Synthesized of PEG-6000 coated MgFe$_2$O$_4$ nanoparticles based on natural iron sand by co-precipitation method

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Abstract. The polymer coated Magnesium Ferrite nanoparticles (MgFe$_2$O$_4$) based on natural iron sand, Mg(CH$_3$COO)$_2$.4H$_2$O, and PEG-6000 have been successfully prepared by co-precipitation method. The mass variation of PEG-6000 content was from 0 to 12 gram. It was prepared at synthesize temperature of 70$^\circ$C. The PEG coating reduced the effect of agglomeration, so the coercivity value can be closed to soft magnets. The nanoparticle of synthesized has MgFe$_2$O$_4$ single phase and cubic spinel structure. The bonding of MgFe$_2$O$_4$ and PEG-6000 as a coating material was confirmed by FTIR curve. The MgFe$_2$O$_4$ density decreased with the increasing of PEG 6000 content. On the other hand, the coercivity value was slightly reduced as the addition of PEG-6000, with the lowest value was obtained on 8 gram PEG content. The optimum condition is obtained at addition of 8 gram PEG 6000 to MgFe$_2$O$_4$, with coercivity, saturation, and remanence are 198.41 Oe, 52.53 emu/g, and 8.51 emu/g, respectively. So that, the sample is widely used as absorbance material of heavy metal.

1. Introduction

The magnetic nanoparticles are widely used in immobilization and separation of proteins or enzymes, drug administration or purification of Deoxyribonucleic Acid (DNA) [1]. It is also used to drugs delivery, hyperthermia treatment, magnetic resonant imaging [2], enhancement agent, manipulating cell membranes, biosensors, bio-labelling [3] and adsorption of metal ions [4]. One of magnetic nanoparticles application which widely developed is nanoparticles based on spinel ferrite. Spinel ferrite is a crystalline structure composed of two substructures such as tetrahedral and octahedral. The chemical formula of spinel ferrite nanoparticles is M-Fe$_2$O$_4$ which M represents a divalent of metal ion. The ionic radius about 0.6-1.0 Å. For spinel ferrite nanoparticles, M is a transition metal such as Cu, Zn, Ni, Co, Fe, Mn, Mg, or a combination of them [5]. The behavior of this material has a high permeability and resistance, but low coercivity. The spinel ferrite nanoparticles is soft ferrites having a cubic crystal structure [6]. Some methods developed for synthesizing magnetic nanoparticles is such as hydrothermal synthesis, thermal decomposition, microwave plasma synthesis [7], sol gel, sonochemical, co-precipitation and others [6]. Morever this nanoparticles has superparamagnetic
behavior when the particles size is nanometer. Superparamagnetic properties of materials have a high saturation magnetization, and the average coercivity equal to zero when those material are not influenced by an external magnetic field.

Natural iron sand is a mineral with a high iron element content. It can be utilized as precursor in the synthesis of magnetic nanoparticles based on ferrite. Many researchers interest to study Magnesium Ferrite (MgFe$_2$O$_4$) because of its great potential for many applications. The MgFe$_2$O$_4$ nanoparticles has high saturation magnetization, Currie temperature and electrical resistivity. The MgFe$_2$O$_4$ nanoparticles are soft magnetic materials (low coercivity) and one of the most important inverse spinel groups [5]. It is also an n-type semiconductor material that can be applied as adsorption, sensor, and used in magnetic technology [8].

The magnetic nanoparticles based on ferrite are obtained under agglomerated conditions. In the other hand, the air which contacts to the surface of the nanoparticles causes oxidation process easily [9]. To overcome these effects, it necessary surface modification of nanoparticles which is coated with a polymer material or an organic material. Some materials that can be used as surface coatings include polyethyleneglycol (PEG), polyvinyl alcohol (PVA), polyethyleneimine (PEI), polyvinylpyrrolidone (PVP) and other ingredients [10]. While reducing agglomeration, these coatings also increase the dispersibility, biocompatibility of chemical stability [11].

Modification of PEG coated magnetite (Fe$_3$O$_4$) is widely used in drugs delivery application. In their research, Bazaan et. al synthesized PEG coated Fe$_3$O$_4$. The Results revealed that the mean diameter of pure Fe$_3$O$_4$ was very high because of the strong interaction between the particles and aggregation phenomena that match well with TEM photograph. By modifying Fe$_3$O$_4$ with different types of PEG, due to the presence of hydrophilic polyethylene glycol on the surface of particles, the mean diameter of nanoparticles significantly decreased and significantly improved their dispersibility which were very favorable for biomedical application [12]. Meanwhile, MgFe$_2$O$_4$ nanoparticles modified with PEG can increased crystallinity by using sol gel method.

In this paper, MgFe$_2$O$_4$ nanoparticles was synthesized with natural iron sand as the precursor. Natural iron sand has an abundance and has a large iron content. The material was prepared by co-precipitation method which one method of synthesis of inorganic compounds based on precipitation of more than one substance. Another advantage of co-precipitation method, it can be processed at room temperature easily and control the particle size, so that the required time is relatively short [6,9]. The addition polyethyleneglycol 6000 (PEG-6000) as the coating is used for reducing the effect of nanoparticle agglomeration at the synthesizing process.

2. Experiment Method
Main material that was used for synthesizing MgFe$_2$O$_4$ nanoparticles coated PEG-6000 is natural iron sand from Buaya River, Deli serdang, North Sumatera, Indonesia. The composition of the natural iron sand is Fe $>$ 90% and < 9% of Ti, Si and others. Mass of PEG-6000 was a varied variable. Iron sand powder of 2.72 gram and 5.91 gram of Mg(CH$_3$COO)$_2$.4H$_2$O was added into 30 mL of 5.1 M HCl solution, followed by stirring at 500 rpm until the mixture of these solution was homogeneous. After that, the mixture of this solution was added dropwise into the mixture of 99 mL of 2 M NH$_4$OH and variation of PEG-6000 of 0, 4, 8, and 12 gram which marked as Sample A, B, C, and D, respectively. The mixture of all these solutions were stirred by using magnetic stirrer at 70°C and 500 rpm for 120 minutes. The result of the mixture was cleaned with aquades until pH neutral. Then, the precipitate sample was dried in an oven at 100°C for 1 hour. After that, the result of MgFe$_2$O$_4$ powder was characterized by using pycnometer, X-ray Diffraction (XRD - Rigaku SmartLab, $\lambda$ = 1.5418 Å), Fourier Transform Infrared Spectrometer (FTIR – Thermo Scientific Nicolet iS10), Field Emission Scanning Electron Microscopy (FE SEM – Jeol JIB 4610F), and Vibrating Sample Magnetometer (VSM – Electromagnetic VSM250).
3. Results and Discussion

Diameter MgFe₂O₄ nanoparticles are black and responsive to the magnetic field. The effect of PEG-6000 addition for powder density of MgFe₂O₄ nanoparticles is shown in Figure 1. The addition of PEG-6000 decreases powder density value. The powder density value is about 4.41-4.66 g/cm³. The decreasing of powder density is resulted by PEG-6000 density that is lower than powder density of MgFe₂O₄.

![Figure 1. The relation between the powder density of MgFe₂O₄ nanoparticles and addition of PEG-6000](image)

XRD diffraction pattern for MgFe₂O₄ nanoparticles is shown in Figure 2. From the result, there is cubic spinel single phase of MgFe₂O₄ with crystal planes of (220), (311), (440), (511) and (440).

![Figure 2. XRD diffraction pattern of MgFe₂O₄ nanoparticles coated PEG-6000.](image)
Lattice parameter and crystalline diameter of MgFe$_2$O$_4$ nanoparticles coated PEG-6000 can show in Table 1.

| Sample | Composition of PEG-6000 (gram) | Lattice Parameter (Å) | Diameter of Crystalline (nm) |
|--------|-------------------------------|-----------------------|-------------------------------|
| A      | 0                             | 8.411                 | 40.20                         |
| B      | 4                             | 8.412                 | 32.22                         |
| C      | 8                             | 8.409                 | 28.22                         |
| D      | 12                            | 8.410                 | 34.02                         |

According to Table 2, it shows that lattice parameter value of all samples is close enough to lattice parameter value of MgFe$_2$O$_4$ standard (a = 8.410 Å). It indicates that the crystal is formed well and the addition of PEG-6000 doesn’t affect to the crystal structure of MgFe$_2$O$_4$. Crystalline diameter is change, and the smallest diameter value is obtained in sample C. This is due to without addition of PEG-6000, nanoparticles will be through agglomeration. Meanwhile, the addition of PEG-6000 reduces effect of agglomeration, so the crystalline size of nanoparticles decreases. However, on the addition of 12 gram PEG-6000, the diameter of crystalline increases because the surface of nanoparticles is getting thicker.

The result of FTIR characterization of sample B (4 gram of PEG-6000) can show in Figure 3. The functional group with wavenumber around 841.94, 962.67, 1111.91, 1242.24, 1280.67, 1342.66, 1466.97, and 2888.83 cm$^{-1}$ is characteristic of PEG [1,13,14]. It indicates that MgFe$_2$O$_4$ particles have been coated. While wavenumber around 528.55 cm$^{-1}$ and 578.45 cm$^{-1}$ is the functional group of the MgFe$_2$O$_4$. The wavenumber is the functional group of metal ion and oxygen (M-O). The functional group of metal and oxygen is on site octahedral (528.55 cm$^{-1}$) and tetrahedral (578.45 cm$^{-1}$) [13,14]. Wavenumber around 1685.28 and 3447.28 cm$^{-1}$ is the functional group of H-O. From the results, it can conclude that sample C and D also has been coated.

![Figure 3. FTIR spectra of PEG-6000 coated MgFe$_2$O$_4$ (Sample B).](image)

The FE-SEM characterization of sample A shows particle size and elements contained in the sample as shown in Figure 4. The Figure 4a shows that most of the particles undergo agglomeration. Meanwhile, the coating of PEG-6000 prevented agglomeration effect. The particle size can be showed
in Figure 4b which is around 65.192 nm. Figure 4c shows composition of O = 76.8, Fe = 22.5 and Mg = 0.7 %At.

![Image a)

Figure 4c](image)

![Image b)

Figure 4c](image)

![Image c)

Figure 4c](image)

**Figure 4.** FE-SEM imaging of sample A a) morphology, b) morphology zoom, and c) EDX.

Hysteresis curve of VSM characterization results is shown in Figure 5. The coercivity and remanence tend to increase at sample A, B, and C. While for sample D, coercivity value increased to 232.26 Oe and remanence value increased to 11 emu/g. Furthermore, the result is shown in Table 2. The increasing of coercivity and remanence on sample D is influenced by crystallite magnification.

In application, the absorbance material of heavy metal need the smaller particle size with the magnetic properties as super paramagnetic for getting the optimum condition. In this research, the optimum condition is obtained on sample C with coercivity value about 198.41 Oe, saturation value about 52.53 emu/g, and remanence value about 8.51 emu/g. Magnetic characterization is influenced by particle size. The increasing of crystalline diameter is in proportion to decreasing of coercivity and remanence value. Meanwhile, the saturation value tends to increase. This is caused by the smaller particle size will be closer to the single domain. Morever, barrier energy is lower [15]. In previous research, the nanoparticle MgFe₂O₄ is prepared by sol-gel combustion method with calcination temperature variation of 400, 500, and 600 °C. The MgFe₂O₄ material has two phases which are cubic and tetragonal phases. In lower temperature, the MgFe₂O₄ material has properties as the smaller diameter of crystallite and the lower coercivity and saturation.
Figure 5. Hysteresis curve of MgFe$_2$O$_4$ nanoparticles

Table 2. Magnetic properties of MgFe$_2$O$_4$ nanoparticles

| Sample | Coercivity (Oe) | Saturation (emu/g) | Remanence (emu/g) |
|--------|-----------------|--------------------|-------------------|
| A      | 382.31          | 48.37              | 13.79             |
| B      | 335.21          | 51.69              | 12.65             |
| C      | 198.41          | 52.53              | 8.51              |
| D      | 232.26          | 51.13              | 11.00             |

4. Conclusion
The MgFe$_2$O$_4$ nanoparticles have been created out with PEG-6000 additive. The powder density of MgFe$_2$O$_4$ nanoparticles is around 4.41-4.66 g/cm$^3$. The MgFe$_2$O$_4$ nanoparticles have a single phase with cubic spinel structure. The lattice parameter of nanoparticles is around 8.410 Å. The addition of PEG6000 additive decreases agglomeration effect and crystalline size. The PEG-6000 coating on MgFe$_2$O$_4$ nanoparticles can be proof with the existing of PEG-6000’s functional group. The particles size is about 65.192 nm with consisting of elements such as O = 76.8, Fe = 22.5 and Mg = 0.7 %At. The optimum condition is obtained at MgFe$_2$O$_4$ with 8 gram PEG 6000 with coercivity, saturation, and remanence are 198.41 Oe, 52.53 emu/g and 8.51 emu/g respectively. So that, the sample is widely used as absorbance material of heavy metal.

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