SYNTHESIS AND CHARACTERIZATION OF FE3O4 MAGNETIC NANOPARTICLES FROM IRON ORE

by Ninis Hadi Haryanti

Synthesis and characterization of Fe$_3$O$_4$ magnetic nanoparticles from iron ore

Synthesis and characterization of Fe_3O_4 magnetic nanoparticles from iron ore

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Abstract. The synthesis of Fe_3O_4 magnetic nanoparticles (MNPs) from iron ore as source of Fe_3O_4 has been done. Fe_3O_4 MNPs were characterized by X-ray diffractometer (XRD) and Transmission Electron Microscope (TEM) for phase and size, Fourier Transform Infrared (FTIR) Spectrometer for bonding, and Vibrating Sample Magnetometer for magnetic properties. XRD pattern confirms the existence of a Fe_3O_4 phase and size average 15 nm and suitable for magnetic nanoparticles. FTIR spectrum shows a band at 418-480 cm^{-1} and 603 cm^{-1} for the Fe-O bond vibration from Fe_3O_4. The coercivity, remanence, and magnetization saturation of the Fe_3O_4 MNPs studied in this investigation are 59.34 Oe, 30.43 emu/g, and 2.68 emu/g respectively and these observations indicate that the sample approaches towards superparamagnetic behaviour. This study agree with the result previously reported.

1. Introduction

Material of Fe_3O_4 magnetic nanoparticles (MNPs) is one of the iron oxides materials beside hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and wustite (FeO). MNPs known as black iron oxide with better magnetic properties than the iron oxide other. MNPs also has high absorption ability, good biocompatibility, non-toxicity, high electron efficiency, easy and simple formation and functionalization, at smaller sizes some nanometers have unique properties than bulk sizes such as superparamagnetic properties and capabilities increasing absorption. MNPs have wide area in applications such as high-density digital recording disks, as adsorbent, drug delivery, hyperthermia treatment, biosensor, iron oxide bio-separation and purification, transfection, magnetic resonance imaging (MRI) materials, and hyperthermia therapy [1-11].

The aim this researches is to determine the results of MNPs characterization of iron ore. There are several methods that can be used to synthesis of MNPs such as co-precipitation method [12], electrochemical method, oxidation hydrolysis method [13], sol-gel method [14], microemulsion [15], oxidation of Fe $(OH)_2$ by H_2O_2 [16], and microwave irradiation [17]. The co-precipitation method was used because it is often used, the method easier, the process using simple equipment, relatively cheap, the process using low temperature (below 100^{0}C) and the time required is relatively short [18-19].

2. Materials and Methods

The materials used are iron ore, HCl 37%, $Fe_2SO_4.7H_2O$ (Merck), NH_4OH (Merck), alcohol, aquadest, aquabides, ethanol 96%. Iron ore is obtained from Tanah Laut regency. The iron ore was washes and then was dried. The sample was crushed to form a powder so that in the process the synthesis of the material can dissolve easily. The powder was separated by impurities using a permanent magnet. Compounded powder that is attracted by magnet, crushed and sieved with a 230 mesh sieve. The powder was then cleaned again using a permanent magnet for impurities to obtain a higher purity level.

Synthesis MNPs used co-precipitation method. 6 g of iron ore was dissolved in 25 mL HCl 5M for 30 min on hotplate at 70^0C. The iron Fe3 + iron salt solution was taken as much as 5 mL and then added with 0.4 g $FeSO_4$ as a Fe^{2+} ion source and was mixed for 30 min at 70^0C and then added NH_4OH 5% or NaOH 2.5 M at 70^0C until formed a solid black solution indicating the Fe_3O_4 solution has been formed. The reaction based on equation (1) and equation (2).

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \tag{1}$$
$$2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \tag{2}$$
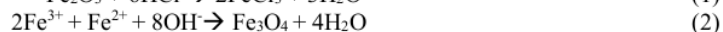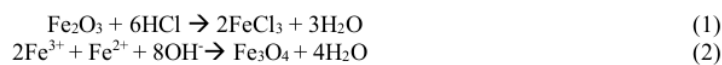
The solution was washed using aquadest for three times and using permanent magnets. Then, the sample dried at temperature of 100^0C.
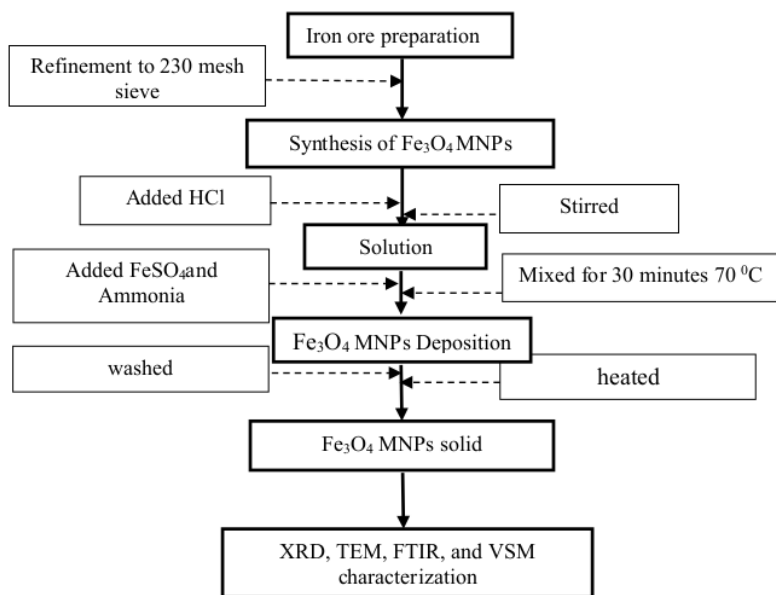
Figure 1. Processing step for Fe_3O_4 MNPs preparation

2.1. Characterizations of MNPs

Characterization sample used X-ray fluorescence (XRF), UV-VIS Spectrophotometer, fluorescence Spectrophotometer, X-ray diffractometer (XRD), vibration sample magnetometer (VSM), Fourier transform infrared (FTIR), and transmission electron microscopy (TEM).

The iron ore was characterized using XRF first. Sample about 1 g of iron ore put in the holder and the characterization process was beginning. 1 g of Fe_3O_4 powder tested using XRD and TEM. The XRD characterization is used to look at the phase and crystallinity of the sample. The characterization of XRD was done in Universitas Negeri Malang, Indonesia. TEM analysis were done in LIPI Indonesia. XRD operated at 35 mA and 40 kV and used Cu-radiation ($\lambda = 1.54060$ Å). XRD using scan speed 0.7 s/step

where step size is 0.02^0 and were recorded from 10 to 90^0 2θ. The average crystallite size D calculated from the full width half maximum (FWHM) of the peaks in radian. Formula to know D used the Debye-Scherrer formula (Eq. 1)

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

For Fe_3O_4, K = 0.94, λ is the wavelength of XRD and θ is the diffraction angle.

FTIR spectra was performed to the dried sample of MNPs from FTIR LIPI Indonesia. Wave range of spectrophotometer are 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. The dried sample was placed on a silicon substrate transparent to infrared, and spectra were measured according to the transmittance method. The magnetization of the dried sample was measured by a VSM with fields from 0 to 25 000 Oe at 295.5 K.

3. Results and Discussion

3.1. MNPs Morphology Characterization

The iron ore obtained has high Fe content of about 98% weight (Table 1). There are another content in the sample becomes a favorable thing to make Fe_3O_4 from natural iron ore. Similar studies have been conducted by some earlier researchers with varying Fe content of which 26.8% [20], 55.78% [21], 68.88% [19]. The XRD results show that Fe_3O_4 has formed (Figure 1a).

Table 1. XRF analysis of iron ore

Elements	Atomic %	Elements	Atomic %
Si	0.30	Br	0.17
P	0.10	La	0.07
Ca	0.15	Yb	0.02
Cr	0.09	Zn	0.04
Mn	0.26	Re	0.05
Fe	98.23	Rb	0.21
Ni	0.10	V	0.01
Cu	0.10	Eu	0.17
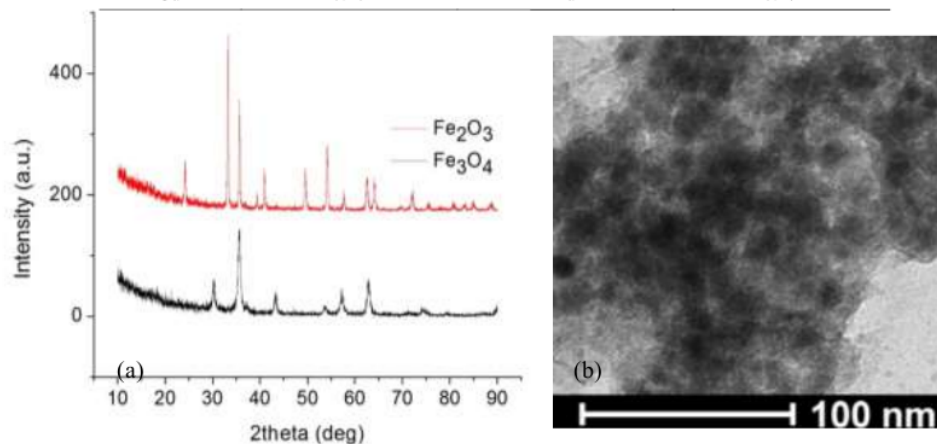
Figure 2. (a) XRD pattern from Fe2O3 and Fe_3O_4 MNPs and (b) TEM analysis for Fe_3O_4 MNPs

The XRD pattern (Figure 2) shows the XRD graph of Fe_2O_3 and Fe_3O_4 MNPs from iron ore. Fe_2O_3 is pure from iron ore and Fe_3O_4 MNPs synthesis form iron ore. XRD pattern for MNPs shows the diffraction peaks at 2θ values of 30.25, 35.64, 43.30, 53.67, 57.19, 62.79, and 74.34 corresponding to (111), (220), (311), (400), (511) and (440) respectively. The plane (111), (220), (311), (400), (511), and (440) are the special plane for Fe_3O_4. This plane are close to standard data JCPDS file no. 19-0629 for bulk Fe_3O_4. The plane (311) was the primary peak. The result indicate Fe_3O_4 has formed. Using Debye-Schrrer formula, the average crystallite sizes (D) of Fe_3O_4 are about 22.1 nm ($\beta=0.3936^0$ and $\theta=17.8196^0$). The results obtained can compare the mean particle sizes determined by TEM image. The average particle size based on TEM results was 10.0 nm. From the results, we can approximately that Fe_3O_4 is nanosize or nanoparticles and we called Fe_3O_4 MNPs.

Lattice parameter a computed from the XRD data applying the following equation shows the value 0.83553 nm or 8.3553 A and this is in suitable with the values reported in the standard JCPDS F.No.19-0629. This research was convenient to the paper previously published [20].

$$a=d\sqrt{h^2+k^2+l^2} \qquad (2)$$
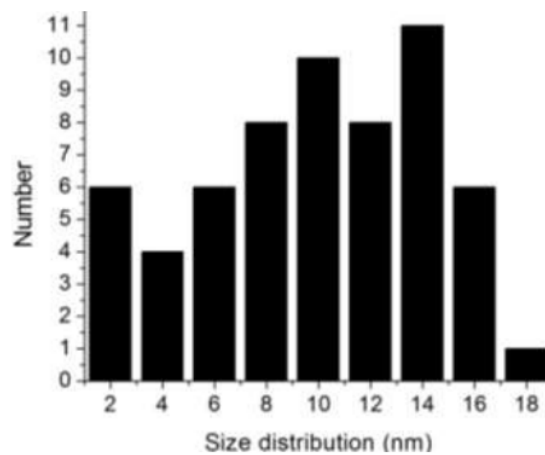
**Figure 3** Size distribution of Fe_3O_4 MNPs

3.2. FTIR Analysis
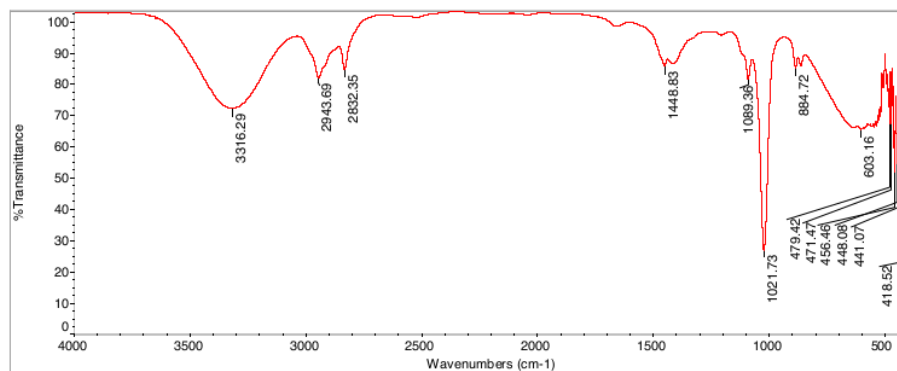
Figure 4. FTIR absorption spectra for Fe_3O_4 MNPs

The results of the infra-red spectral absorption analysis of the Fe_3O_4 sample are shown in the spectrum of Figure 4. The wave number 418-480 cm-1 is related to the vibration of Fe-O octahedral bonds [20, 22]. The large intensity of the wave number is due to the strong Fe-O bond. The wave number 603 cm-1 is the intrinsic vibration of the bond between the tetrahedral Fe-O [20, 22-31]. The appearance of the Fe-O bonding bonds both octahedral and tetrahedral confirms that iron is easy to oxidize. The appearance of the tetrahedral and octahedral neutral Fe-O peaks on the IR spectra proved that the results of XRD analysis that Fe_3O_4 phases have been formed in the synthesized sample. The peaks around 1021 cm-1 is due to the bending vibrations of O-H. The peaks around 1048 cm-1 may be attributed to adsorbed anionic species carbonates on the surface of magnetite [20] Bands round of 1089 cm-1 are stretching vibrations of CO [23]. 2832 cm-1, 2943 cm-1, and 3316 cm-1 related water used as a sample solvent [32] causing stretching of the OH group of water.

3.3. Magnetic Properties of Fe_3O_4 MNPs

Figure 5 shows the hysteresis loop of Fe_3O_4 from iron ore and Fe_3O_4 from materials purchased from Aldrich. The magnetic properties of the sample are known from the test results using the VSM characterization. The Sample was tested in the laboratory of LIPI Physics, Puspitek. VSM type used is VSM250. The external magnetic field of VSM250 has a usage range of H = 0Oe - 25 kOe.
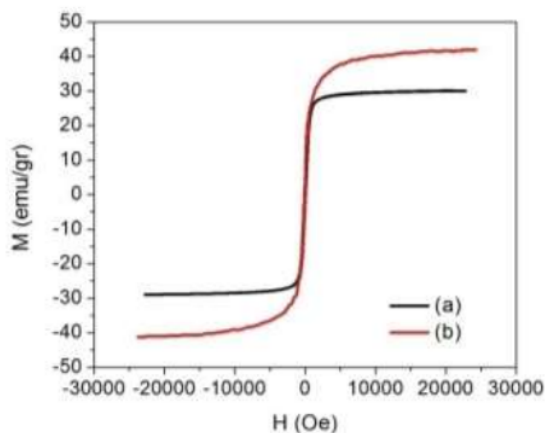
Figure 5. Hysteresis loop of (a) Fe_3O_4 from Iron ore and (b) Fe_3O_4 from aldrich

Table 2. Variations of Fe_3O_4 particle size and the resulting saturation magnetization

Size of Particles Fe_3O_4 MNPs (nm)	Ms (emu/g)
7.20	19.19 [32]*
15	30.43
9-33	45.5 [35]
30	74.86 [19]
36	70.5 [23]
50-60	60 [20]
70	65 [20]

Based on the figure 5, Fe_3O_4 MNPs are superparamagnetic (loop area 4.9 KOe.emu/g) and are soft magnets, since the energy required for magnetization is not greater than 100 Oe. According to previous paper reported, when the size of particles reduced to nanometer range, its magnetic properties reduce and they can exhibit superparamagnetic behavior [33]. Superparamagnetic is a single domain for magnetic material. The coercivity and remanence of the Fe_3O_4 MNPs in this investigation are 59.34

Oe and 2.68 emu/g respectively. Based on coercivity and remanence, the sample approaches towards superparamagnetic behavior [34]. The magnetization saturation (Ms) of the resulting MNPs was 30.43 emu/g. The resulting magnetization value of saturation is smaller than in some previous studies. This may be due to the small size of the MNPs so that the saturation magnetization is also low. Table 2 shows the variations of Fe_3O_4 MNPs particle size and the resulting saturation magnetization.

We can see form table 2 that the size of Fe_3O_4 tends to influence the saturation magnetization results. Table 2 shows that the larger the size of MNPs, the greater the magnetization value of saturation. So the magnetic properties of this study are agreement with the previously reported studies [22, 33].

4. Conclusion

Fe_3O_4 MNPs from iron ore have been successfully synthesized using co-precipitation method. The XRD pattern shows Fe_3O_4 MNPs phase and size average about 15 nm. Fourier Transform Infrared (FTIR) spectrum shows a band at 418-480 cm-1 and 603 cm-1 for the Fe-O bond vibration. The coercivity, remanence, and magnetization saturation of the Fe_3O_4 MNPs studied in this investigation are 59.34 Oe, 30.43 emu/g, and 2.68 emu/g, respectively and these observations indicate that the sample approaches towards superparamagnetic behavior. This study agree with previously reported studies.

Acknowledgement

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