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Silver nanoparticle synthesis using pineapple waste

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Abstract

Silver nanoparticles has been recognised to have numerous advantages for medical, cosmetics and environmental applications. There are three methods to produce nanoparticles namely physical, chemical, and biological. Biological method is preferred because of its eco-friendly, safer, and low operation cost. Usually, plant parts or microorganism used as raw material in biological synthesis. However, plant part is most preferred material due to its simplicity compared to microorganism technique. In this work, silver nanoparticles were synthesised using pineapple peel extract as reducing agent. High phenols content of pineapple extract indicates its potential as reducing and capping agent in the synthesis of silver nanoparticles. The synthesised silver nanoparticles were characterised by FTIR, UV-Vis, and FESEM to verify the presence of nanoparticles. Results demonstrated that the size of AgNPs was formed in range from 20 nm to 30 nm and this work has proven that the pineapple peel has potential in the silver nanoparticles synthesis.

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1.0 Introduction

Nanotechnology has received increasing attention for many years as one of the reliable technologies for pharmaceutical, medical, cosmetics and environmental area. In theory, 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. To maintain and stabilised the size of the nanoparticle, some capping agent is added during the process. It is important to stabilise the silver nanoparticles (AgNP) to avoid it agglomerate and become large particles above 100 nm which is possibly eliminating the benefit of nanoparticles. The function of capping agent is to neutralise the static charge from AgNP and attractive potential to become agglomerate.

Nowadays, varieties type of metallic nanomaterial was explored and produced using copper, zinc, gold, silver, and many more. Different types of metallic nanoparticle material are used in different purposes due to their incredible properties. Nanoparticles have been applied in medical treatment, energy production, environment, agriculture etc. (Hasan, 2015). The nanoparticles can be synthesised from two approaches namely top to bottom and bottom to up. Top to bottom approach usually applied on physical method for example crushing process. The large material is crushed using crusher to reduce to small particle size. This process requires high operating cost due to high energy consumption for the crusher. On the other hand, the bottom up approach is applied in chemical and biological methods as 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 environment. Otherwise, biological method is safer and eco-friendly compared to the chemical method. Even so, the mechanism of biological method is approximately same with chemical method, however biological method utilises biological entities to replace hazardous chemical used for raw material. Examples of biological entities are plant part and microorganism. Plant part is an excellent material than microorganism because it can reduce the isolation cost.

Biological method from plant part is preferred than other methods as it offer numerous advantages such as environmentally friendly, less operation cost, and produces less hazardous chemical waste. In this work, pineapple peel was chosen as nanoparticle material, to reduce the silver nitrate solution as metal ion while silver nanoparticle produced from different parameters was studied in term of sizes, shapes and distributions (Ravichandran et.al., 2016).

Nowadays, nanoparticles have been widely used in the nanotechnology related area. The AgNP had shown moderate antimicrobial and antioxidant activities has make it capable for use in biomedicine, water treatment and nano-biotechnology. Besides, silver nanoparticles are used in electrochemical, sonochemical, and microwave-assisted process (Bindhu & Umadevi, 2014). Moreover, it can be used for an optical sensor to detect the heavy metal in waste water such as Cu^{4+} and Zn^{2+} (Ahmed et.al., 2016).

2.0 Methodology

2.1 Material

Four hundred grams of pineapple peel obtained from pineapple fruit purchased at the Giant Supermarket, Seksyen 7, Shah Alam. Distilled water and deionized water were used to extract the biomolecule from pineapple peel and of silver nitrate solution.

2.2 Preparation for biosynthesis method

Biological method was used to synthesis the silver nanoparticles. In this method, four main steps, namely extraction, synthesis, purification, and analysis were involved.

Preparation for peel extract: Two hundred gram of pineapple peel was collected and washed followed by boiling in 400 ml of distilled water for 20 minutes. The boiled solution was filtered, and the light-yellow peel extract solution was obtained. The peel extract was analysed using FTIR to verify the presence of any biomolecules and polysaccharides in plant extract. After verifying the solution, it was ready to be used for silver synthesizing process.

Preparation for synthesis process: Conical flask was used as mixing equipment in this study. Firstly, silver nitrate solution was put into the conical 0.01 M silver nitrate solution to reduce the silver ion and cap the silver particle. The mixture was stirred for 10 minutes, transferred into a bottle sample and kept within one day. In this duration, the changes of sample colour were observed.

To analyse the prepared solution, 3 ml of sample was taken to undergo the UV-Vis analysis to determine the formation of silver nanoparticle. Furthermore, the sample was characterised by FTIR analysis to analyse the composition in the AgNP. Table 1, 2, 3, and 4 shows the details of parameter used in this study.

Preparation for purification process: The synthesised samples need to be purified to remove impurities and excess reactant materials. The sample was washed and dried prior to the characterisation step. The samples were centrifuged at 10,000 rpm for 15 minutes and discharged the supernatant liquid to obtain the pellet composition. The pellet obtained were silver nanoparticles in agglomerated form. The deionised water (DI) was added to the pellet for washing in a centrifuge, and the process was repeated twice. Finally, the pellet was dried using freeze dryer.

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)	Time complexion (min)
1	500	40	0.005
2	500	40	0.01
3	500	40	0.015

Analysis by field emission scanning electron microscopy (FESEM): Two samples of AgNP (40 ml and 80 ml peel extract) were taken to undergo FESEM analysis. The samples were 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 similar to work done by Benakashani et.al. (2016).

3.0 Results and discussion

3.1 Potential of pineapple peels in silver nanoparticle formation

Biological material is an innovation to improve the nanoparticle synthesis to save the environment by minimizing the hazardous waste produced. It can be any type of plant which are leaves, fruit, peel etc.

Pineapple peel was taken as raw material in this study. The peel extract was analysed using 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, including terpenoids, polyphenols, sugars, alkaloids, phenolic acids and proteins.

Fig. 1 shows the FTIR spectrum for peel extract. There are three peaks of graph that can be detected i.e. are 3270.14 cm^{-1}, 2147.96 cm^{-1} and 1635.69 cm^{-1} which corresponding to the stretch of C–H, *Bromelain* enzymes and C=C (vitamin C), respectively. *Bromelain* enzymes is an important element to separate amino acid in protein. Cysteine residual from broken protein is 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 plays important role to reduce the silver ion to silver particle by reduce the positive charge on the Silver ion (Bindhu & Umadevi, 2014).

Silver in single particle form has the static charge on it. Therefore, the unbalance static charge on that particle tend to attract other particles to be balance and eventually cause an agglomerate until the static charge was balance. Thus, 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. The biomolecule in peel extract acts as stabiliser to control the uniformity of the size of particle.

Fig. 2 shows the FTIR Spectrum for parameter 3. All of three samples were controlled by volume ratio of silver nitrate has shown the almost same spectrum with peel extract. Some changes at the samples peak were compared to the pure peels extract. For example, the absorbance at 3278.35 cm^{-1} of peels extract corresponds to the stretch of C–H that attributes to alkanes group. The compounds comprise of alkanes functional groups is important to cap the nanoparticles. Nevertheless, this peak was shifted to the nearest peak such as 3270.28 cm^{-1}, 3278.26 cm^{-1}, and 3274.15 cm^{-1} could be due to the pure peels extract has underwent reaction when it was mixed with $AgNO_3$.

On the other hand, peak of bromelain at 2149.92 cm^{-1} for peels extract was observed and has been changed to nearest peak position. This happen due to the reaction occurred between $AgNO_3$ that affects the structure of bromelain enzymes.

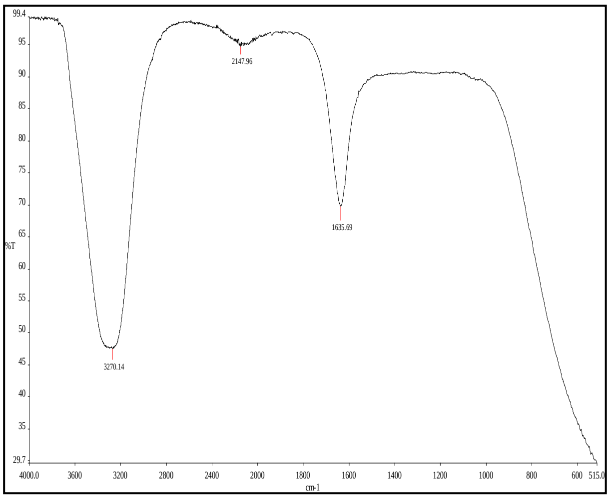

Fig. 1: FTIR Spectrum for peels extract.

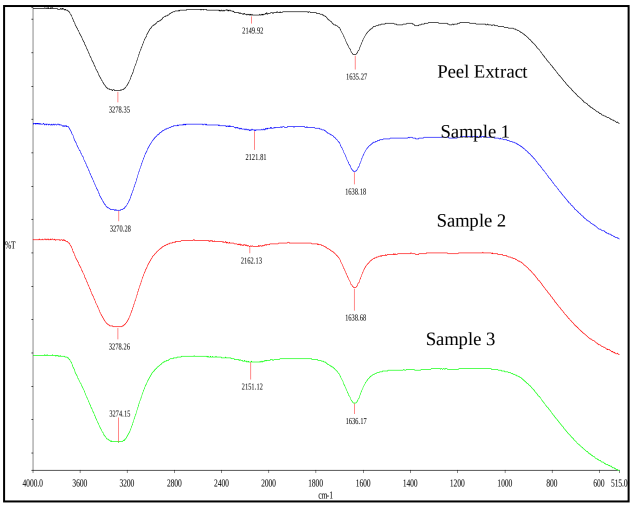

Fig. 2: FTIR Spectrum for volume ratio at 0.01 M silver nitrate solution.

Moreover, C=C group which represent the vitamin C also has small change of the peak at 1635.27 cm^{-1}. The three important peaks of peel extract that used in reaction was changed when underwent biosynthesis process. Therefore, it was confirmed that biomolecule is attached to the silver particle as well and the biosynthesis was occurred.

3.2 Silver nanoparticles characterisation

The synthesised silver nanoparticles were characterised to observe the changing of colour solution during the reaction. It was observed that the colour of solution was changed from colourless of silver nitrate to dark brown AgNP.

Fig. 3 shows path of $AgNO_3$ colour solution changes colourless before mixing the peels extract. After the peels extract was mixed, the mixture was changed to the light brown in colour. After one hour of the mixing, light brown of colour solution changed to the brown colour with the increases of the intensity of colour as time increase until one day completion of complexion time. This indicates the reduction of silver ions, Ag^+ to Silver particle Ag^0 by vitamin C in the peels extract. The reduction process of was assumed complete when no change of colour intensity observed.

However, the intensity of colour is different between parameters. Fig. 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 colour (dark) produced.

Fig. 5 shows the sample of parameter 4 (Table 4) which studied on the effect of silver nitrate at constant volume of silver nitrate and peel extract concentration All of this samples show about same colour intensity. The change from colourless to dark brown was due to the reduction of silver ions. After one day retention time and up to one week, there is no colour variation was observed which indicates that the nanoparticles produced from biological process were very stable (Veerasamy et.al.,2011).

3.3 UV-vis spectroscopy

The absorbance peak of silver nanoparticle was found around 420 nm (Sharma et al., 2015). Several previous studies reports the absorbance peak of silver nanoparticle were found at 438 nm (Veerasamy et al.,2011) and 439–446 nm (Bindhu & Umadevi., 2014). Hence, it can be concluded that absorbance peak within 400 nm to 500 nm. Absorbance peak of four parameters in this study were found in the range of 400–500 nm. Fig. 6 shows the UV-vis spectrum for volume ratio controlled at 0.001 M $AgNO_3$ solution

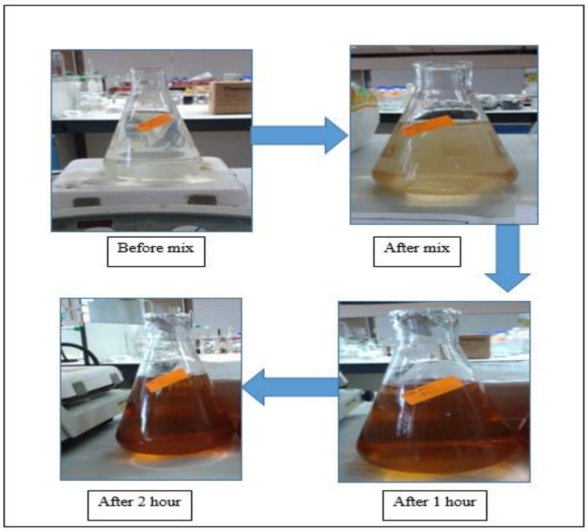

Fig. 3: Path of colour solution changing within 2 hours.

Fig. 4: Samples of volume ratio controlled at 0.01 M $AgNO_3$ solution.(S1 = sample 1, S2 = sample 2, S3 = sample 3)

Fig. 5: Samples of $AgNO_3$ solution concentration controlled at 40 ml of peel extract.

and demonstrated that the absorbance peak is in range 450–475 nm. High volume of peels extract added into $AgNO_3$ solution resulted to the shifting absorbance peak to the 500 nm.

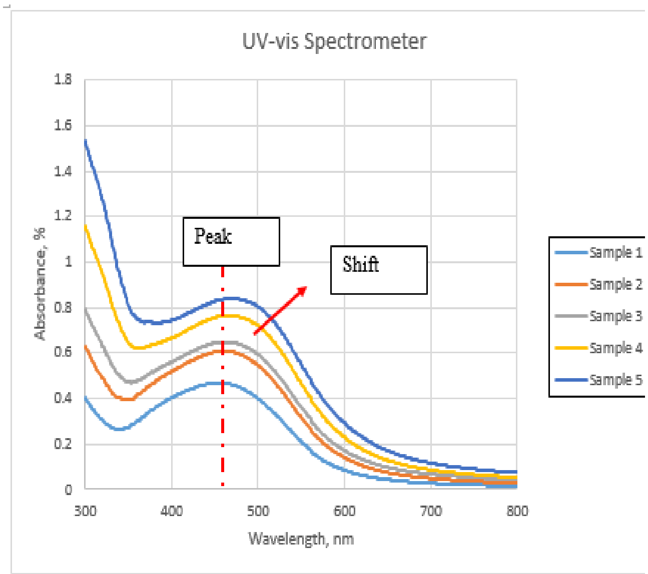

Fig. 6: UV-vis spectrum for volume ratio controlled at 0.001 M $AgNO_3$ solution.

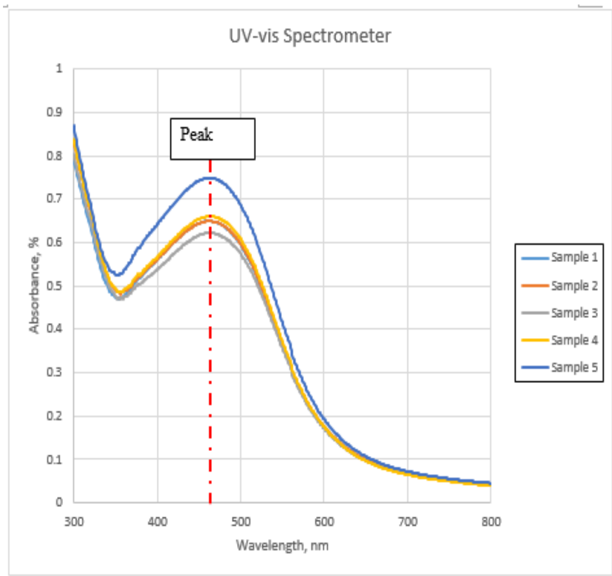

Fig. 7: UV-vis spectrum for stirring time controlled.

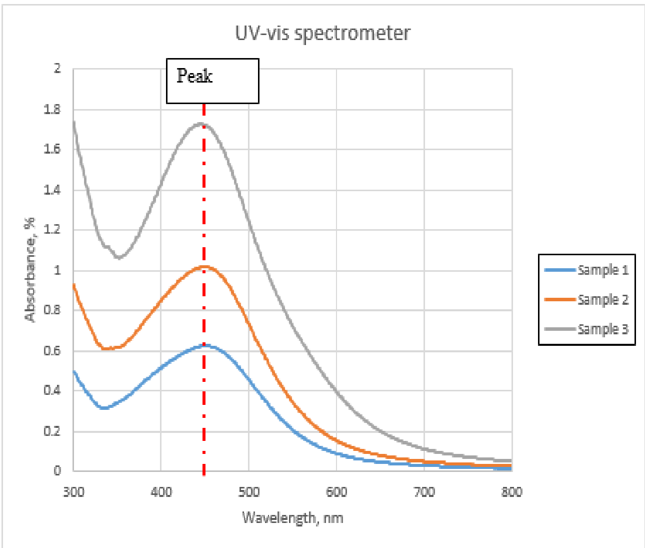

Fig. 8: UV-vis spectrum for volume ratio controlled at 0.01 M $AgNO_3$ solution.

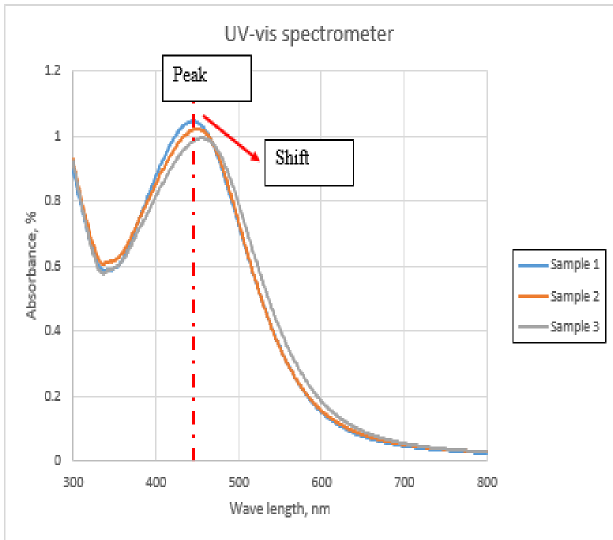

Fig. 9: UV-vis Spectrum for $AgNO_3$ concentration controlled at 40 ml of peels extract.

Fig. 8 shows that the UV-vis spectrum for volume ratio controlled at 0.01 M $AgNO_3$. It is observed that the absorbance peak of this parameter appeared at the 450 nm for all samples. However, When high volume of peels extract was added, the percentage of absorbance was increased. Furthermore, high absorbance value equivalent to the high intensity of colour (dark) corresponds to the high of total particle in the solution. The more concentration of peel extract in constant volume of silver nitrate, the more silver nanoparticles produced. This is due to the high concentration of biomolecule capable to reduce and cap the silver single particle.

Fig. 7 shows the UV-vis spectrum for stirring time of mixer. The absorbance peak of this parameter is in range of 460–463 nm.

In general, the trend of graph shows the high of absorbance value for the long stirring time. This is because the mixture become well mixed when the stirring time was prolonged and has encourage the biomolecule dispersed to each corner of the solution. The use of biomolecule can be maximised in order to reduce the silver ion to silver nanoparticles.

Fig. 9 shows the UV-vis spectrum for $AgNO_3$ concentration controlled at 40 ml of peels extract. The trend of graph is slightly different, as it is observed the absorbance of the peaks have been shifted tremendously from high silver nitrate concentration to low silver nitrate concentration. This indicate that the high concentration of silver nitrate will shift the absorbance peak to 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.

3.4 Field emission scanning electron microscopy, FESEM analysis

The morphology of AgNP was characterised by FESEM analysis using SUPRA 40VP FESEM. The AgNP was scanned using 30 kV of magnification to get the image of particles. Fig. 10 presents the image of AgNP captured by FESEM and showed well distribution in range from 25 nm to 37 nm of size with 31 nm as an average particle size. It is observed that the size and shape of AgNP for both of image A and B has the same particle size. The size of AgNP in this range is corresponding to the 450 nm of absorbance UV-vis spectrum peak (as presented in Fig. 4). It can be observed that volume of peel extract can affect the total formation of AgNP based on value of absorbance percentage in UV-Vis spectrum. However, the size and shape of AgNP could not be affected by changing volume of peel extract.

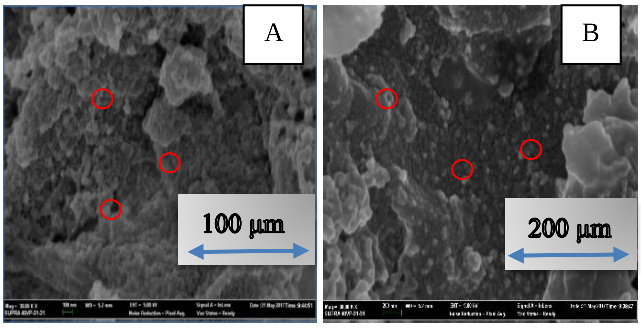

Fig. 10: FESEM images of AgNP using pineapple peel at different volume (A) 40 ml (B) 80 ml.

4.0 Conclusions

Pineapple peel extract has been demonstrated to have a potential for biosynthesis of silver nanoparticle due to content of some of biomolecule that play important role in synthesis process. Several factors that affect the formation of nanoparticle, mainly volume ratio, time stirring, concentration of metal solution are important in order control their size, shape and distribution.

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