Natural magnetite characterization from beach sand prepared by using planetary ball milling

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Abstract. In this paper, the mineral composition and magnetic behavior of nano magnetite ($Fe_3O_4$) extracted from beach were studied. The beach sand was collected from the Gampong Dayah coastal area, Banda Aceh and prepared by mechanical alloying method. The mineral compositions were investigated by XRD and XRF analysis tests. The XRF test showed that the sand mostly contain $Fe_3O_4$ in association with other isomorphous impurities, such as $SiO_2$, $TiO_2$, $Al_2O_3$ and some others minor minerals in varying proportions. Compare to XRD results, it was consistent with XRF, the phase compositions are mainly magnetite ($Fe_3O_4$). The XRD revealed that magnetite is the major mineral components in the Syiah Kuala sand. The electron microscope (SEM) identification showed the fine crystalline structure and the main morphology was micro-crystalline or agglomerate forms. The magnetic properties of the samples after milling showed there has been increasing in coercivity ($Hc$) and remanent ($Br$), while magnetic saturation ($Ms$) was decreased.

1. Introduction

One of the fastest growing industries today is the iron and steel industry, especially for permanent magnet applications. The main raw material is iron sand. Therefore, currently, there are efforts to process iron sand and several types of mineral metals as raw materials for the steel industry [1]. Some studies have been conducted to extract the minerals in the beach sand which dominated by magnetite [2, 3]. Magnetite can be used as a base for dry ink in photo copiers and laser printers. Some researchers do variety identification and characterization of deep to get related information properties magnetic $Fe_3O_4$ [4,5] and the cutting edge is the production of $Fe_3O_4$ nanoparticle-scale natural for the application of ferroelectric materials [6].

A further application is the use of iron oxide as the catalyst in industrial applications [7,8]. Important to note, India is currently exploit iron sand for export-oriented commercial purposes [9, 10]. In order to develop the non-oil and gas utilization business sector, it is necessary to carry out in-depth exploration of local iron sand.

Unfortunately, there are still lack information about the studies related to iron sand in Aceh Province. For such problems, we try to investigate the characteristics of Aceh beach sands. In this work, the data of identification phase, the crystallite size and the magnetic characteristics of natural magnetite from beach sands were studied.
2. Materials and Method
The iron sands were collected from the Gampong Dayah coastal area, Banda Aceh. The iron sands were dried around 4 hours at room temperature. Then, the sample was manually separated by using a permanent magnet. Furthermore, to obtain iron sand in the form of fine powder, the preparation was carried out using mechanical alloying techniques using a ball mill apparatus (Fritsch, P6) and milled for 20 hours at a speed of 450 rpm. The ball and powder ratio (BPR) was 10:1. Afterwards, the phase composition and crystallite size were identified using X-rays diffractometer (XRD Shimadzu, D6000) and the mineral composition was observed by X-ray fluorescence (XRF Brucker, S2-Stranger). The data then compared to the database issued by International Crystallography Diffraction Data (ICDD). The crystallite size was calculated by Scherrer formula. The magnetic properties observed using Permagraph (Magnet Physik, 2T).

3. Results and Discussion
The X-ray Diffraction (XRD) data was conducted the phase identification analysis by observing the angle 2θ, lattice distance factor (d), intensity (I/IO), the phase and the crystallite structure. This identification was approached with the value of the angle 2θ according to certain minerals listed on JCPDS (Joint Committee for Powder Diffraction Standard) file. The analysis is performed by matching technique, the experimental results and JCPDS file. As the results, the XRD patterns informed the dominant phase of Fe₃O₄, whereas SiO₂ and TiO₂ as the minor phase. The diffraction peak profiles XRD test results on the samples are sharps, indicates as crystalline structure. The diffraction peaks began widen after milling for 20 hours. The widening of the peaks can be caused by grain size factor, and also by micro-strains and instrumentation factors.

There were a couple studied on the characteristic of magnetite nanoparticles [11,12] obtained by milling method. They showed that he main characteristic of several peaks impurities was observed in the mineral magnetite, which result in the structural disorder and defect. The strongest peak corresponds to the plane (311) at angle of 35.51, according to the crystallographic plane of the structure. This mainly due to the presence of oxygen that affects the surface concentration of iron (II) in the synthesis product.

![Figure 1. XRD pattern of beach sand after 20 hour milling](image-url)

The mineral composition in beach sands after milling 20 hours obtained by XRF test (as shown in Table 1), indicated that the magnetite (Fe₃O₄) is appeared as the major compound (86.55%), since the minor phases are TiO₂, Cr₂O₃, Al₂O₃ and some others.
Table 1. Mineral composition of Syiah Kuala beach sand

| Compound   | Percentage (%) |
|------------|----------------|
| Fe₂O₄      | 86.55%         |
| TiO₂       | 6.01%          |
| Cr₂O₃      | 2.01%          |
| Al₂O₃      | 0.82%          |
| MnO        | 0.74%          |
| NiO        | 0.62%          |
| SiO₂       | 0.58%          |
| CaO        | 0.40%          |
| Pr₆O₁₁     | 0.40%          |
| P₂O₅       | 0.40%          |
| Nd₂O₃      | 0.33%          |
| K₂O        | 0.30%          |
| CO₂        | 0.25%          |
| Cl          | 0.20%          |
| SO₃        | 0.16%          |
| CuO        | 0.08%          |
| ZnO        | 0.06%          |
| MoO₃       | 0.03%          |
| SnO₂       | 0.02%          |
| ZrO₂       | 0.02%          |

The XRF results consistent with the XRD measurements where magnetite (Fe₃O₄) is the majority phase in the Syiah Kuala coastal area sands. Important to note, by using mechanical alloying method, it is capable to produce the nano-magnetite sand to the smallest crystallite size at the position (311) as 0.111 nm. The XRD diffraction peaks became broader by increasing milling time. The relative intensity decreases due to the particles size reduction and the microstrain accumulation affect [13-15]. It can be stated that the diffraction peaks widen with increasing milling time. This phenomenon is known as peak broadening. Upon this conditions, it is noted that with increasing the milling time, the crystallite size decreases and reaches a nanometric size.

Table 2. Crystallite size of the milling samples

| Milling Time (hour) | Crystal Plane | Crystal Parameter | Crystallite Size (nm) |
|---------------------|---------------|-------------------|-----------------------|
| 0                   | 311           | FWHM: 0.46890     | 2θ: 35.5296           | 0.359956             |
| 10                  | 311           | FWHM: 0.44470     | 2θ: 35.4051           | 0.198                |
| 20                  | 311           | FWHM: 0.79200     | 2θ: 35.4711           | 0.111                |
Furthermore, the grained structure the as-milled samples were carried out by microscopy observation using SEM characterization, as shown in figure 2 (a) and (b). The sample before milling shown a similar grains and after milling (20 hours) the powder becomes smaller and the irregular in shape, due to cracks during the milling process.

![SEM morphology of beach sand before milling](a)

![SEM morphology of beach sand after milling](b)

**Figure 2.** SEM morphology of beach sand before milling (a) and after milling (b) Subsequent observations were obtained by using a Permagraph on an external magnetic field of 2 tesla (T).

The results can be analyses from the hysteresis loop curve, which inform the magnetic saturation (Ms), remanent (Br) and coercivity (Hc), as shown in Figure 3 and Figure 4. The magnetic saturation before milling is 0.333 T and decreased to 0.188 T after milling 20 hours. Afterwards, the remanent value is 0.022 T (before milling) and increased to 0.075 T (after milling), while the coercivity is increasing significantly from 1.34 kA/m to 33.31 kA/m. It is worth to note, as the increasing of milling time, the remanent and coercivity is increases, while the saturation magnetization is decrease.
It is suspected that the finer the crystal size will increase the empty space between the crystals. The increase in the Hc coercive field from 1.34 to 33.31 kA/m could be due to a reduction in cluster size as well as an increase in defect density with increasing milling time [16, 17].

4. Conclusions
The magnetite sand (Fe₃O₄) was successfully extracted from local beach sand using mechanical milling method. The magnetite (Fe₃O₄) was appeared as the major compound of 86.55% in purity. Coercive field was increased from 1.34 to 33.31 kA/m when the particle size decreased. As the increasing of milling time, the remanent (Br) and coercivity (Hc) was increased, while the saturation magnetization (Ms) decreased. The hysteresis loops indicate that the Fe₃O₄ from milled beach sand shows the possibility of a soft magnet application.

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