Effect of Calcination Time on The Formation of Fe3O4 Nanoparticles by Green Synthesis Method Using *Ananas comosus* Leaf Extract

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**Abstract** Recent studies show that Fe3O4 magnetite nanoparticles (M-NPs) can be a great potential in the extraction of liquid waste contaminants. This is caused by extraordinary physical and chemical properties of M-NPs such as high surface area, nanoscale particle size, and their superparamagnetic behavior. These superparamagnetic properties can be enhanced by modifying the surface of the nanoparticles, thereby increasing the adsorptive attraction between the molecules and the liquid waste. Various methods of nanoparticle synthesis have been discovered but have multiple drawbacks, they produce toxic by-products that are not environmentally friendly. Therefore, in this research, M-NPs were synthesized by green approach using Pineapple (Ananas comosus) leaf extract as a capping agent to prevent agglomeration of M-NPs. In this method a ratio of 1:2 is used for the two precursors Fe2+ and Fe3+ which is then varied by the calcination time: 180, 210 and 240 minutes. Magnetite nanoparticles were characterized using XRD, SEM-EDX, and SAA then absorbance tested via UV-Vis spectrophotometry using methylene blue as liquid contaminant. By the results of XRD, it can be confirmed that magnetite (Fe3O4) was formed. Through SEM testing, the average particle size for each calcination variation was 53.73 nm, 71.22 nm and 46.05 nm, respectively. SAA testing showed that the sample surface areas were 130.28 m2/gr, 137.26 m2/gr, and 140.05 m2/gr, respectively. The UV-Vis absorbance test showed the highest degradation percentage shown by a variation of 210 minutes which is 70%.

**Keywords:** *Ananas comosus leaf, Green synthesis, Magnetite, Methylene Blue, Nanoparticles*.

# INTRODUCTION

Water is the most important natural resource and needed by every living creature to meet their needs and support their lives naturally. The need for clean water is one of the basic needs required in everyday life. Almost every day, people use water and indirectly people also produce water waste from their activities. Based on research in 2014 conducted by the Ministry of Environment, Indonesia, 70% - 75% of rivers in 33 provinces of Indonesia have been polluted. River water pollution is basically due to the pollution sources in the neighbor environment, such as batik industry activities which produce methylene blue dye waste.

As a result of the toxicity of dye waste to the environment, it is necessary to process and reduce dye waste before it is released into the environment [[1]](#_bookmark12) Stated that, among several dye waste processing methods, the adsorption process has received more attention because of their simplicity in handling and cost effectiveness. To ensure the success rate of the adsorption process, the suitability of the environment and type of adsorbent is very important. According to [[2],](#_bookmark13) the type of adsorbent that is effective for adsorption has to attain specific characteristics, such as; large adsorption rate and capacity, is chemically stable, can be used repeatedly and is environmentally friendly. Recent studies show that adsorption capacity and efficiency are influenced by the surface area and porosity of the adsorbent. Due to its limited volume, their large surface area and high porosity that consist of a large number of surface vacancies, making nanomaterials one of the adsorbents with great potential for the extraction of contaminants from liquid waste [[3].](#_bookmark14)

Nanomaterials such as magnetite nanoparticles [[4];](#_bookmark15) [[5]](#_bookmark16) and mesoporous materials [[6]](#_bookmark17) have been developed to become adsorbents. Recent studies show that nanoparticle-based adsorbents had excellent performance in removing dyes from aqueous solutions due to their outstanding physical and chemical properties such as high surface area, nanoscale particle size, and chemical composition stability [[7].](#_bookmark18) The purpose and efficiency of this nanomaterial surface can be improved by modifying the nanomaterial surface, thereby increasing the adsorptive attraction between molecules and dyes [[8].](#_bookmark19) Some modification of strong ferromagnetic iron-based nanoparticles (nanomagnetite) has been reported and proven to effectively remove various kinds of organic and inorganic contaminants [[9];](#_bookmark20) [[10];](#_bookmark21) [[11];](#_bookmark22) [[12].](#_bookmark23)

Over the last decade, a promising way to synthesize nanoparticles has developed and is well-known as the green synthesis method. This environmentally friendly method can be carried out using various microorganisms or extracts from various types and parts of plants such as *Azadirachta indica* (neem) leaf [[12],](#_bookmark23) *Dolichos lablab L.* (komak bean) pod [[13],](#_bookmark24) *Phoenix dactylifera L.* (date palm) seeds [[14],](#_bookmark25) *Pontederia crassipes* (water hyacinth) biomass [[15],](#_bookmark26) *Ceratonia siliqua L.* (carob) leaf [[16],](#_bookmark27) various bacteria [[17]](#_bookmark28) and many more. In addition, plant-based green synthesis methods are well accepted because they offer natural, renewable, and safe substances to obtain [[18].](#_bookmark29)

Pineapple *(Ananas comosus L.)* is a fruit plant originating from tropical America and has spread throughout the world, especially in areas around the equator. In Indonesia, pineapple plants are very famous and are widely cultivated in the lowlands and highlands. Especially in East Kalimantan, pineapple production was recorded at 36,641 tonnes in 2022 (Central Statistics Agency BPS, 2022). With the increasing production, agricultural waste from pineapples is quite abundant. The use of pineapple plants so far has only been limited to the fruit. When harvested, these plants must be replaced with the new one and the leaves are discarded as waste. Research conducted by [[19]](#_bookmark30) shows that pineapple leaves contain phytochemical compounds including terpenoids, flavonoids, glycosides, phytosterols, alkaloids and saponins. This phytochemical compound directly reduces metallic salts into nanoparticles and works as a stabilizing agent by inhibiting nanoparticle aggregation [[20].](#_bookmark31)

In green synthesis, active phytochemical compounds provide nanoparticles with their maximal potential and shall not be eliminated. Consequently, a study is needed to determine whether the characteristics of the nanoparticle and their synthesis process are correlated. Thus, this study assesses the most significant step in the synthesis of nanoparticles, which is calcination time, to be the primary goal of this work. In this study, a magnetite nanoparticle was synthesized using *Ananas comosus* aqueous leaf extract (AL-MNPs) which then varied by the calcination time: 180, 210 and 240 minutes. The AL-synthesized magnetite nanoparticles were characterized using FTIR, XRD, SEM-EDX, and SAA then absorbance tested by UV-Vis spectrophotometry using methylene blue as contaminant in aqueous solution.

# MATERIAL

In this study, the precursors used for the synthesis of magnetite nanoparticles (Fe3O4-NPs) are ferric chloride hexahydrate (FeCl3.6H2O) and Ferrous sulfate heptahydrate (FeSO4.7H2O) (Sigma Aldrich, Merck, Indonesia) which both used without further purification. Another following chemical such as: sodium hydroxide (NaOH) and ethanol (CH3CH2OH 99.9%) were all obtained from Merck, Indonesia. The pineapple leaf *(Ananas comosus)* was obtained from a local farm in Balikpapan, East Kalimantan, Indonesia.

# EXPERIMENTAL METHOD

**Preparation of *Ananas comosus* Leaf (AL) Aqueous Extract**

The obtained *Ananas comosus* leaves were washed with tap water to remove surface contaminants such as dust and soil. After that, the leaves were cut into small pieces then air dried before crushed into finer form using a blender. Next, 18 gr of fine *Ananas comosus* leaf (AL) was mixed with 50 mL ethanol in a beaker and heated on a hot plate at 80oC for 30 minutes. The mixture was cooled to room temperature and then filtered using the Whatman no. 42 filter paper. The *Ananas comosus* leaf aqueous extract was obtained and can be stored at 4oC for further use.

## Synthesis of AL-Magnetite Nanoparticle

This procedure was carried out with a green synthesis method using *Ananas comosus* leaf (AL) aqueous extract as a capping agent to produce AL-mediated magnetic nanoparticles (AL-MNPs). At first, a 1:2 mole ratio of Fe2+ and Fe3+ solutions were prepared in separate flasks by dissolving 2.780 gr of FeSO4.7H2O and 5.408 gr of FeCl3.6H2O in each 100 ml of distilled water. The Fe2+ solution was added to the Fe3+ solution with constant stirring at 450 rpm 80oC for 20 min. After that, 20 ml of the AL aqueous extract was added and followed by dropwise addition of 1.0 M NaOH solution until the pH was 11.0. The black-colored mixture was continuously stirred and heated for 60 min then allowed to cool at room temperature. The magnetite precipitate was filtered using Whatman no. 42 filter paper and washed 3 times with distilled water to get rid of excess NaOH. Thereafter, the magnetite precipitate was dried in an oven at 80oC with varying times for 180, 210, and 240 min. The dried precipitate was pulverized using mortar and pestle, and then AL-MNPs was kept in a sample bottle for further characterization analysis.

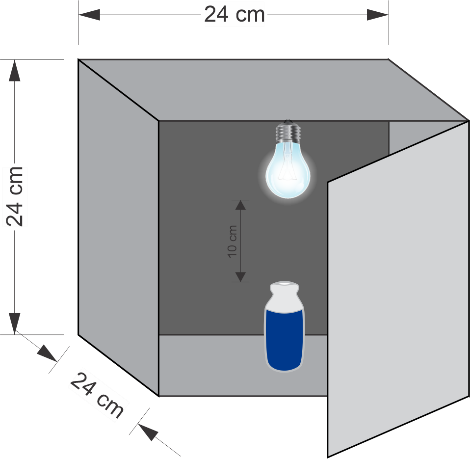
## Characterization of The Synthesized Fe3O4 NPs

The powder of AL-MNPs was characterized to verify the successful green synthesis and also to evaluate their properties such as nanostructure by using X-Ray Diffraction (XRD) technique. This technique can analyze the crystalline structure, lattice parameters, crystallinity, and average crystal size of the synthesized AL-MNPs. Other properties such as surface morphology, particle size distribution and surface elemental can be analyzed using Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX). In addition, the functional group of the *Ananas comosus* leaf extract was characterized using Fourier Transform Infrared Spectroscopy (FTIR). Lastly, the adsorption ability of AL-MNPs using *Methylene Blue* (MB) as liquid contaminant was analyzed based on the absorbance data from UV-Visible spectroscopy (UV-Vis) characterization.

## Preparation of Photocatalytic Degradation of MB

Photocatalytic was a process of decomposing a compound with the help of photon energy (light). In this study, the photocatalytic degradation was carried out in a closed chamber made out of cardboard box covered in aluminum foil with dimension 24 cm ✕ 24 cm ✕ 24 cm (**Figure 1**) Inside the chamber, the dye-containing solution was kept in a 100 ml glass bottle and under radiation of a 15 W white LED lamp placed ±10 cm above the bottle [[21]](#_bookmark32); [[22].](#_bookmark33) The

0.1 gr of powder AL-MNPs samples and 5 ml H2O2 70% solution was added to a 10 ppm of MB test solution. Before exposing the sample to the light, MB solution mixed with photocatalyst was continuously stirred for 30 min in the dark to attain the adsorption-desorption equilibrium. All tests were done by keeping the MB solution under irradiation for 24 h.



**FIGURE 1** Scheme of Photocatalytic Reaction Box

The MB solution was analyzed by taking out approximately 3 ml aliquots at regular intervals of 30 min and filtered through a PVDF filter membrane (0.45 μm pore size) and the dye concentration was measured using UV- Visible spectrophotometer at MB absorbance wavelength λ = 664 nm [[9].](#_bookmark20) The degradation efficiency was calculated by the following equation:

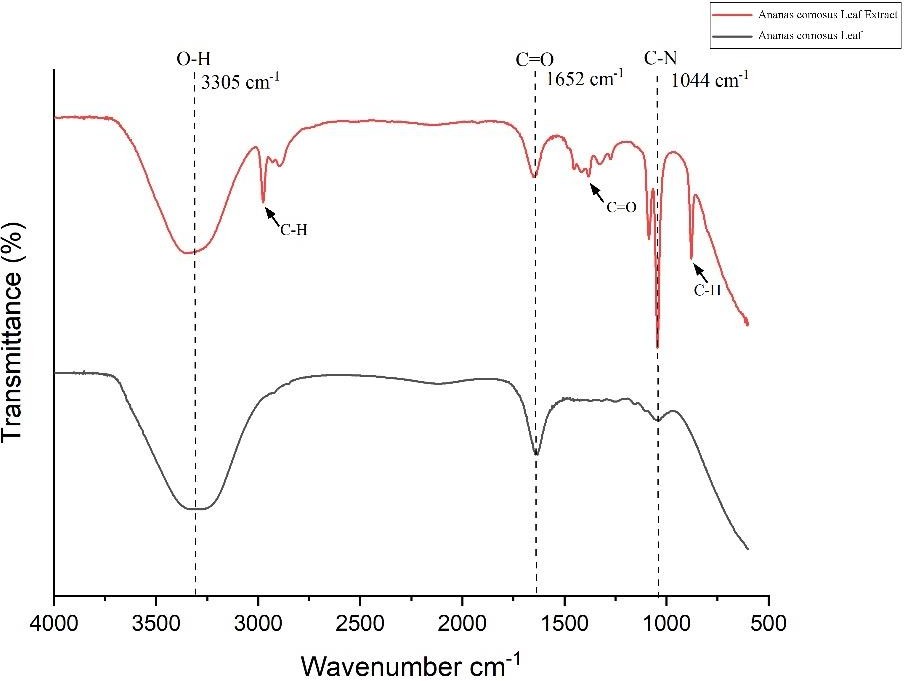
𝐷𝑒𝑔𝑟𝑎𝑑𝑎𝑡𝑖𝑜𝑛 𝑒𝑓𝑓𝑖𝑐𝑖𝑒𝑛𝑐𝑦 (%) = (𝐴𝑜−𝐴𝑡) × 100 (1)

𝐴𝑜

With Ao and At were the initial absorbance and absorbance after the time interval ‘t’ respectively.

# RESULT AND DISCUSSION

## FTIR Spectra Analysis

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed to the *Ananas comosus* leaf and the aqueous extract to verify the presence of functional groups that used as stabilizing and capping agent in the AL- synthesized magnetite nanoparticles (AL-MNPs).

**FIGURE 2** FTIR spectra of AL and AL aqueous extract

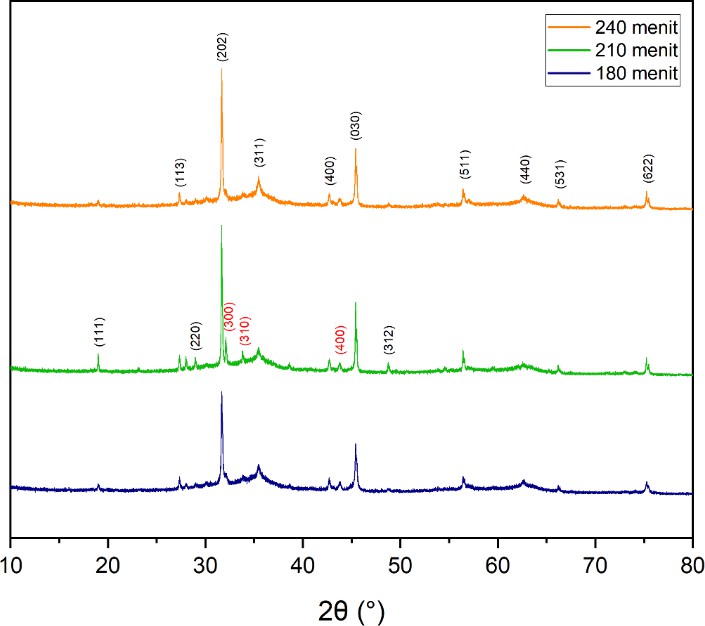
**Fig. 2** shows the FTIR spectra of AL leaf and aqueous extract. It is observed that the AL leaf spectra has two significant peaks at wavelengths of 3305 cm-1 and 1652 cm-1. These peaks were identified as hydroxyl (O-H) and carbonyl (C=O) functional groups, respectively. Meanwhile for the aqueous extract, absorption bands were observed at wavelengths 2972 cm-1 - 2975 cm-1 and 879 cm-1 which could be associated with the alkene (C-H) functional group [[23].](#_bookmark34) The presence of alkene functional groups (C-H) in the extract is due to the usage of ethanol as a solvent. The absorption spectra at a wavelength of 1375 cm-1 - 1385 cm-1 can be identified as the absorption of the aliphatic (C-H) group [[24].](#_bookmark35) Another peak at 1044 cm-1 - 1087 cm-1 can be attributed as aliphatic amine (C-N) functional group [[25].](#_bookmark36)

As reported on [[49]](#_bookmark60) amine group has important part as capping agent and stabilizing formation of nanoparticles. It has been confirmed that the amine group form a layer of proteins that could possibly covering the nanoparticle to prevent agglomeration and by that, also stabilizing the formation of nanoparticles. Research conducted by [[50]](#_bookmark61) stated that the (C=O) functional group plays an important role in the chelation process in nanoparticles synthesis. This process included the interaction of organic molecules with Fe2+ and Fe3+ ions, which necessary to form Fe3O4- NPs. Visual observation in the synthesis process also showed a color change in the solution from brownish-orange to black (**Fig. 3**) when combining AL aqueous extract and NaOH into the two precursors solution. This black- colored solution indicating that magnetite nanoparticles has formed [[51].](#_bookmark62)

|  |  |
| --- | --- |
|  |  |
| a) | b) |

**FIGURE 3** Visual observation during synthesis process; a) Precursors solution before adding AL Extract and NaOH, b) After adding AL extract and NaOH

## XRD Analysis

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**FIGURE 4** XRD spectra of AL-MNPs

The crystallinity, crystal phases and purity of the green synthesized AL-MNPs can be confirmed through the X- Ray Diffractogram (XRD) analysis. XRD spectra shown in **Fig. 4** (2θ, black indicates the magnetite phase and red indicates maghemite phase). The sharp and intense diffraction peaks indicated the high crystalline nature of Fe3O4 nanoparticles [[26].](#_bookmark37) Several peaks were obtained from samples AL-MNPs/180, AL-MNPs/210, AL-MNPs/240 at 2θ

= 18.9o, 27.3o, 28.9o, 31.6o, 35.4o, 42.7o, 45.4o, 48.7o, 56.4o, 62.6o, and 66.2o which corresponding to the magnetite (Fe3O4) crystal planes of (111), (113), (220), (202), (311), (400), (030), (312), (511), (440), and (531), respectively.

This diffraction pattern displayed by the XRD analysis of AL-MNPs is in accordance with the standard magnetite diffraction as indexed in JCPDS no. 19-0629 and JCPDS no. 00-153-2800. Meanwhile, samples AL-MNPs/210 shows the formation of secondary phase which is maghemite (γ-Fe2O3) at 2θ = 32.1o, 33.8o, and 43.7o that corresponds to the maghemite crystal planes of (300), (310), and (400) based on standard maghemite diffraction as indexed in JCPDS no. 04-0755. This result from the XRD diffraction pattern shows that the longer calcination time occurs, until up to 240 min, produces a magnetite phase with higher purity as reported by [[27]](#_bookmark38) at 120 min - 300 min calcination time.

The formation of a secondary phase which is maghemite (γ-Fe2O3) was hard to avoid in mixing both precursors with NaOH solutions. Hence, the Fe2+ and Fe3+ reformed into Fe(OH)2, FeOOH, and Fe(OH)3 as shown by Equation ([2](#_bookmark1))-([3](#_bookmark2)). This phenomenon occurs because of the synthesis that takes place in the air atmosphere, causing Fe(OH)2 to oxidize and become FeOOH and Fe(OH)3 Eq. ([4](#_bookmark3))-([5](#_bookmark4)). Instead of forming a magnetite phase (Fe3O4), this oxidation changes the standard ratio of iron oxide and maghemite phase (γ-Fe2O3) was obtained [[28].](#_bookmark39) In general, it is difficult to differentiate between magnetite (Fe3O4) and maghemite (γ-Fe2O3) phases from XRD diffraction pattern due to their similarity in crystal structure and planes [[29].](#_bookmark40) Nevertheless, based on the selected synthesis method, the color of AL-MNPs powder and the indexed peak of XRD analysis, strongly support the presence of magnetite (Fe3O4).

𝐹𝑒2+ + 2𝑂𝐻− → 𝐹𝑒(𝑂𝐻)2 (2)

𝐹𝑒3+ + 3𝑂𝐻− → 𝐹𝑒(𝑂𝐻)3 (3)

𝐹𝑒(𝑂𝐻)3 → 𝐹𝑒𝑂𝑂𝐻 + 𝐻2𝑂 (4)

2𝐹𝑒𝑂𝑂𝐻 + 𝐹𝑒(𝑂𝐻)2 → 𝐹𝑒3𝑂4 + 2𝐻2𝑂 (5)

It can be observed from **Fig. 4** that the diffraction peaks turn sharper by the intensity as the calcination time increases, meaning that longer calcination time can produce larger crystal sizes [[30].](#_bookmark41) Apart from affecting the crystal size, it can also affect the crystallinity of the Fe3O4 produced. The average crystal size *(D)* of the AL-MNPs was estimated from the XRD pattern by measuring the peak width at half of the peak maximum intensity (FWHM: Full Width at Half Maximum). To acquire the FWHM value, the most intense peak at an angle of 2θ was taken the peak width as half of the peak intensity. It is then calculated using the Debye-Scherrer equation as follows [[31]](#_bookmark42):

𝐷 = 𝐾λ/β cos 𝜃 (6)

Where, D is the average crystal size, *K* = 0.9 is the Scherrer’s constant, λ is the X-Ray wavelength (1.5406 Å), β is the FWHM, and θ is the peak position angle.

Meanwhile, the crystallinity of the as-prepared sample of AL-MNPs was calculated using Eq. ([6](#_bookmark5)), where the area fraction of the crystalline part is divided by the area of diffractogram (crystalline area fraction + amorphous area fraction) [[32]](#_bookmark43) as follows:

%𝐶𝑟𝑦𝑠𝑡𝑎𝑙𝑙𝑖𝑛𝑖𝑡𝑦 = 𝐹𝑟𝑎𝑐𝑡𝑖𝑜𝑛 𝑜𝑓 𝑐𝑟𝑦𝑠𝑡𝑎𝑙𝑙𝑖𝑛𝑒 𝑝𝑎𝑟𝑡 × 100 (7)

𝐴𝑟𝑒𝑎 𝑜𝑓 𝑑𝑖𝑓𝑓𝑟𝑎𝑐𝑡𝑜𝑔𝑟𝑎𝑚

Using the Debye-Scherrer’s equation, the average crystal size of magnetite nanoparticle synthesized using *Ananas comosus* leaf aqueous extract was estimated as 14.8 nm, 25.0 nm, and 21.6 nm for samples AL-MNPs/180, AL-MNPs/210, AL-MNPs/240, respectively. It is found that increasing calcination time from 180 min to 210 min has led to the increase of crystal size (**Table 1**) since the crystallite growth was accelerated thermally [[33].](#_bookmark44) This result were similar to the average crystal size obtained from another study of green-synthesized Fe3O4 nanoparticles using *A. comosus* fruit peel which is 19.8 nm [[4]](#_bookmark15) and *Z. acanthopodium* leaf extract of 20.7 nm [[5].](#_bookmark16)

**TABLE 1** Crystallinity of AL-MNPs

|  |  |  |
| --- | --- | --- |
| **Samples** | **Average crystal size (nm)** | **Crystallinity (%)** |
| AL-MNPs/180 | 14.8 | 31.7 |
| AL-MNPs/210 | 25.0 | 48.0 |
| AL-MNPs/240 | 21.6 | 54.6 |

The crystallinity of as-prepared AL-MNPs samples also increased by the calcination time. Calcination is an important process in the formation of Fe3O4 nanoparticles because it can remove other excess products that can be formed through the synthesis. For example, residual OH- ions can be reduced through calcination since excess OH- ions can decrease the sample crystallinity [[34].](#_bookmark45) The longer the dwelling time, the greater thermal energy can be given to the nanoparticles and thermal diffusion can occur. In this case, the thermal energy takes the role as the driving force that acts on the surface of nanoparticles while in contact with neighboring particles. This phenomenon is well-known as the Ostwald Ripening process; when two surface particles interact, there will occur atomic transport throughout their boundary energy. During this process, the migration from one particle to another through surface diffusion will rotate the direction of their crystal plane. Thus, as an effect of higher thermal energy the surface tension on the nanoparticles will decrease and the lattice parameter becomes shorter due to the atoms that move closer to each other.

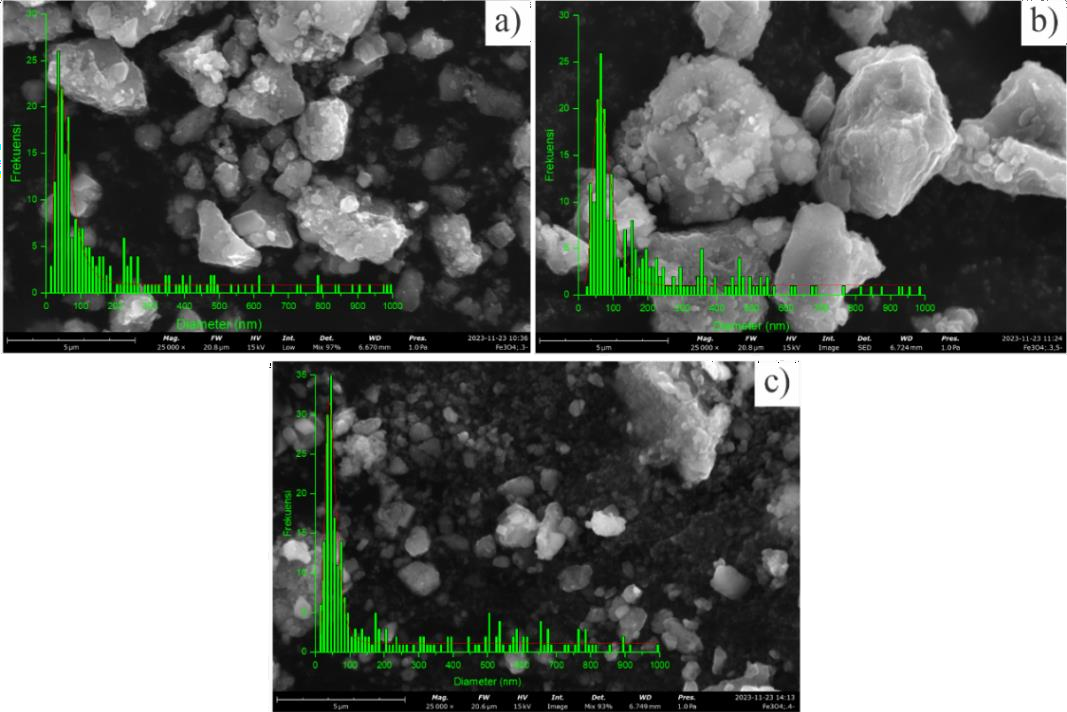
## Morphology, Particle Size, and Surface Area Analysis

*SEM-EDX Analysis*

The SEM images at 25,000x magnification in **Fig. 5 a), b), c)** illustrate the morphology and size distribution histograms of the AL-MNPs/180, AL-MNPs/210 and AL-MNPs/240, respectively.

As can be seen, AL-MNPs exhibited various surface morphology between cubic and irregular structures, with homogeneous particle size distribution. Based on the visual observation, samples AL-MNPs/210 **Fig. 5 b** tended to be more agglomerated compared to the other samples. This could occur due to the remaining phenolic compounds from the aqueous extract that may interact with the nanoparticles’ surface, or their presence on the particle surface could possibly produce H (hydrogen) bonds in the bioactive molecules, thus giving appearance of aggregates [[35]](#_bookmark46);

[[36];](#_bookmark47) [[37];](#_bookmark48) [[38].](#_bookmark49) The agglomeration still occurs in other samples due to the magnetic properties of the nanoparticles in nature and the strong Van der Waals force that acts over the surface of the nanoparticles [[39].](#_bookmark50)



**FIGURE 5** SEM imaging of AL-MNPs magnification at 25000x a) AL-MNPs/180, b) AL-MNPs/210, c) AL-MNPs/240

The data obtained from Energy Dispersive X-Ray (EDX) spectra in summaries by **Table 2** showed the high content of Fe and O elements in all of the as-prepared AL-MNPs samples, which confirmed the successful formation of Fe3O4. [[40]](#_bookmark51) Reported that the high content of Fe and O elements indicates the level of purity on iron oxide nanoparticles. This case has been confirmed through intense magnetite diffraction peaks through XRD spectra.

**TABLE 2,** EDX result of AL-MNPs

|  |  |  |
| --- | --- | --- |
| **Sample** | **Element** | **Weight Concentration (%)** |
| AL-MNPs/180 | Fe | 71.8 |
| O | 28.2 |
| AL-MNPs/210 | Fe | 71.2 |
| O | 28.8 |
| AL-MNPs/240 | Fe | 72.6 |
| O | 27.4 |

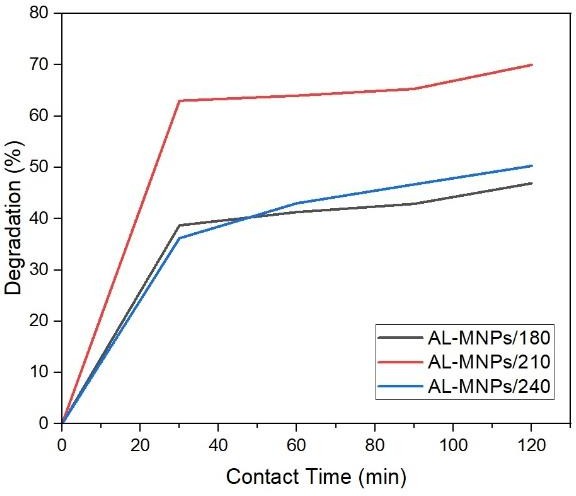
*Particle Size Analysis*

The average particle size distribution of each AL-MNPs/180, AL-MNPs/210 and AL-MNPs/240 samples measured were 53.73 ± 1.62 nm, 71.22 ± 1.87 nm, and 46.05 ± 0.85 nm, respectively. According to [[30],](#_bookmark41) crystal structure and particle size determine the physical and chemical properties of nanoparticles, especially their surface area which can indirectly affect its adsorption ability. A way to control the particle size and crystallinity is through calcination [[34].](#_bookmark45) In correlation with the result of XRD analysis, the longer calcination time shows the highest level of crystallinity amongst the other samples which is 54.6%. Calcination can control the particle size of the nanoparticles with narrow size distribution [[41].](#_bookmark52) In addition, calcination can also increase the crystallinity by removing impurities in the samples [[42].](#_bookmark53) As the dwelling time increases, the average particle size becomes smaller due to oxygen vacancies formed on the surface of the nanoparticles [[27].](#_bookmark38)

*Surface Area Analysis*

The specific surface area was obtained through surface area analyzer testing using Brunauer-Emmett-Teller (BET) method. The specific surface area of as-prepared AL-MNPs/180, AL-MNPs/210 and AL-MNPs/240 samples are 130.282 m2/g, 137.266 m2/g and 140.053 m2/g, respectively. Surface area can influence the adsorption ability of Fe3O4, high surface area and their dispersibility are needed to increase the interfacial interaction between the adsorbent and heavy metal ions [[43].](#_bookmark54) The greater the surface area, the more optimal adsorption activity can occur on the surface due to the amount of adsorbate that is enclosed by the adsorbent surface. However, the surface area is inversely proportional to the particle size of nanoparticles. In agreement with other research, smaller nanoparticles size associated with higher surface area [[44].](#_bookmark55) This argument is related to the result of SEM analysis where the smallest average particle size was obtained by the AL-MNPs/240 sample which has the largest specific surface area.

## Photodegradation of MB

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**FIGURE 6** UV-Vis result of MB in contact with AL-MNPs

**TABLE 3** Degradation percentage of MB in contact with AL-MNPs

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample |  | Degradation by Contact Time (%) | |  |  |
| 0 min | 30 min | 60 min | 90 min | 120 min |
| AL-MNPs/180 | 0 | 38.7 | 41.3 | 42.9 | 46.9 |
| AL-MNPs/210 | 0 | 63.0 | 64.0 | 65.3 | 70.0 |
| AL-MNPs/240 | 0 | 36.2 | 43.0 | 46.7 | 50.3 |

Under the UV-Visible spectrophotometry, the optical properties of AL-MNPs dispersed in MB solution can be determined to verify the successful synthesis of Fe3O4 nanoparticles using aqueous extract of *Ananas comosus* leaf. The degradation percentage of the MB solution are shown in **Fig. 6**. The characteristic of MB at 664 nm was found to decrease with the prolonging the contact time of MB with catalyst AL-MNPs. MB dye degradation efficiency was calculated using Eq. ([1](#_bookmark0)) and shown in **Table 3**. When the photodegradation process occurs, 70% MB dye removal efficiency was obtained at the end of the contact by AL-MNPs/210 sample. Increasing dwelling time in calcination could affect the adsorption by Fe3O4 nanoparticles. This can be attributed by two factors: First, the particle size distribution where larger particle size induces wider photon energy to be absorbed by the nanoparticles. Each particle requires a different amount of photon energy to excite its electrons from the valence band to the conduction band [[34].](#_bookmark45) In this case, the as-prepared AL-MNPs/210 sample has a larger particle size distribution, which suits the previous statement. Second, the non-uniform morphology of the nanoparticles can also affect the shape of adsorption peaks [[45].](#_bookmark56)

## The Photodegradation Mechanism

This photodegradation process was carried out using Advanced Oxidation Process (AOP) method to an MB solution that added 0.1 gr AL-MNPs samples and 5 ml H2O2 70% solution. This whole reaction occurs under an ultraviolet/visible light irradiation, when an oxidizing agent combined with a catalyst such as metal ions or semiconductor [[46].](#_bookmark57) In this process, H2O2 acts as an oxidizing agent, while AL-MNPs as a catalyst. Magnetite nanoparticles play an important role in the Fenton process as precursors of Fe ions and as photocatalysts under visible light irradiation because they have a low band gap of 2.2 eV [[47].](#_bookmark58)

Methylene blue is a cationic dye, which means it can be dissociated into positively charged ions in aqueous solutions. By it means, MB is not an electron donor and it is degraded by hydroxyl radical (•OH). This degradation of MB by photocatalytic reactions takes place due to the absorption of photons present in the radiation, thereby causes electrons (e-) to excite from the valence band to the conduction band, thus forming electron-gap pairs (h+) which are responsible for photo-oxidation of the organic compound [[21].](#_bookmark32)

The Fenton mechanism works when oxygen (O2) adsorbed on the photocatalyst surface, it trapped the electrons and transform it to superoxide radicals (O2-) Eq. ([8](#_bookmark6)). This superoxide radicals react with H2O which produced •OH and hydroperoxide radical (•OOH) Eq. ([9](#_bookmark7)). At the same time, H2O was trapped on the electron-gap on the photocatalyst surface and produced hydroxyl radicals Eq. ([10](#_bookmark8)). The organic compounds are photo-oxidized which then turn into carbon dioxide and water Eq. ([11](#_bookmark9)) [[9].](#_bookmark20)

𝑒− + 𝑂2 → 𝑂•− (8)

2

𝑂•− + 𝐻2𝑂 → • 𝑂𝑂𝐻 + • 𝑂𝐻 (9)

2

ℎ+ + 𝐻2𝑂 → • 𝑂𝐻 + 𝐻+ (10)

* 𝑂𝐻 + 𝑜𝑟𝑔𝑎𝑛𝑖𝑐 𝑐𝑜𝑚𝑝𝑜𝑢𝑛𝑑 → 𝐶𝑂2 + 𝐻2𝑂 (11) In this case, H2O2 is activated by Fe2+ and Fe3+ ions from the magnetite nanoparticles, which produced •OH and

•OOH, both are strong oxidizing agents which decompose the organic molecules. The presence of Fe ions in the

solution turns the process into a heterogeneous Fenton reaction. Eq. ([12](#_bookmark10))-([13](#_bookmark11)) explains the heterogeneous Fenton reaction that occurs in solution [[48].](#_bookmark59)

𝐹𝑒2+ + 𝐻2𝑂2 → 𝐹𝑒3+ + 𝑂𝐻− + • 𝑂𝐻 (12)

𝐹𝑒3+ + 𝐻2𝑂2 → 𝐹𝑒2+ + 𝐻+ + • 𝑂𝑂𝐻 (13)

# CONCLUSION

From the result obtained in this study, it was concluded that green synthesis of magnetite nanoparticles using aqueous extract of *Ananas comosus* leaf extract (AL-MNPs) can be an efficient material for the degradation of methylene blue dye. The FTIR spectrum of the AL extract presented the existence of functional groups which confirm the phytochemicals contained in AL extract. This result was supported by the changed of color in the solution into a black-colored solution after adding AL extract and NaOH. The black-colored solution indicating the presence of magnetite nanoparticle. The XRD result of the synthesized AL-MNPs displayed multiple peaks that correspond to magnetite (Fe3O4) diffraction patterns, which describe the successful synthesis. The obtained SEM pictures of AL-MNPs displayed relatively cubical and irregular nanoparticles with well-dispersed morphology and particle size distribution, indicating the efficient stabilizing action of AL extract. EDX elemental analysis showed the iron and oxygen presented in AL-MNPs as expected to be magnetite spectrum. From the surface area analysis using BET method, showed the longer calcination dwelling time, the larger surface area can be obtained inversely proportional to their particle size. Which can be attributed to thermal diffusion that occurs on the surface of nanoparticles. By the photodegradation process, it is shown that the AL-MNPs act as catalyst for the Fenton reaction. The most significant dye removal obtained in this study was 70.0% in tests carried out with the longer calcination dwell time (AL-MNPs/210). Furthermore, AL-MNPs can become a promising adsorbent for organic pollutants in aqueous solution.

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