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

S Husain$^1$, M Irfansyah$^1$, N H Haryanti$^1$, S Suryajaya$^1$, S Arjo$^2$, A Maddu$^3$

$^1$Physics Department, Lambung Mangkurat University, Banjarbaru, Indonesia
$^2$Physics Education Department, Muhammadiyah Dr. Hamkah University, Jakarta, Indonesia
$^3$Department of Physics, Bogor Agricultural University, Bogor Indonesia

Email: sadanghusain@ulm.ac.id

Abstract. The synthesis of Fe$_3$O$_4$ magnetic nanoparticles (MNPs) from iron ore as source of Fe$_3$O$_4$ has been done. Fe$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$. The coercivity, remanence, and magnetization saturation of the Fe$_3$O$_4$ 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$_3$O$_4$ magnetic nanoparticles (MNPs) is one of the iron oxides materials beside hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$) 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$_2$O$_2$ [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$^\circ$C) and the time required is relatively short [18-19].
2. Materials and Methods

The materials used are iron ore, HCl 37%, Fe$_2$SO$_4$·7H$_2$O (Merck), NH$_4$OH (Merck), alcohol, aquades, ethanol 96%. Iron ore is obtained from Tanah Laut regency. The iron ore was washed 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°C. The iron Fe$^3+$ 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°C and then added NH$_4$OH 5% or NaOH 2.5 M at 70°C until formed a solid black solution indicating the Fe$_3$O$_4$ solution has been formed. The reaction based on equation (1) and equation (2).

$$\text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \quad (1)$$

$$2\text{Fe}^{3+} + \text{Fe}^{2+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (2)$$

The solution was washed using aquades for three times and using permanent magnets. Then, the sample dried at temperature of 100°C.

![Diagram of processing step for Fe$_3$O$_4$ MNPs preparation](image)

**Figure 1.** Processing step for Fe$_3$O$_4$ 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$_3$O$_4$ 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° and were recorded from 10 to 90° 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)

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

For Fe₃O₄, K = 0.94, \( \lambda \) is the wavelength of XRD and \( \theta \) 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 Fe₃O₄ 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 Fe₃O₄ has formed (Figure 1a).

| 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     |

Table 1. XRF analysis of iron ore

![Figure 2. (a) XRD pattern from Fe2O3 and Fe₃O₄ MNPs and (b) TEM analysis for Fe₃O₄ MNPs](image-url)
The XRD pattern (Figure 2) shows the XRD graph of Fe$_2$O$_3$ and Fe$_3$O$_4$ MNPs from iron ore. Fe$_2$O$_3$ is pure from iron ore and Fe$_3$O$_4$ MNPs synthesis form iron ore. XRD pattern for MNPs shows the diffraction peaks at 20 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$_3$O$_4$. This plane are close to standard data JCPDS file no. 19-0629 for bulk Fe$_3$O$_4$. The plane (311) was the primary peak. The result indicate Fe$_3$O$_4$ has formed. Using Debye-Scherrer formula, the average crystallite sizes (D) of Fe$_3$O$_4$ are about 22.1 nm ($\beta=0.3936^\circ$ and $\theta=17.8196^\circ$). 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$_3$O$_4$ is nanosize or nanoparticles and we called Fe$_3$O$_4$ MNPs.

Lattice parameter a computed from the XRD data applying the following equation shows the value 0.83553 nm or 8.3553 Å 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].

\[ a = d \sqrt{h^2 + k^2} \]

(2)

![Figure 3](image-url) Size distribution of Fe$_3$O$_4$ MNPs

3.2. FTIR Analysis

![Figure 4](image-url) FTIR absorption spectra for Fe$_3$O$_4$ MNPs
The results of the infra-red spectral absorption analysis of the Fe$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$ MNPs

Figure 5 shows the hysteresis loop of Fe$_3$O$_4$ from iron ore and Fe$_3$O$_4$ 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.

![Hysteresis loop of Fe$_3$O$_4$ MNPs](image)

**Table 2. Variations of Fe$_3$O$_4$ particle size and the resulting saturation magnetization**

| Size of Particles Fe$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$ 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 Fe₃O₄ MNPs particle size and the resulting saturation magnetization.

We can see from Table 2 that the size of Fe₃O₄ 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
Fe₃O₄ MNPs from iron ore have been successfully synthesized using co-precipitation method. The XRD pattern shows Fe₃O₄ 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 Fe₃O₄ 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.

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