Magnetic iron oxide particles (Fe$_3$O$_4$) fabricated by ball milling for improving the environmental quality

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Abstract. Nowadays magnetic iron oxide particles (Fe$_3$O$_4$) have been extensively used as nanomaterials due to their broad range of applications. One of their applications is to improve the environmental quality by elimination of harmful pollutants in wastewater. Therefore, preparation method of magnetite (Fe$_3$O$_4$) nanoparticles is one of the most important keys to its adsorption efficiency. This study aims to prepare magnetite nanoparticles from natural iron sand of Arta Beach, Pariaman, West Sumatera using ball milling technique. This technique is simple and easy to carry out. The balls used in this milling are the iron balls with the diameter of 1.5 cm. The phase composition, elemental composition, microstructure and magnetic properties of milled powder of magnetic particles were studied by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) respectively. The results showed that the milling time is a key parameter of the magnetite nanoparticles preparation. By increasing the milling time, then high purity magnetite samples can be obtained. Moreover, the magnetic particle size of the sample decreases as the milling time increases. The SEM micrographs showed that the sample has a broad distribution of particle diameters, ranging from around 1 up to 107 μm and 0.5 to 36 μm after 30 and 90 hours of milling respectively.

1. Introduction
Iron sand is kind of mineral that is available in some main Indonesian islands coast such as West Sumatra coast especially Arta Beach, Pariaman, West Sumatera Province. It is commonly known that iron sand consisted of magnetite (Fe$_3$O$_4$), maghemite (γ-Fe$_2$O$_3$) and hematite (α-Fe$_2$O$_3$) phases. These particles in nanometer size show an interesting property such as superparamagnetic in which the value of magnetic moment is high and low value of coercivity. Since the magnetic properties of magnetite nanoparticles can be controlled using external magnetic field, then their application became broad such as environmental materials [1-3], magnetic recording media [4-7], magnetic sensor [8], toners and inks for photocopy machine [9] and magnetic resonance imaging [10,11], biomedicine and bioengineering drug delivery target [12,13]. In environmental point of view, magnetite particles can remove the pollutant in contaminated water based on magnetic extraction technique [14]. One of the

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most important parameters for controlling the magnetic properties of magnetite nanoparticles is the size of the particles. In reality, preparation of magnetite nanoparticles with controllable size and size distribution is a great challenge for researchers [15].

Today there are several methods for preparation of magnetite nanoparticles such as chemical, [16] biological [17] and physical method [18]. One of the physical methods in preparation of magnetite nanoparticles is ball milling method [17]. Ball milling method is a simple and efficient an as well as low cost method in crunching the iron sand concentrate in a rotating tube using metallic or ceramic balls. In this method, ceramic balls that have higher mechanical energy are used to crunch the iron sand concentrate from iron sand separator. The size of magnetic particles obtained through this method depends on the time, speed and weight of the ceramic balls [18]. Previous researchers [16,17] have used this method to synthesize magnetic nanoparticles from iron salt precursor. They found that the size of magnetic nanoparticles is around 10-15 nm. However, they also found that magnetic nanoparticles that synthesize using ball milling resulted higher magnetic saturation (14emu/gr) compared to that of using chemical method that gives magnetic saturation value of 3 emu/gr. In this article, we report the preparation of magnetite particles using ball milling method for improving the environmental quality.

2. Experimental Method

Natural iron sand samples were collected from Arta Beach, Pariaman, West Sumatera. The samples were dried under sun ray until it completely dry before synthesizing them using iron sand separator. The product of iron sand separator called concentrate 1 was milled using ball milling as a function of time. The separation between magnetic and non-magnetic particles, then Neodymium iron boron magnet (NdFeB) was employed. The elemental identification of samples before and after milling was recorded using X- Ray Fluorescence Spectrometer (XRF). Magnetic phases of synthesized samples were studied using X-Ray Diffraction technique equipped with Cu Kα radiation of wavelength of λ=0.15406 nm. Morphological studies were performed using scanning electron microscope (SEM). The magnetic properties of synthesized samples were studied using vibration sample magnetometer (VSM).

3. Results and Discussion

3.1 Elemental composition

Elemental composition of an iron sand before and after ball milling process was determined using X-ray fluorescence (XRF). This composition is presented in Table 1.

Table 1 shows that the elemental composition was affected by processing time. It shows that the Fe contents were increased very significantly after being processed by the ball milling for 90 hours. Some other elements for examples Si, Al, K, and Ca were decreased, however, the other elements such as Ti, V and Mn were increased. This indicates that the ball milling process crunch the iron sand grains into smaller parts so that the non-magnetic and magnetic grain were separated during ball milling process. Moreover, from the table it can be seen that especially Fe and Si concentration improved after being processed by ball milling. Therefore, through ball milling process, some nonmagnetic elements were eliminated from the iron sand.

3.2 X-ray Diffraction Analysis

Magnetic phases for a synthesized iron sand after 30 and 90 hours ball milling times were characterized using X-Ray Diffractometer Phillips that equipped with Cu tube producing x-ray radiation with wavelength of 0.15406 nm. In this measurement, the diffraction angle was selected in interval of 10° to 70° with the step of 0.02°. X-ray diffraction pattern was obtained by applying high voltage source that is around 40 kV and 30 mA. X-ray diffraction patterns of a synthesized iron sand after 30 and 90 hours’ ball milling times are shown in Figure 3.
Table 1. Elemental composition of iron sand before and after ball milling process

| Element | Concentration (%) |
|---------|-------------------|
|         | Before Milling    | After 90 hours milling |
| Mg      | 3.452             | 3.345                  |
| Al      | 10.706            | 8.118                  |
| Si      | 61.182            | 11.246                 |
| P       | 0.908             | 0.591                  |
| Cl      | 2.415             | 0.582                  |
| K       | 7.245             | 0.537                  |
| Ca      | 5.835             | 1.265                  |
| Ti      | 0.472             | 5.836                  |
| V       | 0.006             | 0.403                  |
| Mn      | 0.136             | 0.321                  |
| Fe      | 6.118             | 66.238                 |
| others  | 1.525             | 1.518                  |

Figure 1. X-ray diffraction patterns for a synthesized iron sand after (a) 30 and (b) 90 hours’ ball milling times
Fig. 1 shows two XRD patterns for a synthesized iron sand after 30 and 90 hours ball milling times. In general, it was found that by increasing the ball milling time, then high magnetite purity can be obtained. These XRD results clearly indicate variation of the phase of magnetic iron oxide for these milling times. It can be easily found that the diffraction peaks on a synthesized iron sand after 90 hours milling at 20 value of 30.04°, 32.47°, 35.47°, 43.00°, 53.45°, 57.02° and 62.70° were completely matched the reflections of (220), (311), (400), (422), (511), (440), respectively. It is clear that these crystal planes are remained unchanged as the milling time increases. Moreover, the XRD pattern become broadened and the diffraction peak intensities increased as the particles size decreased with increasing ball milling time as confirmed with scanning electron micrographs Fig 2. From XRD profile, it is clear that no XRD peaks for iron oxide were observed for high ball milling time namely 90 hours. The magnetite iron oxide (Fe₃O₄) phase increased as the ball milling time increased from 30 to 90 hours. Since no obviously peaks observed with increasing ball milling time, then this indicated that FeO phase does not exist for high ball milling time. The comparisons between magnetic phase (Fe₃O₄ and Fe₃O₄) as observed from XRD peaks are presented in Table 2 and 3.

| Diffraction Angle (2θ) | d spacing (Å) | Reflection Plane hkl (for Fe₃O₄) | Magnetic Phase | FWHM Left (°2θ) |
|------------------------|--------------|----------------------------------|---------------|-----------------|
| 21.9228                | 4.05441      |                                  | Fe₃O₄         | 0.1535          |
| 26.6172                | 3.34905      |                                  | Fe₃O₄         | 0.1535          |
| 27.9454                | 3.19282      |                                  | Fe₃O₄         | 0.0768          |
| 30.0392                | 2.97489      | 220                              | Fe₃O₄         | 0.2047          |
| 30.9676                | 2.88777      |                                  | Fe₃O₄         | 0.0768          |
| 32.8377                | 2.72746      |                                  | Fe₃O₄         | 0.4093          |
| 35.3469                | 2.53939      | 331                              | Fe₃O₄         | 0.1791          |
| 42.9686                | 2.10497      | 400                              | Fe₃O₄         | 0.0768          |
| 53.3876                | 1.71616      | 422                              | Fe₃O₄         | 0.4093          |
| 56.7803                | 1.62141      | 511                              | Fe₃O₄         | 0.0768          |
| 62.3647                | 1.48774      | 440                              | Fe₃O₄         | 0.0936          |

Table 2. Diffraction parameters for iron sand milled for 30 hours

| Diffraction Angle (2θ) | d spacing (Å) | Reflection Plane hkl | Magnetic Phase | FWHM Left (°2θ) |
|------------------------|--------------|----------------------|---------------|-----------------|
| 30.0424                | 2.97457      | 220                  | Fe₃O₄         | 0.2558          |
| 32.4741                | 2.75717      | 331                  | Fe₃O₄         | 0.1791          |
| 35.4722                | 2.53072      | 400                  | Fe₃O₄         | 0.2047          |
| 43.0041                | 2.10331      | 422                  | Fe₃O₄         | 0.6142          |
| 53.4531                | 1.71421      | 511                  | Fe₃O₄         | 0.7164          |
| 57.0175                | 1.61523      | 440                  | Fe₃O₄         | 0.3072          |

Table 3. Diffraction parameters for iron sand milled for 90 hours

3.3 Microstructural Properties
The scanning electron microscopy (SEM) images of 30 and 90 hours ball milled samples with 400x magnification are shown in Fig. 2. This analysis was carried out in order to investigate the shape and size of the as-synthesized magnetite particles. Scanning electron microscopy (SEM) images presented in Figure 2 (a) and (b) show the magnetic particle size and the morphology obtained from ball milling with time of 30 and 90 hours. These images show the samples contain particles of different sizes and shapes. SEM images of the sample of 30 hours milled consisted of particles covering the range 1–107 µm and more than 30% of these particles are large approximately 107 µm. The shape of these particles is clearly not systematic shapes. Moreover, SEM image of the samples milled for 90 hours (Figure 2b)
shows particles of smaller size of 0.5-36 µm. From Figure 2 it can be estimated that the average particles size decreases with increasing ball milling time. This result is in agreement with that obtained by previous study [22]. This is a notable result, obtained using this simple method for preparing magnetite particles which might be useful for environmental material applications.

![Figure 2. SEM images of (a) 30 and (b) 90 hours ball milled samples](image)

### 3.4 Magnetic Properties

Magnetic properties of the sample were measured by vibration sample magnetometer (VSM) available at Department of Physics National Atomic Energy Agency (BATAN) Serpong, Tangerang, Banten, Indonesia. Figure 5 below shows the variations of magnetization values and applied magnetic field for the as synthesized iron sand after 30 and 90 hours ball milling times.

![Figure 3. Loop hysteresis for the as synthesized iron sand after (a) 30 and (b) 90 hours ball milling times](image)

The hysteresis loops shown in Fig. 3 are the loop hysteresis of iron oxide prepared by ball milling with time of 30 and 90 hours. The applied magnetic field in this measurement was chosen to be 3000 Oe. These two samples show a nonlinear relationship in magnetization as a function of applied magnetic field. It is clear from Figure 2 that magnetic remanence is almost absent in both sample. It shows almost no remnant magnetization for zero applied magnetic field. This results show
superparamagnetic behaviour of particles. One important parameter of the hysteresis loops shown in Fig 3, is small value of coercivity. It can be noticed from Fig. 3 that the coercivity value of the samples has been found to remain constant (173 Oe) with the increase in milling time. Moreover, it can be seen that as the milling time was increased from 30 hours to 90 hours, the magnetisation values of the samples increase from 31.48 emu/g to 37.80 emu/g. The increase in magnetization values for longer milling time is being thought due to the presence of an additional magnetite iron oxide (Fe₃O₄) phase and reduction of nonmagnetic elements as confirmed by XRF results in Table 1. The loop hysteresis of the as synthesized sample of 90 hours shows magnetization values smaller than the bulk values [28].

4. Conclusion
Magnetite (Fe₃O₄) particles with minimum size of 0.5 μm have been successfully prepared by varying the milling time. The variations of milling time in this study play an important role in preparing magnetite iron oxide particles in which the size of magnetite particles decreases as milling time increases. This method is simple and low cost, however, it takes longer time to obtain a desired result. Moreover, the milled particles show high percentage of magnetite phase for longer milling time as shown by XRD results. The result also showed that the size of particles has become smaller as milling time increased as revealed by SEM images and broadening of the XRD peaks. Furthermore, it was also found that the magnetization of as synthesized sample increases as milling time increase.

5. References
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