SYNTHESIS AND CHARACTERIZATION OF Fe₃O₄ NANOPARTICLES FROM IRON SAND WITH SONOCHEMICAL METHOD

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ABSTRACT

This study conducts Fe₃O₄ nanoparticle synthesis by the sonochemical method with varying its sonication duration. The Fe₃O₄ nanoparticles were made from natural abundance iron sand using a polyethylene glycol -4000 template. The ultrasonic irradiation was carried out in five different durations and characterized by X-ray Diffractometer, scanning electron microscope, Fourier transforms infrared spectrophotometer and vibrating sample magnetometer. At an optimum sonication time of 150 minutes, the sonochemical method produces the minimum size of the Fe₃O₄ nanoparticles. Extending the sonication process from its optimum time yields a crystalline agglomeration that expands the size of the nanoparticles. The magnetic properties test of Fe₃O₄ nanoparticles shows its superparamagnetic properties with low coercivity and remanent magnetization.

Keywords: Fe₃O₄ Nanoparticles, Iron Sand, Sonochemical, Superparamagnetic, Vibrating Sample Magnetometer.

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INTRODUCTION

Fe₃O₄ is known as one of the important transitions of metal oxides with strong magnetic properties.¹ The crystalline structure of Fe₃O₄ nanoparticles is a spinel face-centered cubic (FCC). The structure is arranged by the octahedral sites of Fe²⁺ and Fe³⁺ when coordinated with oxygen ions.^{2,3} In their bulk sizes, Fe²⁺ and Fe³⁺ atoms are ferromagnetic and become superparamagnetic when forming Fe₃O₄ with a diameter below 20 nm.⁴ Many researchers have studied the properties of Fe₃O₄ nanoparticles such as their magnetic, catalytic, biocompatibility, high magnetization saturation, and superparamagnetic behavior.^{5,6} The biocompatibility of Fe₃O₄ nanoparticles is known in the human body and therefore, is used for several applications such as drug delivery, magnetic bioseparation, tumor hyperthermia treatment, cancer treatment, breast cancer cells diagnosis, metastatic liver disease diagnosis, glioma diagnosis, nerve inflammation detection, and neurodegenerative diseases detection.⁷⁻¹²

Fe₃O₄ is easy to produce with a simple and low-cost magnetic separation process.¹³ Several methods to synthesized Fe₃O₄ nanoparticles include hydrothermal, co-precipitation, sonochemical, non-hydrolytic, solvothermal, microemulsion, chemical vapor deposition, and sol-gel.¹⁴⁻¹⁶ As a tropical country, iron sand can easily be found in many Indonesian coastal lines.¹⁷ The main element of iron sand is an iron oxide such as magnetite (Fe₃O₄), hematite (Fe₂O₃), and silica (SiO₂).¹⁸ The advantages of iron sand are its high permeability, high saturation magnetization, easy to get, and have a high thermal conductivity characteristic and can be used to produce Fe₃O₄ nanoparticles.^{19,20}

The sonochemical method is considered as one of the effective methods to synthesized Fe₃O₄ due to its ability to produce a small nanoparticle size, prevent oxidation and agglomeration, perform a short synthesis time with a low temperature and avoid the use of catalysts.²¹⁻²⁵ As reported by some studies, the nanoparticle size and shape can affect the properties of the nanoparticles themselves.²⁶ Even though iron

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sand has been used in the production of Fe_3O_4 by using a sonochemical method, to our knowledge, the variation of the sonication process to optimize the nanoparticle size in the synthesis of Fe_3O_4 nanoparticles were not yet reported. Therefore, this study aims to synthesize Fe_3O_4 nanoparticles from natural iron sand using the sonochemical method with varying the sonication duration and evaluate the characteristic of its crystal structure, particle size, and magnetic properties.

EXPERIMENTAL

The sonochemical method for Fe_3O_4 was conducted in three stages; extraction, synthesis, and characterization. In the first stage, iron sand from natural resources was extracted by using permanent magnets. Next, 10 g of the extracted iron sand was dissolved in 30 mL HCl 37 % and stirred at a temperature of 70 °C for 60 minutes. After that, the solution was filtered and precipitated using NH_4OH solution. Then the resulting black precipitate was washed thoroughly and added with 2.27 g polyethylene glycol (PEG)-4000. After that, the black precipitate was stirred again with a rotating speed of 250 rpm. The synthesis stage starts by conducting ultrasonic irradiation using a 300 watts ultrasonic source (Krisbow, Type: 10039597) at 35 kHz. The irradiation is conducted on the black precipitate samples at 60 °C for five different sonication duration as shown in Table 1. The synthesis ends by drying the irradiated black precipitate using a furnace at 175 °C. The characterization stage is conducted by investigating the crystallinity of the resulting Fe_3O_4 nanoparticles powder using an X-ray diffractometer (Shimadzu, XRD-7000 S with Cu sources and a wavelength of 1.5406 Å). To measure the crystallite sizes, the Scherrer formula is used as follows:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where, D is the crystallite size, λ is the wavelength of X-rays, β is the full width at half maximum (FWHM) of the X-ray diffraction peak, and θ is the diffraction angle of the measured crystal. (REF) By using this formula, the size of the crystal grains is determined by identifying the highest intensity on the diffraction peak. Furthermore, an electron microscope (SEM, Type JEOL-6510LA) was used to investigate the microstructure of the powder while the analysis of the magnetic properties of the powder was conducted by using a vibrating sample magnetometer (VSM) type Oxford VSM1.2H. The characterization of the powder's functional groups was acquired by using a Fourier transforms infrared spectrophotometer (FTIR) Prestige 21 model 8400 S.

Table-1. The Ultrasonic Irradiation Variables and Their connected Sample Name

Composition	Sonication Duration	Sample Name
Fe_3O_4 + PEG 4000	60 minute	A
Fe_3O_4 + PEG 4000	90 minute	B
Fe_3O_4 + PEG 4000	120 minute	C
Fe_3O_4 + PEG 4000	150 minute	D
Fe_3O_4 + PEG 4000	180 minute	E

RESULTS AND DISCUSSION

The XRD spectrum's result of the Fe_3O_4 samples is shown in Fig.-1 for different sonication duration. The 2θ diffraction peaks at 35.74°, 35.84°, 35.78°, 35.86°, and 35.81° showed a dominant diffraction peak of 311 planes of the Fe_3O_4 according to the JCPDS file (JCPDS card no. 19-629), corresponds to several studies that observe the dominant peak around 35.3845° and 35°. ^{7,27} The result shows the spinel cubic structure of magnetic nanoparticles.

The diffraction pattern of Fe_3O_4 nanoparticles has several peaks with low intensity at sonication times of 60 minutes and 90 minutes. The intensity rises at sonication times of 120 minutes, 150 minutes, and 180 minutes. Even though Fe_3O_4 diffraction peaks look like amorphous particles, small diffraction peaks can still be observed. In this study, the low-intensity peaks were acquired due to the use of low furnace temperature below 250 °C to avoid the oxidation of Fe_3O_4 to Fe_2O_3 at higher temperatures. ²² Fe_3O_4 and Fe_2O_3 can be differentiated based on their nanoparticle's color. Fe_3O_4 nanoparticles have a black or brownish color, while Fe_2O_3 nanoparticles are reddish.

Fig.-1: X-ray Diffraction Pattern of Fe_3O_4 Nanoparticles of Sample A to E according to Table-1Table-2: FWHM and crystal grain size of Fe_3O_4

Sample	2θ (°)	FWHM (°)	FWHM (rad)	Crystalline size (nm)
A	35.7473	0.32545	0.00568	49.73
B	35.8475	0.35684	0.00622	45.37
C	35.7827	1.12929	0.01970	14.33
D	35.8661	2.42266	0.04228	6.68
E	35.8103	0.94095	0.01642	17.20

The Fe_3O_4 nanoparticles produced had a size range of 5.6-16.8nm as reported by another study.²⁸ As shown in Table-2, the crystalline size of Fe_3O_4 is decreased to the size of nanoparticle with increasing the sonication time until 150 minutes at sample D. But Table-2 also showed that increasing the sonication time to 180 minutes, at sample E, tends to increase the crystalline size of Fe_3O_4 nanoparticles. This result indicates the need for a maximum time for the sonication process to produce nanoparticles. The grain size was enlarged due to agglomeration as the sonication process exceed the maximum time of Fe_3O_4 particle's breakdown. Figure-2 shows the SEM results of all samples. Even though all samples tend to agglomerate because of the attractive force on the particles, but the generation of nanoparticles in the samples is confirmed by the size of the crystalline measured in Table-2. Figure-2E also illustrated the agglomeration that occurs by extending the duration of the sonication process longer than the maximum time. Our study shows that at 150 minutes, the maximum time for the sonication method is approached and it is interesting to further investigate the optimum maximum sonication time.

Table-3: Magnetic Properties of Fe_3O_4 Nanoparticles acquired from Different Sonication Duration

Sample	Magnetic Properties		
	Ms (emu g^{-1})	Mr (emu g^{-1})	Hc (Oe)
A	17.68	1.75	95.13
B	21.44	2.02	82.20
C	18.04	1.57	91.02
D	16.49	1.56	92.14
E	14.37	1.26	95.68

Based on the SEM analysis, Fe_3O_4 nanoparticles contain 46 % iron atoms and 18 % oxygen atoms. Figure-3 shows the hysteresis curve of Fe_3O_4 nanoparticles that have been synthesized with a magnetic field range from -20.170 kOe to +20.170 kOe at 24 °C. The magnetic properties of Fe_3O_4 nanoparticles are affected by their particle size.²⁹ Based on Table-3, the values of coercivity (Hc), saturation magnetization (Ms), and remanent magnetization (Mr) vary based on the agglomeration process in the samples. It is known that agglomeration inhibits the magnetic moment to fluctuate which affects the direction of the magnetic moment. Therefore, a larger external magnetic field is needed to make a zero magnetization.

Table-3 showed that all samples had a close-to-zero remanent magnetization. Together with the low Hc values, this concludes that the resulted Fe_3O_4 nanoparticles were superparamagnetic.³⁰

Fig.-2: SEM Image of Fe_3O_4 Nanoparticles of Sample A to sample E with 3000 $\times$ magnification

Fig.-3: Hysteresis Curve of Fe_3O_4 Nanoparticles, with its highlighted Remanent, acquired from Different Sonication Duration from 60 minutes (A) until 180 minutes (E) according to Table-1

By using 150 minutes sonication duration, less than 20 nm size nanoparticles was achieved that confirms the optimum superparamagnetic characteristics.⁴ Interestingly, this result was acquired from a simple sonication process with the natural resource of iron sand as its raw material. Superparamagnetic

properties make the nanoparticles have a high magnetic sensitivity which supports the application of the nanoparticles in biomedical applications, for example, as a contrast agent in magnetic resonance imaging.^{22,30}

The FTIR test results showed uniform absorption peaks by all samples as shown in Fig.-4. The absorption peak shows the Fe-O bond at a wavenumber of 552 cm⁻¹. This result corresponds with several studies that identify the Fe-O bonds in the wavenumber absorption of 550-630 cm⁻¹.^{31,32} The absorption wavenumber range of 1050 - 1200 cm⁻¹ shows the bond between C-O while the range of 2850 - 3000 cm⁻¹ shows the bond between C-H.

Fig.-4: FTIR Test results of Fe₃O₄ Nanoparticles of Sample A to E according to Table-1

CONCLUSION

By using the sonochemical method, Fe₃O₄ nanoparticles were successfully synthesized and produced with optimum superparamagnetic size at 150 minutes with low coercivity and remanent magnetization. The nanoparticles were synthesized from natural resource iron sand as its raw material and its superparamagnetic characteristics open the application of the nanoparticles in biomedical applications to provide contrast agents for magnetic resonance imaging.

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