SILVER NANOPARTICLE SYNTHESIS USING PINEAPPLE WASTE

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***Abstract*— Nanoparticles is one of the new technology in this century. This technology help human being to control the behavior of material at molecular level. There are three method to produce nanoparticles which are physical method, chemical method and biological method. Biological method is more preferred from other two methods because it is eco-friendly, safer and low operation cost. Usually, plant parts or microorganism is used as raw material in biological synthesis. However, plant part is preferred to use because it is easy to handle than microorganism. A waste from plant part is suggested instead of fresh part because it can reduce the operation cost and reduce the waste produced. Abundant of pineapple waste is an example of plant part that has potential in biological method. Waste from pineapple which is peel was studies in potential of nanoparticle material. This study was underwent four simple step which are extraction process, synthesis process, purification stage and analyzing stage. Firstly, pineapple peel was extracted to get the biomolecule. The peel extract solution was analyzed using FTIR. Analysis from FTIR was verified the peel has biomolecule such as protein, Bromelain and Vitamin C. So, peel extract was used as reduction and capping agent to prepare Silver Nanoparticles, the process is called biological method. Then, it is added into $AgNO_3$ solution and the mixture was stirred. The colorless of $AgNO_3$ solution was changed to the dark brown solution after peel extract was added. After that, the dark brown solution or called as AgNPs was analyzed by UV-vis instrument. The absorbance peak of UV-vis spectrum in range of 400 nm to 500 nm shows there is AgNPs in that solution. Then, the solution was analyzed by FTIR to verify the changing of functional group. AgNPs solution was dried to get the power form. Then, it was further characterized by using FESEM. The size of AgNPs was formed in range from 20 nm to 30 nm. The peel extract has potential in the synthesis of nanoparticles and the formation of nanoparticles can be controlled by manipulating the volume ratio, stirring time and $AgNO_3$ solution concentration.**

Keywords*— Biological Method, Silver Nanoparticles (AgNPs), Pineapple waste, FTIR, UV-vis, FESEM

I. INTRODUCTION

Nanotechnology is one of the new technology in this century. An object of size in 1- 100 nm range is referred to as nanoparticle material. The size of the nanoparticle is different and depends on their bulk material. In order to maintain and stabilised the size of the nanoparticle, some capping agent is added during the process. It is important to stabilize the AgNPs to avoid it agglomerate and become a big particles above 100 nm which is can eliminate the benefit of nanoparticles. Capping agent is functioning to neutralize the static charge from AgNPs that can be attractive potential to AgNPs become agglomerate. Nowadays, variety type of metallic nanomaterial are being explored and produced using copper, zinc, gold, silver etc. Different types of metallic nanoparticle material will be used in different purpose due to their incredible properties. Nanoparticles have been applied in medical treatment, energy production, environment, agriculture etc [1].

The nanoparticle can be synthesised into two approaches which are top to bottom and bottom to up. Top to down approach usually applied on physical method for example crushing process. The large material is crush using crusher to make it small size of particle. Use of this process cause the high operation cost since the crusher use the high energy consumption. While bottom to up be applied in chemical and biological method. Basically, it is a reduction process of metal ion by reduction agent. Using chemical method, the large quantity of nanoparticles can be produced in short span of time. All materials used in this method is chemical based and produce the hazardous chemical waste that effect the environmental. Otherwise, biological method is safer and eco-friendly compared to the chemical method. Even, the mechanism of biological method is approximately same with chemical method but biological method used the biological entities to replace hazardous chemical used for raw material. Example of biological entities are plant part and microorganism. Plant part is excellent material than microorganism because can reduce the isolation cost. Biological method from plant part is more preferred than others method because that method is environmental friendly, less operation cost and less hazardous chemical waste. Pineapple peel as nanoparticle material was studied to reduce the silver nitrate solution as metal ion while silver nanoparticle produced from different parameters was studied in term of size, shape and distribution [2].

Today, nanoparticles is widely used in the nanotechnology. The AgNPs shown moderate antimicrobial and antioxidant activities has make it capable for use in biomedicine, water treatment and nano-biotechnology. Besides that, silver nanoparticles is used in electrochemical, sonochemical and microwave-assisted process [3]. Moreover, it can use for optical sensor to detect the heavy metal in waste water such as Cu^{4+} and Zn^{2+}[4].

II. METHODOLOGY

A. *Materials*

400 g of Pineapple peel was taken from pineapple fruit that was bought at the Giant supermarket, Seksyen 7, Shah Alam. Distillated water and deionization water were taken from laboratory to extract the biomolecule from pineapple peel and to dilute the Silver Nitrate solution to concentration needed. 0.1 M of Silver Nitrate solution was taken from store chemical laboratory UiTM.

B. Preparation for Biosynthesis method

This study was used the biological method to synthesis the silver nanoparticles. There are four main steps in this method which are extraction, synthesis, purification and analysis.

C. Preparation for peel extract

The small pieces 200 g of pineapple peel was collected and washed. Then, it boiled in 400 ml of distillated water for 20 minutes. The boiled solution was filtered and the light yellow solution obtained (peel extract). The peel extract was analyzed by FTIR to verify existing of the biomolecule and polysaccharides in plant extract**.** After verifying the solution, it ready to be used for synthesis process.

D. Preparation for synthesis process

Conical flask was mixing equipment in this study. Firstly, silver nitrate solution was put into the conical flask. Then, the peel extract was added into silver nitrate solution to reduce the silver ion and cap the silver particle. The mixture was stirred for 10 minutes. After that, the mixture was transferred into the bottle sample and kept within one day. The changes of color of the sample was observed within certain duration. Then, 3 ml of sample was taken to undergo the UV-vis analysis. UV-vis analysis was conducted to confirm the formation of silver nanoparticle. Then, the sample was undergone the FTIR analysis to study the composition in Silver Nanoparticles. Table 1, 2, 3 and 4 shows the detail of parameter used in this study.

Table 1: Parameter 1 – Effect of volume ratio on Silver Nanoparticle formation.

Sample	Volume of Silver Nitrate, $AgNO_3$ (ml)	Volume of Peel Extract (ml)	Time reaction (min)
1	50	1	10
2	50	1.5	10
3	50	2	10
4	50	3	10
5	50	4	10

Table 2: Parameter 2 – Effect of stirring time on Silver Nanoparticle.

Sample	Volume of Silver Nitrate, $AgNO_3$ (mL)	Volume of Peel Extract (mL)	Time complexion (min)
1	50	2	10
2	50	2	20
3	50	2	30
4	50	2	40
5	50	2	50

Table 3: Parameter 3 – Effect of volume ratio on Silver Nanoparticle formation.

Sample	Volume of Silver Nitrate, $AgNO_3$ (mL)	Volume of Peel Extract (mL)	Time complexion (min)
1	500	20	10
2	500	40	10
3	500	80	10

Table 4: Parameter 4 – Effect of Silver Nitrate solution concentration

Sample	Volume of Silver Nitrate, $AgNO_3$ (mL)	Volume of Peel Extract (mL)	Concentration of Silver Nitrate Solution (M)
1	500	40	0.005
2	500	40	0.01
3	500	40	0.015

E. Preparation for Purification process

The sample was undergone purification process by washed and drying method. The samples was centrifuged at 10, 000 rpm for 15 minutes. Then, the supernatant liquid was discharged and the pellet composition was obtain. The pellet obtain are silver nanoparticles in group form. The Deionized water (DI) is added into the pellet and it is repeated the centrifuge process. This process is called washing process and it is repeated in 2 times. Lastly, the pellet was contain 10ml of DI water and further process which is dry process was undergone by Freeze Dryer. For the 5 sample contain of 10 ml water was dried within 3 days.

F. Analysis by Field Emission Scanning Electron Microscopy (FESEM)

2 samples of AgNPs which are 40 ml and 80 ml of peel extract volume used were taken to undergo FESEM analysis at Faculty of Applied Sciences. The samples was coated with gold powder using sputter coater to avoid charging to the samples. After that, the coated samples were scanned with FESEM using 30 kV of magnification [7].

III. RESULTS AND DISCUSSION

A. *Potential of pineapple peels in Silver Nanoparticle formation*

Biological material is an innovation among researchers to improve the nanoparticle synthesis in order to save the environment by minimize the hazardous waste produced. It can be any types of plant which are leaves, fruit, peel etc.

Pineapple peel was taken as raw material to this study. The extraction of peel was analyzed by FTIR to verify the component in that solution. Plant metabolic or other name is biomolecules play important role in reduction and binding the metal ion in nanoparticles production. It including terpenoids, polyphenols, sugars, alkaloids, phenolic acids and proteins [5].

Figure 1 shows the FTIR spectrum for peel extract. There are three peak of graph that can be detected which are 3270.14 cm^{-1}, 2147.96 cm^{-1} and 1635.69 cm^{-1} represented by stretch of C-H, Bromelian enzymes and C=C (vitamin C) respectively. *Bromelain* enzymes is an important element in order to separate amino acid in protein. Cysteine residual from broken protein are able to bind the nanoparticles with hydrogen bond or cap the particle through the electrostatic attraction. This is important to prevent that particle from agglomeration. Vitamin C as well known is a high antioxidant agent. It play important role to reduce the Silver ion to Silver particle by reduce the positive charge on the Silver ion [4].

Silver in single particle form has the static charge on it. So, unbalance static charge on that particle will tend it to attract other particle to be balance. It will agglomerate until the static charge was balance. So, the size and shape of particle cannot be controlled. To overcome this problem, the addictive must be put on that particle such amino acid or other biomolecule in peel extract. Biomolecule in peel extract is functioning to stabilize the size of particle.

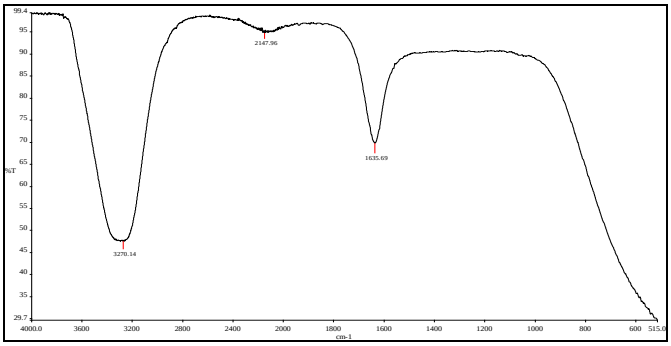

Figure 1: FTIR Spectrum for peels extract.

Figure 2 shows the FTIR Spectrum for parameter 3. All of three sample was controlled by volume ratio has shown the almost same spectrum with peel extract. There was changed some changers at the peak of samples compare to the pure peels extract. For example, peak at 3278.35 cm^{-1} of peels extract that corresponding to the stretch of C-H. The stretch of C-H usually from alkanes group which important to cap the nanoparticles. This peak was shift to the nearest peak such 3270.28 cm^{-1}, 3278.26 cm^{-1} and 3274.15 cm^{-1}. The shifting of peak shows the pure peels extract has underwent reaction when it was mixed with $AgNO_3$. Besides that, peak of *Bromelain* at 2149.92 cm^{-1} for peels extract also was changed to nearest peak position. This is because the reaction happen between $AgNO_3$ was affecting the structure of *Bromelain* enzymes. Moreover, C = C group which represent the vitamin C also has small change of the peak at 1635.27 cm^{-1}. The three important peak of peel extract that used in reaction was changed when underwent biosynthesis. So, it confirmed that biomolecule are attached to the Silver particle as well and the biosynthesis was happen.

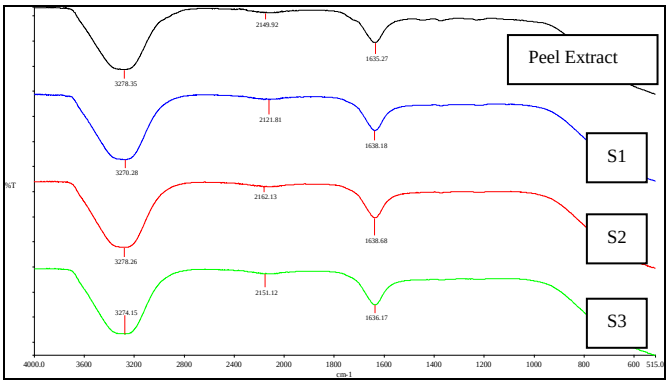

Figure 2: FTIR Spectrum for volume ratio at 0.01 M Silver Nitrate solution

B. *Characteristic*

Characteristic was conducted to observed the changing of color solution during the reaction occur. In generally, the color was changed from colorless of Silver Nitrate to dark brown of Silver Nanoparticle.

Figure 3 shows path of color solution changing. $AgNO_3$ is colorless before mix the peels extract. Then, after mix the peels extract the mixture was changed to the light brown in color. After 1 hour, light brown of color solution was changed to the brown in color and the intensity of color will increase when increasing of time until 1 days. After 1 day, there is no change of color intensity anymore. This is because the reduction of silver ions, Ag^+ to Silver particle Ag^0 by vitamin C in the peels extract. If there is no reduction process, then there is no change in color intensity.

However, the intensity of color is different between parameters. Figure 4 shows the sample of parameter 3 that study effect of volume ratio on the Silver Nanoparticle formation. The high concentration of peel extract added into Silver Nitrate, the high intensity of brown color (dark) produced.

Figure 5 shows the sample of parameter 5 that study on the varied concentration of Silver Nitrate at constant volume of Silver Nitrate and peel extract. All of them shows the same intensity of color.

The change of the color from colorless to dark brown is due to the reduction of Silver ions. After 1 day and up to 1 week, there is no color variation was observed. It shows that the nanoparticles produced from biological process were very stable [6].

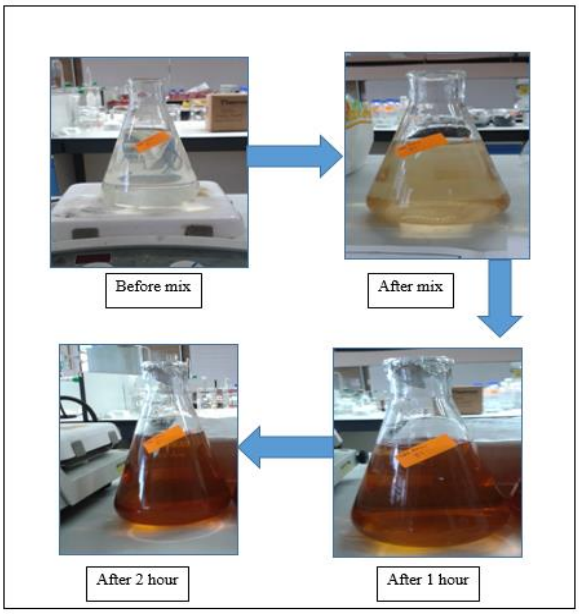

Figure 3: Path of color solution changing within 2 hours

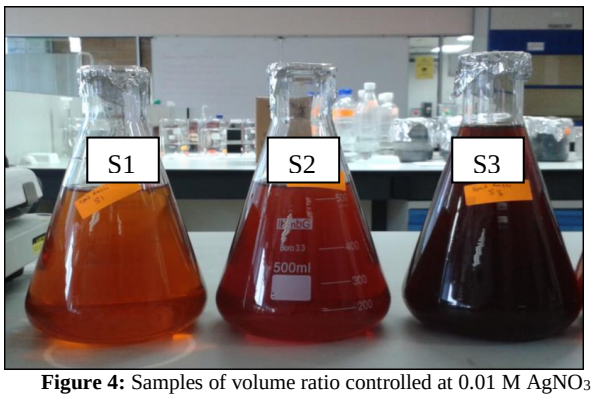

Figure 4: Samples of volume ratio controlled at 0.01 M $AgNO_3$ solution

Figure 5: Samples of $AgNO_3$ solution concentration controlled at 40 mL of peel extract.

C. *UV-vis spectroscopy*

UV-vis was used to verify the formation of Silver Nanoparticle. The absorbance peak of Silver Nanoparticle was found around 420 nm [7]. Besides, other researcher has found absorbance peak of

Silver Nanoparticle around 438 nm [6]. Others researcher was found absorbent peak in range of 439 – 446 nm [4]. So, it can conclude that absorbance peak within 400 nm to 500 nm.

Absorbance peak of four parameters in this study are in range of 400 nm – 500 nm. Figure 6 shows the UV-vis spectrum for volume ratio controlled at 0.001M $AgNO_3$ solution. Absorbance peak for this parameter is in range 450 – 475 nm. More volume of peels extract added into $AgNO_3$ solution, more shifting absorbance peak to the 500 nm. Figure 8 shows the UV-vis spectrum for volume ratio controlled at 0.01 M $AgNO_3$. The absorbance peak of this parameter shows at 450 nm for all samples. However, it is different for the absorbance percentage. More volume of peels extract, more percentage of absorbance. High absorbance value equivalent to the high intensity of color (dark) that meant the total particle of that solution is very high. The more concentration of peel extract in constant volume of Silver Nitrate, the more Silver Nanoparticles will produce. This is due to the more biomolecule capable to reduce and cap the Silver single particle.

Figure 7 shows the UV-vis spectrum for stirring time of mixer. The absorbance peak of this parameter are in range of 460 – 463 nm. In generally, the trend of graph shows the high of absorbance value for the long stirring time. This is because of the mixture become well mix when more time used to stir the mixture. So, the biomolecule dispersed to each corner of the solution. Then, the use of biomolecule can be maximize to turn the Silver ion into Silver Nanoparticles.

Figure 9 shows the UV-vis spectrum for $AgNO_3$ concentration controlled at 40 ml of peels extract. The trend of graph is slightly different from other graph because this graph is more focus on the shifting of absorber peak from high Silver Nitrate concentration to low Silver Nitrate concentration. It is clearly shows that the high concentration of Silver Nitrate will shift the absorbance peak to the 500 nm. According to Bindhu&Umadevi (2014) small wavelength, high frequency and energy shows that size of diameter particle is small. So, it can be concluded that high concentration of Silver Nitrate used will produce the large diameter size of particle.

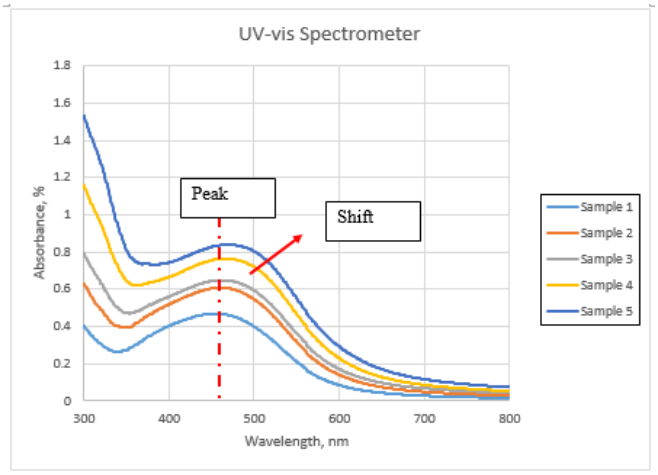

Figure 6: UV-vis spectrum for volume ratio controlled at 0.001 M $AgNO_3$ solution.

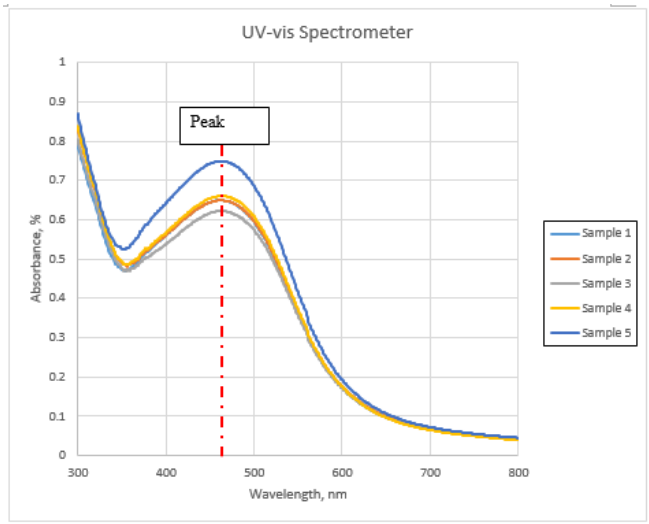

Figure 7: UV-vis spectrum for stirring time controlled.

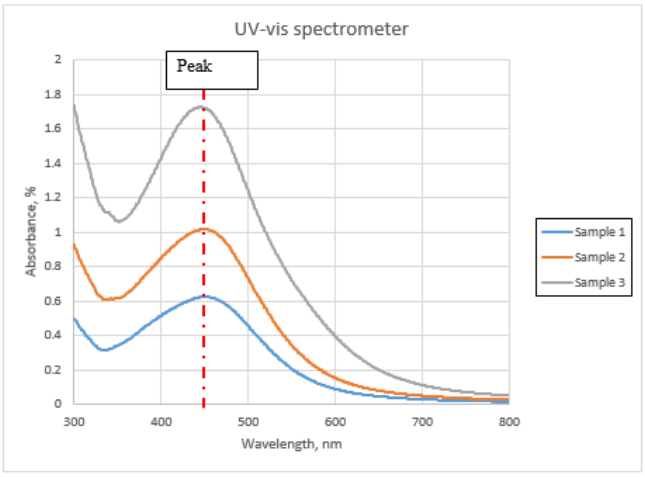

Figure 8: UV-vis spectrum for volume ratio controlled at 0.01 M $AgNO_3$ solution.

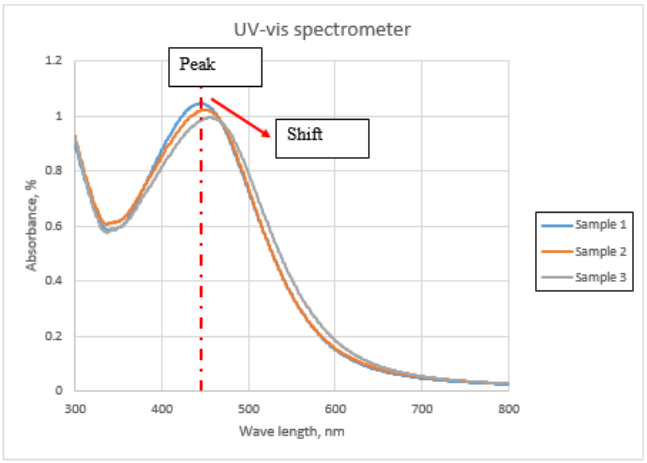

Figure 9: UV-vis Spectrum for $AgNO_3$ concentration controlled at 40 ml of peels extract.

D. Field Emission Scanning Electron Microscopy, FESEM analysis

The morphology of Silver Nanoparticles, AgNPs was viewed by SUPRA 40VP of FESEM. The AgNPs was scanned using 30 kV of magnification to get the image of particles.

Figure 10 shows the image of AgNPs captured by FESEM. The AgNPs is distribution well in range from 25 nm to 37 nm of size at 31 nm of average size. The size and shape of AgNPs for

both of image A and B is same. The size of AgNPs in this range is corresponding to the 450 nm of absorbance UV-vis spectrum peak.

As conclusion, volume of peel extract can affect the total formation of AgNPs based on value of absorbance percentage in UV-vis spectrum. However, the size and shape of AgNPs could not be affected by changing volume of peel extract.

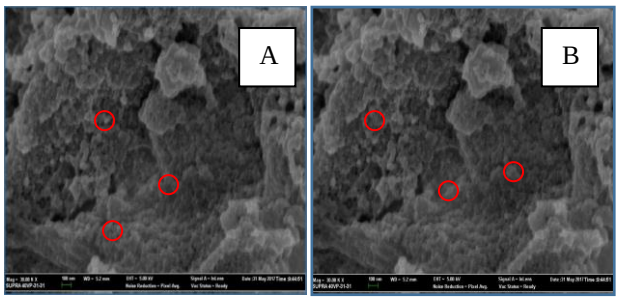

Figure 10: FESEM images of AgNPs using Pineapple peel at different volume (A) 40 ml (B) 80 ml.

IV. Conclusion

As a conclusion, extraction of pineapple peel has a potential in biosynthesis of nanoparticle. This is because the peel extract consist some of biomolecule that play important role in synthesis process. There are several factors that affect the formation of nanoparticle which are effect of volume ratio, time stirring, concentration of metal solution etc. This is important to us to control their size, shape and distribution.

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