Synthesis and characterization of Fe$_3$O$_4$/SiO$_2$ composite with in-situ method: TEOS as SiO$_2$ NPs precursor

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Abstract. The aim study, Fe$_3$O$_4$/SiO$_2$ composites have been synthesized through two stages; first, the synthesis of Fe$_3$O$_4$ particles from iron sand material (from Lumajang area, in Indonesia); second, the synthesis of Fe$_3$O$_4$/SiO$_2$ using the in-situ method by mixing Fe3O4 nanoparticles with ammonia, ethanol, and TEOS (as precursor SiO$_2$ Nanoparticles) in one pot as a chemical reaction site. The Fe$_3$O$_4$/SiO$_2$ composites were then characterized using XRD and FTIR, VSM and TEM. Characterization results showed that the phase structure of the Fe$_3$O$_4$/SiO$_2$ composite was successfully formed. The findings are supported by the functional group vibration data on FTIR, and the identified absorption pattern has Fe-O-Fe and Si-O-Si bonds which states that the surface modification of Fe$_3$O$_4$ has been successfully carried out using SiO$_2$. The VSM test results showed that the magnetization saturation of Fe$_3$O$_4$/SiO$_2$ composites was 18 emus/g and based on the TEM test results it was seen that Fe$_3$O$_4$ particles were coated by SiO$_2$ particles with Fe$_3$O$_4$/SiO$_2$ particle size of ~ 100 nm.

1. Introduction
Magnetite or commonly called Fe$_3$O$_4$ is a compound in the form of iron oxide contained in iron sand minerals, in addition to other iron sand minerals such as hematite ($\alpha$-Fe$_2$O$_3$) and maghemit ($\gamma$-Fe$_2$O$_3$). Magnetite Fe$_3$O$_4$ material has new characteristics such as catalytic, optical and magnetic properties. This material is one of the most commonly used types of magnetic particles. Various examples of the application of Fe$_3$O$_4$ particles include ferrofluid, energy storage, and magnetic data storage [1]. In the medical field the application of Fe$_3$O$_4$ particles can be used as a hyperthermia therapy system [2], Drug Delivery System (DDS) [3], and Magnetic Resonance Imaging (MRI) [4].

In recent years, many studies have discussed the surface modification of Fe$_3$O$_4$ particles with the aim of homogenizing particle shape and size, increasing chemical stability, and compatibility. Surface modification can be done by non-magnetic coating materials [5]. Although there are many types of materials available for particle layers of Fe$_3$O$_4$, such as metal oxides, precious metals, and polymeric materials, silica (SiO$_2$) is still considered the best candidate for modifying the surface of Fe$_3$O$_4$ particles. SiO$_2$ is a material that has a stable nature when reacted. Therefore, SiO$_2$ functions as a composite shell that is ideal for protecting magnetic matter [6]. Also, SiO2 layers can reduce uneven agglomeration and dispersion in Fe$_3$O$_4$ particles [1]. High-quality SiO$_2$ is easily obtained from ethyl silicate hydrolysis or with the common name Tetraethylorthosilicate (TEOS). TEOS will not need a
long time for the synthesis process because in the synthesis process. The silica structure obtained will also be more homogeneous. Fe₃O₄/SiO₂ composites can be synthesized using the wet mixing (ex-situ) method or using the in-situ method. The advantages of the in-situ method itself are the filler, and the matrix can be mixed evenly [7].

Zhang et al. (2016) succeeded in synthesizing Fe₃O₄/SiO₂ using a one-pot process which can be applied as MRI contrast agents [7]. Gao et al. (2011) also summarized and superparamagnetic characterization of composites of Fe₃O₄/SiO₂ Core-Shell nanoparticles with variations in temperature and volume of TEOS so that it has the potential to be applied as DNA purification, targeted drug delivery, and magnetic hyperthermia [8]. Besides, Farmany et al. (2016) synthesized Fe₃O₄/SiO₂ as core/shell by the ultrasound-assisted method using the same SiO₂ material in the form of TEOS which can be applied as absorption material for diazinon removal [9]. In this report, the structure and magnetic properties of Fe₃O₄/SiO₂ composites will be presented, which are synthesized using the in-situ method with silica SiO₂ from TEOS as a precursor; and magnetite particles Fe₃O₄ nanoparticles derived from iron sand using the coprecipitation method.

2. Materials and Methods

2.1. Materials and Synthesis

The materials used in this study include iron sands, Ethanol, Ammonia hydroxide (NH₃•H₂O) powder, Tetraethyl Orthosilicate (TEOS) precursor axles, and DI-water (aquades). And the equipment used in this research is the beaker, measuring cup, magnetic stirrer, filter paper, PH paper, digital balance sheet, spatula, pipette, stopwatch, funnel, aluminum foil, cardboard, and 60-watt lamp or oven. Fe₃O₄ Nanoparticles powder was prepared by co-precipitation method from iron sand taken from Lumajang area-Indonesia. The Fe₃O₄/SiO₂ composite formation was initiated by mixing Fe₃O₄ and aquades with 30 minutes of ultra-sonification. When the solution is mixed, Ethanol is added to the mixture [10]. After stirring evenly, Ammonia and TEOS are added. Then sterilize for 8 hours at room temperature. The composite results were washed with distilled water until PH 7 was then filtered. The precipitate produced is then dried at 60 °C for 24 hours. The result of the combination of the two particles will be obtained Fe₃O₄/SiO₂ composites which are ready to be characterized.

2.2. Characterization

The Fe₃O₄/SiO₂ composite samples that have been made are then tested by the X-Ray Diffraction (Pan Analytical, Type: Expert Pro) to determine the phase and crystal structure formed. The FTIR (Nicolet iS 10 FT-IR Spectrometer) to identify the functional group; VSM (Vibrating Sample Magnetometer) for analysis of hysterical curves, magnetic properties. And The LR-TEM (Low-Voltage Transmission Electron Microscopy) to determine the size, shape, and morphology of particles (sample-powders).

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

The XRD test results showed that the composite diffraction pattern of Fe₃O₄/SiO₂ showed a diffraction pattern of SiO₂ at position 2θ = 21-28 with an amorphous structure and the diffraction pattern of Fe₃O₄ corresponding to each crystal field [6, 8]. The composite diffraction peak Fe₃O₄/SiO₂ which occurs at an angle of 2θ = 30.3 °, 35.5 °, 43.2 °, 57.0 °, 62.8 ° with the respective crystal fields (220), (311), (400), (511), (440 ) which also shows unchanging peaks of Fe₃O₄ [6,8,10]. From the peak results, the samples have similarities with previous studies conducted by [8,10,11]. Based on the results obtained, it shows that the composite has been successfully formed which is characterized by the appearance of characteristic peaks of Fe₃O₄ and SiO₂.
Figure 1. The result of X Ray-Diffraction pattern of samples: Fe$_3$O$_4$ NPs and Fe$_3$O$_4$/SiO$_2$ composite

3.2. Fourier-transform Infrared Spectroscopy Analysis
The FTIR test results showed that the synthesis of Fe$_3$O$_4$ particles and Fe$_3$O$_4$/SiO$_2$ composites revealed wave absorption patterns that were typical of both. The vibration of Fe-O-Fe group found at wave number 580 cm$^{-1}$ indicates an indication of particles Fe$_3$O$_4$ [4,9] and Si-O-Si bonds at wave number 1905 cm$^{-1}$ which states that Fe$_3$O$_4$ surface modification has been successfully carried out using silica [12,13]. The functional groups are similar to the characteristics of the Fe$_3$O$_4$/SiO$_2$ composite functional group obtained from the reference.

Figure 2. The result of FTIR spectroscopy of samples: Fe$_3$O$_4$ NPs and Fe$_3$O$_4$/SiO$_2$ composite

3.3. Vibrating Sample Magnetometer Analysis
Based on the results of the VSM (Vibrating Sample Magnetometer) testing, the magnetic properties of Fe$_3$O$_4$/SiO$_2$ composites are shown in Figure 3. The saturation of the magnetization of Fe$_3$O$_4$/SiO$_2$ composites was 18 emu/g by showing superparamagnetic material properties. When the strength of the
external magnetic field increases, the first magnetization increases rapidly and then reaches saturation. Then, when the external magnetic field strength decreases, the magnetization of the sample returns along the initial route, shows S-type behavior and almost no residual magnetism and stable coercivity forces, these characteristics indicate that this material can be significant for biomedical applications [1,2,8,14].

![Graph showing magnetization vs. applied magnetic field for Fe$_3$O$_4$ and Fe$_3$O$_4$/SiO$_2$ composite](image)

Figure 3. Result of VSM testing of samples: Fe$_3$O$_4$ NPs and Fe$_3$O$_4$/SiO$_2$ composite

3.4. Transmission Electron Microscopy Analysis

![TEM image showing Fe$_3$O$_4$/SiO$_2$ composite](image)

Figure 4. Result of TEM analysis of Fe$_3$O$_4$/SiO$_2$ composite

Based on the TEM analysis results, it was seen that the particles of black Fe$_3$O$_4$ and light gray SiO$_2$ particles were seen covering the entire Fe$_3$O$_4$ particles as shown in Figure 4. Also, Fe$_3$O$_4$/SiO$_2$ particles appeared round and agglomerated between Fe$_3$O$_4$ particles due to the composition of Fe$_3$O$_4$ too much [1,15,16]. The particle size of Fe$_3$O$_4$/SiO$_2$ is around~ 100 nm with a core size (core) of ~ 67 nm, and the thickness of the shell is ~ 16 nm as shown in Figure 4.
4. Conclusion
The Fe₃O₄/SiO₂ composites have been successfully synthesized by the In-situ method, using TEOS as a precursor of SiO₂. The diffraction pattern corresponding to Fe₃O₄ magnetic and SiO₂ phase is amorphous, and absorption of infra-red waves shows the dominant functional groups of Fe-O-Fe and Si-O-Si. The Fe₃O₄/SiO₂ composite magnetization saturation was 18 emu/g which showed superparamagnetic and soft magnetic properties. And the results of morphology analysis, it was known that Fe₃O₄ particles were black (core) and SiO₂ particles with light gray covered Fe₃O₄ particles (shell); and with Fe₃O₄/ SiO₂ particle size around ~ 100 nm.

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