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Synthesis and characterization of magnetite Fe_3O_4 nanoparticles from natural iron sand in Gelar River

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Abstract

Fe_3O_4 nanoparticles made from the natural iron sands of the Gelar River have been successfully synthesized using the coprecipitation method. Test the content of Fe elements in pure iron sand and characterize them using XRF after separation. Fe_3O_4 nanoparticle characterization uses XRD to determine the sample's lattice parameters and crystal size. The nanoparticles' morphology, structure, particle shape, and elemental content were characterized using SEM-E DX. Magnetic properties and magnetic saturation values are characterized using VSM. XRF yield on iron sand before separation contains Fe 59.46%. After separation, the Fe content rose to 84.72%. The synthesis results obtained brownish-black Fe_3O_4 nanoparticle powder that permanent magnets can attract. Based on the XRD results, the crystal structure formed is cubic inverse spinel with crystal lattice $a = b = c = 8.344$ Å with a particle size of 14.8 nm. The SEM-EDX results show the morphology of spherical nanoparticles with multiple agglomerations. Particle size is 40 nm. The EDX spectrum confirmed the formation of Fe_3O_4 nanoparticles in the presence of Fe (51.79%) and O (25.68%). The VSM results show that Fe_3O_4 samples have ferromagnetic properties with saturation magnetization (MS) = 27.36 emu/g, remanent magnetization (Mr) = -0.01 emu/g, and coercivity field (Hc) = 0.01 T.

Introduction

In the last two decades, nanoparticle research has developed rapidly based on its electrical, catalytic, optical, magnetic, and other physical and chemical properties [1]. Nanoparticles are small particles with sizes between 1 and 100 (nm) that have unique properties due to their small size [2]. Magnetic nanoparticles are one of the nanoparticles that are widely studied because of their unique properties [3]. Types of magnetic nanoparticles are magnetite (Fe_3O_4), wustite (FeO), hematite ($\alpha - Fe_2O_3$), and maghemite ($\gamma - Fe_2O_3$) [4].

Fe_3O_4 is widely applied in various fields such as biomedical applications, imaging in MRI, Drug Delivery Systems, antibacterial, and hyperthermia [5], [6], [7], [8]. Apart from being widely applied in the health sector, Fe_3O_4 is also commonly used in the technological industry, namely as a sensor, radar absorber, adsorbent [9], [10], [11]. Research by Taufiq et al. succeeded in synthesizing Fe_3O_4 based on the natural material of Sine Tulungagung iron sand. This research observed that the crystal size was 16.2 nm with a round shape. Fe_3O_4 was successfully applied as an antifibrotic [12].

Crystal size and morphology are influenced by the Fe_3O_4 nanoparticle synthesis method. Several methods can be used in the synthesis of Fe_3O_4 nanoparticles, including the sol-gel method, solvothermal method, hydrothermal method, sonochemical method, coprecipitation method, microemulsion method, and molten salts method [13]. In this research, researchers used the coprecipitation method. The coprecipitation method was chosen because it makes it easier to obtain Fe_3O_4 powder from iron sand base material at a low cost.

Iron sand is mixed with fine iron ore, resembling natural sand [14]. The iron sand is formed due to the meeting of rivers and seas or estuaries. The material from the river (rocks, gravel, and mountain volcanic ash), which contains magnetic minerals, is retained and deposited around it [13]. Iron sand is usually gray or black [15]. One of the iron sands in the Bali region is the Gelar River iron sand. The Gelar River is one of the tourist areas with the red bridge icon [16]. The Gelar River is in Jembrana district, Bali province, in the hamlet of Gelar Sari, Batuagung. The Gelar River offers views and tranquility, flanked by hills with green valleys and clear water. At several points in the Gelar River area, there are deposits of black sand. These black sand deposits are iron sand deposits that undergo a natural deposition process by water. Iron sand contains the main element Fe, which is abundant in the form of iron oxide minerals, namely magnetite (Fe_3O_4), wustite (FeO), hematite ($\alpha - Fe_2O_3$), dan maghemite ($\gamma - Fe_2O_3$) [17].

Based on this, this research needs to be carried out to determine the mineral content in the Gelar River's iron sand by synthesizing Fe_3O_4 using the coprecipitation method. The Gelar River iron sand before and after separation was characterized using X-ray fluorescence (XRF). Then, the synthesis results were described using X-ray diffraction (XRD) to determine the lattice parameters and size, while to determine the morphology of the Fe_3O_4 synthesis results and elemental content using a Scanning Electron Microscope (SEM-EDX) and to choose the magnetic properties a Vibrating Sample Magnetometer test was carried out (VSM).

Theory and Calculation

Fe_3O_4 nanoparticles are tiny particles with sizes between 1 and 100 (nm) that have unique properties due to their small size [2]. The structure of the Fe_3O_4 nanoparticles can be calculated using the XRD test results and analyzed, which are then used to determine peak intensity, 2θ peak location, lattice parameters ($a = b = c$), and crystallite size (D). The following is Scherer's formula used to calculate the size of the crystalline particles, which can be determined by Equation (1).

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

The hysterical curve is used to determine the properties of magnetism. The hysterical curve is analyzed using the Langevin equation as the Equation (2);

$$M = M_s\left(\coth\left(\frac{\mu H}{k_B T}\right) - \left(\frac{k_B T}{\mu H}\right)\right) \quad (2)$$

M is magnetization, M_s is saturation magnetization (emu/g), μ is the magnetic moment, H is the magnetic field, k_B is the Boltzmann constant $(1.38 \times 10^{-23}\ J/K)$, and T is the Room temperature (K).

Experimental Method

This research includes pure experimental research, leading to materials development, synthesis, and characterization. Synthesis of Fe_3O_4 nanoparticles using the coprecipitation method. The Fe_3O_4 synthesis process follows research by Taufiq et al. [18]. Iron sand is used as the primary source in making Fe_3O_4 nanoparticles. NH_4OH *(Merck)* and HCl *(Merck)* were used without further purification. Distilled water was also used during the experiment. The first stage of iron sand from the Gelar River is separated using a permanent magnet to separate the iron sand from its impurities. The second stage is making $FeCl_2$ and $FeCl_3$. The Gelar River iron sand was dissolved in HCl and stirred using a magnetic stirrer at 450 rpm for 1 hour to form $FeCl_2$ and $FeCl_3$. The third stage is the manufacture of Fe_3O_4. FeCl2 and FeCl3 solutions were titrated with NH4OH using a magnetic stirrer at a speed of 450 rpm for 1 hour so that Fe_3O_4 was formed. The pH of Fe_3O_4 titrated shows acidic properties, so Fe_3O_4 is washed repeatedly using Aquadest to keep the pH neutral. Fe_3O_4 is heated at 100°C for 1 hour.

Samples in the form of iron sand before and after separation were characterized using X-ray fluorescence (XRF) PANalytical, Brand to determine the content of any elements contained in iron sand and the percentage of Fe content, sand that had not been separated was given the code P1 and sand that had been separated was given the code P2. The synthesized powdered Fe_3O_4 nanoparticles were characterized using X-ray diffractometry (XRD) *type Bruker eco D8ADVANCE*, which was used to determine the samples' lattice parameters and crystal size. The nanoparticles' morphology, structure, particle shape, and element content were characterized using a scanning electron microscope (SEM-EDX) *type HITACHI FLEXSEM 100*. Magnetic properties were described using a vibrating sample magnetometer (VSM) *type PPMS Quantum Design*.

Result and Discussion

The XRF results of the Gelar River iron sand are shown in Table 1. It can be seen that there is a difference in the Fe element content in the iron sand before separation (P1) and the iron sand after separation (P2). P1 shows a Fe content of 59.46% and P2 of 84.72%. XRF test results also show that iron sand contains other constituent elements in lower percentages. Other magnetic mineral contents in the Gelar River iron sand are Ti and Mn, transition elements with magnetic properties. Other oxide minerals such as Si, Al, Ca, and other components are impurity or non-magnetic. Research Karbeka et al. obtained an XRF test value for iron sand from Pantaru Beach after a separation of 77.80% [19]. Research by Tiwow et al. received a Fe value from

Bontokanang Village of 66.7% and Tanjung Bayang Beach of 79.56%. The higher the Fe value, the more potential it has as a material in synthesizing Fe_3O_4 nanoparticles [20].

Table 1. XRF Test Results Iron Sand of the Gelar River

Element	Percentage (%)	
	P1	P2
Si	15.2	1.6
P	0.36	0.28
K	0.11	-
Ca	16.5	0.904
Ti	5.52	7.83
V	0.41	0.69
Cr	0.17	0.11
Mn	0.78	0.50
Fe	59.46	84.72
Cu	0.091	-
Zn	0.07	0.07
Eu	0.83	0.59
Re	0.09	-
Hg	0.47	-

The diffraction pattern of the Fe_3O_4 nanoparticles is shown in Figure 1. The diffraction pattern shows that Fe_3O_4 has an inverse cubic spinel crystal structure corresponding to AMCSD model data No. 0007423. The diffraction peak of Fe_3O_4 is formed at an angle $2\theta = 35.38°; 41.74°; 50.78°; 63.36°; 67.70°; 74.66°$. which occupies the HKL field (111), (220), (311), (400), (422), (511), (440) respectively. Based on the results of quantitative analysis using the Rietveld method, the crystal size of Fe_3O_4 was found to be 14.8 nm with the lattice parameter $a = b = c = 8.344$ Å [21].

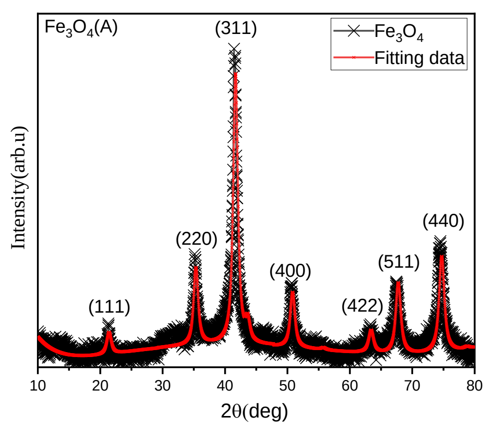

Figure 1. XRD Results of Fe_3O_4 Nanoparticles

The morphology of the particles was observed using SEM, as shown in Figure 2. Based on the picture, it was observed that the surface morphology of Fe_3O_4 nanoparticles is spherical with uneven sizes due to aggregation. Research by Tipsawat et al. also obtained a round morphology [22]. Particle size distribution analysis was carried out using Gaussian fit, and 40-

45 nm particle sizes were obtained. The size obtained from the synthesis process follows research by Packiasamy et al., which received nanoparticle sizes in 20-100 nm [23].

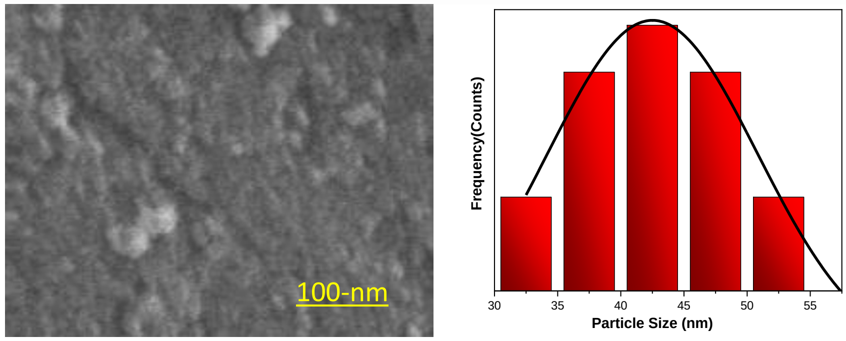

Figure 2. Morphology and Size Distribution of Fe_3O_4 Nanoparticles

The results of the EDX spectrum are shown in Figure 3. It shows that the most dominant nanoparticle elements are Fe and O. The percentage of the elements contained in the nanoparticles is shown in Table 2. Fe elements are 59.7%, and O is 29.61%, which shows that the synthesis of Fe_3O_4 nanoparticles was successful [24]. The EDX results obtained are following research by Kurnia et al., 2021, which obtained Fe elements of 65.86% and O elements of 19.18% [25].

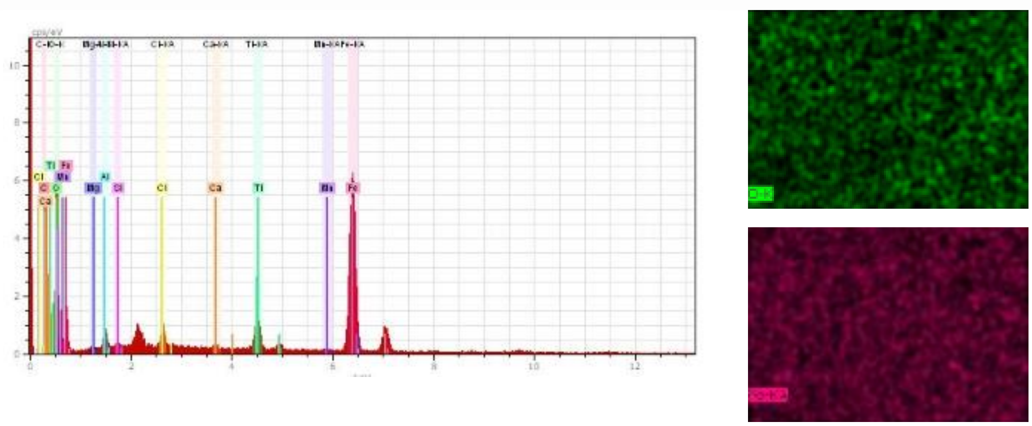

Figure 3. EDX Results of Fe_3O_4 Nanoparticles

Table 2. Percentage Elements EDX of Fe_3O_4 Nanoparticles

Element	**Weight(%)**	**Atom (at.%)**
Fe	59.71	33.09
O	29.61	57.27
Ti	6.11	3.95
Cl	1.63	1.43
Al	1.43	1.64
C	0.79	2.04
Mn	0.32	0.18
Si	0.17	0.18

Ca	0.11	0.09
Mg	0.11	0.14

The magnetic properties of Fe_3O_4 nanoparticles were analyzed using VSM, as shown in Figure 4. The hysteresis curve of Fe_3O_4 nanoparticles displays type S and saturates under the applied magnetic field. Through the hysteresis curve, the coercivity (Hc), saturation magnetization (Ms), and remanence magnetization (Mr) values of Fe_3O_4 nanoparticles can be determined [24]. Hc is the magnetic field value required to reduce the magnetization to zero. Ms is the magnetization value when all magnetic moments have the same orientation. Meanwhile, Mr is the residual magnetization after the magnetic field is reduced to zero.

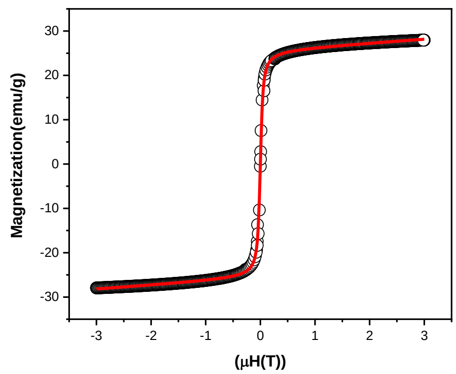

Figure 4. Hysteresis Curve of Fe_3O_4 Nanoparticles

Based on Figure 4. Fe_3O_4 Ms nanoparticles are 27.36 emu/g. Mr is -0.01 emu/g, and a coercivity of 0.01 T shows that Fe_3O_4 nanoparticles have ferromagnetic properties. Research by Ba-Abbad et al. found that Ms was 27.35 emu/g [26]. Fe_3O_4 nanoparticles have different magnetic properties influenced by their structure, including size, morphology, crystallinity, and surface properties [27].

Conclusion

Fe_3O_4 nanoparticles made from natural river iron sand have been successfully synthesized using the co-recipitation method. XRF results on iron sand before separation contained 59.46% Fe. After separation, the Fe content was 84.72%. Based on the XRD results, the crystal structure formed is a cubic inverse with crystal lattice parameters $a = b = c = 8.344$ Å. with a crystal size of 14.8 nm. SEM-EDX shows the morphology of spherical nanoparticles with a particle size of 40 nm. The EDX spectrum confirmed the formation of Fe_3O_4 nanoparticles in the presence of Fe (51.79 %) and O (25.68 %). The VSM results show that the Fe_3O_4 sample has ferromagnetic properties with MS 27.36 emu/g. Mr is -0.01 emu/g, and a Hc of 0.01 T. In future research, it is hoped that we can study the effect of temperature variations in the synthesis of Fe_3O_4 nanoparticles on magnetic properties.

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