Characteristics of Iron Sand Magnetic Material from Bugel Beach, Kulon Progo, Yogyakarta

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Abstract. Magnetic material (MM) of iron sands from Bugel Beach, Kulon Progo, Yogyakarta has been prepared and characterized. Magnetic material was separated from iron sands using a permanent magnet followed by treating with sodium hydroxide (NaOH) solution. The magnetic material product was characterized with X-ray Fluorescence, X-ray Diffraction, Fourrier Transform Infrared spectrophotometry, and Vibrating Sample Magnetometer to determine the chemical composition, crystallinity, presence of functional groups and the magnetization, respectively. Results showed that the investigated iron sand contained magnetic materials up to 89.47% (w/w). The main composition of MM included Fe_2O_3, TiO_2, and SiO_2, with percentages of 72.6, 7.0, and 10.0%, respectively, and the functional groups of material was dominated with Fe−OH and Fe−O. Treatment with NaOH 4M and NaOH 8M increased the content of Fe_2O_3 and TiO_2, otherwise reduced the concentration of SiO_2 and contributed to the improvement of the magnetization from 42.1 to 44.3 emu/g (with 4 M NaOH) and 64.0 emu/g (with 8 M NaOH). Additionally, MM was dominated with mineral of magnetite and contained functional groups of Fe−OH and Fe−O.

1. Introduction

The potential and distribution of iron sand in Indonesia were found on the western coast of Sumatera, Kalimantan, Sulawesi, Maluku islands, and the southern coast of Java [1-2]. Iron sand is generally only used as a building material, whereas it contains magnetic material (MM) constituting the basis for the development of devices in modern life. MM is generally composed of magnetic metals, such as iron, cobalt, nickel, or oxides such as magnetite, maghemite, nickel ferrite, cobalt ferrite, and others [3-5]. MM has been synthesized in different composition and phases such as pure metal (i.e. Fe, Co, Ni), alloys (i.e. FePt, $FePt_3$, $CoPt_3$), metal oxides or spinel ferrites type with general formula MFe_2O_4, where M is a divalent metal cation ($NiFe_2O_4$, $CoFe_2O_4$, $Zn_{0.35}Ni_{0.65}Fe_2O_4$, $MnFe_2O_4$, $MgFe_2O_4$) [3,5,6]. Although pure metals such as Fe, Co, Ni possess the highest magnetization saturation, they receive little interest due to their high characteristic toxicity and are extremely sensitive to oxidation [6-7]. In contrast, iron oxides are less sensitive to oxidation and are able to give a stable magnetic response [3].

The metal oxide of iron sand was found in two phases, magnetite and maghemite. Both are magnetic susceptibility that shows magnetic properties when in a magnetic field [4]. Iron oxide such as magnetite and maghemite last few years has been widely used in various applications, such as

magnetic data storage devices with high density, magnetic resonance image formation, delivery system for medicines, cosmetics, dyes, inks as well as play a role in variation separation processes, including adsorption [7-9]. Several chemical methods can be used to synthesize MM iron oxide: co-precipitation reactions occurred in mixture solution of Fe^{2+} and Fe^{3+}, thermal decomposition of organic iron precursor, solvothermal, hydrothermal and microemulsion methods [8,10,11]. These methods were found to be suitable for synthesis of α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4 with different proportions by controlling the reaction conditions. However, these methods have disadvantages such as difficult to avoid nucleation during reaction, require relatively high temperatures, complicated procedures, relatively slow kinetic due to the relatively low temperature used, and usage of multiple reagents.

Research on the use of natural MM only a few has been reported [12]. High magnetite ingredients in iron sands are certainly encouraging the utilization of iron sand for MM. Iron sands have high economic value, if it can be processed as MMs. Certainly the processing does not need a large scale mining, that the mining and processing can be done selectively [12]. The separation technique by magnetic separator can separate iron sands between magnetic materials and nonmagnetic materials, but MM may still contain minerals such as silica, magnesium oxide, aluminum oxide [13]. Improvement of MM magnetization with an acid solution such as hydrochloric acid, sulfuric acid and hydrofluoric acid can be used to reduce/eliminate the nonmagnetic oxide that may reduce the magnetic susceptibility [15]. However, treatment with acid solutions such as HCl and HF may reduce levels of metal oxide, which is soluble in acid, especially iron oxide. An alternative way to extract silica from the magnetic material is by using an alkaline solution such as sodium hydroxide (NaOH). Silica dissolves in basic condition, especially strong bases, such as alkali hydroxides. The extraction of silica with a solution of NaOH produce sodium silicate (Na_2SiO_3) solution.

This paper reports separation of MM from iron sand using an external magnetic field. To eliminate the nonmagnetic materials such as silica oxide, MM was extracted using a solution of NaOH. Effect of NaOH treatment on the MM characteristic was investigated and evaluated as well.

2. Materials and methods
2.1. Materials
Iron sand was collected from Bugel Beach, Kulon Progo, Yogyakarta. HF and NaOH was supplied from Merck.

2.2. Preparation of magnetic materials
Magnetic material (MM) of iron sand (30 grams) was separated with a permanent magnet and the MM obtained was grounded with a mortal and then sieved with a 200 mesh sieve size. MM size <200 mesh was washed with distilled water and dried in an oven at 95°C for 18 hours. Then, MM refluxed at 75-80°C using HF 10%, NaOH 4 M and NaOH 8M solutions for 2 hours, followed by washing using distilled water until neutral and dried in an oven at 95°C for 18 hours.

2.3. Characterization of magnetic materials

2.3.1. Analysis of oxides with X-ray fluorescence (XRF). The sample was grounded and put in a disposable plastic cell with mylar and analysed with PANalitycal type Minipal 4 (9 W X ray tube, max 30 kV, max 1 mA with high resolution silicon drift detector).

2.3.2. Characterization with Fourrier transform infrared (FT-IR) spectrophotometry. About 0.5 mg of sample was homogenized with 200 mg of KBr powder and was converted into a pellet form with 2000 psi of pressure. The pellet was put in a sample cell and the absorbance was measured using FTIR Spectrometer FTIR-PRESTIGE 21 at a wave number range 400-4000 cm^{-1}.

2.3.3. Identification of structure with X-ray diffraction (XRD). The sample was grounded and put in a sample cell and analyzed with Shimadzu XRD 6100 X-ray diffractometer. Cu kα radiation from 40 kV and 30 mA was applied to the sample with a 2θ range 0f 5-80° (scan speed of 5°/min).

2.3.4. Measurement of magnetization values. The magnetization values of the products were determined with vibrating sample magnetometer (VSM) Oxford types VSM 1.2H at the maximum external magnetic field of 1.2 Tesla at 25°C.

3. Results and discussion
3.1. Magnetic material of iron sand
Magnetic material (MM) was physically separated from iron sand Bugel Beach Kulon Progo Yogyakarta with magnet. Results showed that the investigated row iron sand contained magnetic materials (Figure 1) up to 89.47% (w/w). The content of MM depend on the location and this result is higher than that of iron sand magnetic material from the southern coast of Bantul Yogyakarta (66.32% (w/w)) [15].

Figure 1. Iron sand attracted to the permanent magnet.

3.2. Content of metal oxides
MM separated from iron sand produced material with black colour indicating high content of iron oxide, magnetite [8,10]. However, determination of the phase constituent of iron oxide magnetic material could not be conducted simply only by using visual observation. The oxide content of MM was determined by using X-ray fluorescence (XRF). Table 1 presents analysis results in oxides of iron sand, MM, and HF/NaOH treated MMs (MM-HF 10%, MM-NaOH 4M and MM-NaOH 8M). According to Table 1, iron sand contains dominant metal oxides of Fe_2O_3, SiO_2, TiO_2, Al_2O_3, and CaO, with percentages of 70.18%, 11.00%, 6.61%, 5.00%, and 4.26%, respectively. Moreover, some metal oxides with minor percentages also contain in the sample. The metal oxide content in a region varies depending on several factors such as geographic region, weather, and geologic condition. Iron sand deposits on the south coast of Yogyakarta comprise magnetite and maghemite mineral with levels of 59.97%, 11.7%, 6.48%, 4.34%, and 4.66% for Fe_2O_3, SiO_2, TiO_2, Al_2O_3, and CaO, respectively [15]. After being separated by permanent magnet, magnetic oxide such as iron oxide and titanium oxide content increased to 72.55% and 6.79%, respectively (table 1). However, non-magnetic oxide content such as SiO_2, Al_2O_3 and CaO did not show a significant decreased. This is due to the probability of non-magnetic oxides attached to the grain of iron sand magnetic material and also attracted by an external magnet field.

Non-magnetic oxide such as silica may be removed from magnetic material by extraction using an alkaline solution such as sodium hydroxide (NaOH). Silica reacts with a base to produce sodium silicate (Na_2SiO_3).
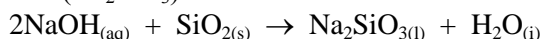
$$2NaOH_{(aq)} + SiO_{2(s)} \rightarrow Na_2SiO_{3(l)} + H_2O_{(i)}$$

Table 1. Metal oxide content in samples analyzed with XRF.

Oxides	Oxide Content (% weight) in sample				
	Iron sand	MM	MM-HF 10%	MM-NaOH 4M	MM-NaOH 8M
Fe_2O_3	70.18	72.55	78.77	80.56	82.73
SiO_2	11.00	10.00	4.00	3.00	2.00
TiO_2	6.61	6.79	7.56	7.39	7.68
Al_2O_3	5.00	5.00	3.00	3.00	4.00
CaO	4.26	3.31	2.86	1.83	1.07
Cr_2O_3	0,13	0.11	0.11	0.11	0.11
MnO	0.57	0.55	0.57	0.56	0.53
V_2O_5	0.48	0.49	0.53	0.55	0.56
NiO	0.12	0.11	0.14	0.09	0.13
P_2O_5	0.78	0.83	0.75	0.55	0.70
K_2O	0.38	0.37	-	0.10	0.07
ZnO	0.04	0.07	0.06	0.06	0.07
Rb_2O	0.23	0.23	0.25	0.26	-
Eu_2O_3	0.59	0.56	0.60	0.62	0.66
Re_2O_7	0.20	0.20	0.20	0.30	0.20
Bi_2O	0.47	0.48	0.53	0.59	0.66

Amorphous silica from rice hull ash (RHA) can be extracted using low temperature alkali extraction. The solubility of amorphous silica is very low at pH < 10 and increases sharply pH > 10. This unique solubility behaviour enables silica to be extracted in pure from RHA by solubilizing under alkaline conditions [16]. Alkali leaching of Kankara Kaolinitic clay is a function of concentration of the extracting agent. NaOH solution 40% w/w leached silica up to 65% [17]. All amorphous silica from soil samples were extracted at room temperature with 0.2M NaOH [18]. In this study, solutions of NaOH 4M and NaOH 8M are used as the leaching agents by refluxing the sample at 80°C for 2 hours. As a comparison, solution of HF 10% was also used for silica extraction. Silica leached from MM by NaOH 4M and NaOH 8M decreased the weight of MM up to 1.18% and 6.95%, respectively, while by HF 10% was 1.04%. XRF analysis results in Table 1 show that the iron oxide content after treated with HF 10%, NaOH 4M and NaOH 8M increased up to 78,77%, 80,56% and 82.73%, respectively. Furthermore, the titanium oxide content also increased significantly by activation. In contrast, silica oxide content decreased up to 4.00%, 3.00% and 2.00%, by HF 10%, NaOH 4M and NaOH 8M, respectively. Although hydrofluoric acid can be used to reduce the nonmagnetic oxide such as silica, treatment with hydrofluoric acid solutions may reduce levels of metal oxide, which is soluble in acid, especially iron oxide.

3.3. Functional groups
Analysis with infrared spectroscopy is aimed to identify the change of functional groups presence due to treatment of MM. FTIR spectra resulted from iron sand, MM, MM-HF 10%, MM-NaOH 4M and MM-NaOH 8M is presented in Figure 2. In FTIR spectra of iron sand (Figure 2(a)) is observed an absorbance band at 553.50 cm^{-1} corresponding Fe–O bond and it is attributed to the formation of ferrite phase. Similar with iron sand, FTIR spectra of MM, MM-HF 10%, MM-NaOH 4M and MM-NaOH 8M (Figure 2(b), (c), (d), (e)) Fe–O bond appears in absorbance band 570.93 cm^{-1} corresponding of magnetite mineral. The presence of silica was showed with characteristic bands at 493.78 cm^{-1} and 918.12-925.83 cm^{-1} coming from bending vibration of Si–O–Si and stretching vibration of Si–O–H (Figure 2(a) and (b)). The intensity of this spectrum decreased at Figure 2 (c), (d), and (e) indicating reduction of silica content by treating with HF and NaOH. FTIR spectra around 1627.92-1643.35 cm^{-1} and 3448.72 cm^{-1} come from bending and stretching vibration, respectively, of –OH groups from both Fe–OH and Si–OH [19].
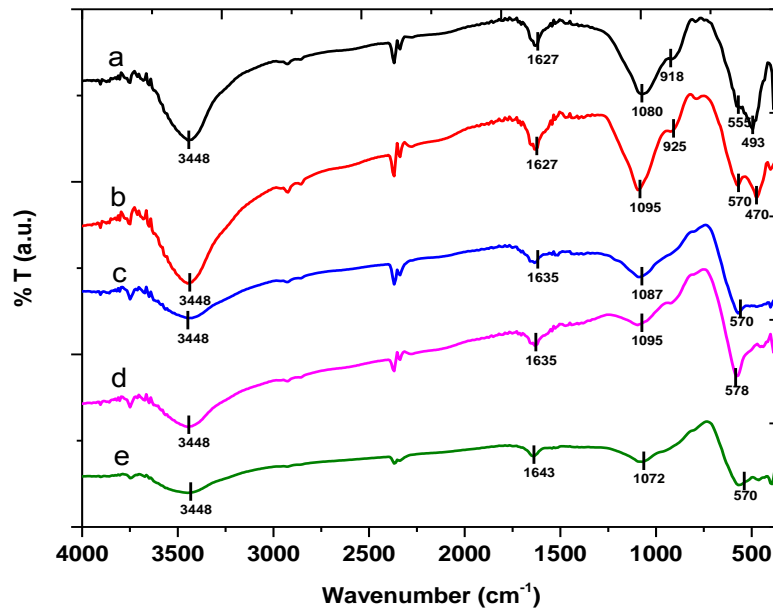
Figure 2. Infrared spectra of (a) Iron sand, (b) MM, (c) MM-HF 10%, (d) MM-NaOH 4M and (e) MM-NaOH 8M.

3.4. Structure of MM

XRD characterization was performed to obtain an X-ray diffraction pattern of the material indicating the crystallinity. Identification is based on the iron oxide phase matched with database. XRD measurements was performed in a range of $2\theta = 0\text{-}80°$. The XRD characterization results and characteristic peaks of iron sand, MM, MM-NaOH 4M and 8M-NaOH are presented in Figure 3 and Table 2, respectively. Almost the diffraction peaks can be indexed to an inverse spinel structure of magnetite (Fe_3O_4) particles (PDF file no 19-0629), except peak at $2\theta = 27.72°$ which is confirmed to quartz (SiO_2) particles [10]. This peak intensity decreased after separation with permanent magnet and treatment with NaOH. This suggests that treatment of MM with NaOH reduced the content of silica. The strong diffraction peak at $2\theta = 35.44\text{-}35.58°$ related to the spinel phase of Fe_3O_4 crystals. The sample appear high crystalline with sharp and intense peaks. The lattice parameters is about 8.32-8.39 Å, whereas crystal field spacing estimated using the Scherrer's formula at $\lambda = 1.54$ Å is 0.243-0.258 Å. It should be noted that the diffraction patterns of magnetite and maghemite ($\gamma\text{-}Fe_2O_3$) are almost identical due to their analogous inverse cubic spinel crystal structure [12].

Table 2. Crystal field spacing and lattice parameters of material sample.

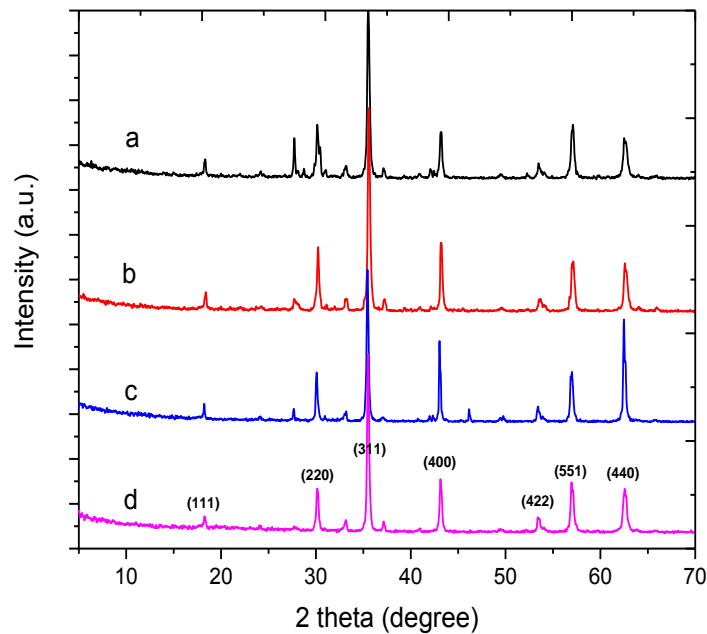| Material sample	2θ (deg)	d_{311} (Å)	a (Å)
Magnetite	35.42	0.246	8.38
Iron sand	35.52	0.246	8.37
MM	35.58	0.258	8.36
MM-NaOH 4M	35.44	0.246	8.39
MM-NaOH 8M	35.50	0.243	8.32

Figure 3. XRD spectra of (a) Iron sand, (b) MM, (c) (e) MM-NaOH 4M and (d) MM-NaOH 8M.

3.5. Magnetization values

Magnetic properties of the particles are studied using VSM at a room temperature and sweep width of external magnetic field from -1 to 1 T. VSM yields a magnetic hysteresis curve, which confirms relationship between magnetization, M (emu/g) and an external magnetic field, H (T). Important parameters in determining the magnetic properties based on the hysteresis curve are saturation magnetization, M_s, remanent magnetization, M_r and coercivity field, H_c. Measurements of magnetization versus applied external magnetic field of iron sand, MM, MM-NaOH 4M and MM-NaOH 8M are shown in Figure 4 and magnetic parameters of iron sand, MM, MM-NaOH 4M and MM-NaOH 8M are listed in Table 3. From Figure 4 seems that all samples give small curve area indicating low energy for magnetization and are classified as soft magnet. Magnet with low coercivity are expressed 'soft'. The term 'hard' refers to magnets having both a high permanent magnetization and a high coercivity [12]. This assumption is supported by the low H_c values of the samples. The value of $H_c \neq 0$ for iron sand, MM, MM-NaOH 4M and MM-NaOH 8M indicates ferrimagnetic properties of the samples. From Table 3, based on the M_s values, can be seen that treatment of MM with NaOH improves the magnetic property.

Table 3. Magnetic parameters of material samples.

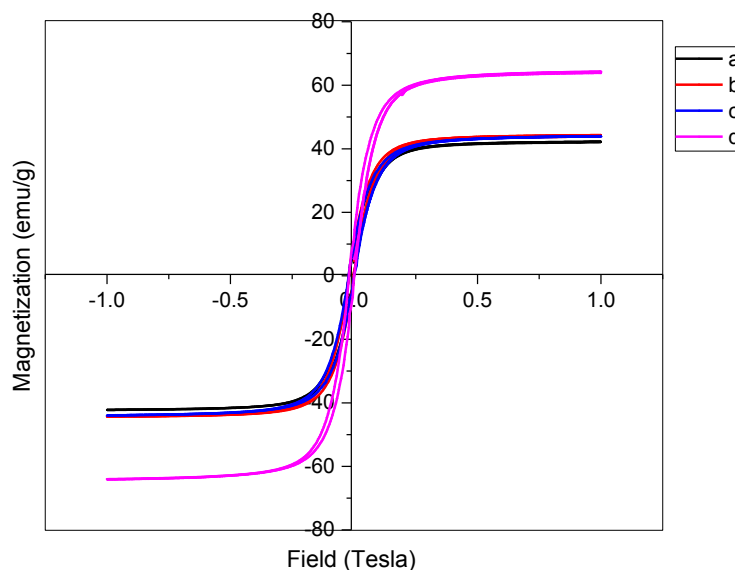| Material samples	M_s (emu/g)	H_c (x 10^{-2} Tesla)	M_r (emu/g)
Iron sand	42,08	1.52	8.39
MM	43.95	1.8	10.39
MM-NaOH 4M	44.32	2.09	10.71
MM-NaOH 8M	64.28	1.76	12.18

Figure 4. VSM hysteresis curve of (a) Iron sand, (b) MM, (c) MM-NaOH 4M and (d) MM-NaOH 8M.

4. Conclusions

In this research, iron sand collected from Bugel Beach, Kulon Progo, Yogyakarta contains 89.47% (w/w) magnetic material. Treatment with NaOH 4M and NaOH 8M increased the concentration of Fe_2O_3 and TiO_2, magnetization from 42.1 to 44.3 emu/g (with 4 M NaOH) and to 64.0 emu/g (8 M NaOH) and reduced the concentration of SiO_2. Additionally, MM was dominated with mineral of magnetite and contained functional groups of Fe−OH and Fe−O.

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