Avilia & Hilda, 2022).

$CuSO_4$ Volume Variation

$CuSO_4$ solutions with various volumes (0.5, 1, and 2 mL) were mixed with a reducing agent in the form of dragon fruit extract. This was done to determine the effect of $CuSO_4$ concentration on the formation of copper nanoparticles (Cu-NPs). In Figure 2, it appears that the solution from left to right becomes darker in blue.

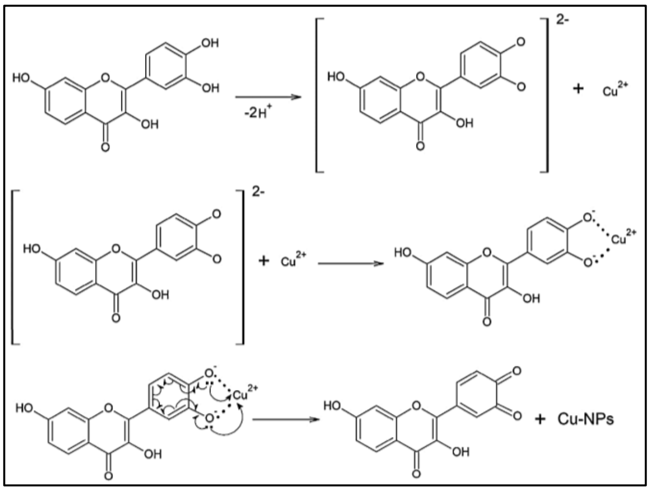

Figure 1. Prediction of the reaction mechanism for the formation of copper nanoparticles

The solution on the far left uses the $CuSO_4$ solution with the lowest concentration, and the further to the right, the greater. This affects the color of the resulting solution, where the greater the volume of $CuSO_4$, the more concentrated the color of the solution, which indicates that more nanoparticles were formed.


Figure 2. Synthesis of Cu-NPs with various concentrations of $CuSO_4$

Measurements of colloidal copper nanoparticles using a UV-visible Spectrophotometer were carried out in the wavelength range of 400 – 800 nm (Figure 3). The characteristics of the formation of copper nanoparticles by UV-Visible Spectrophotometer analysis can be observed from the formation of the absorbance spectrum at a wavelength of 200-650 nm. The change in peak intensity is related to the concentration of the reducing agent. The higher the reduced concentration, the smaller the intensity (Fatiha et.al, 2022). The wavelength 400 nm was obtained. The optimum concentration of the reducing agent shows the highest intensity. At the optimum concentration, the amount of reducing agent is sufficient to reduce Cu^+ ions in solution. This is what causes a sufficient number of nanoparticles to form a lot so that the reducing agent used is effective in the formation of nanoparticles copper. The reducing concentration below the optimum shows a small intensity. This matter This is because the amount of reducing agent available is not sufficient to reduce the ion Cu^+ to Cu^0 so that little silver nanoparticles are formed. A concentration-reducing agent that exceeds the optimum concentration results in a capable reducing agent that reduces Cu^+ ions quickly. This can accelerate growth particles and cause aggregation which results in enlarged copper nanoparticles, so that the size of the copper nanoparticles is more varied. The absorbance peak for $CuSO_4$ variation was formed at a wavelength of 700-750 nm. And it can be seen that the highest $CuSO_4$ concentration produces a high absorbance value as well.

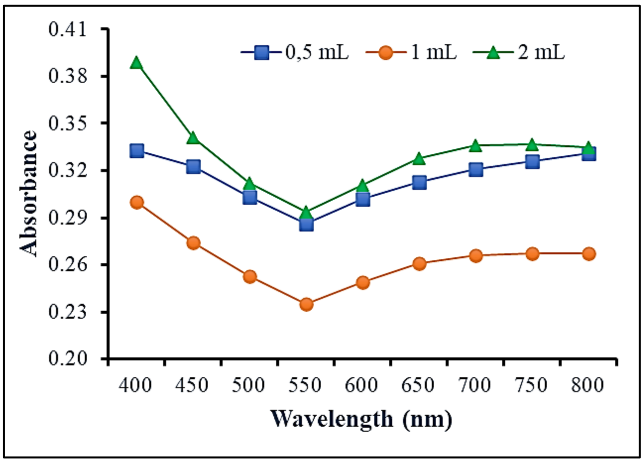

Figure 3. UV-Visible spectrum of Cu-NPs at volume comparison of $CuSO_4$

The change in peak intensity is related to the concentration of the reducing agent. The higher the reduced concentration, the smaller the intensity (Fatiha, Dwyana, & Johannes, 2022). The wavelength 400 nm was obtained. The optimum concentration of the reducing agent shows the highest intensity. At the optimum concentration, the amount of reducing agent is sufficient to reduce Cu^+ ions in solution. This is what causes a sufficient number of nanoparticles to form a lot so that the reducing agent used is effective in the formation of nanoparticles copper. The reducing concentration below the optimum shows a small intensity. This matter This is because the amount of reducing agent available is not sufficient to reduce the ion Cu^+ to Cu^0, so little silver nanoparticles are formed. A concentration-reducing agent that exceeds the optimum concentration results in a capable reducing agent that reduces Cu^+ ions quickly. This can accelerate growth particles and cause aggregation which results in enlarged copper nanoparticles, so that the size of the copper nanoparticles is more varied.

pH Variation

The $CuSO_4$ solution was mixed with the dragon fruit extract. Then, 1 M NaOH was added to vary the pH with a pH variation of 6, 9, and 12. The purpose of pH variation was to determine the optimum pH for the formation of copper nanoparticles (Cu-NPs). As shown in Figure 4, the color of the resulting solution with different pH values did not experience a significant color difference.

Based on the results of measurements using a UV-Visible Spectrophotometer, it can be seen that at the lowest pH (pH 6). Thus, the optimum pH for the synthesis of copper nanoparticles (Cu-NPs) with dragon fruit extract was 6. The pH of reducing compounds and capping agents can affect the copper ion reduction process into nanoparticles. The phenolic functional group from dragon fruit extract can be deprotonated to form a group a new functional unit that is negatively charged under alkaline conditions. The phenolic groups can remove H^+ to form a conjugate base. Negatively charged functional groups can bond with Cu^+ through electrostatic interactions or covalent bond coordination as in Figure 1. The use of dragon fruit extract in the synthesis of copper nanoparticles can save valuable materials used and reduce the waste produced because dragon fruit extract has two functions simultaneously a reducing agent and a capping agent.

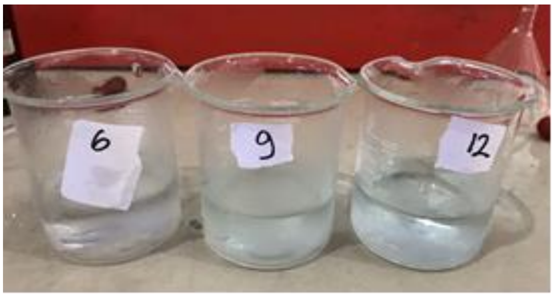

Figure 4. Synthesis of Cu-NPs with variations in pH

At pH of 6, the absorbance value is the highest, with the absorbance peak obtained at a wavelength of 750 nm. The quantity of the reducing agent is adequate to decrease the Cu^+ ions in the solution at the ideal concentration. This is what results in a large enough quantity of nanoparticles being produced, allowing the copper nanoparticles to be effectively generated by the reducing agent. Below the optimal concentration, the decreasing concentration has a weak intensity. This issue This happens because there is not enough reducing agent to change the ion Cu^+ to Cu^0, leading to the formation of tiny silver nanoparticles. A reducing agent that has a concentration that is higher than the ideal concentration can swiftly decrease Cu^+ ions. This may speed up particle growth and lead to aggregation, which results in larger copper nanoparticles and a wider range of copper nanoparticle sizes.

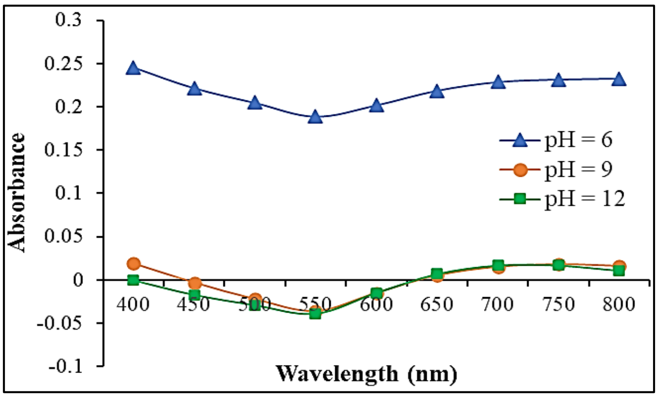

Figure 5. Cu-NPs UV-Visible spectrum with variations in pH

Stirring Time Variation

The synthesis of copper nanoparticles (Cu-NPs) using dragon fruit extract was carried out by varying the stirring time to determine the effect of stirring time on the formation of copper nanoparticles (Cu-NPs). Reaction time is also related to the stability of the nanoparticles. Reaction times were analyzed using a UV-Vis spectrophotometer after the storage process of nanoparticles. The stability of nanoparticles can be expressed in terms of aggregation. Aggregation occurs when the nanostructures experience clustering due to interactions between the particles nearby. Thus, the stability of the nanoparticles depends on the prevention aggregation process. This prevention can be modified using a capping agent.

The capping agent can be an anion or a polymer. Nanoparticles are otherwise not aggregation occurs when the solution does not experience extreme color changes and no precipitate appears. The longer the storage time for nanoparticles and no aggregation occurs, the better the stability. Based on Figure 6, the color of the resulting solution remains the same with different stirring times. This indicates that the color of the synthesized solution had no significant effect on the stirring time. Next, it was analyzed using a UV-Visible Spectrophotometer.

As shown in Figure 7, at 15 min, the stirring time shows the highest absorbance value, with the absorbance peak formed at a wavelength of 400 nm. At 15 minutes, it showed that the copper nanoparticles were successfully formed. Because reaction time affects agglomeration, it is possible that by 25 minutes, particle agglomerates have formed so that the absorbance decreases.

Figure 6. Synthesis of Cu-NPs with variations in stirring time: 5, 15, and 25 minutes

Whereas at 5 minutes of reaction, it was also possible that nanoparticles had not formed. The wavelength of 400 nm is the highest which is also related to Figure 3 which was previously explained.

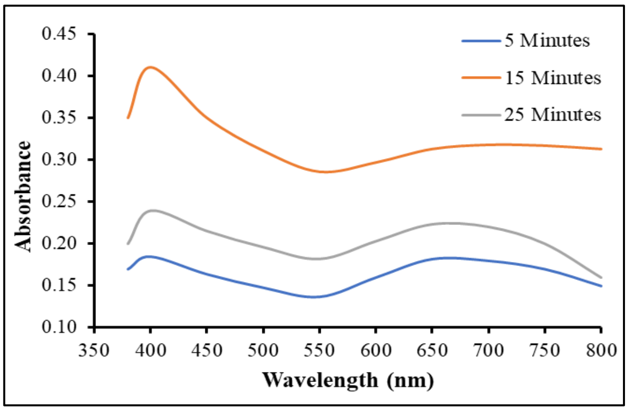

Figure 7. The UV-Visible spectrum of Cu-NPs with stirring time variation

CONCLUSION

Based on the above research, the highest absorbance value was obtained at a wavelength of 700-750 nm with a variation in the $CuSO_4$ volume of 2 mL. The optimum pH obtained was 6, with a peak absorbance at a wavelength of 750 nm. The most effective time for the synthesis of Cu-NPs with dragon fruit extract was 15 min, with an absorption peak at 700 nm. These results indicate the successful synthesis of copper nanoparticles using a natural reducing agent, dragon fruit.

ACKNOWLEDGMENT

The author would like to thank the Chemical Laboratory of the Banyuwangi Institute of Health Sciences for facilitating the research equipment and materials. The author also thanks the dragon fruit farmers in Pesanggaran Village, Banyuwangi Regency, who provided dragon fruit for research purposes.

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