Synthesis of magnetite nanoparticles from iron sand by ball-milling

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Abstract. The research aims to synthesis of magnetite nanoparticle from iron sand by mechanomhemical route. The XRF graph of showed the dominant mineral content of the iron sand is SiO₂ (36.09%), Fe₂O₃ (34.015%) and Al₂O₃ (10.034%). Hereinafter, the Iron oxide nanoparticle synthesized by the ball mill method at different milling time. The XRD graph of samples after milling showed there is no diffraction peak correspond to SiO₂, and it only corresponds to Fe₃O₄ and α-Fe₂O₃, also showed there is increasing magnetite (Fe₃O₄) purity as increasing of milling time and homogenous magnetite phase reached at 30 h milling time. The milling time affects the size of crystallites, morphology, and magnetic properties of magnetite nanoparticles. In this paper we will describe the effect of grinding time on these properties in detail.

1. Introduction

In Indonesia, there are approximately 83 active volcanoes [1] so that volcanic minerals are available in abundance. One of them is iron sand mineral. Recently, intensive nanomaterials research has been conducted around the world. Nanomaterials are a very interesting study, because nanomaterials have physical, chemical, and biological properties that change dramatically compared to bulk material, giving more application opportunities.

New discoveries in the field of nanomaterials impact on new applications in areas such as electronics, energy, chemistry, health and medicine, the environment, and so on. One of the potential nanomaterials for some applications is iron oxide. Iron is an element that is abundant in the earth's crust (about 6.3% by weight), and because iron easily oxidizes in the air to an iron state of +2 (ferrous) and iron +3 (ferric), thus iron oxide is easy to find. Iron can be oxidized to different valence states. The three main phases of iron oxide are FeO or iron (II) oxide, Fe₂O₃ or iron (III) oxide and Fe₃O₄ or iron (II, III) oxide.

Applications of nanomaterials can not be separated from the two aspects of synthesis and functionalization. How to synthesize materials efficiently, near monodispers, easy handling, and high stability is an unresolved problem.

In fact, iron oxide contains only Fe and O, where Fe is present in a divalent (ferrous) state, trivalent (ferric) state, or in a mixed valence state. Currently, there are four known natural iron oxide minerals, namely; magnetite, hematite, maghemit and wüstite. Magnetite (Fe₃O₄) contains Fe2+ and Fe3+, with a stoichiometric ratio of 1: 2. Hematite (α-Fe₂O₃) and maghemite (γ-Fe₂O₃) both have unique trivalent iron, while wüstite (FeO) consists of unique divalent iron.

Currently, the iron oxide, intensively studied for its application to photocatalysts [2], gas sensors [3], super capacitors [4], Li-ion battery electrodes [5], biosorption [6] and biomedicine [7, 8]. Magnetite is one form of iron oxide known as black iron oxide, which is the most powerful metal oxide of its magnetic properties [9] and magnetite thin film shown semiconductor properties [10]. The last few years of magnetite have been the subject of study that attracts the attention of experts because of the wide application opportunities, especially in industry.

The highly superior magnetic properties in the nano-sized Fe₃O₄ have extensive applications in modern technology. Along with the development and increasing technology needs of Fe₃O₄ nanoparticles is needed as an alternative raw materials electronics industry. The Fe₃O₄ nano-sized has
applications in industrial fields such as; ceramics, catalysts, energy storage, magnetic data storage, ferrofluids, as well as magnetic sensor materials.

2. Experimental
The processing of iron sand minerals into magnetite nanoparticles aims to regulate particle size, eliminate unwanted parts, improve quality, and purity of magnetite. The process is mechanomechanic which consists of destruction, milling, washing, filtering, and sorting with permanent magnets.

The iron sand samples were taken from Pantai Tiram in West Sumatra Province, Indonesia is then drawn with permanent magnets 30 times to separate the ferrite with other materials mixed in iron sand (residue), then the iron sand that has been drawn is dissolved in aquabidest, this serves to clean the iron sand. After washing, the iron sand is pulled back using a permanent magnet 20 times.

Furthermore, the samples that have been separated from the residue in the next process of resizing to nanoparticles by milling. The length of time the milling is varied 5, 15, 20, 25 and 30 hours. Fe$_3$O$_4$ nanoparticle structures were analyzed using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Vibrating Sample Magnetometer (VSM).

3. Results and discussion
3.1. Microstructure of Magnetite
Based on the results of XRF characterization shows that iron sand samples contain iron oxide in addition to the presence of other oxides. The main component of the iron sand from Pantai Tiram in West Sumatra is shown in Table 1. To get iron oxide only more pure, then the iron sand sample is drawn with permanent magnet several times then washed and dried.

| No | Oxides     | Percentage |
|----|------------|------------|
| 1  | SiO$_2$    | 36.09 %    |
| 2  | Fe$_2$O$_3$| 34.015 %   |
| 3  | Al$_2$O$_3$| 10.034 %   |
| 4  | MgO        | 8.068 %    |
| 5  | TiO$_2$    | 7.804 %    |
| 6  | CaO        | 1.136 %    |

The XRD characterization of samples before milling have been performed to determine the iron oxide phases present in the sample as shown in figure 1. The XRD analysis show that the iron sand from Pantai Tiram in West Sumatra does contain magnetite and hematite in addition to other minerals, such as Albite and Quartz and do not show maghemite phase.

The magnetite phase of iron sand that has been analyzed has a cubic crystalline system with lattice values $a = b = c = 8.4045$ Å. The hematite has a Rhombohedral crystal system with $a = b = 5.1120$ Å and $c = 13.8200$ Å. The Albite has a Triclinic crystal system with lattice values $a = 8.1260$ Å, $b = 12.9960$ Å and $c = 7.1640$ Å. Meanwhile, Quartz has a Hexagonal crystal system with lattice values $a = b = 4.9030$ Å and $c = 5.3930$ Å.

After milling, the sample were analyzed qualitatively by XRD as shown in figure 1. The diffraction patterns were quantitatively analyzed with High Score Plus software to know its crystalline size and microstrain. Figure 1 shows the XRD pattern of iron sand samples in milling with variations of time 5 hours, 15 hours, 20 hours, 25 hours and 30 hours. Seen after milling, the iron oxide has a mixture of the magnetite (Fe$_3$O$_4$) phase and the hematite ($\alpha$-Fe$_2$O$_3$) phase. However, in the 30 hour sample the peak $\alpha$-Fe$_2$O$_3$ disappears and there is only one phase of Fe$_3$O$_4$. The loss of the hematite phase is caused by a high-energy milling process which can increase the reaction kinetics associated with the magnetite formation of the hematite [11].
Table 2 shows data of crystalline size of Fe$_3$O$_4$ for each milling time variation. The crystalline size has increased from the time milling 5 hours to 15 hours. This is due to the agglomeration process at the beginning of the milling process. This process occurs because of the magnetite powder compaction that has been solved that results in greater crystalline magnetite.

At milling time 20 hours yielded the smallest crystalline size that is 19.9 nm. In general, the crystalline size will decrease as the milling time increases. However, samples with a 25-minute milling time experienced an increase in crystalline size of 23.5 nm. The SEM results of magnetite nanoparticles for variation of milling time are shown in figure. 2 and the particle size of magnetite of the sample is shown in Table 3.

Table 2. XRD data analysis of milling results against crystalline size of magnetite

| Milling time (hour) | Crystallite (nm) |
|---------------------|------------------|
| 5                   | 22.4             |
| 15                  | 25.4             |
| 20                  | 19.9             |
| 25                  | 23.5             |
| 30                  | 20.5             |

Table 3. Particle size of iron oxide for some variations of milling duration

| No. | Milling time (hour) | Average particle size (µm) |
|-----|---------------------|----------------------------|
| 1   | 5                   | 1.57                       |
| 2   | 15                  | 1.61                       |
| 3   | 20                  | 1.30                       |
| 4   | 25                  | 1.57                       |
| 5   | 30                  | 1.47                       |
3.2. Magnetic properties of Magnetite

The magnetic properties of the Fe₃O₄ nanoparticles were investigated by measuring the magnetization dependence on applied field at 300 K. We found that coercive of Fe₃O₄ varies with particle size as shown in figure 3. The coercive decreases with increasing particle size. Lin et al. [12] was reported the Hc value of Fe₃O₄ particles decrease as the crystallite size increased. Meanwhile, Dunlop [13] and Moskowitz [14] reported that two different regions existed (single domain and multidomain) where the Hc of magnetic nanoparticles was dependent on the particle diameter.

Figure 2. SEM image of iron oxide nanoparticles for milling time: (a) 5 hours, (b) 15 hours, (c) 20 hours, (d) 25 hours and (e) 30 hours

Figure 3. Graph of coercive (Hc) versus particle size
4. Conclusions
It has been synthesized and characterized iron oxide from Pantai Tiram in West Sumatra Province, Indonesia, where iron sand samples have the most dominant composition of Si 36.09%, Fe 34.015%, and Al 10.034%. The X-ray diffraction pattern after the milled sample showed diffraction peaks corresponding to Fe₃O₄ and α-Fe₂O₃. There is an increase in Fe₃O₄ purity as milling time increases and homogeneous Fe₂O₃ phases are achieved at 30 hours of milling. The crystal size of the milling sample was 5 h, 15 h, 20 h, 25 h, and 30 h respectively 22.4 nm, 25.4 nm, 19.9 nm, 23.5 nm, 20.5 nm.

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