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Fabrication of Fe_3O_4/PEG 4000/Oleic Acid Ferrofluids on Crystal Structure and Magnetic Properties Using Rhee Sumbawa Iron Sand

Syamsul Bahtiar[1*], Izzul Islam[2], Adella Ulyandana Jayatri[3], Risky Pratama[1], Emsal Yanuar[1], Fauzi Widyawati[1]

[1]Department of Mettalurgy, Faculty of minerals and environment technology, Sumbawa University of Technologi, Sumbawa, Indonesia.
[2]Department of Biotecnology, Faculty of lifescience of technology, Sumbawa University of Technologi, Sumbawa, Indonesia
[3]Department of Physics, Faculty of Mathematics and Natural Sciences
, University of Mataram, Mataram, Indonesia
[*]e-mail: syamsul.bahtiar@uts.ac.id

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Abstract: The fabrication of ferrofluid using Fe_3O_4 nanoparticles synthesized from Rhee Sumbawa iron sand has been successfully carried out. This fabrication was conducted to study the crystal structure characteristics and magnetic properties of the ferrofluid from Rhee iron sand. The fabrication used the co-precipitation method at room temperature to synthesise Fe3O4 nanoparticles. In contrast, the ferrofluid fabrication employed a magnetic stirrer with the addition of PEG 4000/Oleic Acid as a surfactant. The structure and magnetic characteristics of the Fe_3O_4/PEG 4000/AO ferrofluid will be investigated in this work. The results of the XRF characterization show an Fe content of 91.73%, indicating that the purity of Fe has been successfully increased using a permanent magnet separation method. The XRD characterization results show the formation of a cubic crystal system with lattice parameters a=b=c = 9.3797 Å, α=β=γ = 90°, and the crystal size obtained from the refinement is 8.42 nm. The TEM characterization results indicate that the morphology of the nanoparticles is spherical with a particle size of 7.34 nm. The VSM characterization results obtained the ferrofluid magnetization value in the 0.08–0.34 emu/g range.

Keywords: Co-presipitation; Ferrofluids; Fe3O4; Iron Sand; Magnetization.

Introduction

The abundance of natural resources presents a challenge for researchers to conduct in-depth studies on the physical properties, synthesis methods, and applications of the existing natural resources. One of the abundant natural resources currently being studied is the physical properties of iron sand. Iron sand is one of the commodities in demand today because it can be used in various fields[1], [2]. Iron sand in Indonesia is partly located on the island of Sumbawa, specifically on the shores of Rhee Beach [3].

Iron sand, in general, is an iron oxide consisting of the minerals Fe_2O_3, Fe_3O_4, FeTiO, SiO_2, and several other impurities in small amounts [4]. Separating Fe_3O_4 minerals from other minerals presents its own challenge. The selection of the wrong synthesis method will prevent the formation of the Fe_3O_4 phase. Factors such as stoichiometric calculations and other parameters like leaching temperature and solution pH must also be considered [5].

The world of technology is moving towards material sizes on the order of nanometers. Similarly, Fe_3O_4 in the nanometer scale has unique characteristics compared to its bulk form. The superparamagnetic phenomenon is one of the interesting physical properties studied in Fe_3O_4 nanoparticles[6]. This phenomenon arises because the nanoparticles are single-domain, easily influenced by an external magnetic field. Fabricating Fe_3O_4 on the nanometer scale is necessary for synthesis using the appropriate method.

The patented synthesis method used in the synthesis of Fe_3O_4 particles based on iron sand is the coprecipitation method. This method combines the reductive leaching method and precipitation. Researchers often use the coprecipitation method because it has advantages such as being easy to operate and control and can be performed at low temperatures. Some researchers have successfully obtained sizes in the nanometer range using the coprecipitation method [7], [8], [9].

The significance of particle sizes in the nanoscale range is essential for various applications. Fe_3O_4 can be used as a raw material for ferrofluid, a ferromagnetic liquid with a nanometer size[10]. Research on ferrofluids becomes interesting due to their advanced applications in various fields, including energy harvesting[11], [12], [13], magnetic hyperthermia[14], [15], biosensing, and biomedical applications. Further research on ferrofluids needs to be enhanced to discover the wide applications.

The fabrication of ferrofluid can be done using nano Fe_3O_4 particles combined with surfactant liquid as a particle stabiliser and liquid carrier as a ferrofluid stability controller. PEG is one of the surfactants that acts as a stabilizer, . The method enhances colloidal stability and prevents the agglomeration of nanoparticles. It also increases the biocompatibility of the ferrofluid [17].

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Meanwhile, using oleic acid as a coating on Fe_3O_4 nanoparticles provides additional stability and dispersibility in the ferrofluid, which can be used for a long time [18]. Thus, using two surfactants can control the dispersion of nanoparticles in ferrofluid. In addition, these two non-toxic surfactants can be well applied in the biomedical field.

Research Methods

The primary material used in this research is Rhee Sumbawa iron sand. The iron sand was collected from the beach using a permanent magnet. The following are the steps involved in fabricating ferrofluid:

Magnetic Separation

Iron sand is purified using the magnetic separation method. This process is carried out physically using an external magnet. The iron sand is dried in sunlight to facilitate the separation from its impurities. Next, the separation process is done manually using a permanent magnet. This process is repeated until a high concentration of iron sand is obtained, characterized by its black and shiny appearance.

Sintesis Partikel Nano Fe3O4

20 grams of iron sand are prepared and placed in a 250-ml measuring glass for leaching. HCL PA 37% amounting to 60 ml was prepared and poured into the measuring cup containing iron sand. Next, the leaching process is carried out on a magnetic stirrer with a stirring speed of 750 rpm and at room temperature. The reaction equation is as follows [7]:

$$Fe_3O_4+8HCl \rightarrow 2FeCl_3.FeCl_2+4H_2O \quad (1)$$
$$2FeCl_3.FeCl_2+4H_2O+8NH4OH \rightarrow Fe_3O_4+8NH_4Cl+ 8H_2O \quad (2)$$

The leaching process lasts 30 minutes with a constant stirrer speed. Next, the leaching results of iron sand with HCl in the form of filtrate are filtered using filter paper. The obtained FeCl filtrate is prepared again in 15 ml, and a coprecipitation process will be carried out using 30 ml of NH_4OH. NH_4OH is continuously dripped during precipitation until a precipitate of Fe_3O_4 nanoparticles is formed. Next, the precipitate is washed with aquades until it has a neutral pH. After that, the Fe3O4 nanoparticles are collected with the help of filter paper. The final stage of the sample involves drying one part for testing and the other for the ferrofluid fabrication process.

Fabrication of Ferofluida Fe3O4

The fabrication of ferrofluid consists of three components: magnetic nanoparticles, surfactants, and a carrier liquid. The function of the surfactant is to prevent the magnetic nanoparticles from agglomerating. Meanwhile, the carrier fluid serves as a fluid to control viscosity, surface tension, and stability at low temperatures[19]. This study used a double surfactant system, namely PEG 4000 and oleic acid, with aquades as the carrier fluid [12]. The PEG 4000 to oleic acid ratio used in this study was 0.75:0.25 (FF1), 0.5:0.5 (FF2), and 0.25:0.75. (FF3)

Characterization

The characterisation techniques employed in this work include TEM to view the morphology and particle size, VSM to ascertain the magnetization value of Fe_3O_4 nanoparticles, XRF equipment to observe the elemental composition, and XRD to analyze the phases and crystal structure.

Results and Discussion

Analysis of Elemental Composition Results from X-Ray Fluorescence (XRF)

X-ray fluorescence (XRF) analysis was conducted to determine the content of synthetic iron sand using the coprecipitation method, which employs the sample's fluorescence method. The characterization results of Rhee Sumbawa iron sand are presented in Table 1.

Table 1. XRF Characterization Results of Rhee Iron Sand

No	Unsur	Komposisi (%)
1	P	0.35 %
2	Ca	0.80 %
3	Ti	2.65 %
4	V	0.48%
5	Cr	0.13 %
6	Mn	0.94 %
7	Fe	91.73 %
8	Zn	0.06 %
9	Rb	0.56 %
10	Eu	0.61 %
11	Re	0.20 %
12	Bi	0.74 %

Table 1 shows the components of elements resulting from the synthesis of Fe_3O_4 nanoparticles from Rhee Sumbawa iron sand. The results show the highest Fe composition at 91.73%, Ti with a composition of 2.65%, and several other trace elements. The Ti element is always associated with Fe to form the mineral Ilmenite. Researchers from various regions have also reported the high Fe content in iron sand, including Tulung Agung iron sand at 86% [7] and Hais Beach in North Sulawesi at 73% [20] . Unlike the iron sand content from Buton, which is 47%, and Kulon Progo, which is 45%. The separation technique used determines the high Fe content, among other things; repeatedly employing a permanent magnet can increase the Fe content. Sunaryono et al. 2020 reported that the FeTi content increased from 23% to 63% after separation using an external magnet of 0.3 tesla [21]. The increase in Fe content was also successfully achieved from 27.96 to 96.79 using an external magnet[22].

X-Ray Diffraction (XRD) Data Analysis

XRD data is needed to determine the phase, crystal structure, and crystal nano size of Fe_3O_4. The XRD characterization results of Fe_3O_4 from Rhee Sumbawa iron sand is shown in Figure 1.

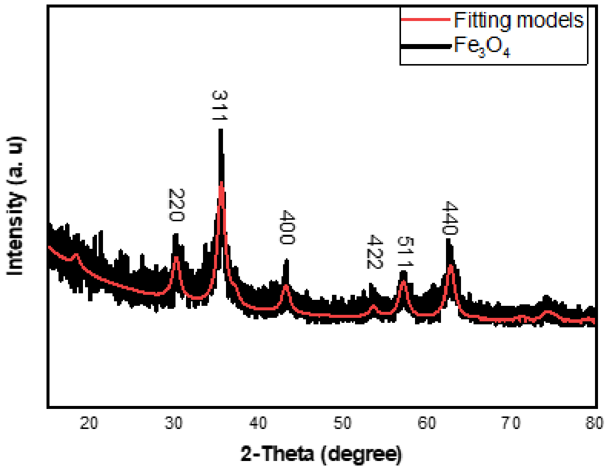

Figure 1. Diffraction pattern of Fe3O4 nanoparticles

Based on the diffraction pattern of Fe_3O_4 in Figure 1, 2 diffraction patterns can be observed, namely the black and red patterns. Both diffraction patterns are the data and the result of the refinement. The diffraction patterns formed correspond to the Miller indices of Fe_3O_4: 220, 311, 400, 422, 511, and 440 [23]. We can also conclude that the synthesized Fe3O4 does not contain impurity phases based on the refinement results. This is in accordance with the XRF data showing the highest Fe content. Quantitative analysis is needed to prove that the data is in accordance with the reference. The reitica software was used for data analysis using reference code 0002402. The results show that Fe_3O_4 forms a system of cubic crystals, space group FD-3M, with lattice parameter values obtained as (a=b=c) = 9.3797 Å, α=β=γ = 90°, while the crystal size from the refinement results is obtained as 8.42 nm. As a comparison, the crystal size can also be calculated using the Debye-Scherer equation as follows [24]:

$$D = \frac{K\lambda}{BCos\theta} \quad (3)$$

D represents the crystal size, K is the constant, λ is the wavelength of the X-ray, B is the FWHM value, and θ is the formed Bragg angle. Based on the equation, the crystal size of the Fe_3O_4 nanoparticles is 5.52 nm.

Analysis of Particle Size Data with Transmission Electron Microscope (TEM)

TEM characterization was performed to measure the diameter of nanoparticles of Fe_3O_4.This technique clearly visualizes the size of metal particles. It uses light sourced from electrons to transmit the size of metal particles easily. The results of the TEM characterization of nanoparticles of Fe_3O_4 are shown in Figure 2.

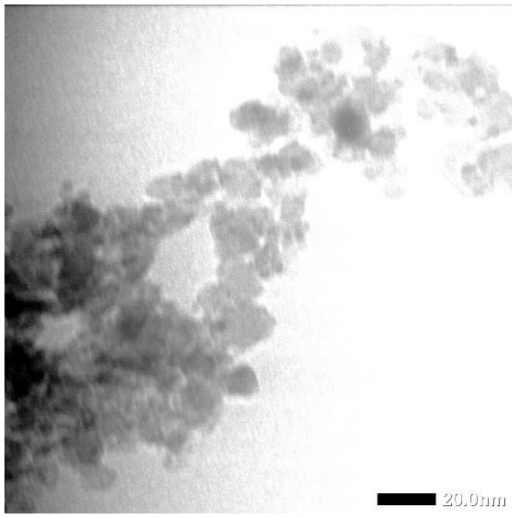

Figure 2. Morphology of Fe_3O_4 nanoparticles

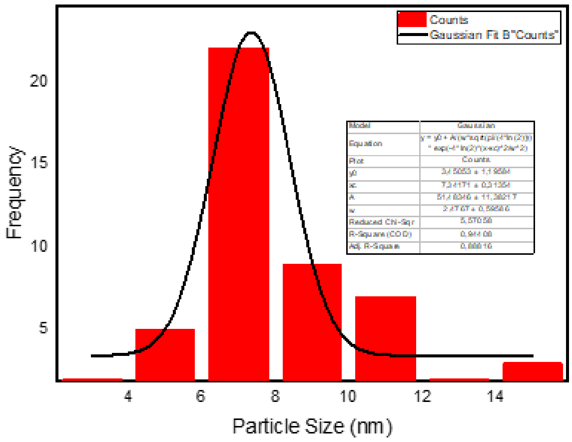

Figure 3. Distribution of nano Fe_3O_4particle size

Figure 2 shows the morphology and particle size of the Fe_3O_4 mineral in powder form. Qualitative analysis shows that the morphology of the Fe_3O_4 nanoparticles is spherical. According to previous research by Bahtiar et al., the shape is caused by using natural sand as the material. Morphology also shows agglomeration caused by the magnetic dipole-dipole attraction between magnetic [25]. In addition, The clustering of Fe3O4 nanoparticles was ascribed to the van der Waals forces acting between the magnetic particles, resulting in aggregates of primary particles[26]. The particle size distribution from the analysis is shown in Figure 3. Quantitative analysis using ImageJ software yielded an average particle size of 7.34 nm. Based on TEM characterization, it can be concluded that the fabrication of Fe3O4 nanoparticles has been successfully carried out and can be applied to ferrofluids.

Magnetic data analysis

The material's magnetic characteristics were identified by VSM analysis. A graph illustrating the correlation between magnetization values and the external field was produced by the VSM test of the Fe_3O_4sample, which was conducted at room temperature and with an external field of 1 T. Figure 4 displays the VSM curve pattern for the Fe3O4/PEG 4000/Ao ferrofluid sample. The

Langevin equation method was used to evaluate the study data. The pattern of the experimental data will be statistically followed using the Langevin equation [27] . Figure 4 shows a hysteresis curve representing the results of the Fe3O4 sample's VSM characterization.

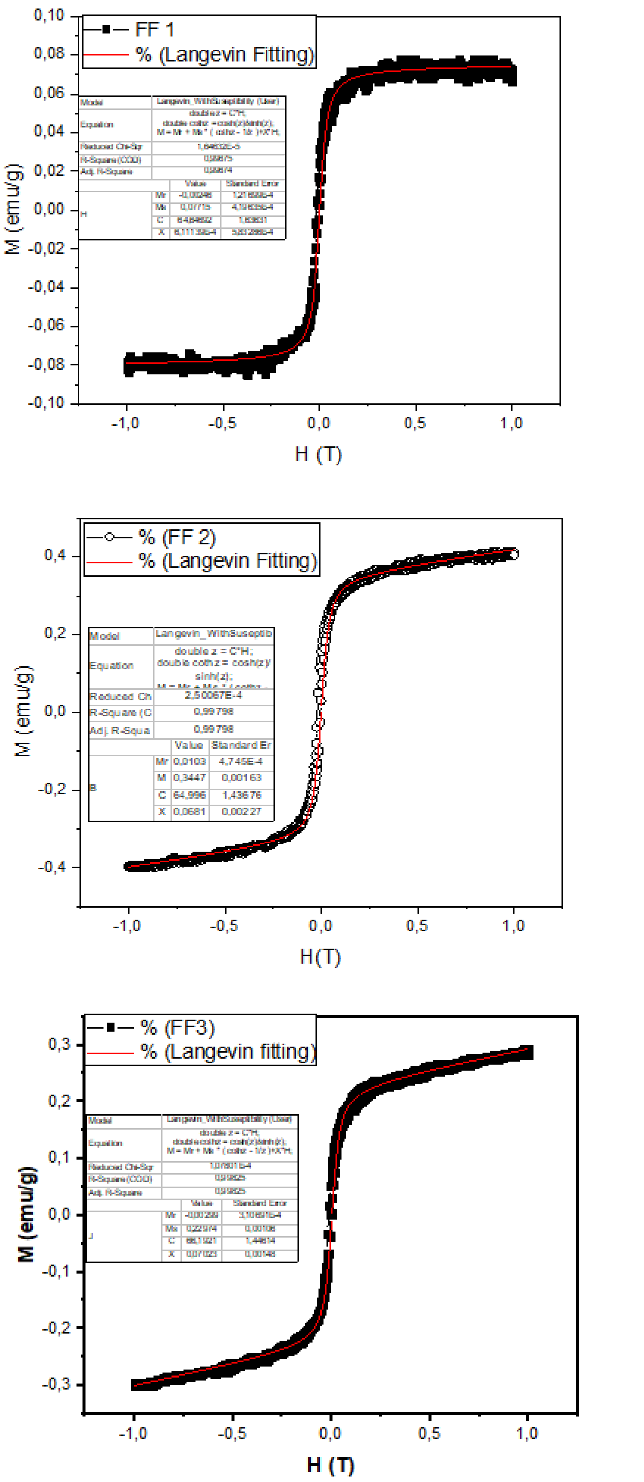

Figure 4. Hysteresis curve of Fe_3O_4/PEG 4000/Ao ferrofluid

Figure 4 is the hysteresis curve of the Fe Fe_3O_4/PEG4000/Ao ferrofluid at room temperature. Qualitative analysis shows that all ferrofluid curves form an S shape, a characteristic that indicates a superparamagnetic pattern. Superparamagnetic curves will appear in magnetic materials with particle sizes on the order of nanometers. The magnetization value of the ferrofluid is relatively lower than that of the solid form due to the nanoparticles in the ferrofluid being single particles affected by surfactants and carrier liquid in the ferrofluid. Futhermore, PEG and magnetite most likely interact because of dipole-cation binding between the polymer's ether group and magnetite's positive charge[28]. The magnetization values for each are FF1 0.08 emu/gr, FF2 0.34 emu/gr, and FF3 0.3 emu/gr. Following a number of research, ferrofluid's magnetization value at room temperature varies between 0.3 and 1 emu/gr[6]. That behaviour is caused by the size of the nanoparticles Fe_3O_4 being in the single domain phase [2]. The remanent magnetization (Mr) value obtained is close to zero, consistent with the behaviour of superparamagnetic materials.

Conclusion

The fabrication of Fe_3O_4/FEG 4000/AO ferrofluid using Rhee Sumbawa iron sand was successfully carried out using the coprecipitation method. The characterization results demonstrate the success of this research. XRD characterization for identification of the Fe_3O_4 phase was successfully confirmed through analysis using reitica, forming a cubic crystal system with lattice parameters a=b=c = 9.3797 Å, α=β=γ = 90°, and a crystal size of about 8.42 nm. VSM characterization for identifying magnetic properties of the Fe3O4/PEG 4000/AO ferrofluid was successfully created with a magnetization value of 0.08–0.34 emu/g. The value of magnetization is influenced by the nanoparticles in the ferrofluid, which are in the form of single particles affected by surfactants. Other physical characteristics of iron sand purity were successfully used using XRF, which amounted to 91.73%. Furthermore, the particle size calculation based on TEM characterisation yielded a size of 7.34 nm.

Contributor Authors

Syamsul Bahtiar: created the experiments, analyzed data, and wrote the paper. Izzul Islam: analyzed data; and wrote the paper. Adella bandana Jayanti: analyzed the data; and wrote the paper. Emsal Yanuar: analyzed the data; and wrote the paper. Fauzi widyawati:analyzed the data; and wrote the paper. Risky pratama : Performed the experiments; Wrote the paper.

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