Nanoparticle Synthesis from Pineapple Waste Using Copper (II) Sulphate Pentahydrate

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***Abstract*— Nanoparticles have been widely used especially metallic type as they have many potential applications that can be applied. Copper-based nanoparticles have been chosen to be synthesized by biological method. This green synthesizing method is easy, efficient and eco-friendly compared to chemical-mediated or microbe-mediated synthesis. Copper is highly conductive metal and less expensive compare to silver and gold also, they have excellent physical and chemical properties and also low cost of preparation. In this research project, different volume of ratio of $CuSO_4.5H_2O$ and pineapple extract; 1:2, 1:3, 1:4 and temperature at room to 80ºC were used to synthesize CuNPs. The result from UV-Vis shows that the broad peak was obtained mostly around 341 to 343 nm . Plus, large amount of aqueous pineapple and high range of temperature were required to make the reduction of Cu^{2+} effectively. FTIR result shows that the stretching frequency region contains phenols and alcohol, alkyne and amide. These CuNPs were in shape of spherical through observation from FESEM. Plus, the size of sample with ratio ($CuSO_4.5H_2O$: pineapple extract) 1:2 was within the range of 40-70 nm while for ratio 1:4 the size was in between 30-50 nm.**

Keywords*— copper *nanoparticles, green synthesis, pineapple waste

I. INTRODUCTION

"Nano" term is basically derived from the Greek word, "nanos" which means small and it is used as the prefix for one billionth parts (10^{-9}). Generally, the size of a nanoparticle spans the range between 1 and 100nm. Nanoparticles have been widely used in many fields such as electronics, photochemical, biomedicine and chemistry[6].Metallic nanoparticles have fascinated by scientist for over a century and are now heavily utilized in biomedical sciences and engineering[5].It has excellent and physical and chemical properties, such as high surface-to-volume ratio and high heat transfer (thermal conductivity). Metallic nanoparticles can be divided by two, noble metal and non-noble metal. Noble metals such as gold, silver platinum and palladium have been widely used in products ranging from cosmetics to medical and pharmaceuticals [1]. Iron, Copper, Zinc Oxide and Selenium are from non-noble metallic. They have been used in medical treatments, cosmetics formulations and antibacterial applications. Nowadays, Copper nanoparticles have been considered as an alternative for noble metals in many applications as it is a low cost and also a conductive material compared to noble metal like gold and silver

Different physical and chemical processes are widely used to synthesize nanoparticles. However, these methods give impacts in production cost and hazardous to the environment and living organisms. In this research, nanoparticles have been synthesized by green or biological approach using pineapple waste. Synthesizing nanoparticles using plant has been chosen for its eco-friendly and economically viable compared to the microbial systems like fungi and bacteria because of their pathogenecity and also the chemical and physicals methods used to synthesize nanoparticles[8]. Plant extract has been used as capping and reducing agent for copper nanoparticles synthesis due to their reducing properties present in the leaf and fruit extract.

Pineapple or ***Ananas Comosus L.*** belongs to Bromeliacee family. Pineapple mostly contains considerable amount of calcium, potassium, vitamin C, carbohydrates, crude fibre, water and different minerals that is good for digestive system, maintaining ideal weight and balanced nutrition. Also, pineapple contains phytochemicals which include antioxidant substances that fight against free radical cell damage [2]. Malaysia is also one of the world major producers of pineapple. In Malaysia, Malaysian Pineapple Industry Board (MPIB) is responsible to handle all about pineapple. Nanoparticles have been widely used in many fields such as cosmetics, medical, electrical, environmental and optical because they have special and enhanced physical and chemical properties as compared to their bulk materials due to their large reactive and exposed surface area and quantum size effect as a result of specific electronic structures [6].Nanoparticle are discovered as to be promising multi-functional platform by its small size. Also, nanoparticles also can possess the property of diffusion especially at higher temperature and not affect the density of final product.

There are a few main scopes that being focus on for achieving the objectives of this research. The pineapple wastes extract are used as reducing agent of $CuSO_4.5H_2O$ for nanoparticle synthesizing. Then, two parameters; volume ratio and temperature effect use for synthesizing nanoparticles are observed during this research. The different volume ratio of $CuSO_4.5H_2O$ and pineapple extract; 1:2, 1:3, 1:4 are used. For temperature, two different temperatures; room temperature and 80ºC are observed. Then, all the information obtains from the synthesizing will be analyzed. The reduction Cu^{2+} ion was monitored by UV-Vis Spectrophotometer for the metal ions stability. The FTIR is used to find the molecules and their functional group present in the synthesized nanoparticles. Besides that, the morphology of the synthesized nanoparticles is being done by using FESEM where it is used to determine the shape and size distribution colloidal particles characterization.

II. METHODOLOGY

Material and Method

The chemical reagent used in this experiment was copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) which acts as precursor while pineapple waste was used as reducing agent for synthesizing of the nanoparticles.

A. Preparation of Pineapple Extract

The peels of the pineapple were washed thoroughly and dried to remove the residue moisture. The 100 g dried peel of pineapple were cut into small pieces and washed with distilled water. After

that, the peel was taken into a 1000 ml beaker with 200 ml of distilled water and boiled for 20 minutes at 80ºC until the colour change from watery to light yellow. Then, the extract of the peel was cooled to room temperature and filtered using Whatman filter no. 1 and stored at 4ºC. This extract can be used within a week.

B. Preparation of Copper (II) Sulphate Pentahydrate

The accurate amount of 0.01M copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) was prepared by dissolving 0.25g of $CuSO_4.5H_2O$ together with 100 ml distilled water. Then the mixture was stored in clean and dried reagent bottle.

C. Synthesis of Copper Nanoparticles

The 44 ml of pineapple extract was added into 22 ml of 0.01 M copper (II) sulphate pentahydrate solutions. Next, the colour of sky blue $CuSO_4.5H_2O$ was change to green colour due to the excitation of surface Plasmon vibrations with the CuNPs[3]. The solution was left at room temperature. The mixture was then centrifuged for 20 minutes at 10,000 rpm at 4ºC. Then, the residue was dispersed in deionized water. Lastly, the solution was freeze dried and the powder produced was stored in dried sample bottle for further used.

D. Effect of Parameters for Biosynthesis of Copper Nanoparticles

- Synthesizing of CuNPs using different composition of pineapple extract (volume ratio of $CuSO_4.5H_2O$: Extract):

The different volume ratios of $CuSO_4.5H_2O$ and pineapple extract (1:2, 1:3, and 1:4) were used. Then, the formation of nanoparticles was monitored carefully by UV-Vis Spectrophotometer.

- Synthesizing of CuNPs at different temperature in their range of room to 80ºC:

The different temperatures; room temperature and 80ºC were used and analyzed using the UV-Visible spectrum.

E. The Analysis of Synthesized Copper Nanoparticles

- UV- Visible Spectroscopy Analysis

The analysis was done by using model Lamda 750, Perkin Elmer. UV-Vis Spectral analysis was done to monitor the reduction of copper (II) sulphate pentahydrate to CuNPs. The wavelength range for this analysis is set from 300 to 600 nm.

- Fourier Transform Infrared Specroscopy (FTIR) Analysis

This analysis used to identify the possible biomolecules responsible for capping and efficient stabilization of the metal nanoparticles synthesis. Also, to identify the functional group of the nanoparticle synthesis. The FTIR was conducted using model Spectrum one, Perkin Elmer by putting small amount of synthesized CuNPs on the FTIR plate. Then, the FTIR spectrum was recorded using at 4000-400 cm^{-1} resolution and 20 scans per sample.

- Field Emission Scanning Electron Microscopy (FESEM) Analysis

The size and structure analysis of the synthesized copper nanoparticles was done FESEM machine with magnification of 30000x. The CuNPs were uniformly distributed on the surface of the film. Thin films of the samples were prepared by putting a very small amount of the sample and then, the sample was being coating with gold. This is to prevent or overcome the charging from nanoparticles.

III. RESULTS AND DISCUSSION

A. Characterization of Copper Nanoparticles

The characterization of CuNPs was made through visual inspection (colour changes), UV-Visible spectral analysis, FTIR and FESEM.

- By colour changes (Visual inspection)

The sky blue colour of copper (II) sulphate pentahydrate that shows in Fig.1 was changing to pale green colour when adding pineapple extract. This was due to the excitation of surface Plasmon vibrations with the CuNPs[3].The appearance of this colour shows that the reduction has started.

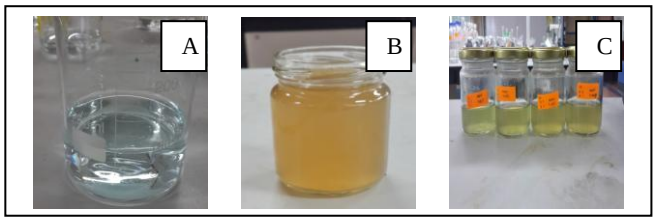


Figure 1: Formation of copper nanoparticles by visualization; a) copper (II) sulphate pentahydrate solution, b) pineapple extract and c) CuNPs synthesis.

- UV-Visible Spectral analysis

The reduction of copper has been made by analysing the sample using UV-Vis Spectroscopy at range 300 to 700 nm. The absorbance is measured at each wavelength. UV-visible spectrophotometer's optical measurement has variance absorbance peak. The observation was made at both paramaters; volume ratio and temperature in synthesizing of CuNPs.

Effect of different volume ratio for synthesizing of CuNPs (volume ratio of $CuSO_4.5H_2O$: Extract):

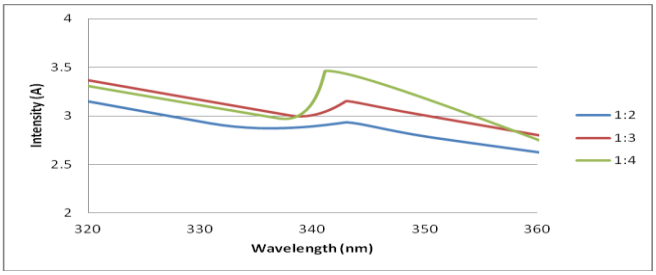


Figure 2: Graph of UV-Vis Spectra of copper nanoparticles at different volume ratio ($CuSO_4.5H_2O$: Extract):

The reduction of Cu^{2+} ions was monitored to analyze the metal ion stability. In this research, the volume ratio was manipulated by increasing the volume of pineapple extract. For this analysis, the range was set from 300 to 700 nm with different volume of pineapple extract. Based on the result obtain, the volume ratio at 1:4 of ($CuSO_4.5H_2O$: Extract) has the highest absorbance while volume ratio of 1:2 was the lowest one. This shows that the absorbance was increased by increasing the amount of pineapple extract. Fig.2 shows that the broad peak was obtained mostly around 341 to 343 nm. Mercy Ranjitham et.al, 2015 stated that when the biosynthesis was carried out in the ratio of vice versa as Fig.3, where the plant extract was less than $CuSO_4.5H_2O$, the composition will remain blue in colour. Thus, it shows that the composition of the solution definitely not ideal or suitable for the formation of CuNPs due to less amount of antioxidant and other secondary metabolites present in the plant extract[2]. Basically, the pineapple extract as reducing agent plays an important role in the formation of nanoparticles. Therefore, the different volume ratio of pineapple extract result an effect on reduction of copper.

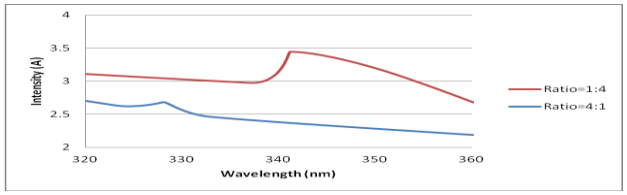


Figure 3: Graph of UV-Vis Spectra of CuNPS at different volume ratio ($CuSO_4.5H_2O$: Extract); 1:4 and 4:1.

Effect of different temperature for synthesizing of copper nanoparticles with volume ratio 1:4 ($CuSO_4.5H_2O$: Extract):

The UV-visible absorption spectra in Fig.4 show the CuNPs synthesis at different temperature. For this part the ratio at 1:4 where the solution was with composition 56 ml of $CuSO_4.5H_2O$ and 14 ml of pineapple extract has been chosen as this ratio gives an optimum result before. The result shows that the absorbance peak was higher at temperature 80°C compared to room temperature where the absorbance was 3.446 and 2.918 respectively. Based on the results obtain, the reaction was more favourable at 80°C. Therefore, when the temperature increases, the absorbance will increase [7]. Further research on effect of temperature for synthesizing CuNPs can be done by using other range of temperature.

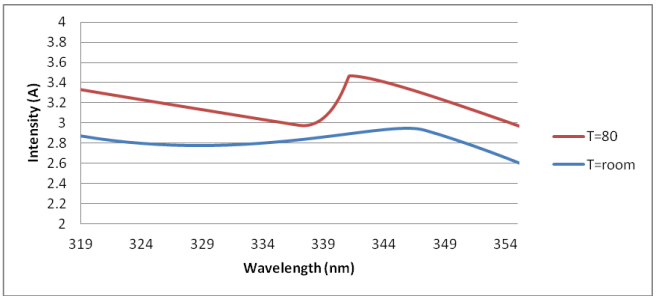


Figure 4: Graph of UV-vis spectra of CuNPs at different temperature; room temperature and 80°C.

- FTIR analysis

The FTIR analysis was conducted to identify the of associated functional groups and structural features of biological extracts with nanoparticles where it's actually about measures infrared intensity vs. wavelength of light. Besides that, the calculated spectra clearly reflect the well-known dependence of nanoparticle optical properties [4]. This usually used for green synthesis, where FTIR used and showed characteristic peaks.

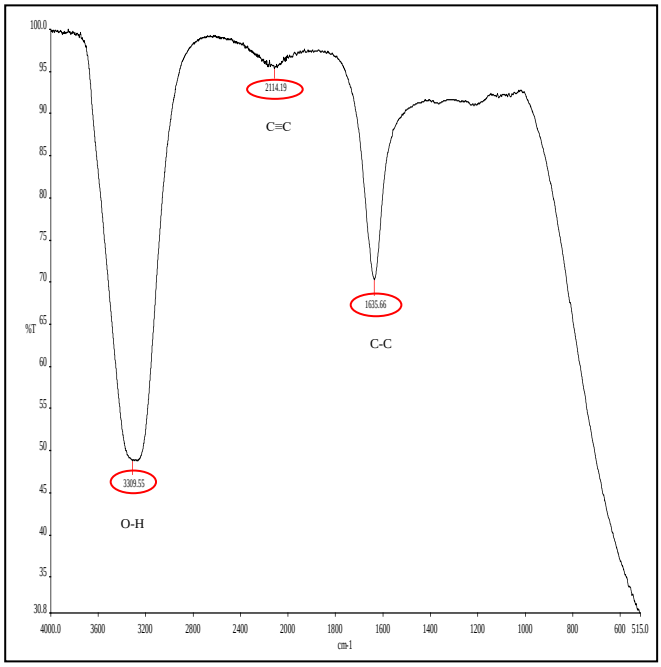


Figure 5a: FTIR spectra of fresh pineapple extract

The FTIR spectra of the fresh pineapple extract and synthesized CuNPs are shown in Fig.5a and b. The wavelength of the graph was set from 400 cm^{-1} to 4000 cm^{-1}. Fig.5a shows the spectrum of aqueous fresh pineapple extract. The graph shows that the peaks were happened at wave number 3309.55 cm^{-1}, 2114.19 cm^{-1} and 1635.66 cm^{-1}. The peak at 3309.55 cm^{-1} was due to the O-H stretching of phenolic compound. The peak at 2114.19 cm^{-1} was due to the stretching of alkyne while at 1635.66 cm^{-1} was due to C=O stretching of amide.

Fig.5b shows the spectrum of fresh pineapple extract and synthesized CuNPs sample in different ratio. The absorption peaks for sample with ratio 1:1, 1:2, 1:3 and 1:4 were at 3275.86, 2114.05 and 1636.65 cm^{-1}; 3270.66, 2160.40 and 1636.15 cm^{-1}; 3288.86, 2164.44 and 1636.19 cm^{-1} respectively. The peaks at 3275.86, 3270.66 and 3288.86 cm^{-1} were corresponded to the stretching of phenolic compound while peaks at 2114.05, 2160.40 and 2164.44 cm^{-1} were because of the stretching of the alkyne. Peaks at 1636.65, 1636.15 and 1636.19 cm^{-1} were due to C=O stretching of amide.

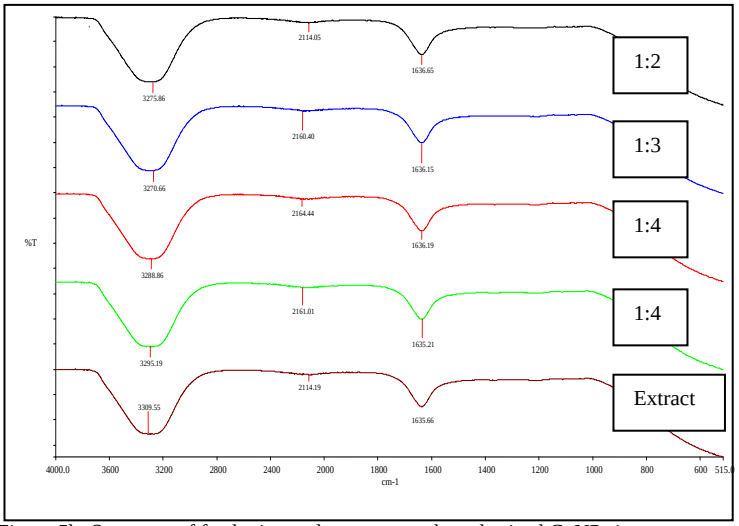
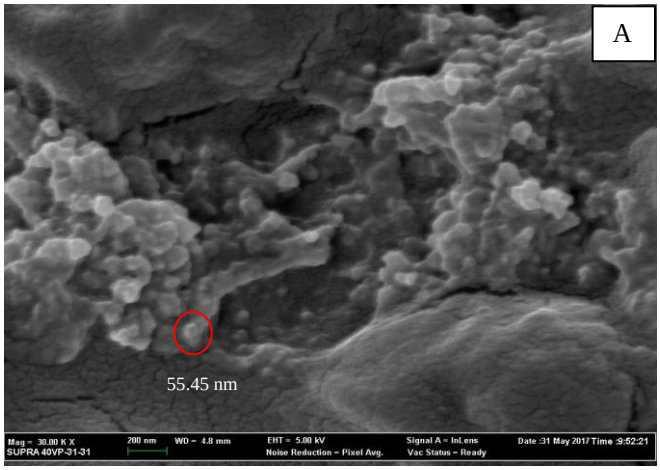


Figure 5b: Spectrum of fresh pineapple extracts and synthesized CuNPs in different ratio.

Mercy et.al, 2015 stated that biosynthesized CuNPs might be surrounded by any one of these organic molecules such as polyphenols, terpenoids and alkaloids by the peak obtained. Plus, the presents of phyto constituents in the fresh pineapple extract such as alkaloids, terpenoids and flavanoids might be responsible for the reduction of copper ions to CuNPs due to their reducing capacity.

- FESEM analysis

FESEM or Field Emission Scanning Electron Microscopy provides visualizes of very small topographic details on the surface or entire or fractionated objects. In this research, the morphology of CuNP was done by using FESEM analysis. The size and structure analysis of the synthesis CuNPs was done using Field Emission Scanning Electron Microscope machine with magnification of 30000x.



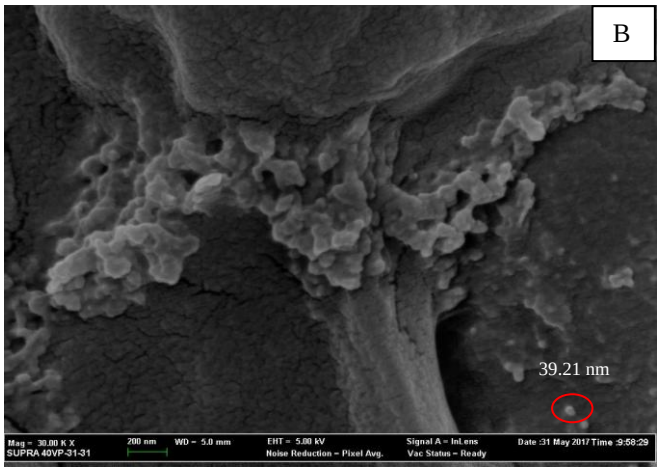


Figure 6: a) and b) FESEM analysis of CuNPs

Fig.6a and b shows the size and shape of synthesized copper nanoparticles. For this part, the CuNPs with the different volume ratio of pineapple extract had been used; ratio of 1:2 and 1:4. The shape of the nanoparticles cannot be described more accurate as the nanoparticles had been agglomerated but they still can be determined. Based on the figure above, the copper nanoparticles were dominated by the shape of spherical for both samples [2]. The size for sample with ratio 1:2 was within the range of 40 – 70 nm while for ratio 1:4 the size was in between 30 – 50 nm. Previous study stated that the different volume ratio of extract can affect the shape and size of nanoparticles[1]. Further research on size distribution was needed for having the constant size of nanoparticles.

IV. CONCLUSION

In the conclusion, this research has achieved all the objectives targeted at the start of the study. The CuNPs was successfully synthesized by using green synthesis method where pineapple extract has been used as reducing agent of copper (II) Sulphate Pentahydrate. The extract will reduce the Cu^{2+} metal ions by exhibition of dark colour. The formation CuNPS was confirmed by colour change from sky blue to pale green colour due to excitation of Surface Plasmon Vibrations. The characterization of synthesized CuNPs was made by using UV-Vis, FT-IR spectral studies and their size and shape was determined by FESEM analysis. UV-Vis absorption study shows that the broad peak was obtained mostly around 341 to 343 nm and. It shows that the sample with high amount of aqueous pineapple and temperature have the highest absorbance peak. This means that the large amount of aqueous pineapple and high temperature were needed to make the reduction of Cu^{2+} effectively. FTIR studies of copper nanoparticles showed that the stretching frequency region contains functional group of phenols and alcohol, alkyne and amide. FESEM observation with high magnification shows that these CuNPs were in shape of spherical. The size for sample with ratio ($CuSO_4.5H_2O$: Extract) 1:2 was within the range of 40 – 70 nm while for ratio 1:4 the size was in between 30 – 50 nm. The different volume ratio of pineapple extract can affect the shape and size of nanoparticles. Therefore, green synthesis method is the most suitable method to synthesize CuNPs. This method has several advantages over other methods which include cost effectiveness, simplicity, use less temperature, less toxicity materials and compatible and save for medical and food uses.

ACKNOWLEDGMENT

Thank you to my supervisor, Madam Syafiza Abd Hashib for the support, patience and ideas in assisting me with this project. Thank you to LESTARI Grant (600-IRMI/MYRA 5/3 LESTARI (0143/2016) from Universiti Teknologi MARA for supporting this research. Thank you to all who may contribute directly or indirectly towards making this research successful.

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