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Green Preparation of Cu Nanoparticles with Bioreductor of Red Dragon Fruit Peel Extract: Visible Spectroscopy Properties

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Abstract

Copper nanoparticles have been successfully synthesized using the green synthesis method by utilizing red dragon fruit peel extract as a bioreductor. Red dragon fruit peel contains secondary metabolites that can reduce Cu^{2+} ions to Cu^0. Physically, the formation of copper nanoparticles is indicated by a color change from light blue to green. In addition, the success of copper nanoparticles of red dragon fruit peel extract can be analyzed using a Visible and Fourier Transform Infrared (FTIR) spectrophotometer. The measurements using a Visible spectrophotometer showed the formation of copper nanoparticles at absorption peaks in the wavelength range of 400-450 nm. The stability of copper nanoparticles can be determined through the SPR peak absorption for 30 minutes, which shows that copper nanoparticles have good stability and have an estimated particle range of 46.43-92.93 nm, with a band gap value of 2.45 eV. The results of the FTIR spectrum on copper nanoparticles-red dragon fruit peel extract show a shift in the absorption peak of the wave number 3412.07 cm^{-1} to a wave number of 3439.07 cm^{-1} indicating a reduction of $Cu^{2+}$to Cu^0.

Keywords: Copper Nanoparticles, Red Dragon Fruit Peel Extract, Visible Spectroscopy

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1 Introduction

Nanotechnology has experienced very rapid development in the last few decades, this is inseparable from its use in various fields. Nanotechnology is the process of synthesizing particles that are in the nano range of about 1 to 100 nm [1]. Metal/metal oxide nanoparticles can be synthesized using the to-down and bottom-up method approaches. Synthesis of metal/metal oxide nanoparticles using a physical and chemical approach requires high radiation, reducing agents and toxic stability which can be harmful to humans and the environment. Due to these limitations, synthesis is carried out using a biological approach or better known as green synthesis. Green synthesis is considered more energy efficient, non-toxic and environmentally friendly because it utilizes natural ingredients (e.g., bacteria, fungi, algae and plant extract) in the reduction process. In the green synthesis method for metal/metal oxide nanoparticles, the use of plant extracts is a simpler and easier process to produce large-scale nanoparticles than using bacteria or fungi.

Plant extracts can be used as reducing agents due to the presence of phytochemicals in plant extracts, especially in leaves such as ketones, aldehydes, flavonoids, terpenoids, phenols, carboxylic acids and other organic compounds [2] where these secondary metabolites can reduce metal ions into nanoparticles and envelop them thereby preventing agglomeration. Red dragon fruit peel is one of the plants that can be used as a bioreductor, red dragon fruit peel contains antioxidants such as vitamin C, flavonoid compounds, and polyphenols which have the potential as bioreductors. Anthocyanins derived from flavonoids are the most abundant secondary metabolites in red dragon fruit peels of 18.16 to 100 mg/100 g of red dragon fruit peel [3]. Among the metal nanoparticles obtained by synthesis, copper nanoparticles stand out with diverse applications such as electronics, biomedical applications, sensors, environment, etc. [4].

The use of nanoparticles in various fields is inseparable from their good characteristics, there are several methods for characterizing metal nanoparticles, for example, particle size analysis using Scanning/Transmission Electron Microscopy (SEM/TEM), Fourier Transform Infrared Spectroscopy (FTIR) for functional group analysis, and UV-Visible Spectroscopy for stability analysis and band gap absorption shift. However, using UV-Visible Spectroscopy it is possible to determine particle size, stability and band gap shift, so this is a new alternative in determining the characteristics of metal nanoparticles [5],[6].

2 Methods

2.1 Materials

The tools used in this study were beakers (Iwaki Pyrex) 250, 500 and 1000 mL, measuring cups (Iwaky Pyrex) 10, 50 and 100 mL, volumetric flasks (Iwaki Pyrex) 100 and 250 mL, oven (Gallenkamp England), pipette, hot plate, vial, dark bottle, stir bar, spray bottle, analytical balance, spatula, funnel, petri dish (Iwaki Pyrex), knife, blender, strainer, jar, cuvette, desiccator, centrifuge, magnetic stirrer, rotary evaporator, micropipette, Fourier Transform Infrared (FTIR) (Shimadzu), UV-Vis Spectrophotometer (Spectroquant Pharo 300 M) and optical microscope.

The materials used in this study were, red dragon fruit peel (Hylocereus polyrhizus), distilled water (H_2O), copper sulfate ($CuSO_4$), 96% ethanol (C_2H_5OH), Whatmann filter paper no.42, label paper, tissue, plastic wrap and aluminum foil.

2.2 Preparation of Red Dragon Fruit Peel Extract

Extraction of red dragon fruit skin was carried out using maceration technique, to obtain the anthocyanin content of red dragon fruit skin using 96% ethanol solvent. Extract the red dragon fruit skin into small pieces (fresh sample) and grind it using a blender. Furthermore, 500 g of red dragon fruit skin paste was extracted with 1 L of 96% ethanol. Furthermore, it was allowed to stand for 3 × 24 hours by stirring 2 times a day. Furthermore, filtering was carried out to separate the filtrate and residue from maceration using filter paper. The extract obtained was then concentrated using a rotary evaporator at 50 °C for approximately 3 hours. Furthermore, the reduction of water content was carried out using the oven method, where the sample was heated in the oven at 50 °C for approximately 30 minutes.

2.3 Synthesis of Copper Nanoparticles-Red Dragon Fruit Peel Extract

The synthesis of copper nanoparticles was carried out using the green synthesis method with the reduction method by reacting a 0.1 M $CuSO_4$ solution as a precursor and red dragon fruit peel extract as a bioreductor. The 0.1 M $CuSO_4$ precursor solution and red dragon fruit peel extract were put into a beaker according to the ratio shown in table 1. The mixture was then stirred with a magnetic stirrer for 2 hours. The precipitate was then centrifuged at 3,000 rpm for 30 minutes. The centrifuged filtrate is put into the vials according to the comparison. The precipitate is then dried in an oven at 50°C for 1 hour until a shiny black powder is obtained. The results of the synthesis were then analyzed for their functional groups using an FTIR spectrophotometer, their stability and particle size estimation using a UV-Vis spectrophotometer.

Table 1. Synthesis composition copper nanoparticles

Sample Comparison (v/v)	Precursor $CuSO_4$ 0,1 M (mL)	Red Dragon Fruit Peel Extract (mL)
1:1	5	5
1:2	5	10
1:3	5	15
1:4	5	20
1:5	5	25
1:6	5	30

3 Results and Discussion

3.1 Red Dragon Fruit Peel Extract

The results of extracting red dragon fruit skin as shown in Figure 1(b) have a dark brown-black color due to evaporation with a yield value of 7.495%, while Figure 1(a) is a sample of red dragon fruit skin with a bright red color with a volume of 500 mL.

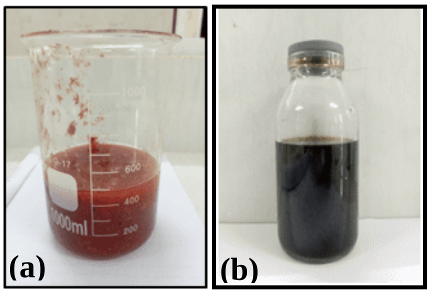

Figure 1. (a) Red dragon fruit peel extract and (b) CuNPs colloid solution-Red dragon fruit peel extract

3.2 Synthesis of Copper Nanoparticles-Red Dragon Fruit Peel Extract

The results of the synthesis of copper nanoparticles-red dragon fruit skin extract have different colors in each comparison as shown in Figure 2.

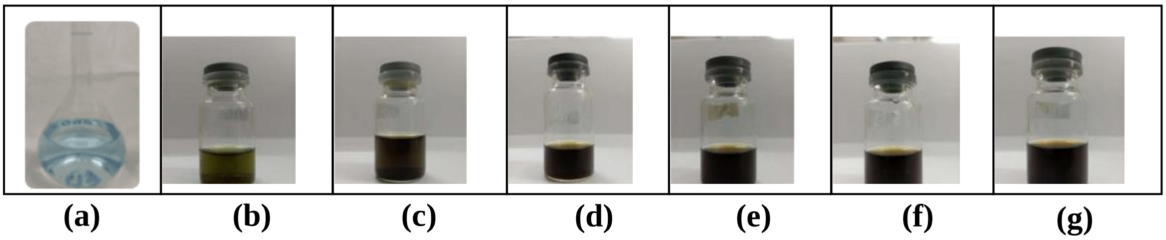

Figure 2. Product of synthesis copper nanoparticles-red dragon fruit peel extract (a) $CuSO_4$ 0,1 M, (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:4, (f) 1:5 and (g) 1:6

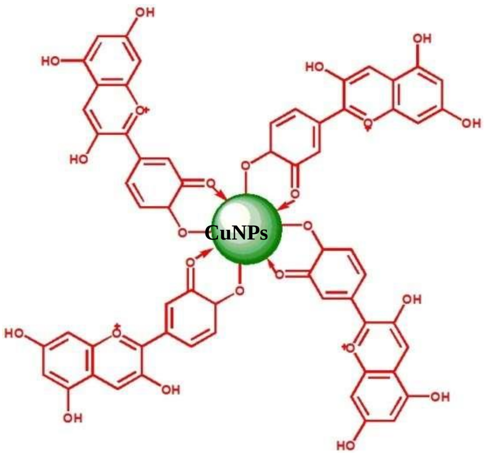

Figure 3. Illustration of the capping mechanism of anthocyanin compounds on copper nanoparticles

The formation of copper nanoparticles is indicated by a color change from light blue to green, but the color change will become more concentrated with the addition of extracts as shown in Figure 2. The color change occurs based on ion transfer which indicates the successful reduction of Cu^{2+} ions to copper nanoparticles (CuNPs), according to previous research conducted by Chandraker *et al*. [7]. The reduction process occurs presumably due to the work of a bioreductor in red dragon fruit peel extract which contains compounds such as anthocyanins.

The anthocyanin compound in red dragon fruit peel extract can reduce Cu^{2+} ions because it has a hydroxyl group (-OH), which is able to donate its electron pair so that it will reduce Cu^{2+} to Cu^0. In addition, due to the release of hydrogen atoms by the hydroxyl groups, anthocyanin compounds will undergo oxidation so that the hydroxyl groups will turn into ketones. Anthocyanin compounds in red dragon fruit peel extract reduce Cu^{2+} ions to Cu^0 in the bioreduction process. Once formed, the copper atoms tend to group together with the formation of nanoparticles. When the maximum size of the nanoparticles is reached, the copper nanoparticles will try to attract anthocyanin compounds which act as capping agents to the surface of the copper nanoparticles to stabilize the surface, so that the formation of the nanoparticles can stop, and agglomeration of copper nanoparticles can be avoided according to the results of research previously conducted by Watoni *et al.* [8]. The capping agent works by interacting electrostatically with copper nanoparticles so that the cluster growth that occurs is not significant, which will affect the size diversity of the synthesized copper nanoparticles. An illustration of the mechanism of the capping agent for anthocyanin compounds against copper nanoparticles is shown in Figure 3.

3.3 Stability Analysis of Copper Nanoparticles-Red Dragon Fruit Peel Extract

The stability of the copper nanoparticle solution is known by looking at changes in the absorption peak. The synthesized nanoparticles have a maximum absorption that varies between 400-450 nm, which indicates the formation of copper nanoparticles based on the reduction of Cu^{2+} to Cu^0 by polyphenolic compounds in red dragon fruit peel extract. In Figure 4 the absorption peaks in the 10 minute time range show consistent wavelengths, this indicates that the nanoparticle mixture formed has good stability.

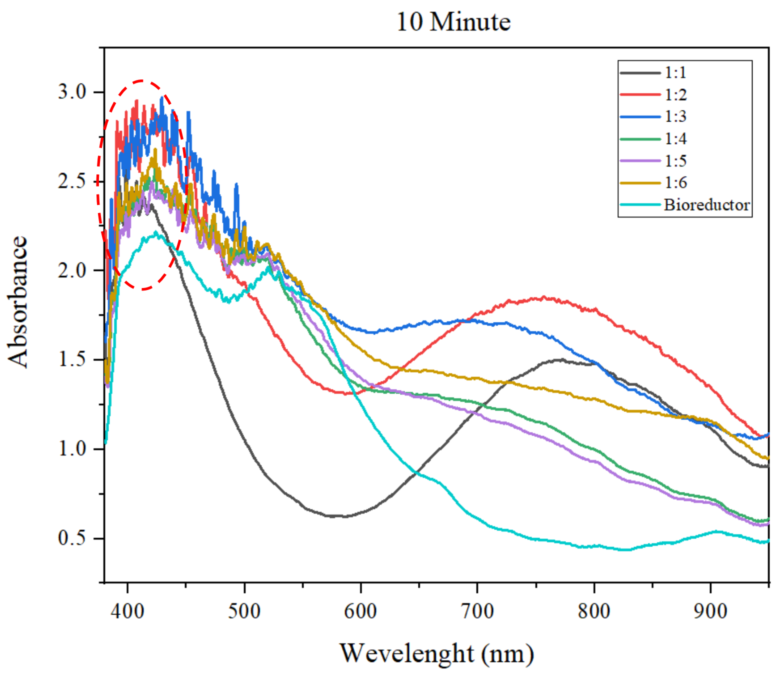

Figure 4. UV-Vis spectrophotometer absorption spectrum from the synthesis of copper nanoparticles-red dragon fruit peel extract at a time interval of 10 minutes.

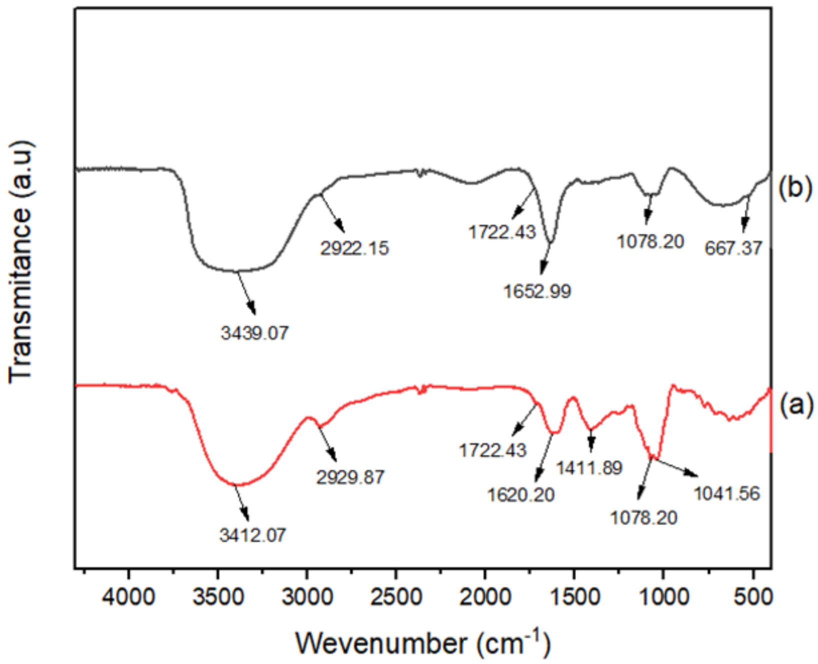

Figure 5. FTIR spectrum comparison between (a) red dragon fruit peel extract and (b) copper nanoparticles-red dragon fruit peel extract.

If there is a shift in the absorption peak to a longer wavelength it indicates that the nanoparticles are relatively less stable due to agglomeration [8]. Conversely, a shift in the maximum wavelength to a lower wavelength indicates that the interaction energy of copper nanoparticles with bioreductor compounds increases [9]. This is due to changes in the optical properties of the copper nanoparticles when the particles are agglomerated and the conduction electrons that approach the surface of the particles become delocalized and shared with other particles, so that the SPR experiences a shift to a lower energy causing the absorption peak to move at a longer wavelength.

3.4 Functional Group Analysis of Copper Nanoparticles-Red Dragon Fruit Peel Extract using FTIR Spectrophotometer

Based on the FTIR data in Figure 5, it shows the presence of functional groups at wave numbers between 450 to 4000 cm^{-1}.

Figure 5 (a) at wave number 3412.07 cm^{-1} shows the presence of –OH groups with absorption supported at wave number 2929.87 cm^{-1} C-H alkane bonds. Meanwhile the absorption at wave number 1722.43 cm^{-1} indicates the presence of a C=O group, 1620.20 cm^{-1} C=C alkene bonds, 1411.89 and 1078.20 cm^{-1} are C-H alkanes bonds and 1041.56 cm^{-1} which is the C-O bond. The results obtained are in accordance with the results of previous research conducted by Sambasevam et al. [10].

Figure 5 (b) shows a shift in the absorption of wave numbers in the Cu nanoparticles of red dragon fruit peel extract, where the –OH group is at wave number 3439.07 cm^{-1}, and the C-H alkane functional groups, C=O and C=C each alkene experienced a shift to 2922.15, 1722.43 and 1652.99 cm^{-1}. The shift in the absorption peak of wave number 3412.07 cm^{-1} to wave number 3439.07 cm^{-1} indicates the reduction of Cu^{2+} to Cu^{0} colloidal nanoparticles [11]. This is reinforced by the presence of absorption at wave number 667.37 cm^{-1} which indicates Cu-O interactions. According to El-Masry and Imam [12] the emergence of absorption wave numbers in the FTIR spectrum between 500-700 cm^{-1} is the vibration of the Cu-O bond.

3.5 Particle Size Estimation of Copper Nanoparticles using Spectrophotometer UV-Vis

The size of the nanoparticles in this study was predicted using a UV-Vis spectrophotometer based on SPR which is a characteristic characteristic of a material [13]. The resonance peak of metal nanoparticles depends on the diameter of the nanoparticles and the refractive index of the surrounding medium. The absorption peak wavelength shifts to longer wavelengths as the nanoparticle size increases. The position of the plasmonic resonance peak has a quadratic dependence on the nanoparticle diameter. This shift occurs due to the reduced force that restores electron oscillations when the size of the nanoparticles increases [14].

A computational method for estimating the diameter of copper nanoparticles is carried out by applying the equation according to Haiss *et al*. [15] approximate size estimates of metal nanoparticles can be calculated by using a combination of theoretical equations and fitting experimental data. Estimation of the size of metal nanoparticles can be calculated from the position of the absorption peak using equation 1.

$$d = \frac{\ln\left(\frac{\lambda_{SPR}-\lambda_0}{L_1}\right)}{L_2} \qquad \text{(Equation 1)}$$

where d is the particle diameter (nm), λ_{SPR} is the wavelength at which absorption is maximum, λ_0 is the wavelength at which absorption is minimum at the start of SPR, L_1 and L_2 are values taken from fitting TEM data vs UV-Vis. Using the fit parameters determined from theoretical values for d > 25 nm (L_1 = 6.53 and L_2 = 0.0216) [15]. The following is an example of estimating the size of nanoparticles using the UV-Vis spectrum, which can be seen at Figure 7 in supplementary data.

The estimated data of copper nanoparticle size in Table 4.2 shows that copper nanoparticles have sizes that vary between 46-92 nm. This size proves the success of the synthesis of copper nanoparticles using red dragon fruit peel extract, which has reached a nanoparticle size of 1-100 nanometers.

Table 2. Particle Size Estimation Results of Copper-Red Dragon Fruit Peel Extract Nanoparticles

Nanoparticle Composition	λ_{SPR}	λ_0	L_1	L_2	d (nm)
1:1	398.3	380.5	6.53	0.0216	46.43
1:2	407.5	380.5	6.53	0.0216	65.72
1:3	429.1	380.5	6.53	0.0216	92.93
1:4	423.7	380.5	6.53	0.0216	87.47
1:5	419.9	380.5	6.53	0.0216	83.21
1:6	423.7	380.5	6.53	0.0216	87.47

The results of UV-Vis spectrophotometer analysis can also be used to calculate the size of the band gap. Band gap measurement is an important parameter because the semiconductor performance is affected by the band gap value. The measurement results show that the band gap value obtained is 2.45 eV as shown at Figure 8 in supplementary data.

4 Conclusions

Synthesis of copper nanoparticles by applying the green chemical method using red dragon fruit peel extract as a bioreductor has been successfully carried out. The results of UV-Vis spectrophotometer analysis indicate the formation of copper nanoparticles which tend to be stable with a maximum wavelength of 398.3-423.7 nm. Characterization using a UV-Vis spectrophotometer also showed an estimate of the particle size of copper nanoparticles for each precursor : bioreductor ratio of 1:1-1:6 (v/v) respectively 46.43; 65.72; 92.93; 87.47; 83.21 and 87.47 nm with a band gap value of 2.45 eV. The results of the characterization using FTIR showed that there was oxidation of the –OH group in the vibration wave number 3412.07 cm^{-1} to wave number 3439.07 cm^{-1} which indicated a reduction of Cu^{2+} to Cu^0.

5 Declarations

5.1 Acknowledgments

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5.2 Author Contributions

The names of the authors listed in this journal contributed to this research.

5.3 Funding Statement

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5.4 Conflicts of Interest

The authors declare no conflict of interest.

6 Supplementary Data

Supporting information article can be accessed online.

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