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Hydrothermal Method to Synthesize Nanomagnetite by Water Extract of *Averrhoa bilimbi* : Effect of Time and Reactor Size

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Abstract—Nanomagnetite was synthesized using water extract of bilimbi (*Averrhoa bilimbi*). The high citric acid content has the potential as a reducing agent in the synthesis of magnetite using the hydrothermal method. The synthesis was conducted using different sizes of hydrothermal reactors, 50, 150, and 1700 mL. The results showed that a reactor with a volume of 150 mL and a synthesis time of 12 h was the best condition for synthesis. The results obtained from X-ray diffraction analysis showed that in the best conditions, the crystallinity level was 74.4%, the ratio of product to volume was 3.7×10^{-2} g/mL, the Fe content in magnetite was 22.0%, the Fe content in the remaining liquid was 0.02%, the Fe ratio was 96.9%, and the ammonium content in the solution was 1.24%w/v. The best conditions were 150 mL reactor and 12 h synthesis.

Keywords—*Averrhoa bilimbi*; Citric acid; Magnetite; Reactor size

1. INTRODUCTION

Magnetite is an iron oxide particle with various properties, such as magnetism, catalytic ability, current conductivity ability, large surface area, and relatively high temperature stability [1]. The diverse characteristics of magnetite can be applied for various purposes, such as catalysts, high-density magnetic recording media, medical diagnostic aids [2], biosensors, and data storage in the form of CDs [3]. Magnetite can also be used as an adsorbent for harmful substances [4]. Magnetite can be synthesized using various methods, namely coprecipitation, microemulsion technology, precursor thermolysis, hydrothermal, and magnetic nanocomposites [5].

Cheng et al. (2010) have synthesized nanomagnetite hydrothermally with precursors of iron(III) chloride ($FeCl_3$), sodium citrate, polyacrylamide, and urea [6]. The resulting magnetite is spherical and dispersed in water. The advantages of the hydrothermal technique are that it is easy, cheap, produces nanomagnetite with high crystallinity [7], and the materials used are nontoxic [6]. In addition, magnetite can be synthesized from the reduction reaction of $FeCl_3$ by sodium citrate or citric acid as a reducing agent [1] and urea as a precipitator that produces an alkaline atmosphere in the reaction [8]. Magnetite has two Fe oxidation states, namely Fe^{2+} and Fe^{3+}. Fe^{2+} and some Fe^{3+} ions are octahedrally bonded, while other Fe^{3+} are tetrahedrally bonded to form face-centered cubic spinel crystals [9].

Citrate is commonly found in fruits with a sour taste, one of which is bilimbi. The citric acid content in bilimbi as an organic acid component is about 92.6–133.8 meq/100 g fresh material [10]. Bilimbi water extract can be a good source of citrate for nanomagnetite synthesis. Previous studies have never used bilimbi as a reducing agent, so this study tried to use bilimbi as a source of citrate. Kalifawi used hund fruit extract (*Citrus medica*) as source citrate for nanomagnetite production [11]. Athitan et al. used extract of *Annona muricata* as source of citrate for synthesis [12]. Variations in the size of different reactors have never been tried to affect the degree of crystallinity produced, so the effects of variations in time and reactor size need to be studied further for large-scale development in synthesizing nanomagnetite with bilimbi as a reducing agent.

2. EXPERIMENTAL SECTION

2.1. Materials

The materials used in this study were bilimbi (*Averrhoa bilimbi*), Iron(III) Chloride hexahydrate (Nacalai Tesque, Japan), urea (Merck, Germany), distilled water, ethanol 96% (Merck, Germany), oxalic acid (Merck, Germany), Sodium hydroxide (Merck, Germany), potassium-sodium tartrate (Merck,

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Germany), Phenol (Merck), Ammonium sulfate (Merck, Germany), sodium hypochlorite (Merck, Germany), and concentrated HNO_3 (Merck, Germany).

2.2. Instrumentations

The tools used in this study were a four-decimal digital analytical balance (sartorius), a grinder (Philips blender), a glassware set (pyrex), an oven (Memmert), a furnace (Nabertherm Furnace, L1/12), a desiccator, a pH meter (Eutech 510), hydrothermal vessel, X-Ray Diffractometer (GBC EMMA), UV-vis Spectrophotometer (SHIMADZU UV-VIS 1700), centrifugation (Ohaus Frontier Series) and Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA 7000).

2.3. Procedures

2.3.1. Preparation of water extract of bilimbi fruit

Fresh bilimbi fruit was washed and then cut into small pieces and pulverized with a blender without the addition of distilled water. The milled extract was filtered and separated from the settled suspension by centrifugation for 20 min at 1000 rpm. The filtrate was analyzed for acid content using titration and as a base material for making nanomagnetite. Five kg of bilimbi can produce a filtrate of about 1700–1800 mL.

2.3.2. Determination of water, ash, and acid content of bilimbi fruit water

The acid content of bilimbi was determined through the titrimetric method using NaOH as the titrant. 1 mL of bilimbi fruit water extract filtrate was diluted using distilled water to a volume of 10 mL. Then, 2-3 drops of phenolphthalein indicator were added to the sample and titrated using standardized NaOH until the colour changed to light pink.

The determination of the water content of the bilimbi fruit was conducted as follows using the AOAC 2007 standard method guidance. Bilimbi fruit was weighed 2 g and then put into a porcelain cup whose empty weight was known. The cup was stored in an oven at 105 °C for 5 h. Next, it was cooled in a desiccator and weighed. Determination of the ash content of bilimbi was carried out as follows, 2 g was put into a cup and then ignited over the flame of a Bunsen burner until it was not smoking. The cup was placed in a furnace at 600 °C for 2 h until ash was obtained. The ash cup was cooled in a desiccator for 30 min and weighed.

2.3.3. Synthesis of nanomagnetite

The synthesis was carried out Cheng et al. (2010)[6] with three composition variations according to the reactor size. The mixture was made in a total volume of 1700 mL with a concentration of of 0.1 M $FeCl_3$, 0.35 M urea, and 0.3 M acid. The composition was listed in **Table 1**.

The mixture was put into a beaker and stirred using a magnetic stirrer until the whole mixture was homogeneous. Stirring was carried out for ± 30 min. Once homogeneous, the solution was put into the reactor. The hydrothermal reactor was tightly closed until it was confirmed that no leakage occurred during the heating process. After that, the hydrothermal vessel was put into an oven at 200 °C. The nanomagnetite synthesis used three different synthesis time treatments, namely 9, 12, and 15 h. After the synthesis was completed, the hydrothermal reactor was cooled. The synthesis results were separated between solids and liquids. The solids formed were washed with distilled water and ethanol. The precipitate was then dried at 70 °C.

Table 1. Nanomagnetic precursor material composition

Reactor	Reactor Size		Material Composition (mmol)			Fluid volume (mL)
	Diameter (cm)	Height (cm)	$FeCl_3$	Urea	Acid	
A	5	10	5	20	15	50
B	5	20	15	52.5	45	150
C	10	30	150	525	450	1500

2.3.4. Characterization of synthesized results

Solids hydrothermally synthesized crystals were characterized using an X-ray diffractometer (XRD) at a wavelength of 0.15406 nm (CuKα).

2.3.5. Determination of Fe and ammonium content

Determination of Fe content was carried out on hydrothermally synthesized solids and liquids. The synthesized powder was weighed 0.5 g and added 5 mL of HNO_3 and heated. The filtrate was filtered and diluted in a 100 mL measuring flask using distilled water and then diluted. The solution was measured using AAS. Fe measurement in the liquid was carried out by mixing 5 mL of synthesized liquid plus 5 mL of HNO_3, and shaking until homogeneous and diluted. Furthermore, the solution was analyzed using AAS.

One mL of the synthesized liquid was put into a test tube and added 2 mL each tartrate and Na-phenate buffer solutions. The solution was shaken and stored for 10 min. Next, the solution was added with 2 mL of 5%, NaOCl and the absorbance was measured using a UV-Vis spectrophotometer at a wavelength of 629 nm.

3. RESULT AND DISCUSSION

3.1. Bilimbi Water Filtrate

Bilimbi is a highly acidic fruit with high water content (**Fig. 1**) [12]. The sour taste of bilimbi comes from the organic acids contained in it. The acid determination results of the water extract filtrate of bilimbi fruit for nanomagnetite synthesis for the time treatment of 9, 12, and 15 h were 0.3289; 0.2680; and 0.3040 N. These acid concentrations indicate the total acid in the fruit water, not just citric acid.

Citric acid is one of the organic acid components in bilimbi fruit that gives it a sour taste [13]. Novak et al. (2023) stated that citric acid is the most organic acid component in bilimbi fruit, with levels of 92.6–133.8 meq/100 g fresh material [10]. Citric acid, as the main component of organic acids in bilimbi fruit, is displayed in **Fig. 2.**

Fig. 1. (a) Bilimbi (*A. bilimbi*), and (b) Bilimbi water filtrate

The study water content measurement obtained water content of bilimbi fruit of 95.45%. The high value of water and citric acid content as the most organic acid component in bilimbi is the main reason that bilimbi fruit filtrate has potential as a reducing agent in the hydrothermal synthesis of nanomagnetite. The ash content in the bilimbi shows the mineral content contained in the fruit. The ash content in bilimbi fruit obtained in this study was 5.87%. Minerals contained in bilimbi fruit are phosphorus, iron, calcium, and potassium [14].

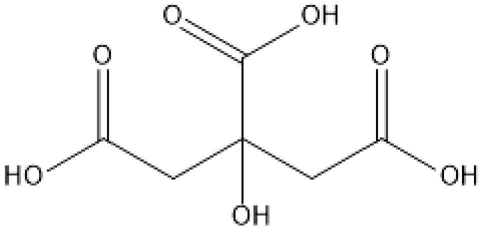

Fig. 2. Citric acid structure

In this study, it was synthesized nanomagnetite using bilimbi fruit water stored for a week as a citrate source. Bilimbi water is effective in synthesizing nanomagnetite but not the suspension of bilimbi water extract. Therefore, a precipitation process was carried out using a centrifuge to precipitate the suspension from bilimbi extract for better results. After centrifugation, the filtrate is separated, which will be used as a source of citrate.

3.2. Scale-up of Nanomagnetite Synthesis Method with Bilimbi Filtrate

The use value of bilimbi fruit needs to be increased using bilimbi fruit filtrate as a reducer in nanomagnetite synthesis. Nanomagnetite synthesis was developed by observing the effect of variations in time and reactor size used in nanomagnetite synthesis. A synthesis time of 12 h is the best time for nanomagnetite synthesis. To discover the pattern of synthesis results from time variations, two synthesis time points were taken with an interval of 3 h before 12 h and 3 h after 12 h. Therefore, the nanomagnetite synthesis has a time variation of 9, 12, and 15 h.

The reactor size is expected to affect the results of nanomagnetite synthesis, especially the degree of crystallinity of the resulting product. The reactor sizes used in the synthesis have a total volume of 50, 150, and 1500 mL. These volumes are not the total volume that each reactor can accommodate but they are used for a comparison that is easy to calculate after producing the product. The reactor used is shown in **Fig. 3**.

Fig. 3. Hydrothermal reactor used in nanomagnetite synthesis: (a) 50 mL, (b) 150 mL, and (c) 1500 mL.

The hydrothermal synthesis of nanomagnetite was carried out in a hydrothermal reactor at 200 °C. The main ingredients were citric acid, urea, and $FeCl_3$ [6]. A heating temperature of 200 °C is given to the system so that the crystals are formed perfectly [6]. The synthesis of nanomagnetite required 12 h, but within 3 h, nanomagnetite had been produced, which was still amorphous. Theoretically, the degree of crystallinity of nanomagnetite will increase as the synthesis time increases. The process of crystal formation occurred gradually [8].

Laurent et al. (2008) [7] stated that there are two important pathways in the hydrothermal synthesis of nanomagnetite, namely hydrolysis and oxidation or neutralization in a mixture of metal oxides. In this process, reaction conditions, such as solvent, temperature, and heating time greatly affect the obtained results. The following are the reactions that occur during the formation of nanomagnetite hydrothermally.

$$C_6H_5O_7^{3-} + 2Fe^{3+} \rightarrow C_5H_4O_5^{2-} + H^+ + CO_2 + 2Fe^{2+} \quad (1)$$

$$(NH_2)_2CO + 3H_2O \rightarrow 2NH_3.H_2O + CO_2 \quad (2)$$

$$Fe^{2+} + 2(NH_3{\cdot}H_2O) \rightarrow Fe(OH)_2 + 2NH_4^+ \quad (3)$$

$$Fe^{3+} + 3(NH_3{\cdot}H_2O) \rightarrow Fe(OH)_3 + 3NH_4^+ \quad (4)$$

$$Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 + 4H_2O \quad (5)$$

The perfect composition of materials in synthesizing nanomagnetite must be considered so the reaction runs stoichiometrically well. Therefore, it is necessary to determine the acid first. Nanomagnetite synthesis using bilimbi water was conducted by mixing it with $FeCl_3$ and urea. The mixture was stirred for 30 min using a magnetic stirrer and slightly heated until the solution became homogeneous. A homogeneous solution produced a brownish-green colour (**Fig. 4**). The mixture was put into small, medium, and large sizes reactors and then baked for 9, 12, and 15 h. The difference in reactor size will show the pattern of weight gain of the synthesis along with the increase in reactor size. In contrast, variations in synthesis time can affect the degree of crystallinity of the resulting nanomagnetite.

Citric acid from bilimbi fruit water will reduce Fe^{3+} from $FeCl_3$ to Fe^{2+}. Citric acid will undergo decarboxylation due to heating, so the alcohol group in the citric ion will turn into a ketone group. Citrate is oxidized, and Fe^{3+} is reduced to Fe^{2+} (**Reaction 1**) [14]. Hydrothermal synthesis of nanomagnetite uses a liquid medium placed in a closed container with a pressure of up to 2000 psi and generally uses a temperature of 200 °C or more [5]. High pressure can increase the solubility of solids and increase the reaction speed, which then promotes the minimization of surface energy so that the particles will start to crystallize [6]. Based on this, the use of different reactor sizes will affect the nanomagnetite yield obtained. The larger the reactor size, the smaller the pressure that can be generated in the container. In addition, the effectiveness of heat flowing into the reactor and collisions in the reactor also affect the synthesis results.

Urea will decompose at high temperatures to form ammonia. Urea is an effective precipitator because it produces reactions in an alkaline atmosphere from slow hydrolysis at 70 °C (**Reaction 2**). The synthesis temperature was 200 °C, so urea is completely hydrolyzed [8]. The alkaline atmosphere resulted in the formation of $Fe(OH)_2$ and $Fe(OH)_3$ (**Reactions 3 and 4**), which further formed magnetite (Fe_3O_4) by releasing water (**Reaction 5**) [15].

Magnetite is formed when mixing 0.1 M $FeCl_3$, 0.35 M Urea, and about 0.3 M total acids from bilimbi fruit water. Citrate in the hydrothermal formation of nanomagnetite functions as a reducing agent, forming crystal morphology, and preventing aggregation [15]. Without citrate, Fe_3O_4 will not be formed but α-Fe_2O_3. The amount of citrate in the synthesis must be considered. If the amount of citrate is small, some citrates will react with dissolved oxygen in the water, so it is not strong enough to reduce Fe^{3+}. Thus Fe_2O_3 will be formed. However, if the citrate is too much, it will lower the pH value of the system so that most of the Fe^{3+} will be reduced to Fe^{2+}. Thus Fe_3O_4 is not formed [8].

Nanomagnetite solids synthesized using bilimbi water all produce black solids and are attracted when approached by a magnet following Liang et al. (2006) [14] (**Fig. 4**). The number of solids produced increases with increasing reactor size. Citrate ions will complex Fe and produce a slow reaction that is good for crystal formation. Fe^{3+} will be reduced by citrate to Fe^{2+}, which turns into magnetite. Citrate also functions in forming the pure Fe_3O_4 phase and supporting the success of the resulting magnetite products [6].

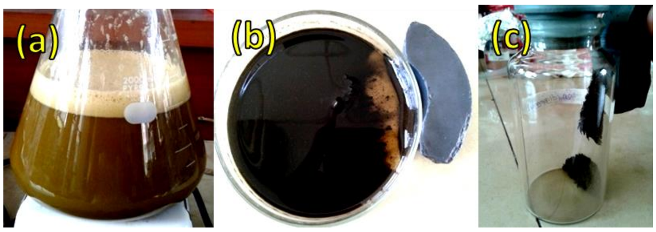

Fig. 4. (a) Solution mixture before synthesis, (b) Retraction test of synthesized product, and (c) Synthesized solids that have been separated from the filtrate and dried.

3.3. Characterization Results with XRD

Characterization was performed on the synthesis results at various reactor sizes (50, 150, and 1500 mL) and numerous synthesis times (9, 12, and 15 h). The first step was to characterize the results using an X-ray diffractometer (XRD). Characterization using XRD determines the crystal phase, crystal size, and degree of crystallinity. The analysis compared the typical peaks of the synthesized solids with the standard crystal peaks.

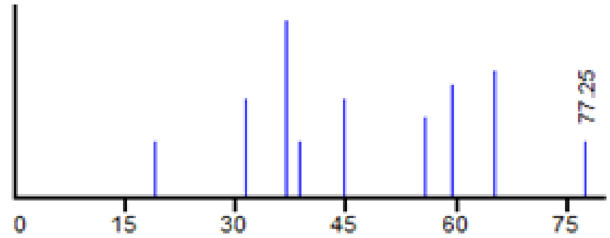

Fig. 5. Nanomagnetite standard JCPDS 19-0628

The results of the X-ray diffractograms were compared with the magnetite standard JCPDS No. 19-0629 [16] (**Fig. 5**). The nine samples had similarities with the standard. However, some showed different diffractogram peak intensities with nanomagnetite samples. These peaks are likely to be impurities present in the sample. The suspected impurity peaks are displayed in the diffractograms of A1, B1, C1, and A2, B3 (**Fig. 6–8**). The magnetite standard showed a peak with a typical intensity at an x-axis value (2θ) of 18.27° which had a smaller intensity than when the x-axis value (2θ) was 30.09°. In contrast, the peak intensities produced by samples A1, B1, C1, A2, and B3 were greater when the x-axis value was about 18.27° than when the x-axis value was about 30.09° (**Fig. 6–8**). Based on Gergely et al. (2010) [15], the peak that has a typical intensity at a 2θ value of 18° is the $Ca(OH)_2$ compound. Ca metal is one of the minerals found in bilimbi [10]. The best diffractogram peaks were found in the synthesis of B2, C2, and C3 (**Fig. 6 and 7**). The diffractogram of sample A3 (**Fig. 8**) still had a small intensity in the peaks, and possibly there were still many amorphous

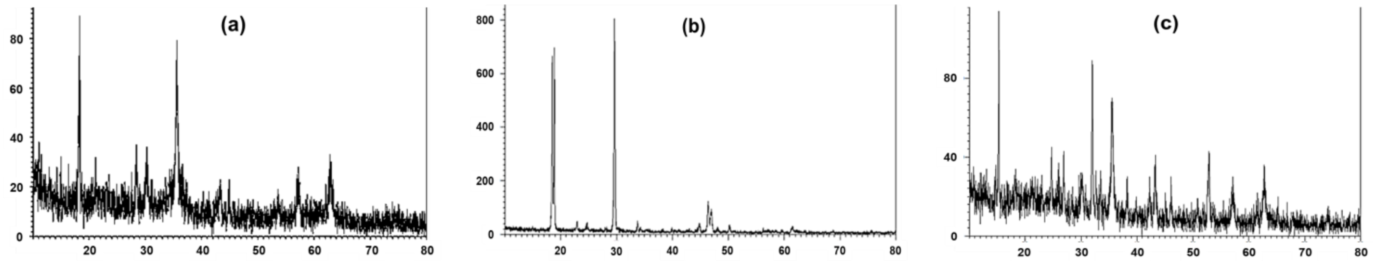

Fig. 6. Nine-hours synthesis nanomagnetite diffractogram of (a) 50 mL, (b) 150 mL, and (c) 1500 mL reactor

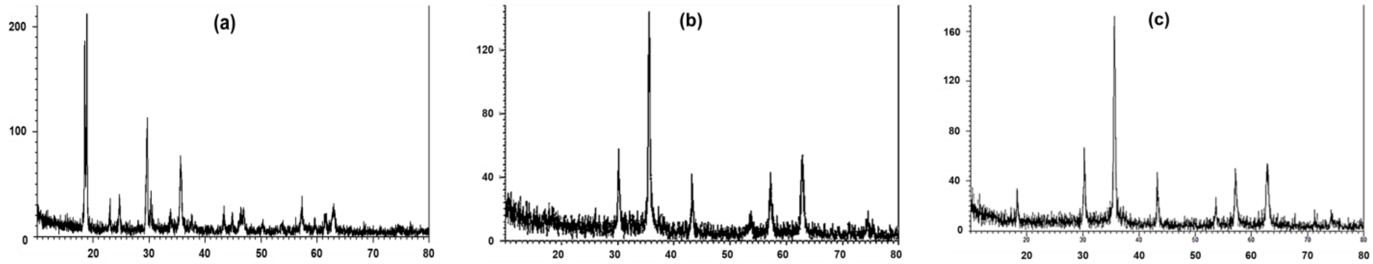

Fig. 7. Twelve-hours synthesis nanomagnetite diffractogram of (a) 50 mL, (b) 150 mL, and (c) 1500 mL reactor

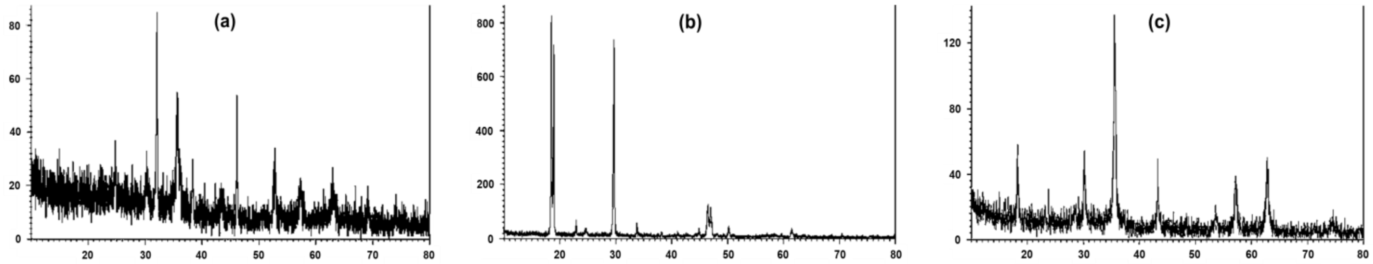

Fig. 8. Fifteen-hours synthesis nanomagnetite diffractogram of (a) 50 mL, (b) 150 mL, and (c) 1500 mL reactor

particles. Determination of crystal size using the Debye-Scherrer equation resulting crystal size ranged from 19.17–34.04 nm.

The sample's crystallinity degree was obtained based on the ratio of the crystalline area to the total area (crystalline and amorphous) produced by the sample. The crystallinity of nanomagnetite particles formed during synthesis is affected by synthesis time, reactor size, and the material used.

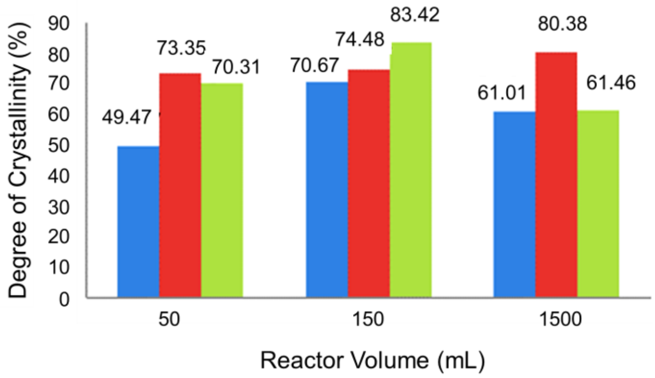

Fig. 9. Relationship curve between synthesis time (hour) and degree of crystallinity (%) (blue = 9 h, red = 12 h, green = 15 h).

Fig. 9 and **Fig. 10** show that the nanomagnetite produced had the highest degree of crystallinity of 83.42% at a synthesis time of 12 h using reactor C with a volume of 1500 mL. **Fig. 9** shows the effect of time on the degree of crystallinity, while **Fig. 10** shows the effect of reactor size on the degree of crystallinity. Reactors A and C showed an increase in crystallinity at 9 to 12 h and then decreased at 15 h. Reactor B showed an increase in the degree of crystallinity as time increased.

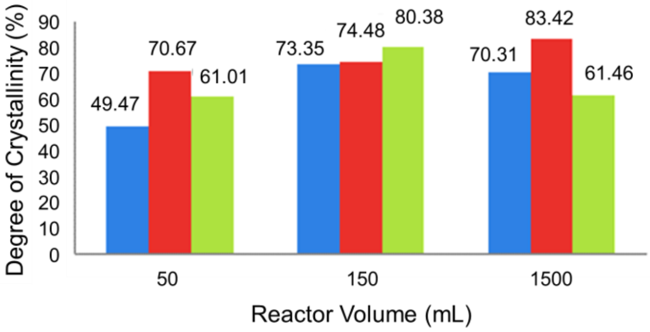

Fig. 10. Relationship curve between reactor volume (mL) and degree of crystallinity (%) (blue = 9 h, red = 12 h, green = 15 h).

The longer synthesis time will result in better crystallinity because the reaction is considered perfect [5]. Therefore, the synthesis time of 9 h showed a smaller degree of crystallinity than 12 h. Synthesis for 9 h still produced more amorphous crystals. However, the synthesis time of 15 h did not obtain a sufficiently large degree of crystallinity compared to the 12 h synthesis. This indicates that the synthesis time of 15 h is less effective in forming nanomagnetite crystals. In addition, the synthesis results are also influenced by the volume of the reactor used. Reactor volume is closely related to the amount of precursor material added during the hydrothermal process. The more materials are included, the greater the energy during the reaction. This energy will affect the formation of nanomagnetite crystals. When the synthesis occurs, a large amount of material generates considerable energy to produce pressure that pushes the sides of the hydrothermal reactor. Based on the previous description, the best time to synthesize nanomagnetite to have a high degree of crystallinity was for 12 h and used a 150 mL medium-sized reactor.

3.4. Effect of Filtrate Volume on Yield Weight

The longer synthesis time will cause the reaction to run more perfectly, thus increasing the weight of the resulting solids. The reactor volume is closely related to the amount of solids produced. The enlargement of the reactor volume is expected to be proportional to the amount of solids produced (**Table 2**). The comparison between the weight of the synthesized solids and the reactor volume illustrates the success of the reactor scale-up method.

Table 2. Weight of solid produced in nanomagnetite synthesis

Time (hour)	V (mL)	Weight of solid produced (g)	Weight of solid/V (g/mL)
9	50	0.9934	1.99×10^{-2}
	150	1.0212	0.68×10^{-2}
	1500	28.9907	1.93×10^{-2}
12	50	1.4672	2.93×10^{-2}
	150	5.5789	3.72×10^{-2}
	1500	25.0253	1.67×10^{-2}
15	50	2.8996	5.80×10^{-2}
	150	5.5657	3.71×10^{-2}
	1500	23.2706	1.55×10^{-2}

Based on **Fig. 11**, the 50 mL reactor produced an increasing weight/volume ratio, but the resulting degree of crystallization was not better than the 150 mL reactor. The 1500 mL reactor produced a weight/volume ratio value that decreased with synthesis time. This result is not theoretically appropriate. The pressure during this reactor's synthesis process affects the decreasing results. Therefore, if we want to use a larger reactor, we must pay attention to the effect of the pressure in it. The best reactor is a reactor with a volume of 150 mL because it produces a weight/volume ratio that tends to be constant at 12 and 15 h. Based on this, the best time is 12 h synthesis time.

Fig. 12 shows the relationship between synthesized weight and volume enlargement. All treatments with the addition of synthesis time of 9, 12, and 15 h increased the synthesized weight. At 9 h, the volume expansion of 10 times resulted in a weight increase of 28.39 times. This is far beyond the volume increase. In the synthesis for 12 h, the weight enlargement increased and did not exceed the value of volume enlargement. In the synthesis for 15 h, the volume enlargement also increased and did not exceed the volume enlargement, but when the volume enlargement was 30 times, the weight gain was only 8.03 times obtained. This value was too small. Based on this, the best time was 12 h.

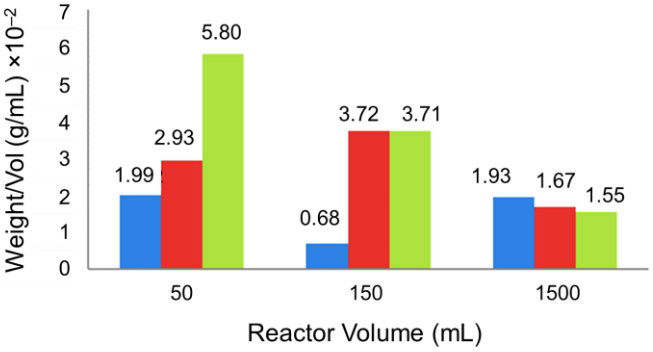

Fig. 11. Relationship curve between reactor volume (mL) and weight of solid/volume (g/mL) (blue = 9 h, red = 12 h, green = 15 h).

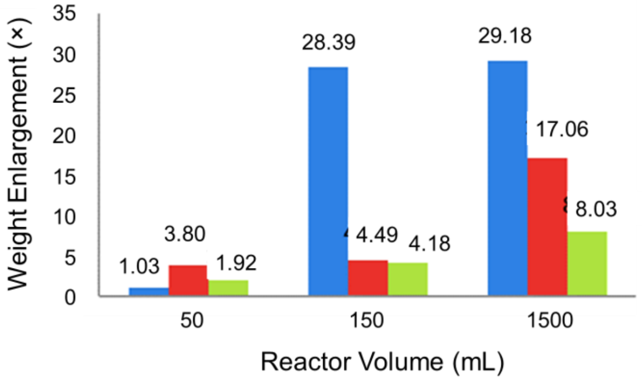

Fig. 12. Relationship curve between reactor volume (mL) and synthesized weight enlargement (blue = 9 h, red = 12 h, green = 15 h).

3.5. Fe Content

The Fe content in solids and liquids illustrates the presence of total Fe in them. The more effective the hydrothermal reaction, the greater the Fe content in the solid and the smaller the Fe value in the liquids.

In **Fig. 10**, reactors A and B had the same bar graph pattern at the time of synthesis for 9, 12, and 15 h. The Fe content in the solid, when synthesizing for 9 and 12 h, increased and then decreased when synthesizing for 15 h. Reactor B had the same pattern in **Fig. 11**. However, reactor A had an increasing pattern from 9 to 12 h and then decreased at 15 h. Reactor C increased Fe solids and liquids at 9, 12, and 15 h (**Fig. 10** and **Fig. 11**).

The Fe content is closely related to the amount of product formed. However, the targeted product is nanomagnetite (Fe_3O_4). The determination of total Fe does not clearly illustrate whether all Fe has been completely converted during the hydrothermal reaction. Based on **Fig. 13**, the largest Fe content was obtained when synthesizing for 12 h using a small reactor, namely 55.58% w/v. However, the degree of crystallinity was only 70.67%. This indicates that the Fe formed in the solid has not perfectly formed nanomagnetite. In the results shown in **Fig. 13**, reactor C had Fe content that tend to be constant at 12 and 15 h. The degree of crystallinity in reactor C at 12 h was 83.42%. The ratio between the solids weight produced and the reactor volume showed an unfavourable result of $1.67{\times}10^{-2}$ g/mL. Thus, the scale-up was less effective.

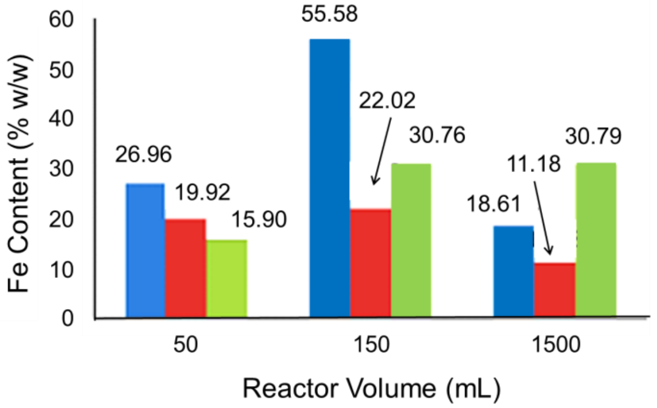

Fig. 13. Relationship curve between synthesis time (hour) and Fe content in solid (% w/w) (blue = 9 h, red = 12 h, green = 15 h).

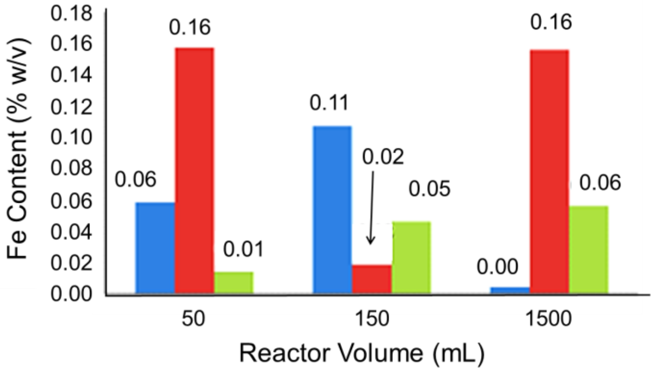

Fig. 14. Relationship curve between synthesis time (hour) and Fe content in liquid (% w/v) (blue = 9 h, red = 12 h, green = 15 h).

The Fe content of solids in reactor B for 12 h was 22.02% w/v, and liquid Fe was 0.02% w/v. Reactor B at 12 h had a fairly high degree of crystallinity of 74.48% with a ratio of the number of solids per volume of $3.72{\times}10^{-2}$ g/mL, which increased 4.49 times and was constant after more than 12 h. This indicates that the best time for nanomagnetite synthesis was 12 h, while volume enlargement could be effective when the reactor volume was enlarged ten times from 50 mL to 150 mL. In addition to Fe content in solids and liquids (**Fig. 14**), the effectiveness of the reaction could also be observed based on the Fe yield value, ranging from 72.54% – 99.31%. The Fe yield value at 12 h using the medium reactor was 96.89%. This value was quite good.

3.6. Ammonium Content of Synthesized Liquid

Ammonium is a side product produced in the hydrothermal nanomagnetite synthesis reaction with bilimbi fruit as a reducing agent. Yang et al. (2010) [17] stated that the longer the synthesis time, the greater the ammonium content contained in the filtrate.

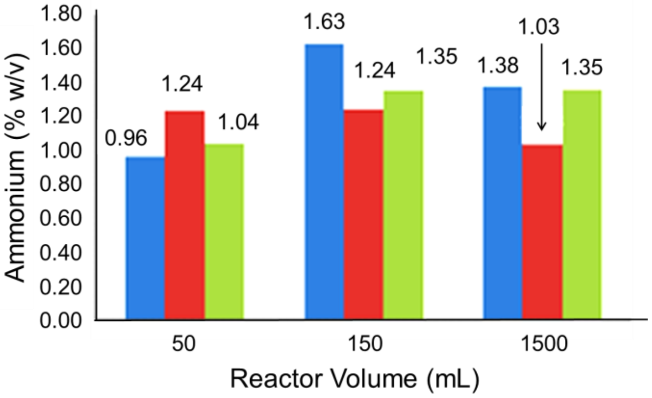

Fig. 15. Relationship curve between synthesis time (hour) and ammonium content (%w/v) (blue = 9 h, red = 12 h, green = 15 h).

Fig. 15 shows the pattern of increasing ammonium content based on increasing synthesis time and reactor size. Reactor A at 12 h had the highest ammonium value of 1.63 %w/v. This pattern is similar to the Fe content in the solids. However, as discussed previously, the degree of crystallinity and the ratio of yield weight per volume showed small values. When synthesizing for 12 h, reactors B and C showed similar results. However, the ratio of weight per volume results when using reactor B was more effective for scaling up the synthesis. The ammonium content of reactor B in the 12 h synthesis was 1.24% w/v.

CONCLUSION

Based on the characterization and synthesis results obtained, scale-up in nanomagnetite synthesis using bilimbi filtrate had an effective time of 12 h using a 150 mL reactor. This result was reinforced by X-ray diffractograms, a fair good degree of crystallinity of 74.48%, the ratio of the weight of the results per volume of 3.72x10-2 g/mL, the Fe content in the solid of 22.02% w/w, the Fe content of the liquid of 0.02%w/v, the Fe yield value of 96.89%, and the ammonium content in the synthesized liquid of 1.24%w/v. The acid content value of bilimbi filtrate at 12 h of synthesis was 0.2680 N.

SUPPORTING INFORMATION

There is no supporting information of this paper. The data that support the findings of this study are available on request from the corresponding author (D.Saprudin).

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CONFLICT OF INTEREST

No potential conflicts of interest were reported by the authors.

AUTHOR CONTRIBUTIONS

A.N. Hikmah and **I. Ismawati** conducted the experiment, **Z. Arif** and **D. Saprudin** conducted writing and revised the manuscript. All authors agreed to the final version of this manuscript.

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