The Role of pH in Synthesis Silver Nanoparticles Using Pometia pinnata (Matoa) Leaves Extract as Bioreductor

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Abstract. Green synthesis of silver nanoparticles (AgNPs) using plant extract have been developed due to ecological friendly and their simple procedure. Plant contains bioreductor to reduce silver precursor into nanoparticles. Plant compound beside of their medicinal properties also can be functional for this biosynthesis process. The synthesis process can be affected by pH, which can determine the shape and size from AgNPs. Therefore, in this research biosynthesis of AgNPs has been done to study the effect of aqueous extract pH on the AgNPs synthesize on acidic and alkaline condition. The synthesis was done by mixing 2% Matoa aqueous extract and 1 mM AgNO₃ each solution adjusted to 4 and 11, and 5 as the nature pH for comparison. The AgNPs were characterized based on color changes, UV-Vis spectrophotometers, TEM (Transmission Electron Microscopy), and PSA (Particle Size Analyzer). The UV-Vis spectrum had absorption between 400-500 nm. The TEM results showed that the shape of the nanoparticles produced varies considerably from triangles, spherical, and hexagons. The PSA results show that increasing pH tend to produce the small size of nanoparticles, which had moderately stable nanoparticle and moderate stability. This result showed that the AgNPs synthesized can be optimized by adjusting the pH to obtain particular shape and size from the AgNPs.

1. Introduction
Nanoparticle biosynthesis is a method of fabricated nano-sized particles by utilizing extracts from microorganisms [1] and plants [2], as reducing agents. The biosynthetic method is simpler and green [3]. Reducing agents derived from metabolites compounds are more easily to extract and no toxic effect, making them more environmentally friendly. The advantage of using plants as the source of reducing agent in the biosynthesis process due to their abundance in nature and tend to be sustainable sources. In general, plants used for biosynthesis are plants that contain metabolite compounds such as polyphenols, saponins [4], flavonoids, alkaloids [5], and terpenoids. Pometia pinnata (Matoa) leaves are known to contain flavonoid, phenol, and saponin groups [6]. In this study, Matoa leaves extract will be used as a reducing agent to reduce silver ions (Ag⁺) to silver nanoparticles (Ag⁰). Silver nanoparticles are nanoparticles that have broad applications and are used in health as an antimicrobial material [7,8] and the environment as to detect pollutants [9]. The role of extracts as an attractive
reducing agent to be studied is related to methods which are quite simple but have quite complex mechanisms to be studied [10].

Besides the source of reducing agent, other factors that can influence the reduction process are reaction conditions such as pH, temperature, substrate concentration, and reaction time. This factor will determine the character of the AgNPs resulting from the synthesis. The size and shape of nanoparticles can be controlled by modifying process variables, one of which is pH [7, 11, 12]. Several studies have shown that pH can affect the size of nanoparticles produced, whereas at the alkaline condition, the size of nanoparticles can be smaller [13, 14]. Nanoparticles can exhibit an effective charge change in aqueous conditions, from positive (at low pH) to negative (at high pH,) with an isoelectric point in equilibrium. Near the isoelectric point, the average particle size is typically larger than those conditions where the particle charge (or zeta potential) is higher, which will determine the AgNPs stability and will prevent aggregation [14, 15]. In this research, the pH variation of Matoa extract was carried out to determine its role in the process of biosynthesis of silver nanoparticles. The results observed were related to the effect of pH on the shape, size, and stability of the silver nanoparticles produced.

2. Material and method

2.1. Extract preparation. The sample of Matoa leaves obtained from the Matoa tree at Science Park, Universitas Indonesia. The cleaned and dried powdered [13] leaves then extracted by boiled 10 grams of Matoa leaves in 500 mL double-distilled water for 15 minutes. After that, the solution filtered using Whatman filter paper No.1. The filtrate then stored at 4°C and ready to use for the synthesis process.

2.2. Synthesize of silver nanoparticles. All the chemicals used for this research were from Merck. After we prepared the Matoa leaves extract, the nature pH from the extract measured using pH meter (Horiba P-1000). For the treatment, the pH of the extract adjusted to 4 using 0.1 M HCl and to 11 using 0.1 M NaOH for the alkaline condition. Then, the extract mixed with 1 mM AgNO₃ as the silver precursors. The ratio between the extract and precursor were 1:2 (v/v) — the reaction conditioned at room temperature and dark condition. After 24 hours, the mixed solution observed for further characterization.

2.3. Characterization of silver nanoparticles. After 24 hours of reaction, the solution observed for their color change which indicates the AgNPs have been formed. Further characterization was done using a UV–Vis spectrophotometer (Thermo Genesys 10S) to confirm the AgNPs spectrum absorption. Particle Size Analyzer (Malvern Zetasyr Nano series Nano-ZS) used to study the dispersity and zeta potential from the AgNPs. TEM used in this research were JEOL JEM 1400 at Department of Chemistry, Universitas Gadjah Mada, Yogyakarta dan TEM FEI Tecnai G2 Supertwin at Balai Besar Penelitian dan Pengembangan Pascapanen Pertanian (BB-Pascapanen), Bogor. Transmission electron microscopy (FEI Tecnai G2 SuperTwin). The image from TEM result used to observe the size and shape of the AgNPs, the picture analyzes using image-J to analyze the particles size.

3. Results and discussion

After 24 hours, the synthesis solution of silver nanoparticles using pH variations from Matoa leaves extract showed various colors. The colors formed at pH 4 were yellow, brown at pH 5 and dark brown at pH 11 are (Fig1.a). This color is the characteristic from the surface plasmon resonance of AgNPs [8,13,16]. The UV-Vis spectra were subtracted to show the equalize baseline between treatments (Fig. 1b). There were differences in λmax from each sample, where at pH 4 there was a peak at λmax 359 nm. Meanwhile, at pH 5 and 11, there are 2 peaks from the max peak, at 360 and 447 nm respectively, while at pH 11 at 422 and 673 nm. The difference in the value of λmax and the number of λmax can indicate differences related to the size and shape of AgNPs [7]. The AgNPs absorbance value increases with the increasing of pH, where at pH 11 there is a high absorption value, and there were 2
peaks that indicate different sizes of AgNPs. A higher absorption value can also indicate a higher number of nanoparticles [17].

![Figure 1](image1.png)

**Figure 1.** (a) Silver nanoparticles colloids in each pH reaction condition after 24 hours, (b) The subtracted UV-Vis spectra showed a peak between 300-500 nm. The peak show the LSPR spectrum from AgNPs.

Furthermore, based on the TEM results showed that at pH 4 AgNPs tends to produce spherical shape AgNPs. Meanwhile from TEM results at pH 5, it was found that there were triangular and spherical AgNPs with sizes 80 nm and 50 nm respectively. At pH 11, the TEM result showed spherical and hexagonal shape nanoparticles with various the range size from 10-50 nm (Fig.2). Based on research by Alqadi et al. [18] Silver nanoparticles with small size and more regular shape were produced at an alkaline condition (high pH). In this research, nanoparticles with various sizes and shapes can be obtained in high pH because the reaction conditions that direct the growth of AgNPs, into nanosphere or nanocluster forms through the nucleation stage until coalescence happened. Hence this mechanism can obtain nanoparticles with small sizes, a faster reactions are needed. This pH adjustment changed the chemical nature of the extract. It can affect its performance as well as the rate of reduction [15].

![Figure 2](image2.png)

**Figure 2.** TEM image showed a possible variety of AgNPs shape and size in different pH condition; the bar represents 50 nm.

Based on the PSA results (Table 1.) the AgNPs had zeta potential values between -10--16 mV, which showed that all samples were in the relatively stable category. The Zeta potential that is less negative than -15 mV represents the initiation of nanoparticles aggregation, and when the zeta-
potential equals to zero the colloid will precipitate [19]. Meanwhile the Polydispersity Index (PDI) values of AgNPs at pH 4 and 5 are in the moderately disperse and pH 11 highly polydisperse distribution category [20]. The High PDI values on pH11 supported by UV-Vis and TEM results which showed AgNPs of various shapes and sizes. The peak width of the UV-Vis spectra represents the homogeneity of the size of the nanoparticles produced. The narrower the absorbance peak, the more homogeneous the size of the silver nanoparticles produced [7]. Thus, AgNPs at pH 5 and 11 tend to have a more heterogeneous size distribution (polydisperse). Nanoparticles can exhibit an effective charge change in aqueous conditions, from positive at low pH to negative at high pH, with an isoelectric point in between. Near the isoelectric point, the average particle size is typically larger than those where the effective or zeta potential is stronger [14,15]. At low zeta potential AgNPs will tend to be easier to experience agglomeration and precipitation. This condition explains that the shape, size and stability are strongly affected by the experimental conditions [8, 21].

### Table 1. Particle size analyzer (PSA) result and category from each sample

| Samples | PDI value | PDI category | Zeta potential value (mV) | Zeta potential category |
|---------|-----------|--------------|--------------------------|------------------------|
| pH 4    | 0.303     | moderately disperse distribution | -14.8 |  |
| pH 5    | 0.274     |              | -10.9 | relatively stable |
| pH 11   | 0.491     | highly polydisperse distribution | -16.1 |  |

These results confirm that the formation of AgNPs was better in alkaline conditions than in acid. This condition can be caused due to functional groups ionizing process at higher pH and reduction rates. However, to produce small size AgNPs, the nucleation process tends to be slow. This mechanism can be related to the electrostatic repulsion of anions present in the reaction mixture [14,15]. AgNPs tend to aggregate; some nanoparticles may aggregate without strong electrostatic repulsion keeping the nanoparticles apart. The samples were more stable on alkaline and neutral than on acidic pH. With the increase of pH, the free organic functional groups on the AgNPs surfaces reach a higher degree of deprotonation; thus, the amount of negative surface charge increases simultaneously. This would enhance the electrostatic repulsion between particles resulting in smaller aggregate diameters, explaining the lower Z-average values compared to the measurements on acidic conditions [19] specific control of the shape, size, and distribution of the produced nanoparticles could be achieved by changing the methods of synthesis, the reducing agents and stabilizers [8].

### 4. Conclusion

Silver nanoparticles biosynthesis tend to produce spherical silver nanoparticles. However, the extract reaction conditions at pH 5 and 11 have the potential to produce AgNPs in a triangle and hexagonal form. Alkaline condition tends to produce small size nanoparticles. Meanwhile, the stability of AgNPS include in the category of relatively stable. For further improvement, the process needed to be modified to optimize the reaction condition to get a monodisperse size and shape from the AgNPs with high stability.

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