**ORIGINAL ARTICLE**

# The Influence of pH on Structural, Morphological, and Optical Properties of Al₂O₃ Nanoparticles Synthesized by *Syzygium aromaticum* Leaf Extract

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**ABSTRACT** – Aluminum oxide (Al₂O₃) nanoparticles have been synthesized through a biosynthesis approach, employing *Syzygium aromaticum leaf* extracts prepared under varying acidic conditions as bioreductants in the reaction with aluminum nitrate nanohydrate. The Al₂O₃ nanoparticles were annealed at 450 °C for one hour to facilitate the formation. Then, the samples were characterized for their crystal structure, morphology, and optical properties using X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), and UV-visible (UV-Vis) spectrophotometry, respectively. XRD analysis confirmed that the Al₂O₃ nanoparticles possess an orthorhombic crystal structure, corresponding to Inorganic Crystal Structure Database (ICSD) entry #98-009-4485. The average crystallite sizes were measured to be 37.36 nm, 15.47 nm, and 12.52 nm for nanoparticles synthesized at pH-9, pH-10, and pH-11, respectively. Morphologically, the pH condition affects the morphology of Al₂O₃ nanoparticles. The reflectance spectrum peak of Al₂O₃ nanoparticles in the wavelength range of 328–336 nm is observed with the band gap energy of 2.92-3.01 eV. According to these results, it is believed that the Al₂O₃ nanoparticles have potential applications as photocatalysts.

## INTRODUCTION

Because of the rapid development of science and technology, nanotechnology research is now a trend and attracts the attention of many researchers. Nanotechnology, a subdiscipline of material science, involves the synthesis and fabrication of nanoparticles that exhibit specific properties through the utilization of physical and chemical methodologies [1]. Aluminum oxide (Al₂O₃) is one of the most extensively developed metal oxides, because the aluminum element is abundant in the Earth's crust, where it is the third most prevalent element in the lithosphere [2]. Aluminum oxide has a wide band gap and high exciton binding energy, which is 4.40 eV for the γ-Al₂O₃ crystal structure and 9.5 eV for the α-Al₂O₃ crystal structure [3]. Basically, Al₂O₃ is very interesting and important because it has good physical properties such as high electrical resistance [4], high hardness, resistance to corrosion, a high melting point of 2345 K, low thermal conductivity, and resistance to high environmental temperatures [5].

Aluminum oxide can be synthesized through a range of methods, including sol-gel, precipitation, hydrolysis, and wet chemical [6]. However, these methods have disadvantages, such as taking a long time, requiring relatively expensive base materials, and requiring high temperatures [6]. Recently, researchers around the world showed their interest in synthesizing metal oxide nanoparticles through an environmentally friendly method by utilizing green synthesis with plants, bacteria, fungi, and algae [7]. Clove leaf (*Syzygium aromaticum*) is one of the plants that can be used as a bioreductor to biosynthesize aluminum oxide nanoparticles. Clove leaves contain phenolic compounds, flavonoids, tannins, and eugenol [6], [7]. Parameters such as pH can influence the green synthesis of metal nanoparticles using plant-based methods. Specifically, pH is of significant experimental importance because it has been demonstrated to affect the size and morphology of the resulting nanoparticles [8]. Several studies report that the biosynthesis of nanoparticle methods using plant extracts can produce crystal structures, morphologies, and particle sizes that are controlled, more effective, and easier

[8]. In a study by Sutradhar et al., aluminum oxide nanoparticles synthesized using tea leaf extract were found to have crystallite sizes ranging from 50 to 100 nm [9]. Aluminum oxide nanoparticles were synthesized by Ansari et al. using lemongrass leaf extract and produced a crystal size of 34.5 nm [10]. Hasanpoor et al. also reported that aluminum oxide nanoparticles synthesized with oregano leaf extract, marjoram leaves, cocoa leaves, and yellow lettuce leaves produced crystal sizes of 2–9 nm [11]. Duraisamy et al. also reported that nanoparticles synthesized with Aerva lanata leaves produced a crystal size of about 50–70 nm [12]. Goutam, Pratap et al. synthesized aluminum oxide nanoparticles with rose leaf extract, producing a crystal size of 24.53 nm [13].

Due to the high concentrations of eugenol, tannins, and flavonoids in Syzygium aromaticum leaf extract, it shows considerable potential as a bio-reductant in the synthesis of $Al_2O_3$ nanoparticles. This paper investigates the effect of pH on the biosynthesis process and examines the crystal structure, morphology, and optical properties of $Al_2O_3$ nanoparticles produced using *Syzygium aromaticum* leaf extract.

## EXPERIMENTAL METHOD

### Materials and Instruments

The instruments and materials used in this experiment were a digital balance, 100 ml and 250 ml beakers, Whatman filter paper, a hotplate magnetic stirrer, a drop pipette, a furnace, a spatula, a mortar and pestle, a centrifuge, clove leaf powder, aluminum nitrate nanohydrate ($[Al(NO_3)_3.9H_2O]$) Merck, sodium hydroxide (NaOH), and deionized water (DI water).

### Method and Procedure

Aluminum nitrate nanohydrate $[Al(NO_3)_3.9H_2O]$ and liquid extract of clove leaves were mixed in a ratio of 1:4. The solution was continuously stirred on a hotplate stirrer for 30 minutes and heated to 60 °C. The pH solution was adjusted to 9, 10, and 10 by adding specific amounts of NaOH to investigate the impact of pH on the fabricated material. The whole mixture was stirred constantly until the mixture changed color from brown to yellowish. After allowing the mixture to cool to room temperature, it was centrifuged and thoroughly washed with deionized water (DI water) for 10 minutes at 4000 rpm. This washing process was repeated three times to eliminate contaminants. Next, the precipitate was dried at 90 °C for 4 hours using a furnace and continued with the annealing process at 450 °C for 1 hour using a furnace to produce aluminum oxide ($Al_2O_3$) nanoparticles powder. After that, the sample can be characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV–visible (UV-Vis) spectroscopy.

## RESULT AND DISCUSSION

The biosynthesis of aluminum oxide ($Al_2O_3$) nanoparticles was successfully achieved using clove leaf extract under varying pH conditions. In the manufacture of $Al_2O_3$ nanoparticles (Figure 1), the temperature used in crystal formation is 450 °C for 1 hour. The results of the annealing process with pH 9, pH 10, and pH 11 are white powder. This is due to the annealing process, which releases water molecules and converts hydroxide into pure oxide, which is white in color. Following their synthesis, the $Al_2O_3$ nanoparticles were characterized using X-ray diffraction (XRD), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDX), and UV-Visible (UV-Vis) spectrophotometry.
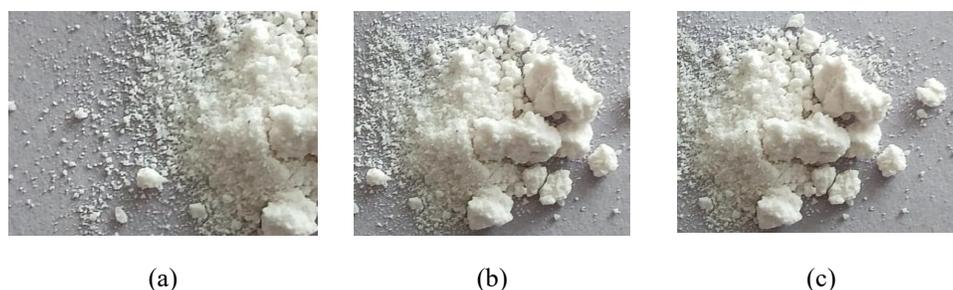


(a)  (b)  (c)

**Figure 1.** $Al_2O_3$ nanoparticles powder using clove leaf extract with variations of pH: (a) 9, (b) 10, and (c) 11

### Crystal Structure of $Al_2O_3$ Nanoparticles

Figure 2 shows the XRD pattern of $Al_2O_3$ nanoparticles synthesized using clove leaf extract under different pH conditions, following annealing at 450 °C for one hour. The XRD analysis identified eight distinct crystal planes in each sample, based on the Inorganic Crystal Structure Database (ICSD) entry #98-009-4485. It was identified that the crystal structure of $Al_2O_3$ nanoparticles is an orthorhombic polycrystal with space group Pna21. However, additional peaks were

observed at different pH values: at pH 9, peaks appeared at hkl (001) and (21-3); at pH 10, a peak was observed at hkl (100); and at pH 11, a peak was detected at hkl (110). The multiple peaks observed in the XRD data were attributed to aluminium hydroxide ($Al(OH)_3$), as referenced by ICSD entries #98-003-6233 and #98-001-6018. This means that $Al_2O_3$ nanoparticles do not have high purity. In this study, the average crystallite size values at pH 9, 10, and 11 were 37.36 nm, 15.47 nm, and 12.52 nm, respectively. The average micro strain values at pH 9, 10, and 11 were 0.34%, 0.51%, and 0.92%, respectively. This observation is consistent with existing literature, which demonstrates an inverse relationship between crystallite size and micro strain. Specifically, as the crystallite size increases, the micro-strain values decrease. This means that the larger the crystallite size, the less micro strain occurs in the material. The addition of pH to the solution also affects the crystallite size. At alkaline pH conditions, the surface of the $Al_2O_3$ particles will be negatively charged due to the presence of ionized hydroxyl (-OH) groups, which cause the crystallite size to become larger [8]. Lower pH conditions will create environmental conditions that favor the formation of new crystal nuclei rather than the growth of larger crystallites, resulting in smaller $Al_2O_3$ crystallites. According to the Debye–Scherrer equation, the full width at half maximum (FWHM) in XRD patterns is influenced by peak intensity, with greater intensities producing smaller FWHM values [14]. The FWHM, together with the wavelength, intensity, and $2\theta$ angle from XRD data, is then used to estimate the crystal size of the material. The concentration of sodium hydroxide (NaOH) used in the process of forming $Al_2O_3$ nanoparticles can affect the crystallite size. A high concentration will increase the reaction rate in the formation of nanoparticle nuclei, so the size of nanoparticles will tend to be smaller.
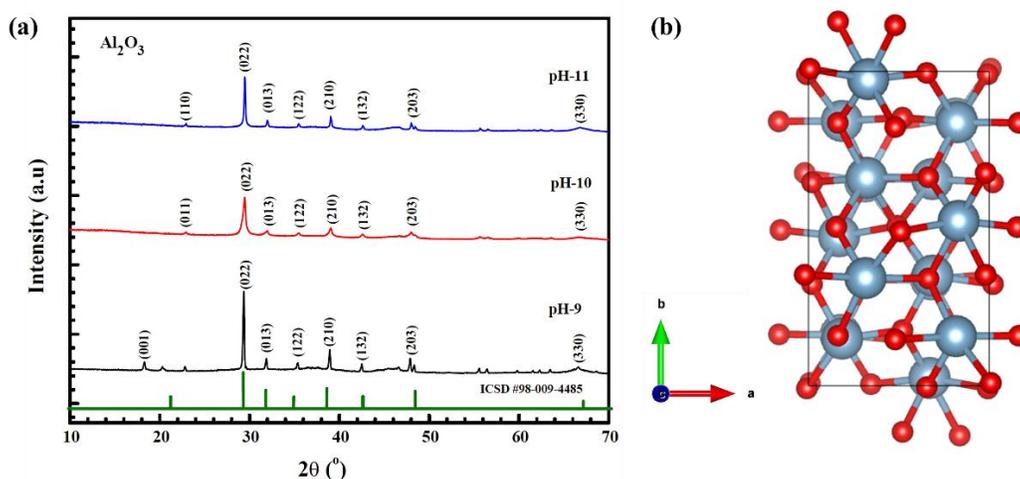


**Figure 2.** (a) Diffraction pattern of $Al_2O_3$ nanoparticles with pH variation and (b) orthorhombic crystal structure of $Al_2O_3$ nanoparticles material

### Morphology and Elemental Composition of $Al_2O_3$ Nanoparticles

Figure 3 shows the morphology and particle size distribution of $Al_2O_3$ nanoparticle samples synthesized at different pH levels, as observed using SEM. As can be seen from Figure 3 (a), Figure 3(b), and Figure 3(c), all SEM images of $Al_2O_3$ nanoparticles indicate strong agglomeration. This may be due to environmental conditions, such as increasing the pH value. Hence, the nanoparticle size could not be clearly observed.
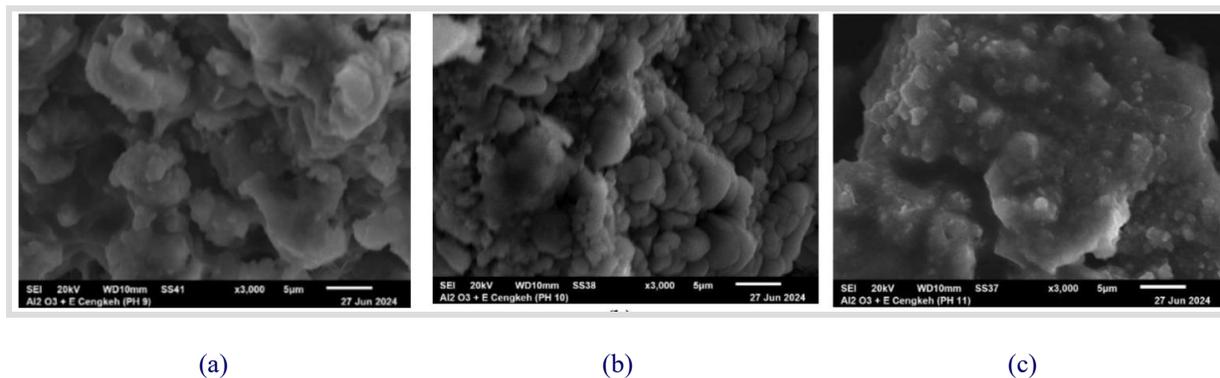


(a)        (b)        (c)

**Figure 3.** SEM images of $Al_2O_3$ Nanoparticles: (a) pH 9, (b) pH 10, and (c) pH 11

However, it is believed that the use of pH influences particle size [8]. Under base conditions, high concentrations of OH-ions cause coagulation, and particle sizes tend to be smaller [15]. Meanwhile, our results strongly influenced the chemical condition during the growth process, which causes strong agglomeration, and the grain boundary could not be clearly observed.

**Table 1.** Element composition of $Al_2O_3$ nanoparticle under different pH

| Sample $Al_2O_3$ | | | |
|---|---|---|---|
| pH | Element | Weight % | Atomic % |
| 9 | C | 9.44 | 14.19 |
| | O | 51.57 | 58.17 |
| | Na | 13.48 | 10.59 |
| | Al | 25.51 | 17.06 |
| 10 | C | 7.82 | 11.92 |
| | O | 48.95 | 56.03 |
| | Na | 23.08 | 18.38 |
| | Al | 20.15 | 13.68 |
| 11 | O | 50.72 | 61.95 |
| | Na | 18.72 | 15.91 |
| | Al | 30.57 | 22.14 |

Table 1 shows that the three samples exhibit similar atomic percentages, and the elemental weights are almost the same. The element Al has a smaller weight. The O atom has a larger atomic percentage compared to the Al element in the $Al_2O_3$ pH 9 and pH 11 samples. In $Al_2O_3$, pH 9 has an excess of O atoms possibly due to impurity or contamination with oxygen-containing compounds which can react with oxygen in the environment to make the surface of $Al_2O_3$ more stable, where the surface of $Al_2O_3$ can react with oxygen in the environment to form additional oxide layers hydrated oxides such as aluminium oxyhydroxide (AlOOH) or aluminium hydroxide ($Al(OH)_3$) which increases the amount of oxygen detected [8].

The characteristic peaks for Al and O were clearly observed. This identifies that in the process of synthesizing $Al_2O_3$ nanoparticles, there are other elements detected using EDX, namely the presence of elements carbon (C) and natrium (Na). This indicates that the $Al_2O_3$ nanoparticle structure grows with low purity. The presence of other elements in the EDX analysis of $Al_2O_3$ nanoparticles may indicate the presence of impurities and side reactions in the nanoparticle synthesis process. This is likely due to the carbon element originating in the tube holder in spectroscopy and the sodium element present due to side reactions in the precipitation process.

## Optical Properties of $Al_2O_3$ Nanoparticles

The reflectance test results of $Al_2O_3$ nanoparticle samples with clove leaf extract at various acidity with wavelength spectrum range 250–800 nm are shown in Figure 4. The reflectance spectra of $Al_2O_3$ nanoparticles with variations in pH 9, pH 10, and pH 11 are at wavelengths of 336 nm, 335 nm, and 328 nm, respectively. Nanoparticles with smaller sizes will have a higher intensity of peak reflectance. This is because in alkaline pH conditions, the reflectance peak of $Al_2O_3$ nanoparticles tends to be sharper and symmetrical. In alkaline conditions, the nanoparticle surface has a strong negative charge. This negative charge causes a repulsive force between particles, so the nanoparticles will be well dispersed [6].
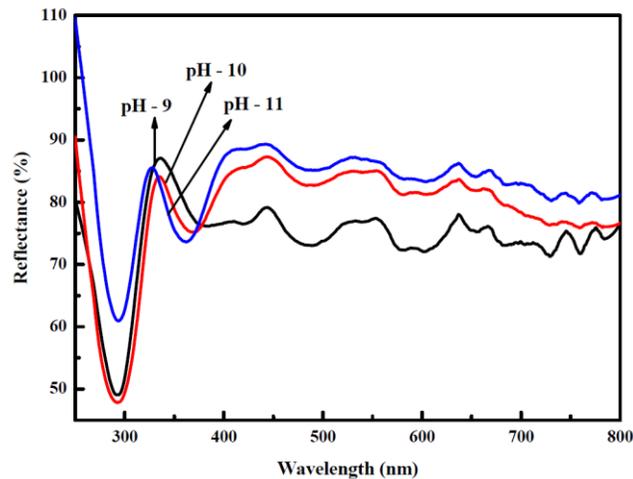
**Figure 4.** Reflectance spectrum of $Al_2O_3$ nanoparticles with clove leaf extract

The optical band gap energy of $Al_2O_3$ nanoparticles was determined using the Kubelka-Munk method [14], as illustrated in Figure 5. The magnitude of the energy gap is done by drawing a linear line from the curve until it intersects the horizontal coordinate (energy). The intersection of the linear line that offends the linear part of the curve with the horizontal axis (energy axis) is the energy gap value of $Al_2O_3$ nanoparticles with clove leaf extract.
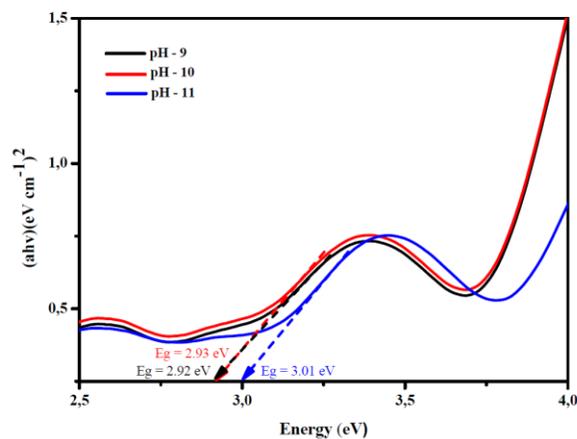


**Figure 5.** Bandgap energy of $Al_2O_3$ nanoparticles with variations of pH

Figure 5 shows that $Al_2O_3$ nanoparticles synthesized at pH 9, pH 10, and pH 11 exhibit band gap energies of 2.92 eV, 2.93 eV, and 3.01 eV, respectively. The pH value can change the crystal structure of $Al_2O_3$ nanoparticles and affect the optical band gap energy. As observed, Al2O3 nanoparticles tend to have a larger optical band energy. The higher pH value will cause the crystal structure to be more ordered and have a higher optical band gap energy [7].

**Table 2.** Effect of pH variations on nanoparticles $Al_2O_3$

| Sample $Al_2O_3$ | Average size of crystallites (nm) | Peak maximum reflectance (nm) | Bandgap energy (eV) |
|---|---|---|---|
| pH 9 | 37.36 | 336 | 2.92 |
| pH 10 | 15.47 | 335 | 2.93 |
| pH 11 | 12.52 | 328 | 3.01 |

Table 2 shows the effect of pH variation on $Al_2O_3$ nanoparticles. The pH value can affect the wavelength at the maximum peak and band gap energy. Nanoparticles with a high pH (alkaline) tend to have a smaller size. The crystal size of nanoparticles becomes small because electrons and holes in the material are limited to movement in a narrow volume, resulting in a greater increase in band gap energy [8]. In this study, $Al_2O_3$ nanoparticles synthesized at pH 9 exhibited an average crystallite size of 37.36 nm, a maximum peak wavelength of 337 nm, and a band gap energy of 2.92 eV. At pH 10, the crystallite size was 15.47 nm with a peak wavelength of 335 nm and a band gap energy of 2.93 eV. For pH 11, the nanoparticles had an average crystallite size of 12.52 nm, a peak wavelength of 327 nm, and a band gap energy of 3.01 eV.

## CONCLUSION

Clove leaf extract can be used as a bio-reductor in the biosynthesis process of $Al_2O_3$ nanoparticles because it contains antioxidant compounds such as flavonoids, phenolics, and eugenol. The variation of acidity in the biosynthesis process of $Al_2O_3$ nanoparticles affects the crystal structure, morphology, and optical properties, namely the crystal structure formed in the biosynthesis of $Al_2O_3$ nanoparticles with clove leaf extract is orthorhombic, the crystallite size of $Al_2O_3$ nanoparticles with pH 9 is 37.36 nm, pH 10 is 15.47 nm, and pH 11 is 12.52 nm. The higher the pH, the smaller the crystallite size obtained. pH affects particle size, which can cause agglomeration. Effect of pH on band gap energy. The higher the pH, the band gap energy will increase, whereas the size of the nanoparticles will be smaller. The band gap energies at pH 9, 10, and 11 are 2.92 eV, 2.93 eV, and 3.01 eV, respectively.

## ACKNOWLEDGEMENT

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