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DIFFRACTION AND MAGNETIZATION PROPERTIES OF Fe_3O_4 NANOPARTICLE FROM NATURAL IRON SAND IN VARIOUS STIRRING RATE FOR POTENTIAL BIOMEDICAL APPLICATIONS

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ABSTRACT

This study aims to synthesize Fe_3O_4 nanoparticles using the co-precipitation method using variations in the synthesis process's stirring rate. Fe_3O_4 nanoparticles are made from natural iron sand with an abundance of Fe (Iron). The stirring rate variation was carried out at five different rpm rates, from 270 rpm to 470 rpm. X-ray diffraction is used to determine the crystal size, and the contained phase with a vibrating sample magnetometer is used to determine the nanomaterial's magnetic properties. At the stirring rate of 370 rpm, a minimum Fe_3O_4 crystal size of 4.156 nm is produced by the co-precipitation method, as shown in the sample's 2D crystal diffraction. At the stirring rates below and above 370 rpm, the resulting crystalline size is much larger in the range of 7 nm. The phase test results showed that elements other than Fe_3O_4 had degraded, resulting in a pure magnetite (Fe_3O_4) phase. The magnetic properties test showed superparamagnetic properties of Fe_3O_4 with low coercivity field values and magnetic saturation values in the range of 19-26 emu/g. The crystal characteristics and magnetic properties of the pure magnetite phase of the Fe_3O_4 nanoparticles have the potential for applications in the biomedical field.

Keywords: Superparamagnetic, Iron Sand, Diffraction, Stirrer Rate, Co-precipitation.

INTRODUCTION

The nanoscale materials, on which nanoscience and nanotechnology are based, recently have become one of the most popular research topics. Nanoscale materials can be defined as materials with at least one of its dimensions exists at the nanometer scale and materials whose properties are affected by these dimensions.[1] Materials with relevant physical measurements at the nanometer scale have unique and different chemical and physical properties (thermodynamic, dynamic, mechanical, optical, electronic, and magnetic properties) compared to materials in their bulk form. Nanoparticles have broad and comprehensive applications for various fields of nanoparticles as biomedical applications.[2]

Fe_3O_4 is known as the transition in metal oxides with strong magnetic properties. Fe_3O_4 nanoparticles have a characteristic face-centered cubic (FCC) spinel crystal structure. Its structure is governed by the tetrahedral (dA) and octahedral (dB) sites of Fe^{2+} and Fe^{3+} when coordinated with oxygen ions. Fe_3O_4 nanomaterials are unique materials due to their magnetic properties, low toxicity, biodegradability, catalytic, biocompatibility, high magnetization saturation, low Currie temperature, and superparamagnetic behavior.[3-5] Because of these properties, magnetite nanomaterials are suitable for use in medical applications. Some applications of magnetite nanomaterials are neutron cancer therapy,[6,7] antibacterial applications,[8] drug delivery,[4,9] contrast

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magnetic resonance imaging (MRI) agents,[10-12] hyperthermia application,[13] and analysis of uric acid content.[14] The applications of magnetite nanomaterials are increasing, especially for its potential in biomedical applications.

Iron sand is a natural material that contains iron or commonly called magnetite, which exists along the coastline. As an archipelago, Indonesia has the advantage of abundant natural iron sand resources.[15] Elements contained in natural iron sand include Fe_2O_3, TiO_2, Al_2O_3, and MnO_2. The low utilization of natural iron sand as a source of material for Fe_3O_4 formation is due to the complicated synthesis process and many costs. Therefore the necessity to optimize the use of natural iron sand as the initial material for the synthesis of Fe_3O_4 nanoparticles is still needed.

A method known for its fast, easy, efficient and affordable cost in producing nanomaterials is co-precipitation synthesis. Many studies have reported the advantage of the technique in producing Fe_3O_4 nanoparticles.[16-18] However, a suitable synthesis composition in the co-precipitation method to produce Fe_3O_4 nanoparticles from natural iron sand is still a challenge as a potential material in biomedical applications. The Fe_3O_4 nanoparticles' specific properties are needed in biomedical applications, such as biocompatibility, nano-size, low toxicity, high magnetic saturation, sterically and electrostatically stable, not agglomerated, and superparamagnetic.[19]

There are several options to synthesize Fe_3O_4 nanomaterials. The choice includes varying the degree of acidity (pH),[20] adding stabilizing agents,[21] changing the heating rates,[22] or alter the temperature during the calcination process.[23,24] However, to our knowledge, the variation in lower stirring rate (under 500 rpm) during the synthesis process of Fe_3O_4 nanoparticles has not been reported, mainly to produce its specific properties for biomedical applications. Therefore, this study aims to acquire the synthesis process's optimum stirring rate to make crystal-size Fe_3O_4 nanoparticles for biomedical applications using natural iron sand as its initial material.

EXPERIMENITAL

Preparation and Synthesis Process of Fe_3O_4 Nanoparticles

Natural iron sand from Kulon Progo beach is used to synthesize Fe_3O_4 nanoparticles. Figure-1 explains the co-precipitation method that used 37% hydrochloric acid (HCl) (Mallinckrodt Baker, Paris, USA), ammonium hydroxide (NH_4OH) (Merck KGaA, Darmstadt, Germany), and distilled water to wash the synthesis product. The raw material of Fe_3O_4 nanoparticles from the natural iron sand is acquired firstly by filtering the sand using gauzes with a specific mesh size to separate the sand from its remaining impurities. Next, a magnet bar is used to extract the sand from its organic contaminants before it is washed and dried. The resulting iron sand becomes the material in the synthesis process of Fe_3O_4 nanoparticles using the co-precipitation method with varying the synthesis's stirring rate.

30 ml Hydrochloric acid is prepared using a magnetic stirrer. Natural iron sand is dissolved in HCl for 6 hours with a magnetic stirrer rate variation of 270 rpm, 320 rpm, 370 rpm, 420 rpm, and 470 rpm. The stirring rate variation is labeled by R1 for 270 rpm to R5 for 470 rpm, respectively. The suspension results are iron sand deposits and a solution containing Fe_3Cl, Fe_2Cl, Fe_2O_3, H_2O, and H_2 gases. The suspension results are then filtered using a filter paper to obtain ferric chloride ($FeCl_3$). The filtering process is also used to avoid the incomplete decomposed iron sand to form maghemite (Fe_2O_3) and follow the chemical formulation**.** After that, by using chemical reactions and neutralizes colloidal acidity, the colloids are added in NH_4OH solution with a ratio of 1:1 to form Fe_3O_4 compounds. The base solution's addition will undergo an exothermic reaction to create a pure Fe_3O_4 and NH_4Cl salts. The sample result is then washed with distilled water to dissolve the remaining salt from the pure Fe3O4 and stabilize the pH until it reaches a neutral pH (pH 7). The resulted black Fe_3O_4 deposit is tested using a permanent magnet to see the produced magnet's properties. The obtained ferrofluid was then dried using a furnace for 2 hours at 175 degrees Celsius C to create a bulk of Fe_3O_4. The drying temperature is set not to be too high to avoid an unwanted Fe_2O_3 compound in the sample**.** The bulk of Fe_3O_4 is grounded with a mortar to obtain a fine powder. The chemical formulation of the process is described as follow:

Natural iron sand dissolves process

$$3Fe_3O_4 + 8HC \rightarrow FeCl_2 + 2FeCl_3 + 3Fe_2O_3 + 3H_2O + H_2 \quad (1)$$

Filtrating the sample

$$FeCl_2 + 2FeCl_3 + 3Fe_2O_3 + 3H_2O \rightarrow FeCl_2 + 2FeCl_3 + H_2O \quad (2)$$

$$FeCl_2 + 2FeCl_3 + H_2O + 8NH_4OH \rightarrow nano - Fe_3O_4 + 8NH_4Cl + 5H_2 \quad (3)$$

Washing the sample using distilled water

$$nano - Fe_3O_4 + 2H_2O \rightarrow nano - Fe_3O_4 + 2H_2 + O_2 \quad (4)$$

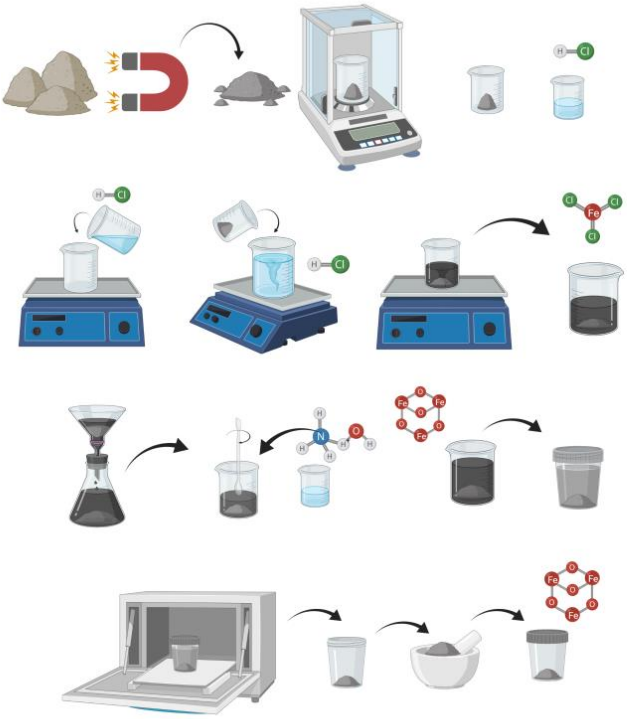


Fig.-1: Synthesis Fe_3O_4 nanoparticles using co-precipitation method

Characterization of Nanoparticles Fe_3O_4

X-ray diffraction (XRD) characterization of the sample is conducted by using Bruker D8 Advance diffractometer with an operated Cu X-ray anode at 1.6 kW (40 kV, 40 mA), line focus of 0.04 x 8 mm, arm radius of 250 mm (primary and secondary), divergence slit of 1°, Soller slit of 2.5° (primary and secondary) and LYNXEYE-XET position-sensitive detector (PSD) without $K\beta$ filter. Data acquisition was collected at 2θ range of 20° - 100°, with step size of 0.02° 2θ (4000 data points) and scan speed of 1 second per data. Due to LYNXEYE-XET PSD's advantage, each sample only needs a short acquisition time of about 6 minutes. Using Bruker – EVA v5.1 phase identification (ICDD PDF-4+ database) and Bruker – Topas v.6 for Rietveld refinement, the XRD data were analyzed. The phase data is processed by using phase ID software EVA v5.1 and QPA software Bruker-Topas v6. The Fe3O4 nanoparticle samples' magnetic properties are characterized by using Electromagnetic Dexing Magnet Tech VSM250 (Banten, Indonesia). The structural characterization of Fe_3O_4 nanomaterials is performed by using a D-8 diffractometer (Bandung, Indonesia) involving a Cu Kα radiation source (λ = 1.5405 Å) with radiation beams between the Bragg angles of 20˚ to 100˚.

RESULTS AND DISCUSSION

Structural Analysis

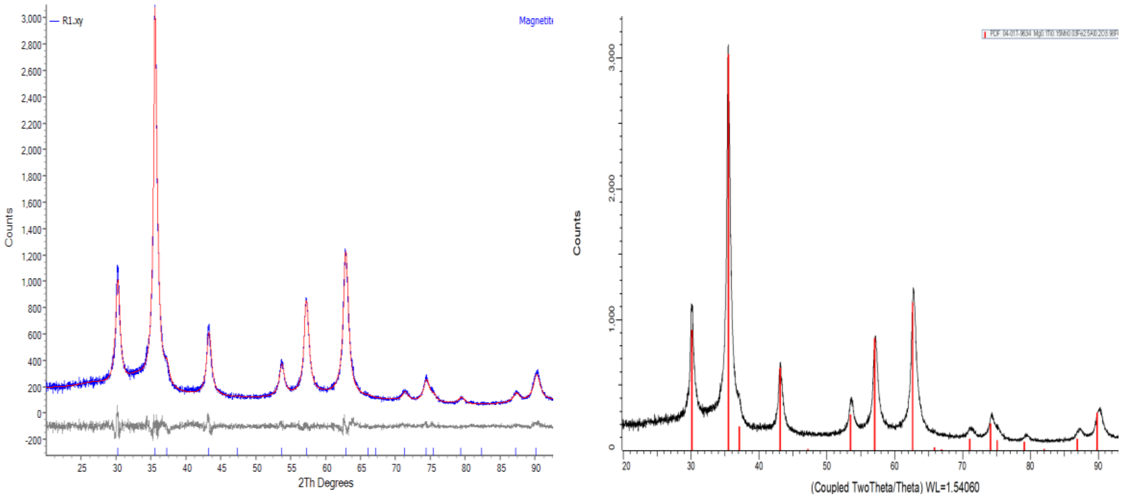
There is a good agreement between the experimental data of the Rietveld refinement[25] of Fe_3O_4 and the simulated pattern from the International Centre for Diffraction Data (ICDD) reference database PDF 04-017-9634 (face-centered cubic Fd-3m;2) as shown in Figure-2. In Figure-2, The X-ray graph plot produces by the Bragg reflection also confirmed the finding of a single-phase cubic spinel structure nanoparticle without impurities as previously reported.[26] In this study, the determined crystallite in the Rietveld refinement analysis is based on the fundamental parameter of approach line profile fitting[27-29] that indirectly determined the broadening sample without 2-dimensional defects. The analysis shows that the sample's resulting phase belongs to the Fd3m group (confirmed in ICDD PDF-4), with all samples containing magnetite (Fe_3O_4) without any contaminant. The magnetite nanoparticles' crystal size was confirmed using the intensity's peaks with the Miller index result of 311.

Figure-3 shows a diffractogram generated from the XRD characteristics with 2D XY-offset, 2D-view, and peak (311) depiction with 10-isoline levels. A decrease in intensity is shown in the Figure, with the stirring rate elevation from R1 to R3. Meanwhile, elevating the stirring rate at R4 and R5 increasing the intensity. The value of full-width half maxima (FWHM) is increased from R1 to R3 and decreased from R4 to R5. The sample's crystal size was in the range of 4 to 7 nm for each different variation of the stirring rate. The crystal size is decreased slowly for samples with stirring rates of R1 to R3 with the smallest crystal size of 4 nm (shown in Table-1). However, there was an increase in the nanoparticle crystals' size to 7 nm at the R5 stirring rate. The increase may be due to variations in the stirring rate, which affected the amount of Fe (ferrite) formation that was different as previously reported.[30]

Crystal lattice parameters are calculated through the following Equation-5 and summarized in Table-1.

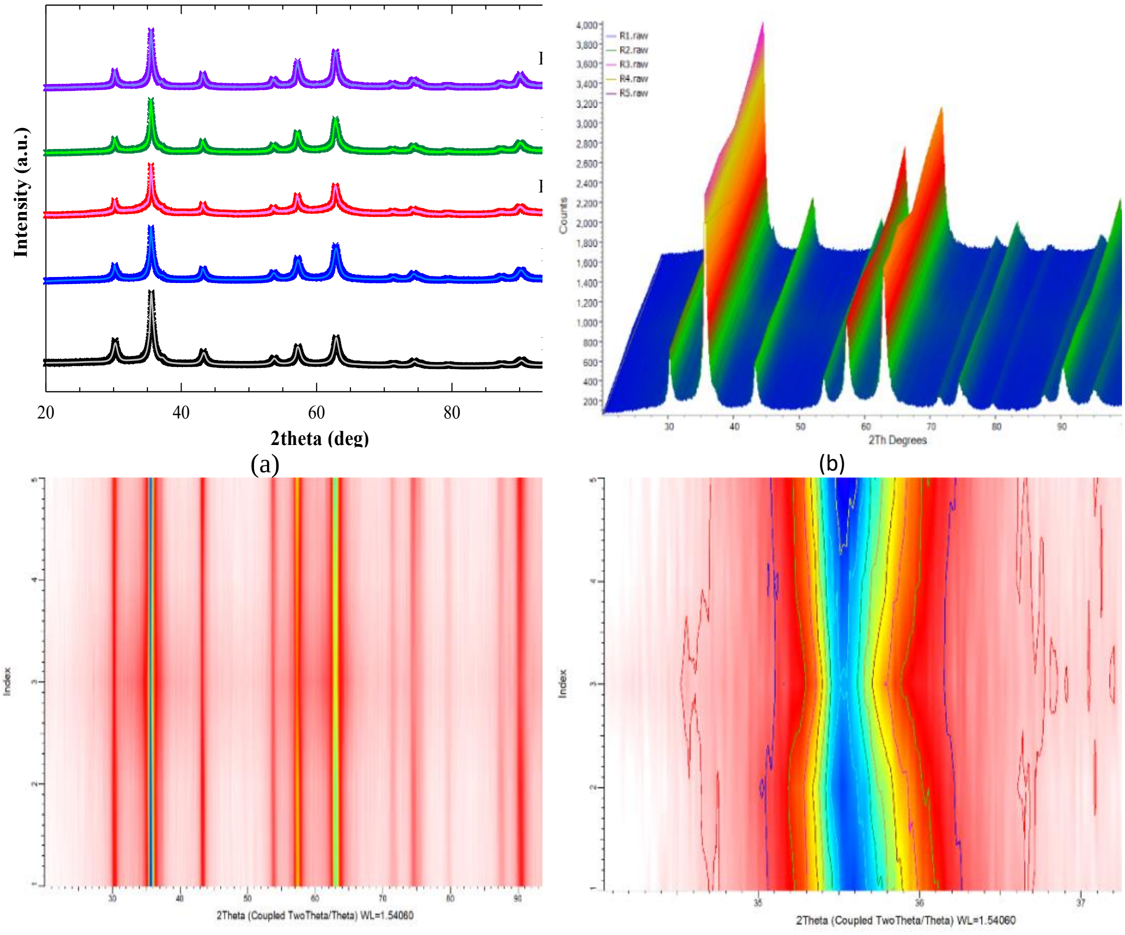
$$a = d\sqrt{h^2 + k^2 + l^2}\ \text{Å} \qquad (5)$$

where α is the lattice constant, where (hkl) is the miller's index, and d is the distance between the lattices. Crystallite size is closely related to particle size. When the particles are in the order of nanometers, the particles will tend to have a single domain that makes their crystallite size is the same as the particle size. However, when the particle size is large enough to form a polycrystalline, the particle size may be larger than the crystallite size. Therefore, further research is needed to produce Fe_3O_4 nanoparticles with suitable particle sizes in the biomedical field.



(a) (b)

Fig.-2: (a) Qualitative analysis result from nanoparticle Fe_3O_4 with Bruker-EVA,
(b) Rietveld quantitative analysis nanoparticle Fe_3O_4 with Bruker-Topas



(a) (b)

(c) (d)

Fig.-3**:** Diffractograms nanoparticle Fe_3O_4 of (a) Rietveld refinement, (b) 2D xy-offset, (c) 2D- view and (d) peak (311) with 10-isoline level

Table-1: Values of crystallite size, the goodness of fitting, R-Bragg, lattice parameter (a), X-ray density (dx), and hopping length at a tetrahedral site (A-site) and octahedral site (B-site).

Sample (rpm value)	The crystallite size (nm)	χ^2	R-Bragg	Lattice parameter (Å)	d_x [g/cm^3]	V (Å^3)	d_A (Å)	d_B (Å)
R1 (270)	7.762	1.00	0.759	8.355446	4.930	583.327	3.618023	2.954104
R2 (320)	7.068	1.35	0.667	8.355228	4.931	583.289	3.617946	2.95404
R3 (370)	4.165	1.13	0.494	8.322829	4.989	576.518	3.603891	2.942565
R4 (420)	6.886	1.07	0.372	8.293374	5.042	570.411	3.59112	2.932138
R5 (470)	7.731	1.06	0.326	8.315418	5.002	574.979	3.600682	2.939944

χ^2: The goodness of fitting, d_x: X-ray density, V: The volume of a unit cell, d_A: Hopping length at a tetrahedral site, d_B: Hopping length at an octahedral site**.**

Figure-4 shows the lattice parameters (α) with different stirring rates (rpm). Figure-4 shows that the lattice parameter decreases with increasing the stirring rate, but the lattice parameter increases after the stirring rate of 470 rpm (R5). The lattice parameters' decrease can be attributed to Fe^{3+} ions from a tetrahedral site (site A) to an octahedral site (site B). The reduction of lattice parameters is also due to Fe^{3+}, which is superior to Fe^{2+} even though its sufficient nuclear charge is the same (0.64Å). However, the number of electrons in Fe^{2+} is more than in Fe^{3+}. The outer electrons in Fe^{3+} are attracted to it so that the radius of Fe^{2+} is more significant, which causes a decrease in lattice parameters accompanied by an increasing amount of Fe^{3+}.

X-ray density or called crystal density (dx), is obtained through the following formulation at Equation-6,[31]

$$\mathrm{X-ray\ density\ (d_x)} = \frac{[\text{molecular weight x Number of molecules per unit cell}]}{[\text{Volume of unit cell x Avogadro's number}]} \qquad (6)$$

Figure-4 showed an inverse relationship between the lattice parameter and the X-ray density in the increasing stirring rate. The X-ray density of magnetite nanoparticles is recorded in Table-1, namely at 4.9 g cm^{-3} to 5.0 g cm^{-3}. Compared to this study, another study has reported a different density of 5.2 g/cm^3,[32] which can be explained due to the larger crystallite size in the resulting sample in this study that creates a heavier molecular weight. The unit cell volume is obtained through the following Equation-7,

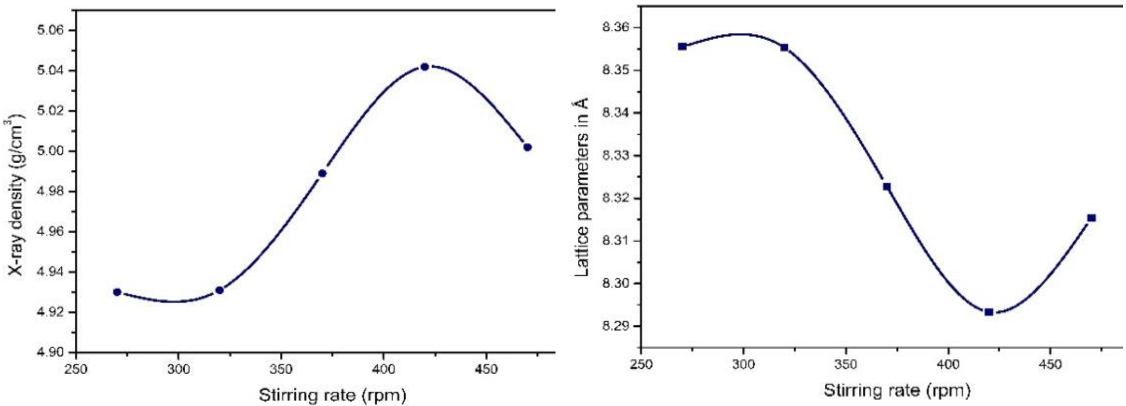
$$V = a^3\ (\text{Å}^3) \qquad (7)$$

with the value shown in Table-1. It is shown that the unit cell volume value decreases with the increase of the stirring rate because the volume of the unit cell depends on the decrease of the lattice parameter (a).

The distance between the magnetic ion at the octahedral and the tetrahedral site is called the length of the jump at site A (tetrahedral) and site B (octahedral). The jump length values for site A and site B follow the following Equation 8 for each site,

$$d_B = 0.25\, a\sqrt{2} \qquad d_A = 0.25\, a\sqrt{3} \qquad (8)$$

where α is the lattice parameter.[33] Table-1 shows the value of each site's jump length, indicating the importance of site A at 3.6 Å and site B at 2.9 Å. These results match the results in the report of Rani et al..[32] The distance between the magnetic ions (jump length) at the tetrahedral and octahedral sites is decreased with the increase of the stirring rate due to the number of Fe^{3+} ions formed. The Fe^{3+} ion has a smaller ionic radius than the Fe^{2+} ion because fewer electrons are around it. The outer electrons tend to be attracted inward, making the magnetic ions closer to another, reducing the jump length.



(a) (b)

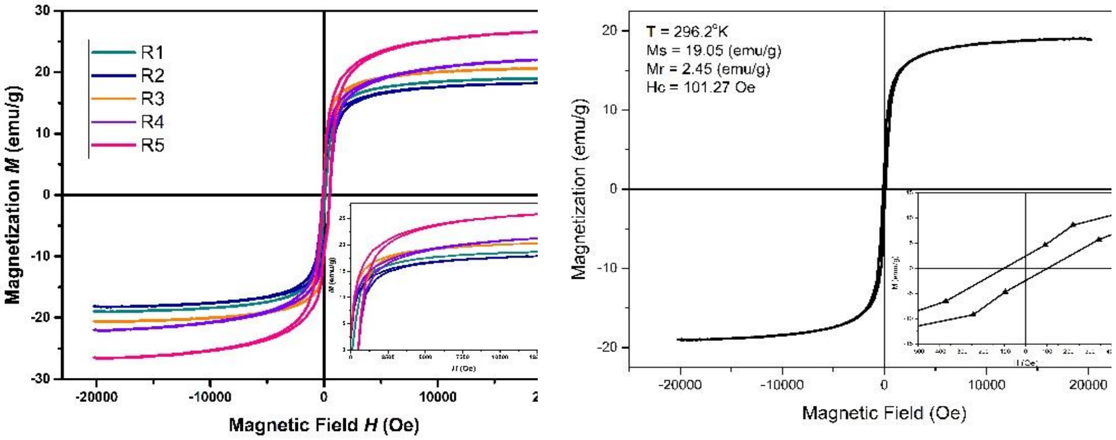
Fig.-4: (a) Plot graph X-ray density (dx) at various stirring rate, (b) Plot graph lattice parameter at various stirring rate

Magnetic Properties

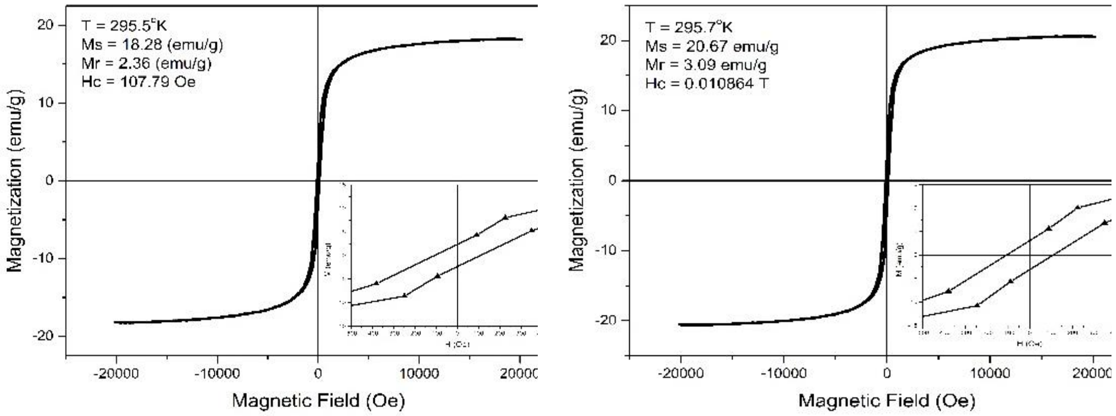
The sample hysteresis loop was obtained via a vibrating sample magnetometer (VSM). The hysteresis loop is used to determine the magnetic properties of the sample from the synthesis process. Each VSM sample is measured at room temperature, as shown in Figure-5. The magnetic stirring rate variation results in a hysteresis loop with the magnetic saturation value (Ms), increasing the stirring rate. The greater the stirring speed, the resulting coercivity field (Hc) tends to increase, and when the stirring speed is 470 rpm (R5), the Hc drops significantly. In an experiment by Goya et al.,[34] Hc will decrease with decreasing particle size. The Ms value increases due to the increase in the mass of the nanoparticles due to surface interactions. The interaction surface disturbance is caused by the spin magnetic moment and the inversion disturbance of the spinel structure coupled with an increase in the weight volume of Fe_3O_4 nanoparticles.[35]

The Magnetization properties are shown in Figure-6. at the stirring rate of R1, the Ms value decreased. Ms value if the sample size of the nanoparticles is small, the particles will tend to have a single domain, which means that the magnetic moment can quickly return to its original state when the external magnetic field is released.[36] According to the previous study,[37] the decrease in Ms value was caused by the size of the ultrafine particles, the monodisperse of particles, abnormalities on the nanoparticle samples' surface, and the presence of cation distribution.

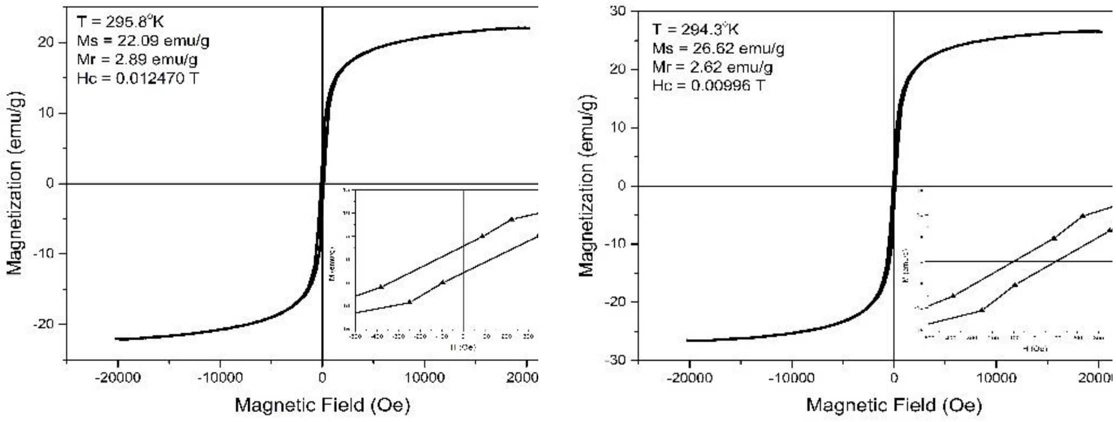
The magnetization plot with an applied magnetic field (M-H) shows superparamagnetic properties. In Table-2., it is known that the samples show close to zero coercivity values at room temperature, meaning that when the sample is placed in an external magnetic field, the sample cannot hold the residual magnet when the magnetic field is released. According to a study conducted previously,[38] values of zero coercivity are superparamagnetic characteristics. If the magnetic material has a particle size smaller than the critical superparamagnetic size (25 nm); these particles will exhibit superparamagnetic properties.[39] In another study report by Chatterjee et al.,[40] Fe_3O_4 nanoparticles measuring below 15 nm will have a single magnetic domain, which means that the particles have uniform magnetization.



(a) (b)



(c) (d)



(e) (f)

Fig.-5: (a) Magnetic hysteresis loop with the value of magnetic saturation (emu/g), remanent magnetization (emu/g), and coercivity field (T) at (b) 270 rpm, (c) 320 rpm (d) 370 rpm, (e) 420 rpm, (f) 470 rpm.

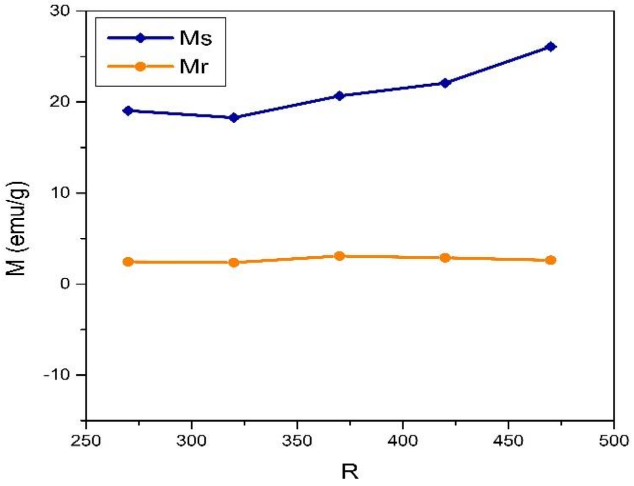


Fig.-6: The magnetization remanent and saturation magnetic properties at a various stirring rate

Table-2 Values of magnetic saturation (Ms), remanent magnetization (Mr), coercivity field (Hc), and the correlation with crystallite size

Stirring rate	Magnetic Properties		
	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
R1	19.05	2.45	101.27
R2	18.28	2.36	107.79
R3	20.67	3.09	108.64
R4	22.09	2.89	124.70
R5	26.62	2.62	99.60

The magnetic saturation value produced by the sample is smaller than the magnetic saturation value in the Fe_3O_4 bulk (88-92 emu/g).[23,41] Fe_3O_4 nanoparticles as biomedicine applications must have a Ms value in the range of 5-20 emu/g [3] In another study, Brusentsov et al.[42] stated that Ms values of around 7-22 emu/g could be used for biomedical applications. This statement is supported by Ma et al.,[43] that a magnetic saturation of 16.3 emu g^{-1} tends to be sufficient to separate Fe_3O_4 magnetic nanoparticles from water when an external magnetic field is applied. Particles that have a nanoscale size have physical and chemical properties that describe the characteristics of their atoms.[44] Experiments of Zhang et al.,[45] stated that changes in nanoparticles' magnetic properties are based on two factors, namely changes in size and changes in the state of the surface layer of nanoparticles. The quantum effect of nanoparticles and the nanoparticles' magnetic surface area will change their magnetic properties. The changes indicate a superparamagnetic phenomenon, namely quantum magnetization, showing that the particles are considered a single magnetic domain.[34] Superparamagnetic nanomaterials have a high potential for biomedical applications due to their unique physical, thermal, mechanical, chemical, and mesoscopic properties.[46]

CONCLUSION

The synthesis of Fe_3O_4 nanoparticles by co-precipitation method using natural iron sand as the starting material has been successfully carried out to produce powdered Fe_3O_4 nanoparticles with sizes under 10 nm. The stirring rate variation was described from 270 rpm (R1) to 370 rpm (R3); the crystallite size was getting smaller, and then the crystallite size increased when the stirring rate was 420 rpm (R4). The lattice parameter decreases with the increasing stirring rate, inversely proportional to X-ray density, decreasing with the rising stirring rate. The lattice parameters are in the 8.3 Å range, and the X-ray density is at 5.0 g cm^{-3}. The structure formed shows that the sample contains 100% magnetite nanoparticles without any contaminants. The resulting magnetic property is a coercive field close to zero in a superparamagnetic magnet with Ms value in the standard for biomedicine applications. The application of Fe_3O_4 nanoparticles in the biomedical field requires nanoparticle sizes below 15 nm with Ms values 7-22 emu g^{-1} and superparamagnetic magnetic properties. The magnetite nanoparticles' results in this experiment with the smallest crystallite size of 4.156 nm at 370 rpm (R3) and a Ms value of 20.67 emu g^{-1} with a Hc value close to zero superparamagnetic, so that the magnetite nanoparticles from the experiment are potentially for future biomedical applications.

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DIFFRACTION AND MAGNETIZATION PROPERTIES OF Fe_3O_4 NANOPARTICLE FROM NATURAL IRON SAND IN VARIOUS STIRRING RATE FOR POTENTIAL BIOMEDICAL APPLICATIONS

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ABSTRACT

This study aims to determine the effect of synthetic stirring rate on the diffraction and magnetization properties of Fe_3O_4 nanoparticles. Materials made from natural iron sand were synthesized using the co-precipitation method with variations in stirring rate 270 to 470 rpm. At stirring up to 370 rpm (R3), the crystalline size of Fe_3O_4 decreases. Increasing the stirring rate caused the lattice parameters to decrease in the range of 8.3 A° and the X-ray density to increase in the range of 5.0 g cm^{-3}. The structure formed indicates that the sample contains 100% magnetite nanoparticles without any contaminants. The magnetite nanoparticles in this experiment with the smallest crystal size of 4.156 nm and the Ms value of 20.67 emu g^{-1} with a Hc value close to zero superparamagnetic, have the potential for future biomedical applications.

Keywords: Superparamagnetic, Iron Sand, Diffraction, Stirrer Rate, Co-precipitation.

INTRODUCTION

Nanoparticles have broad applications for various fields of nanoparticles as biomedical applications.[1,2] Fe_3O_4 is known as the transition in metal oxides with strong magnetic properties. Fe_3O_4 nanomaterials are unique materials due to their magnetic properties, low toxicity, biodegradability, catalytic, biocompatibility, high magnetization saturation, low Currie temperature, and superparamagnetic behaviour.[3-5] Because of these properties, magnetite nanomaterials are suitable for use in medical applications. Some applications of magnetite nanomaterials are neutron cancer therapy,[6,7] antibacterial applications,[8] drug delivery,[4,9] contrast magnetic resonance imaging (MRI) agents,[10-12] hyperthermia application,[13] and analysis of uric acid content.[14] The applications of magnetite nanomaterials are increasing, especially for their potential in biomedical applications.

Iron sand is a natural material containing iron, commonly called magnetite, which exists along the coastline. As an archipelago, Indonesia has the advantage of abundant natural iron sand resources.[15] Elements contained in natural iron sand include Fe_2O_3, TiO_2, Al_2O_3, and MnO_2. The low utilization of natural iron sand as a source of material for Fe_3O_4 formation is due to the complicated synthesis process and many costs. Therefore the necessity to optimize the use of natural iron sand as the initial material for synthesising Fe_3O_4 nanoparticles is still needed.

Co-precipitation is a fast, easy, efficient and affordable method of producing nanomaterials. Fe_3O_4 particle size can be controlled using this method.[16] Many studies have reported the advantage of the technique in producing Fe_3O_4 nanoparticles.[17-19] However, a suitable synthesis composition in the co-precipitation method to produce Fe_3O_4 nanoparticles from natural iron sand is still a

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challenge as a potential material in biomedical applications. The Fe_3O_4 nanoparticles' specific properties are needed in biomedical applications, such as biocompatibility, nano-size, low toxicity, high magnetic saturation, sterically and electrostatically stable, not agglomerated, and superparamagnetic.[20]

Several researchers have previously synthesized Fe_3O_4 with various developments, including varying the degree of acidity (pH),[21] adding stabilizing agents,[22] changing the heating rates,[23] or altering the temperature during the calcination process.[24,25] Hidayanto et al[15] synthesized Fe_3O_4 from natural iron sand, using a sonochemical method by varying sonication time. Nalle et al[26] and Wulandari et al[27] synthesized Fe_3O_4 using the co-precipitation method from commercial materials by varying polymer, oleic acid (OA) and chitosan as stabilisers agent on the surface of nanoparticles. Magnetization properties of their nanoparticles were measured using electron spin resonance (ESR). Kamakshi et al[16], also synthesized Fe_3O_4 nanomaterial using a stirring rate of 900 rpm, for catalyst or biomedical diagnosis.

However, a study about the variation in lower stirring rate (under 500 rpm) during the synthesis process of Fe_3O_4 nanoparticles has not been reported, mainly to produce its specific properties for biomedical applications. Therefore, this study aims to synthesize Fe_3O_4 nanoparticles with various stirring rates using natural iron sand as its initial material via co-precipitation method. This paper profoundly discusses the diffusion and magnetization properties of the synthesis process at an optimum stirring rate to make the crystallite size of Fe_3O_4 nanoparticles suitable for biomedical applications.

EXPERIMENTAL

Preparation and Synthesis Process of Fe_3O_4 Nanoparticles

Natural iron sand from Kulon Progo beach is used to synthesize Fe_3O_4 nanoparticles. Figure-1 explains the co-precipitation method that used 37% hydrochloric acid (HCl) (Mallinckrodt Baker, Paris, USA), ammonium hydroxide (NH_4OH) (Merck KGaA, Darmstadt, Germany), and distilled water to wash the synthesis product. The raw material of Fe_3O_4 nanoparticles from the natural iron sand is acquired firstly by filtering the sand using gauzes with a specific mesh size to separate the sand from its remaining impurities. A magnet bar is used to extract the sand from its organic contaminants before washing and drying. The resulting iron sand becomes the material in the synthesis process of Fe_3O_4 nanoparticles using the co-precipitation method with varying the synthesis's stirring rate.

30 ml Hydrochloric acid is prepared using a magnetic stirrer. Natural iron sand is dissolved in HCl for 6 hours with a magnetic stirrer rate variation of 270 rpm (R1), 320 rpm (R2), 370 rpm (R3), 420 rpm (R4), and 470 rpm (R5). The suspension results are iron sand deposits and a solution containing Fe_3Cl, Fe_2Cl, Fe_2O_3, H_2O, and H_2 gases. The suspension results are then filtered using a filter paper to obtain ferric chloride ($FeCl_3$). The filtering process is also used to avoid the incomplete decomposed iron sand to form maghemite (Fe_2O_3) and follow the chemical formulation**.** The colloids are added in NH_4OH solution with a ratio of 1:1 to form Fe_3O_4 compounds. The base solution's addition will undergo an exothermic reaction to create pure Fe_3O_4 and NH_4Cl salts. The sample result is then washed with distilled water to dissolve the remaining salt from the pure Fe_3O_4 and stabilize the pH until it reaches a neutral pH. The resulted black Fe_3O_4 deposit is tested using a permanent magnet to see the produced magnet's properties. The obtained ferrofluid was then dried using a furnace for 2 hours at 175 ^oC. The drying temperature is set not to be too high to avoid an unwanted Fe_2O_3 compound in the sample**.** The chemical formulation of the process is described as follow:

Natural iron sand dissolves process

$$3Fe_3O_4 + 8HC \rightarrow FeCl_2 + 2FeCl_3 + 3Fe_2O_3 + 3H_2O + H_2 \qquad (1)$$

Filtrating the sample

$$FeCl_2 + 2FeCl_3 + 3Fe_2O_3 + 3H_2O \rightarrow FeCl_2 + 2FeCl_3 + H_2O \qquad (2)$$

$$FeCl_2 + 2FeCl_3 + H_2O + 8NH_4OH \rightarrow nano - Fe_3O_4 + 8NH_4Cl + 5H_2 \qquad (3)$$

Washing the sample using distilled water

$$nano - Fe_3O_4 + 2H_2O \rightarrow nano - Fe_3O_4 + 2H_2 + O_2 \qquad (4)$$

Characterization of Nanoparticles Fe_3O_4

X-ray diffraction (XRD) characterization of the sample is conducted by using Bruker D8 Advance diffractometer with an operated Cu X-ray anode at 1.6 kW (40 kV, 40 mA), line focus of 0.04 x 8 mm, arm radius of 250 mm (primary and secondary), divergence slit of 1°, Soller slit of 2.5° (primary and secondary) and LYNXEYE-XET position-sensitive detector (PSD) without $K\beta$ filter. Data acquisition was collected at 2θ range of 20° - 100°, with step size of 0.02° 2θ (4000 data points) and scan speed of 1 second per data. Due to LYNXEYE-XET PSD's advantage, each sample only needs a short acquisition time of about 6 minutes. The XRD data were analysed using Bruker – EVA v5.1 phase identification (ICDD PDF-4+ database) and Bruker – Topas v.6 for Rietveld refinement. The phase data is processed by using phase ID software EVA v5.1 and QPA software Bruker-Topas v6. The Fe3O4 nanoparticle samples' magnetic properties are characterized using Electromagnetic Dexing Magnet Tech VSM250 (Banten, Indonesia). The structural characterization of Fe_3O_4 nanomaterials is performed by using a D-8 diffractometer (Bandung, Indonesia) involving a Cu Kα radiation source (λ = 1.5405 Å) with radiation beams between the Bragg angles of 20˚ to 100˚.

RESULTS AND DISCUSSION

Structural Analysis

There is a good agreement between the experimental data of the Rietveld refinement[28] of Fe_3O_4 and the simulated pattern from the International Centre for Diffraction Data (ICDD) reference database PDF 04-017-9634 (face-centered cubic Fd-3m;2) as shown in Figure-1. The X-ray graph plot produced by the Bragg reflection also confirmed the finding of a single-phase cubic spinel structure nanoparticle without impurities as previously reported.[29] In this study, the determined crystallite in the Rietveld refinement analysis is based on the fundamental parameter of approach line profile fitting[30-32] that indirectly determined the broadening sample without 2-dimensional defects. The analysis shows that the sample's resulting phase belongs to the Fd3m group (confirmed in ICDD PDF-4), with all samples containing magnetite (Fe_3O_4) without any contaminant. The magnetite nanoparticles' crystal size was confirmed using the intensity peaks with the Miller index result of 311.

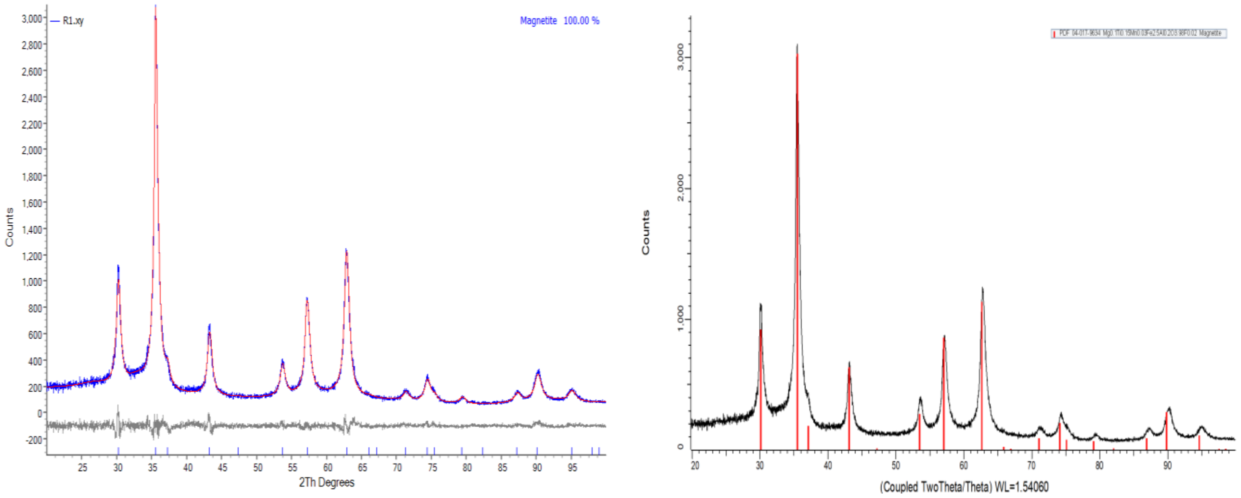
Figure-2 shows a diffractogram generated from the XRD characteristics with 2D XY offset, 2D-view, and peak (311) depiction with 10-isoline levels. A decrease in intensity is shown in the Figure, with the stirring rate elevation from R1 to R3. The value of full-width half maxima (FWHM) is increased from R1 to R3 and decreased from R4 to R5. The sample's crystal size was in the range of 4 to 7 nm for each different variation of the stirring rate. The crystal size is decreased slowly for samples with stirring rates of R1 to R3 with the smallest crystal size of 4 nm (shown in Table-1). However, there was an increase in the nanoparticle crystals' size to 7 nm at the R5 stirring rate. The increase may be due to variations in the stirring rate and different times to form a dry gel of spinel ferrit which prevents particles growth[16] which affected the amount of Fe (ferrite) formation that was different as previously reported.[33]

Crystal lattice parameters are calculated through the following Equation-5 and summarized in Table-1.

$$a = d\sqrt{h^2 + k^2 + l^2}\ \text{Å} \qquad (5)$$

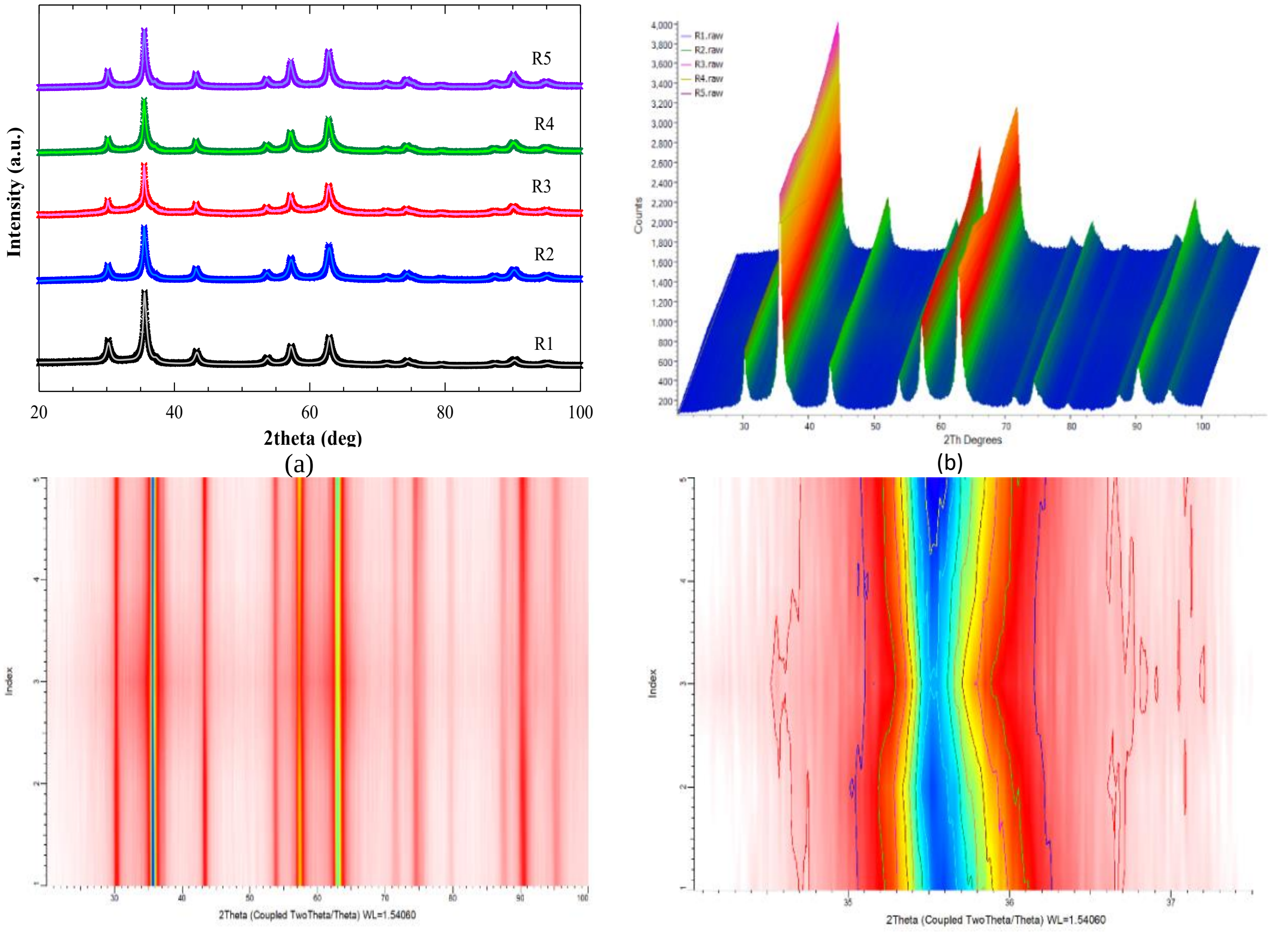
where α is the lattice constant, where (hkl) is the miller's index, and d is the distance between the lattices. The resulting lattice parameter has a lower value than the bulk size of Fe_3O_4, and this is due to the presence of slight oxidation of Fe^{2+} ions on the surface of magnetite nanoparticles

Crystallite size is closely related to particle size. When the particles are in the order of nanometers, the particles will tend to have a single domain that makes their crystallite size is the same as the particle size. However, when the particle size is large enough to form a polycrystalline, the particle size may be larger than the crystallite size. Therefore, further research is needed to produce Fe_3O_4 nanoparticles with suitable particle sizes in the biomedical field.



(a) (b)

Fig.-1: (a) Analysis of nanoparticle Fe_3O_4 with Bruker-EVA,
(b) Rietveld quantitative analysis nanoparticle Fe_3O_4 with Bruker-Topas



(a) (b)

(c) (d)

Fig.-2**:** Diffractograms nanoparticle Fe_3O_4 of (a) Rietveld refinement, (b) 2D xy-offset, (c) 2D- view and (d) peak (311) with 10-isoline level

Table-1: Values of crystallite size, the goodness of fitting, R-Bragg, lattice parameter (a), X-ray density (dx), and hopping length at a tetrahedral site (A-site) and octahedral site (B-site).

Sample (rpm value)	The crystallite size (nm)	χ^2	R-Bragg	Lattice parameter (Å)	d_x [g/cm^3]	V (Å^3)	d_A (Å)	d_B (Å)
R1 (270)	7.762	1.00	0.759	8.355446	4.930	583.327	3.618023	2.954104
R2 (320)	7.068	1.35	0.667	8.3552[28]	4.931	583.289	3.617946	2.95404
R3 (370)	4.165	1.13	0.494	8.322829	4.989	576.518	3.603891	2.942565
R4 (420)	6.886	1.07	0.372	8.293374	5.042	570.411	3.59112	2.932138
R5 (470)	7.731	1.06	0.326	8.315418	5.002	574.979	3.600682	2.939944

χ^2: The goodness of fitting, d_x: X-ray density, V: The volume of a unit cell, d_A: Hopping length at a tetrahedral site, d_B: Hopping length at an octahedral site.

Figure-3 shows that the lattice parameter decreases with increasing the stirring rate, but the lattice parameter increases after the stirring rate of 470 rpm (R5). The lattice parameters' decrease can be attributed to Fe^{3+} ions from a tetrahedral site (site A) to an octahedral site (site B). The reduction of lattice parameters is also due to Fe^{3+}, which is superior to Fe^{2+} even though its sufficient nuclear charge is the same (0.64Å). However, the number of electrons in Fe^{2+} is more than in Fe^{3+}. The outer electrons in Fe^{3+} are attracted to it so that the radius of Fe^{2+} is more significant, which causes a decrease in lattice parameters accompanied by an increasing amount of Fe^{3+}.

X-ray density or called crystal density (dx), is obtained through the following formulation at Equation-6,[34]

$$\text{X} - \text{ray density } (\mathrm{d_x}) = \frac{[\text{molecular weight x Number of molecules per unit cell}]}{[\text{Volume of unit cell x Avogadro's number}]} \qquad (6)$$

Figure-3 showed an inverse relationship between the lattice parameter and the X-ray density in the increasing stirring rate[26]. The X-ray density of magnetite nanoparticles is recorded in Table-1, namely at 4.9 g cm^{-3} to 5.0 g cm^{-3}. Compared to this study, another study has reported a different density of 5.2 g/cm^3,[35] which can be explained due to the larger crystallite size in the resulting sample in this study that creates a heavier molecular weight. The unit cell volume is obtained through the following Equation-7,

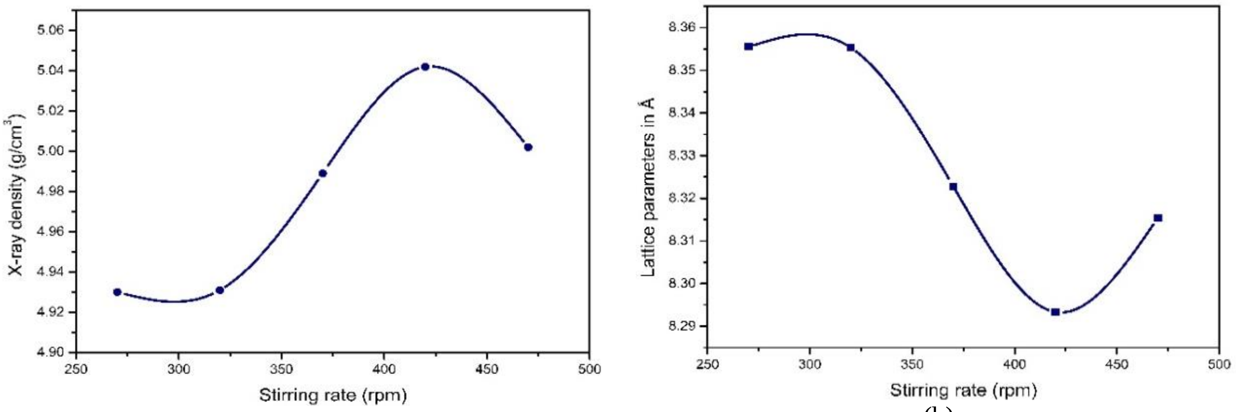
$$V = a^3 \ (\text{Å}^3) \qquad (7)$$

with the value shown in Table-1. It is shown that the unit cell volume value decreases with the increase of the stirring rate because the volume of the unit cell depends on the decrease of the lattice parameter (a).

The distance between the magnetic ion at the octahedral and the tetrahedral site is called the length of the jump at site A (tetrahedral) and site B (octahedral). The jump length values for site A and site B follow the following Equation 8 for each site,

$$d_B = 0.25\, a\sqrt{2} \qquad d_A = 0.25\, a\sqrt{3} \qquad (8)$$

where α is the lattice parameter.[36] Table-1 shows the value of each site's jump length, indicating the importance of site A at 3.6 Å and site B at 2.9 Å. These results match the results in the report of Rani et al.[35] The distance between the magnetic ions (jump length) at the tetrahedral and octahedral sites is decreased with the increase of the stirring rate due to the number of Fe^{3+} ions formed. The Fe^{3+} ion has a smaller ionic radius than the Fe^{2+} ion because fewer electrons are around it. The outer electrons tend to be attracted inward, making the magnetic ions closer to another, reducing the jump length.



(a) (b)

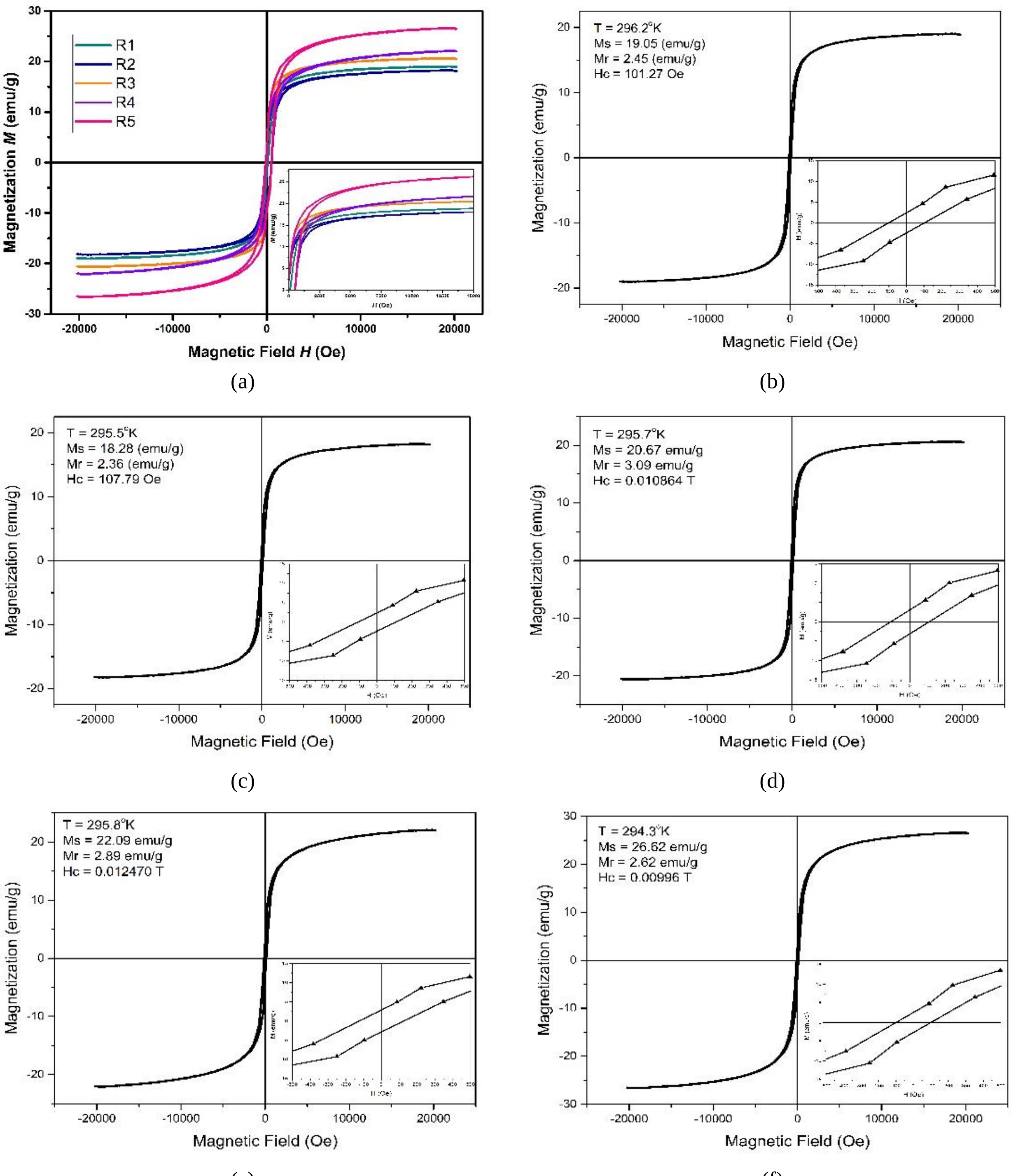
Fig.-3: (a) Plot graph X-ray density (dx) at a various stirring rate, (b) Plot graph lattice parameter at a various stirring rate

Magnetic Properties

The sample hysteresis loop was obtained via a vibrating sample magnetometer (VSM). The hysteresis loop is used to determine the magnetic properties of the sample from the synthesis process. Each VSM sample is measured at room temperature, as shown in Figure-4. The magnetic stirring rate variation results in a hysteresis loop with the magnetic saturation value (Ms), increasing the stirring rate. The greater the stirring speed, the resulting coercivity field (Hc) tends to increase, and when the stirring speed is 470 rpm (R5), the Hc drops significantly. In an experiment by Goya et al.,[37] Hc will decrease with decreasing particle size. The Ms value increases due to the increase in the mass of the nanoparticles due to surface interactions. The interaction surface disturbance is caused by the spin magnetic moment and the inversion disturbance of the spinel structure coupled with an increase in the weight volume of Fe_3O_4 nanoparticles.[38]

The Magnetization properties are shown in Figure-5. at the stirring rate of R1, the Ms value decreased. Ms value if the sample size of the nanoparticles is small, the particles will tend to have a single domain, which means that the magnetic moment can quickly return to its original state when the external magnetic field is released.[39] According to the previous study,[40] the decrease in Ms value was caused by the size of the ultrafine particles, the monodisperse of particles, abnormalities on the nanoparticle samples' surface, and the presence of cation distribution.

The magnetization plot with an applied magnetic field (M-H) shows superparamagnetic properties. In Table-2., it is known that the samples show close to zero coercivity values at room temperature, meaning that when the sample is placed in an external magnetic field, the sample cannot hold the residual magnet when the magnetic field is released. According to a study conducted previously,[41] values of zero coercivity are superparamagnetic characteristics. If the magnetic material has a particle size smaller than the critical superparamagnetic size (25 nm); these particles will exhibit superparamagnetic properties.[42] In another study report by Chatterjee et al.,[43] Fe_3O_4 nanoparticles measuring below 15 nm will have a single magnetic domain, which means that the particles have uniform magnetization.



(a) (b)

(c) (d)

(e) (f)

Fig.-4: (a) Magnetic hysteresis loop with the value of magnetic saturation (emu/g), remanent magnetization (emu/g), and coercivity field (T) at (b) 270 rpm, (c) 320 rpm (d) 370 rpm, (e) 420 rpm, (f) 470 rpm.

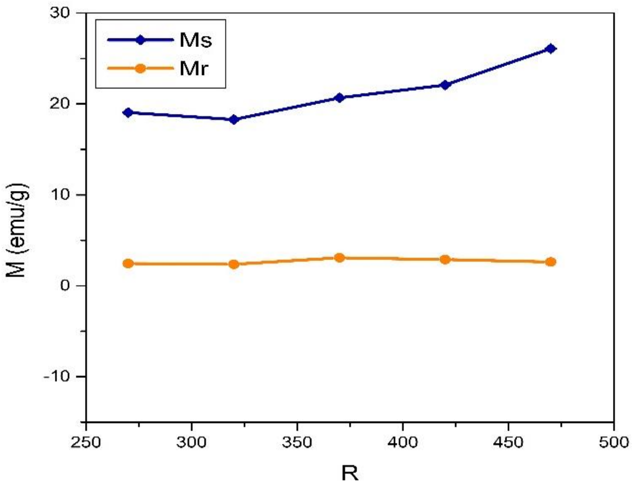


Fig.-5: The magnetization remanent and saturation magnetic properties at a various stirring rate

Table-2 Values of magnetic saturation (Ms), remanent magnetization (Mr), coercivity field (Hc), and the correlation with crystallite size

Stirring rate	Magnetic Properties		
	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
R1	19.05	2.45	101.27
R2	18.28	2.36	107.79
R3	20.67	3.09	108.64
R4	22.09	2.89	124.70
R5	26.62	2.62	99.60

The magnetic saturation value produced by the sample is smaller than the magnetic saturation value in the Fe_3O_4 bulk (88-92 emu/g).[24,44] Fe_3O_4 nanoparticles as biomedicine applications must have a Ms value in the range of 5-20 emu/g[3]. In another study, Brusentsov et al.[45] stated that Ms values of around 7-22 emu/g could be used for biomedical applications. This statement is supported by Ma et al.,[46] that a magnetic saturation of 16.3 emu g^{-1} tends to be sufficient to separate Fe_3O_4 magnetic nanoparticles from water when an external magnetic field is applied. Particles that have a nanoscale size have physical and chemical properties that describe the characteristics of their atoms.[47] Experiments of Zhang et al.,[48] stated that changes in nanoparticles' magnetic properties are based on two factors, namely changes in size and changes in the state of the surface layer of nanoparticles. The quantum effect of nanoparticles and the nanoparticles' magnetic surface area will change their magnetic properties. The changes indicate a superparamagnetic phenomenon, namely quantum magnetization, showing that the particles are considered a single magnetic domain.[37] Superparamagnetic nanomaterials have a high potential for biomedical applications due to their unique physical, thermal, mechanical, chemical, and mesoscopic properties.[49]

CONCLUSION

Synthesis of Fe_3O_4 nanoparticles by co-precipitation method using natural iron sand as a starting material has been successfully carried out to produce Fe_3O_4 nanoparticle powder. A stirring rate affects the decrease in lattice parameters but increases the X-ray density. Magnetite nanoparticles at 370 rpm had the smallest crystal size of 4.156 nm and Ms value of 20.67 emu g-1. These Fe_3O_4 nanoparticles have near-zero coercive fields in superparamagnetic magnets and standard Ms values, making them potential biomedical applications.

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Title of Manuscript: Diffraction and Magnetization Properties Of Fe_3O_4 Nanoparticle from Natural Iron Sand in Various Stirring Rate for Potential Biomedical Applications

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DIFFRACTION AND MAGNETIZATION PROPERTIES OF Fe_3O_4 NANOPARTICLE FROM NATURAL IRON SAND IN VARIOUS STIRRING RATE FOR POTENTIAL BIOMEDICAL APPLICATIONS

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ABSTRACT

This study aims to determine the effect of synthetic stirring rate on the diffraction and magnetization properties of Fe_3O_4 nanoparticles. Materials made from natural iron sand were synthesized using the co-precipitation method with variations in stirring rate 270 to 470 rpm. At stirring up to 370 rpm (R3), the crystalline size of Fe_3O_4 decreases. Increasing the stirring rate caused the lattice parameters to decrease in the range of 8.3 A° and the X-ray density to increase in the range of 5.0 g cm^{-3}. The structure formed indicates that the sample contains 100% magnetite nanoparticles without any contaminants. The magnetite nanoparticles in this experiment with the smallest crystal size of 4.156 nm and the Ms value of 20.67 emu g^{-1} with a Hc value close to zero superparamagnetic, have the potential for future biomedical applications.

Keywords: Superparamagnetic, Iron Sand, Diffraction, Stirrer Rate, Co-precipitation.

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INTRODUCTION

Nanoparticles have broad applications for various fields of nanoparticles as biomedical applications.[1,2] Fe_3O_4 is known as the transition in metal oxides with strong magnetic properties. Fe_3O_4 nanomaterials are unique materials due to their magnetic properties, low toxicity, biodegradability, catalytic, biocompatibility, high magnetization saturation, low Currie temperature, and superparamagnetic behavior.[3-5] Because of these properties, magnetite nanomaterials are suitable for use in medical applications. Some applications of magnetite nanomaterials are neutron cancer therapy,[6,7] antibacterial applications,[8] drug delivery,[4,9] contrast magnetic resonance imaging (MRI) agents,[10-12] hyperthermia application,[13] and analysis of uric acid content.[14] The applications of magnetite nanomaterials are increasing, especially for their potential in biomedical applications.

Iron sand is a natural material containing iron, commonly called magnetite, which exists along the coastline. As an archipelago, Indonesia has the advantage of abundant natural iron sand resources.[15] Elements contained in natural iron sand include Fe_2O_3, TiO_2, Al_2O_3, and MnO_2. The low utilization of natural iron sand as a source of material for Fe_3O_4 formation is due to the complicated synthesis process and many costs. Therefore, the necessity to optimize the use of natural iron sand as the initial material for synthesizing Fe_3O_4 nanoparticles is still needed.

Co-precipitation is a fast, easy, efficient and affordable method of producing nanomaterials. Fe_3O_4 particle size can be controlled using this method.[16] Many studies have reported the advantage of the technique in producing Fe_3O_4 nanoparticles.[17-19] However, a suitable synthesis composition in the co-precipitation method to produce Fe_3O_4 nanoparticles from natural iron sand is still a challenge as a potential material in

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biomedical applications. The Fe_3O_4 nanoparticles' specific properties are needed in biomedical applications, such as biocompatibility, nano-size, low toxicity, high magnetic saturation, sterically and electrostatically stable, not agglomerated, and superparamagnetic.[20]

Several researchers have previously synthesized Fe_3O_4 with various developments, including varying the degree of acidity (pH),[21] adding stabilizing agents,[22] changing the heating rates,[23] or altering the temperature during the calcination process.[24,25] Hidayanto et al[15] synthesized Fe_3O_4 from natural iron sand, using a sonochemical method by varying sonication time. Nalle et al[26] and Wulandari et al[27] synthesized Fe_3O_4 using the co-precipitation method from commercial materials by varying polymer, oleic acid (OA) and chitosan as stabilizers agents on the surface of nanoparticles. Magnetization properties of their nanoparticles were measured using electron spin resonance (ESR). Kamakshi et al[16], also synthesized Fe_3O_4 nanomaterial using a stirring rate of 900 rpm, for catalyst or biomedical diagnosis.

However, a study about the variation in lower stirring rate (under 500 rpm) during the synthesis process of Fe_3O_4 nanoparticles has not been reported, mainly to produce its specific properties for biomedical applications. Therefore, this study aims to synthesize Fe_3O_4 nanoparticles with various stirring rates using natural iron sand as its initial material via the co-precipitation method. This paper profoundly discusses the diffusion and magnetization properties of the synthesis process at an optimum stirring rate to make the crystallite size of Fe_3O_4 nanoparticles suitable for biomedical applications.

EXPERIMENTAL

Preparation and Synthesis Process of Fe_3O_4 Nanoparticles

Natural iron sand from Kulon Progo beach is used to synthesize Fe_3O_4 nanoparticles. Figure-1 explains the co-precipitation method that used 37% hydrochloric acid (HCl) (Mallinckrodt Baker, Paris, USA), ammonium hydroxide (NH_4OH) (Merck KGaA, Darmstadt, Germany), and distilled water to wash the synthesis product. The raw material of Fe_3O_4 nanoparticles from the natural iron sand is acquired firstly by filtering the sand using gauzes with a specific mesh size to separate the sand from its remaining impurities. A magnet bar is used to extract the sand from its organic contaminants before washing and drying. The resulting iron sand becomes the material in the synthesis process of Fe_3O_4 nanoparticles using the co-precipitation method with varying the synthesis's stirring rate.

30 ml Hydrochloric acid is prepared using a magnetic stirrer. Natural iron sand is dissolved in HCl for 6 hours with a magnetic stirrer rate variation of 270 rpm (R1), 320 rpm (R2), 370 rpm (R3), 420 rpm (R4), and 470 rpm (R5). The suspension results are iron sand deposits and a solution containing Fe_3Cl, Fe_2Cl, Fe_2O_3, H_2O, and H_2 gases. The suspension results are then filtered using a filter paper to obtain ferric chloride ($FeCl_3$). The filtering process is also used to avoid the incomplete decomposed iron sand to form maghemite (Fe_2O_3) and follow the chemical formulation**.** The colloids are added in NH_4OH solution with a ratio of 1:1 to form Fe_3O_4 compounds. The base solution's addition will undergo an exothermic reaction to create pure Fe_3O_4 and NH_4Cl salts. The sample result is then washed with distilled water to dissolve the remaining salt from the pure Fe_3O_4 and stabilize the pH until it reaches a neutral pH. The resulting black Fe_3O_4 deposit is tested using a permanent magnet to see the produced magnet's properties. The obtained ferrofluid was then dried using a furnace for 2 hours at 175 ^{o}C. The drying temperature is set not to be too high to avoid an unwanted Fe_2O_3 compound in the sample**.** The chemical formulation of the process is described as follow:

Natural iron sand dissolves process

$$3Fe_3O_4 + 8HC \rightarrow FeCl_2 + 2FeCl_3 + 3Fe_2O_3 + 3H_2O + H_2 \tag{1}$$

Filtrating the sample

$$FeCl_2 + 2FeCl_3 + 3Fe_2O_3 + 3H_2O \rightarrow FeCl_2 + 2FeCl_3 + H_2O \tag{2}$$

$$FeCl_2 + 2FeCl_3 + H_2O + 8NH_4OH \rightarrow nano - Fe_3O_4 + 8NH_4Cl + 5H_2 \tag{3}$$

Washing the sample using distilled water

$$Nano - Fe_3O_4 + 2H_2O \rightarrow Nano - Fe_3O_4 + 2H_2 + O_2 \tag{4}$$

Characterization of Nanoparticles Fe_3O_4

X-ray diffraction (XRD) characterization of the sample is conducted by using Bruker D8 Advance diffractometer with an operated Cu X-ray anode at 1.6 kW (40 kV, 40 mA), line focus of 0.04 x 8 mm, arm radius of 250 mm (primary and secondary), divergence slit of 1°, Soller slit of 2.5° (primary and secondary) and LYNXEYE-XET position-sensitive detector (PSD) without $K\beta$ filter. Data acquisition was collected at 2θ range of 20° - 100°, with a step size of 0.02° 2θ (4000 data points) and a scan speed of 1 second per data. Due to LYNXEYE-XET PSD's advantage, each sample only needs a short acquisition time of about 6 minutes. The XRD data were analyzed using Bruker – EVA v5.1 phase identification (ICDD PDF-4+ database) and Bruker – Topas v.6 for Rietveld refinement. The phase data is processed by using phase ID software EVA v5.1 and QPA software Bruker-Topas v6. The Fe3O4 nanoparticle samples' magnetic properties are characterized using Electromagnetic Dexing Magnet Tech VSM250 (Banten, Indonesia). The structural characterization of Fe_3O_4 nanomaterials is performed by using a D-8 diffractometer (Bandung, Indonesia) involving a Cu Kα radiation source (λ = 1.5405 Å) with radiation beams between the Bragg angles of 20˚ to 100˚.

RESULTS AND DISCUSSION

Structural Analysis

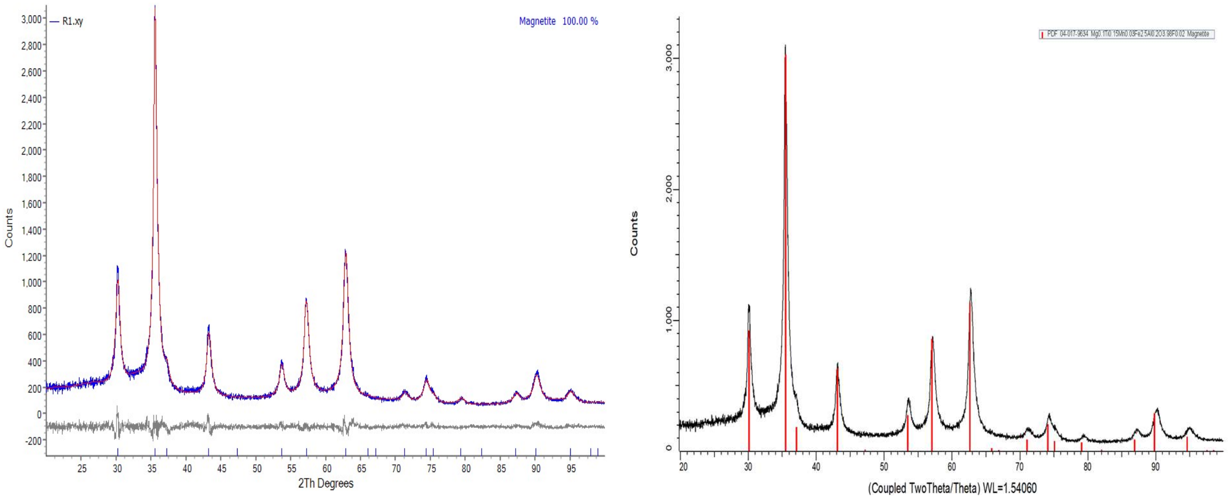
There is a good agreement between the experimental data of the Rietveld refinement[28] of Fe_3O_4 and the simulated pattern from the International Centre for Diffraction Data (ICDD) reference database PDF 04-017-9634 (face-centered cubic Fd-3m;2) as shown in Fig.-1. The X-ray graph plot produced by the Bragg reflection also confirmed the finding of a single-phase cubic spinel structure nanoparticle without impurities as previously reported.[29] In this study, the determined crystallite in the Rietveld refinement analysis is based on the fundamental parameter of approach line profile fitting[30-32] that indirectly determined the broadening sample without 2-dimensional defects. The analysis shows that the sample's resulting phase belongs to the Fd3m group (confirmed in ICDD PDF-4), with all samples containing magnetite (Fe_3O_4) without any contaminant. The magnetite nanoparticles' crystal size was confirmed using the intensity peaks with the Miller index result of 311.

Figure-2 shows a diffractogram generated from the XRD characteristics with 2D XY offset, 2D-view, and peak (311) depiction with 10-isoline levels. A decrease in intensity is shown in the Figure, with the stirring rate elevation from R1 to R3. The value of full-width half maxima (FWHM) is increased from R1 to R3 and decreased from R4 to R5. The sample's crystal size was in the range of 4 to 7 nm for each different variation of the stirring rate. The crystal size is decreased slowly for samples with stirring rates of R1 to R3 with the smallest crystal size of 4 nm (shown in Table-1). However, there was an increase in the nanoparticle crystals' size to 7 nm at the R5 stirring rate. The increase may be due to variations in the stirring rate and different times to form a dry gel of spinel ferrit which prevents particle growth[16] which affected the amount of Fe (ferrite) formation that was different as previously reported.[33]

Crystal lattice parameters are calculated through the following Equation-5 and summarized in Table-1.

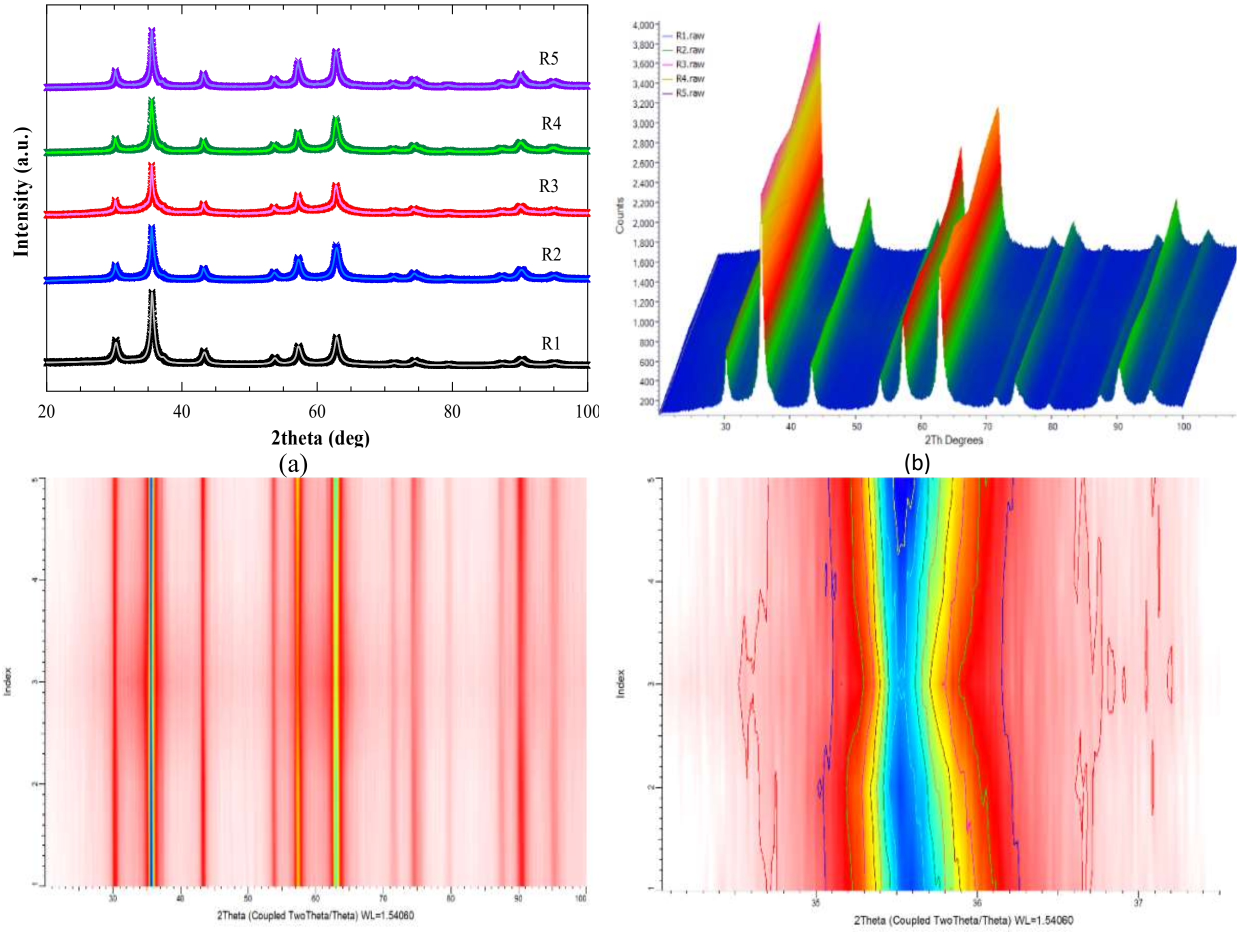
$$a = d\sqrt{h^2 + k^2 + l^2}\ \text{Å} \tag{5}$$

Where, α is the lattice constant, where (hkl) is the miller's index, and d is the distance between the lattices. The resulting lattice parameter has a lower value than the bulk size of Fe_3O_4, and this is due to the presence of slight oxidation of Fe^{2+} ions on the surface of magnetite nanoparticles Crystallite size is closely related to particle size. When the particles are in the order of nanometers, the particles will tend to have a single domain that makes their crystallite size is the same as the particle size. However, when the particle size is large enough to form a polycrystalline, the particle size may be larger than the crystallite size. Therefore, further research is needed to produce Fe_3O_4 nanoparticles with suitable particle sizes in the biomedical field. Figure-3 shows that the lattice parameter decreases with increasing the stirring rate, but the lattice parameter increases after the stirring rate of 470 rpm (R5). The lattice parameters' decrease can be attributed to Fe^{3+} ions from a tetrahedral site (site A) to an octahedral site (site B). The reduction of lattice parameters is also due to Fe^{3+}, which is superior to Fe^{2+} even though its sufficient nuclear charge is the same (0.64Å). However, the number of electrons in Fe^{2+} is more than in Fe^{3+}.



(a) (b)

Fig.-1: (a) Analysis of Nanoparticle Fe_3O_4 with Bruker-EVA,
(b) Rietveld Quantitative Analysis Nanoparticle Fe_3O_4 with Bruker-Topas



(a) (b)

(c) (d)

Fig.-2**:** Diffractograms Nanoparticle Fe_3O_4 of (a) Rietveld Refinement, (b) 2D xy-offset, (c) 2D- View and (d) Peak (311) with 10-isoline Level

The outer electrons in Fe^{3+} are attracted to it so that the radius of Fe^{2+} is more significant, which causes a decrease in lattice parameters accompanied by an increasing amount of Fe^{3+}.

X-ray density or called crystal density (dx), is obtained through the following formulation at Eqn.-6,[34]

$$\text{X}-\text{ray density }(\text{d}_\text{x}) = \frac{[\text{molecular weight x Number of molecules per unit cell}]}{[\text{Volume of unit cell x Avogadro's number}]} \qquad (6)$$

Table-1: Values of Crystallite Size, the Goodness of fitting, R-Bragg, Lattice Parameter (a), X-ray Density (dx), and hopping length at a Tetrahedral Site (A-site) and Octahedral Site (B-site).

Sample (rpm Value)	The Crystallite Size (nm)	χ^2	R-Bragg	Lattice Parameter (Å)	d_x [g/cm^3]	V (Å^3)	d_A (Å)	d_B (Å)
R1 (270)	7.762	1.00	0.759	8.355446	4.930	583.327	3.618023	2.954104
R2 (320)	7.068	1.35	0.667	8.3552^{28}	4.931	583.289	3.617946	2.95404
R3 (370)	4.165	1.13	0.494	8.322829	4.989	576.518	3.603891	2.942565
R4 (420)	6.886	1.07	0.372	8.293374	5.042	570.411	3.59112	2.932138
R5 (470)	7.731	1.06	0.326	8.315418	5.002	574.979	3.600682	2.939944

χ^2: The goodness of fitting, d_x: X-ray density, V: The volume of a unit cell, d_A: Hopping length at a tetrahedral site, d_B: Hopping length at an octahedral site.

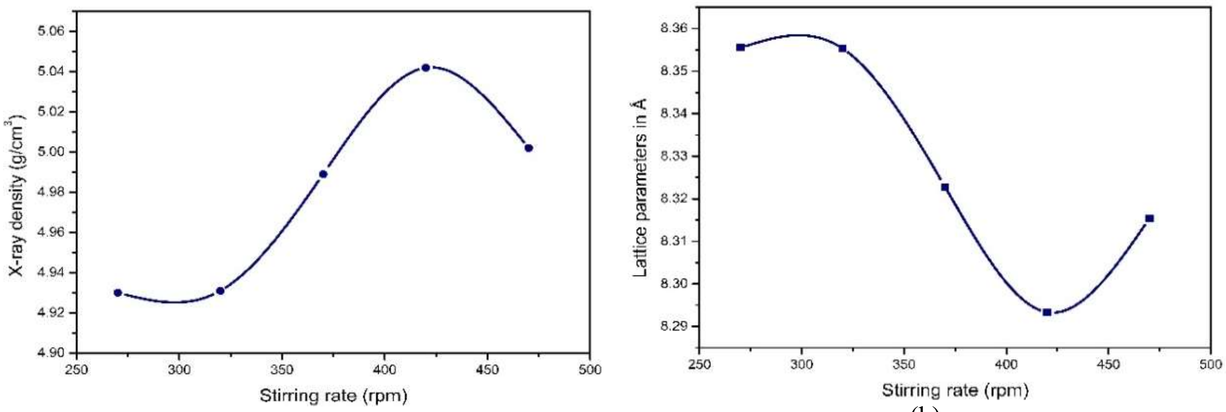
Figure-3 showed an inverse relationship between the lattice parameter and the X-ray density in the increasing stirring rate[26]. The X-ray density of magnetite nanoparticles is recorded in Table-1, namely at 4.9 g cm^{-3} to 5.0 g cm^{-3}. Compared to this study, another study has reported a different density of 5.2 g/cm^3,[35] which can be explained due to the larger crystallite size in the resulting sample in this study that creates a heavier molecular weight. The unit cell volume is obtained through the following Eqn.-7,

$$V = a^3 \ (\text{Å}^3) \qquad (7)$$

with the value shown in Table-1. It is shown that the unit cell volume value decreases with the increase of the stirring rate because the volume of the unit cell depends on the decrease of the lattice parameter (a). The distance between the magnetic ion at the octahedral and the tetrahedral site is called the length of the jump at site A (tetrahedral) and site B (octahedral). The jump length values for site A and site B follow the following Eqn.-8 for each site,

$$d_B = 0.25\, a\sqrt{2} \qquad d_A = 0.25\, a\sqrt{3} \qquad (8)$$

Where α is the lattice parameter.[36] Table-1 shows the value of each site's jump length, indicating the importance of site A at 3.6 Å and site B at 2.9 Å. These results match the results in the report of Rani et al.[35] The distance between the magnetic ions (jump length) at the tetrahedral and octahedral sites is decreased with the increase of the stirring rate due to the number of Fe^{3+} ions formed. The Fe^{3+} ion has a smaller ionic radius than the Fe^{2+} ion because fewer electrons are around it. The outer electrons tend to be attracted inward, making the magnetic ions closer to another, reducing the jump length.



(a) (b)

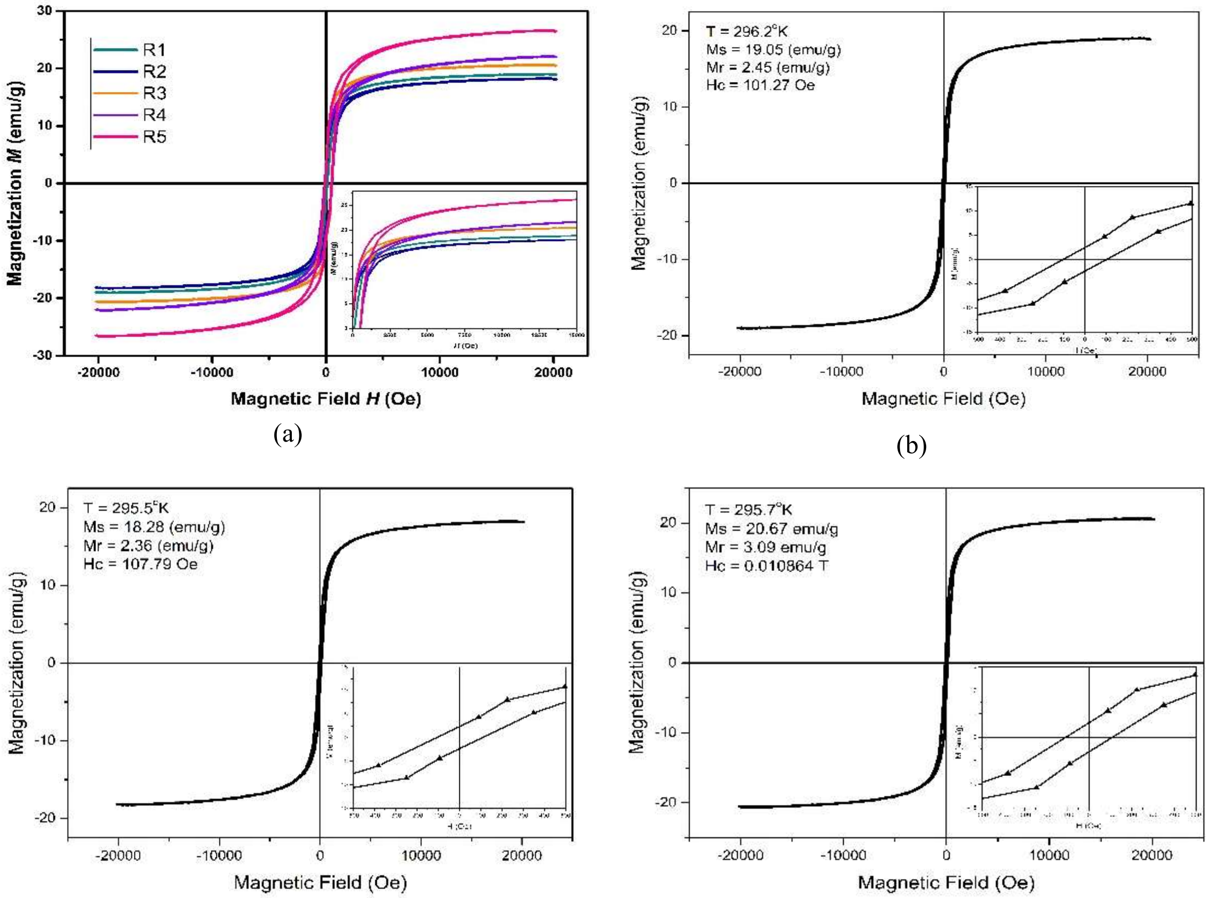
Fig.-3: (a) Plot Graph X-ray Density (dx) at a Various Stirring Rates, (b) Plot Graph Lattice Parameter at a Various Stirring Rate

Magnetic Properties

The sample hysteresis loop was obtained via a vibrating sample magnetometer (VSM). The hysteresis loop is used to determine the magnetic properties of the sample from the synthesis process. Each VSM sample is measured at room temperature, as shown in Fig.-4. The magnetic stirring rate variation results in a hysteresis loop with the magnetic saturation value (Ms), increasing the stirring rate. The greater the stirring speed, the resulting coercivity field (Hc) tends to increase, and when the stirring speed is 470 rpm (R5), the Hc drops significantly. In an experiment by Goya et al.,[37] Hc will decrease with decreasing particle size. The Ms value increases due to the increase in the mass of the nanoparticles due to surface interactions. The interaction surface disturbance is caused by the spin magnetic moment and the inversion disturbance of the spinel structure coupled with an increase in the weight volume of Fe_3O_4 nanoparticles.[38]

The Magnetization properties are shown in Figure-5. at the stirring rate of R1, the Ms value decreased. Ms value if the sample size of the nanoparticles is small, the particles will tend to have a single domain, which means that the magnetic moment can quickly return to its original state when the external magnetic field is released.[39] According to the previous study,[40] the decrease in Ms value was caused by the size of the ultrafine particles, the monodisperse of particles, abnormalities on the nanoparticle samples' surface, and the presence of cation distribution.

The magnetization plot with an applied magnetic field (M-H) shows superparamagnetic properties. In Table-2, it is known that the samples show close to zero coercivity values at room temperature, meaning that when the sample is placed in an external magnetic field, the sample cannot hold the residual magnet when the magnetic field is released. According to a study conducted previously,[41] values of zero coercivity are superparamagnetic characteristics. If the magnetic material has a particle size smaller than the critical superparamagnetic size (25 nm); these particles will exhibit superparamagnetic properties.[42] In another study report by Chatterjee et al.,[43] Fe_3O_4 nanoparticles measuring below 15 nm will have a single magnetic domain, which means that the particles have uniform magnetization.



(a)

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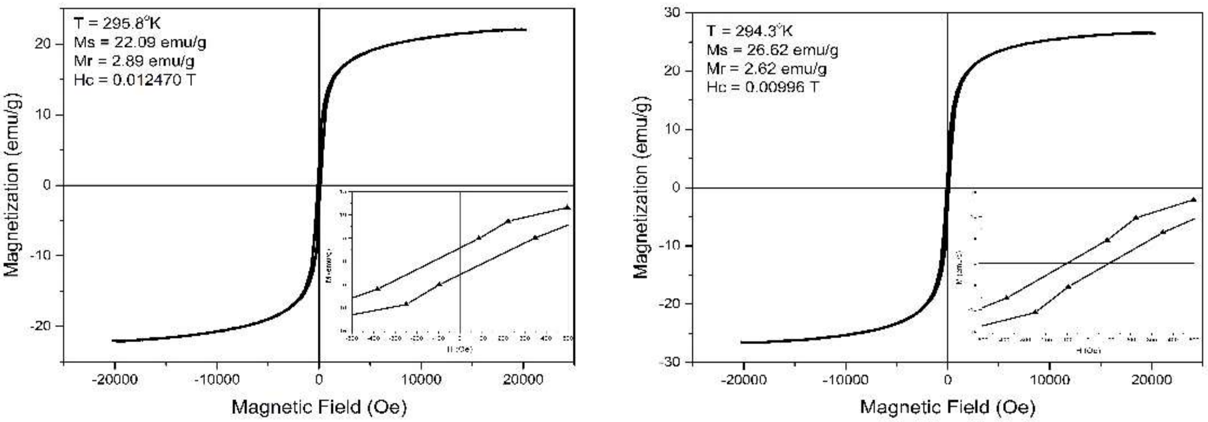

(e) (f)

Fig.-4: (a) Magnetic Hysteresis Loop with the Value of Magnetic Saturation (emu/g), remanent magnetization (emu/g), and Coercivity Field (T) at (b) 270 rpm, (c) 320 rpm (d) 370 rpm, (e) 420 rpm, (f) 470 rpm.

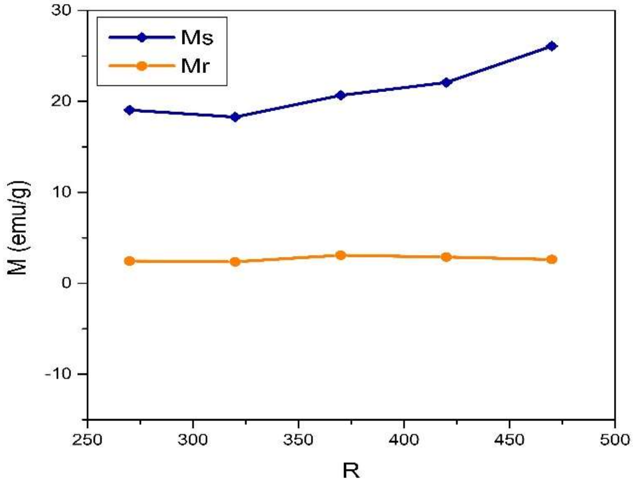

Fig.-5: The Magnetization Remanent and Saturation Magnetic Properties at A Various Stirring Rate

Table-2 Values of Magnetic Saturation (Ms), Remanent Magnetization (Mr), Coercivity Field (Hc), and the Correlation with Crystallite Size

Stirring Rate	Magnetic Properties		
	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
R1	19.05	2.45	101.27
R2	18.28	2.36	107.79
R3	20.67	3.09	108.64
R4	22.09	2.89	124.70
R5	26.62	2.62	99.60

The magnetic saturation value produced by the sample is smaller than the magnetic saturation value in the Fe_3O_4 bulk (88-92 emu/g).[24,44] Fe_3O_4 nanoparticles as biomedicine applications must have a Ms value in the range of 5-20 emu/g[3]. In another study, Brusentsov et al.[45] stated that Ms values of around 7-22 emu/g could be used for biomedical applications. This statement is supported by Ma et al.,[46] that a magnetic saturation of 16.3 emu g^{-1} tends to be sufficient to separate Fe_3O_4 magnetic nanoparticles from water when an external magnetic field is applied. Particles that have a nanoscale size have physical and chemical properties that describe the characteristics of their atoms.[47] Experiments of Zhang et al.,[48] stated that changes in nanoparticles' magnetic properties are based on two factors, namely changes in size and changes in the state of the surface layer of nanoparticles. The quantum effect of nanoparticles and the nanoparticles' magnetic surface area will change their magnetic properties. The changes indicate a superparamagnetic phenomenon, namely quantum magnetization, showing that the particles are considered a single magnetic domain.[37] Superparamagnetic nanomaterials have a high potential for biomedical applications due to their unique physical, thermal, mechanical, chemical, and mesoscopic properties.[49]

CONCLUSION

Synthesis of Fe_3O_4 nanoparticles by co-precipitation method using natural iron sand as a starting material has been successfully carried out to produce Fe_3O_4 nanoparticle powder. A stirring rate affects the decrease in lattice parameters but increases the X-ray density. Magnetite nanoparticles at 370 rpm had the smallest crystal size of 4.156 nm and Ms value of 20.67 emu g-1. These Fe_3O_4 nanoparticles have near-zero coercive fields in superparamagnetic magnets and standard Ms values, making them potential biomedical applications.

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