Characterization structure of Fe$_3$O$_4$@PEG-4000 nanoparticles synthesized by co-precipitation method

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Abstract. Magnetic nanoparticles (Fe$_3$O$_4$) from natural iron sand with PEG-4000 have been successfully synthesized by the co-precipitation method. Natural iron sand was from Kulon Progo beach. Extraction of natural iron sand was separated with a magnet permanent as a precursor. The result of extraction was dissolved by acid chloride (HCl) solution. Precipitation process has been finished after added ammonium hydroxide (NH$_4$OH) solution and added polyethylene glycol (PEG)-4000. This solution was dried until it formed a black precipitate. Magnetic nanoparticles were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), and Fourier Transform Infra-Red (FTIR). The quantitative and qualitative analyzes on XRD were using the Profex 4.2.0 application and Joint Committee Powder on Diffraction Standards (JCPDS) No. 19-0629, respectively. Fe$_3$O$_4$ nanoparticles were successfully formed as indicated by the bonding of Fe-O. The results obtained in this study were the crystalline size of 11-13 nm with lattice parameters of 8.3758 Å for Fe$_3$O$_4$ and 8.3589 Å for Fe$_3$O$_4$ added with PEG. Fe nanoparticles were more dominant with wt% above 65%, which was confirmed by the EDX results. The addition of PEG mass resulted in the smaller crystallite size of the nanoparticles.

1. Introduction

In recent years, magnetic nanoparticles (Fe$_3$O$_4$) have been developed because of their potential properties in various sector, especially for bio applications such as selective protein separation, hyperthermia therapy, Magnetic Resonance Imaging (MRI) contrast agent, drug delivery, cell labeling, manipulating membranes, biosensor, and tracking of cell [1,2]. The Fe$_3$O$_4$ is the strong magnetic nanoparticles based on natural’s minerals on earth, well known as iron sand [2]. Iron sand is widespread along the southern coast of Java island in Indonesia. It consists of many minerals, including silica, titania, alumina, and iron oxide [3]. Natural iron sand contains magnetic minerals such as magnetite (Fe$_3$O$_4$), hematite (α-Fe$_2$O$_3$), and maghemite (γ-Fe$_2$O$_3$) [4-6].

Magnetic nanomaterials are inseparable from surface stabilization and functionalization of Fe$_3$O$_4$ nanoparticles for biomedical applications [7]. Fe$_3$O$_4$ is a magnetic nanoparticle that tends to be unstable. To increase their surface stabilization of Fe$_3$O$_4$ nanoparticles, formed polymer layer using dextran, polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and polyethylene glycol (PEG) [8-10]. Fe$_3$O$_4$ coated by PEG polymer has the physical size and crystal size which smaller with increasing weight of
PEG [2,9]. The methods for synthesis Fe₃O₄ powder include cathodic electrochemical deposition [5], direct sono electrochemical [10], hydrothermal [11], and co-precipitation [12]. The co-precipitation method has great advantages such as nano-crystallized, high purity, homogeny, simple and low cost [13-15].

Fe₃O₄ material tends to be unstable and agglomerate in nano size. The agglomeration of these nanoparticles can be minimized by modifying the surface using polymers. Radoń (2017) synthesized Fe₃O₄ nanoparticles with polymer wrapping resulting in a smaller nanoparticle crystallite size compared to bare Fe₃O₄ [16]. Previous research was carried out by Yang (2014) who synthesized Fe₃O₄ with surface modification using PEG which showed that the crystallite size of the nanoparticles was 15 nm and had better dispersion with the addition of PEG [17]. Anbarasu's (2015) study resulted in a Fe₃O₄ crystallite size of about 10-15 nm with a weight addition of PEG using commercial raw material [2]. The addition of PEG with mass variation 0, 0.1, 0.2, and 0.3 grams of natural iron sand as raw material to obtain stable Fe₃O₄ nanoparticle material with an optimal amount of PEG-4000 have never been done. Therefore, this study aims to obtain nano-sized magnetite particles from natural iron sand and to show the effect of adding PEG-4000 on the characteristics of Fe₃O₄ nanoparticles.

2. Methods

2.1. Materials
The main precursor in this research is natural iron sand from Kulon Progo beach of Indonesia, chloride acid 37% (HCL), ammonium hydroxide (NH₄OH) solution, aquadest, and polyethylene glycol - 4000 (PEG-4000) as coatings. The first step is the extraction of natural iron sand using a permanent magnet to obtain Fe₃O₄ and remove its impurities.

2.2. Synthesis of Fe₃O₄ nanoparticles
The iron sand was extracted by magnetic permanent to remove the impurity of Fe₃O₄. The extracted iron sand is taken as 15 gram and dissolved with 30 ml chloride acid (37%), then stirred using a hot plate by a temperature 70 °C for 6 hours. The solution is formed and then filtered to obtain FeCl₃. Next, NH₄OH solution was added slowly while stirring and wait a few moments until form black sediment. The sample was washed by aquadest three times to reduce residual salts from the reaction. The black precipitate from the solvent using a permanent magnet. Manufacture Fe₃O₄@PEG, black precipitate was added by PEG. Dissolved 0.1 gram, 0.2 gram, and 0.3 gram of PEG with aquadest, heated at temperature 100 ºC and put into Fe₃O₄ solution while stirred. Sample of Fe₃O₄ was named sample A, Fe₃O₄ with 0.1 gram of PEG were named sample B, Fe₃O₄ with 0.2 gram of PEG were named sample C, and Fe₃O₄ with 0.3 gram of PEG was named sample D. Samples was dried at the furnace for 2 hours at a temperature below than 200 ºC.

2.3. Characterization
Characterization was used X-ray diffraction (Shimadzu XRD-7000) for obtaining the XRD pattern, Fourier transform infra-red (FTIR) spectrometer (PerkinElmer Spectrum IR 10.6.1), and analytical scanning electron microscopy – energy dispersive X-ray (SEM – EDX) (JEOL JSM-6510LA) at Laboratorium Terpadu Diponegoro University. Quantitative analysis used Profex 4.2.0 for measuring the crystallite size and obtain the fraction of all phases in the XRD pattern.

3. Results and discussion
The XRD pattern of the Fe₃O₄ and Fe₃O₄ synthesis is shown in figure 1. XRD diffraction images of Fe₃O₄ nanoparticle is indicated by letter A, Fe₃O₄@PEG nanoparticles with a PEG mass of 0.1 gram is indicated by letter B, PEG mas of 0.2 gram is indicated by letter C, and PEG mass of 0.3 gram is indicated by letter D. All diffraction peaks of the nanoparticles were according with Joint Committee Powder on Diffraction Standards (JCPDS) No. 19-0629. The diffraction peaks obtained at an angle of
2θ for the Fe₃O₄ phase are as follows 30.22°, 35.59°, 37.23°, 43.26°, 53.67°, 57.22° respectively according to the miller's index (220), (311), (222), (400), (422), and (511), respectively. The maximum intensity of the Fe₃O₄ diffraction pattern formed at an angle of 2θ is 35.5932°, which corresponds to miller's index (311). The result of phase using profex 4.2.0 for Fe₃O₄ has a lattice parameter value of 8.3758 Å and for Fe₃O₄@PEG is 8.3589 Å with a cubic crystal structure. The lattice parameter from No. 19-0629 reference is for bulk (8.397 Å). The lattice parameters in this study are below standard because the effect of the smaller particle size affects the lattice parameter values [14]. The average crystal size of the nanoparticles was calculated using Debye Scherrer’s formula:

$$d = \frac{0.89 \lambda}{\beta \cos \theta}$$

Where d (in nm) is the crystallite size, λ is the wavelength emitted by the X-ray source (Cu Kα = 1.5406 Å), θ is the Bragg’s angle, and β (in radian) is the full width half maximum (FWHM) of the diffraction peak.

![X-ray diffraction pattern](image)

Figure 1. The X-ray diffraction pattern of Fe₃O₄ and Fe₃O₄@PEG nanoparticles with different amount

The peak at 2θ angle of 32.7° in XRD pattern is the highest peak in the presence of salammoniac (NH₄OH). The existence of the salammoniac phase because the FeCl₃ solution is added with NH₄OH to form NH₄Cl. NH₄Cl can be trapped between Fe₃O₄ nanoparticle sediments even though the sample has been washed with distilled water because the nanomaterial of Fe₃O₄ has a relatively large surface area which causes the remaining distance between small particles. This causes NH₄Cl to be evenly distributed. Samples C and D in Figure 1 show that adding the mass of PEG to the Fe₃O₄ solution can
reduce the intensity of NH$_4$Cl because of the characteristic of PEG is a hydrophilic and biocompatible polymer [18].

Table 1. Crystallite size of Fe$_3$O$_4$ nanoparticle and Fe$_3$O$_4$@PEG

| Sample | Crystallite size (nm) |
|--------|-----------------------|
| A      | 12.98                 |
| B      | 12.65                 |
| C      | 11.91                 |
| D      | 12.35                 |

Table 1 showed that the average crystallite size of Fe$_3$O$_4$ and Fe$_3$O$_4$@PEG nanoparticles. The crystallite size of Fe$_3$O$_4$ nanoparticles is bigger compared to Fe$_3$O$_4$ coated by PEG polymer. In our study, the addition of PEG made the particle size is smaller, but in sample D the size was even bigger. This is related to the PEG function which is used to control the particle size as a template and exhibit better dispersion [17]. PEG could work according to its function if the PEG added has the right composition and ratio. The magnetite fraction was calculated by profex 4.2.0. The result of magnetite fraction formed was dominated by Fe at 72.36% and O at 27.64%.

![Figure 2. FTIR spectra of (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$@PEG nanoparticles](image-url)

Figure 2 is present FTIR spectra of the sample of Fe$_3$O$_4$ and Fe$_3$O$_4$@PEG with mass of 0.3 gram. The bands in the range of 400 – 650 cm$^{-1}$ are characteristic of Fe-O bond in Fe$_3$O$_4$ [16]. The peak absorption of sample Fe$_3$O$_4$ located at 556 cm$^{-1}$ and Fe$_3$O$_4$@PEG located at 577 cm$^{-1}$ that implicates Fe$_3$O$_4$ nanoparticles have been successfully synthesized. The peak at 1096 cm$^{-1}$ is the stretch of C-O in the Fe$_3$O$_4$@PEG nanoparticles [4] which indicates that PEG was coated Fe$_3$O$_4$ nanoparticle, and there is a residue exist at PEG in the final product [19]. The absorption peak at 2810 cm$^{-1}$ is related to 3400-2400 cm$^{-1}$ are O-H bonds of the polyphenols group of water molecules bond in Fe-O surface [8].
The morphology of Fe$_3$O$_4$ and Fe$_3$O$_4$@PEG nanoparticles was determined using scanning electron microscopy (SEM) with a magnification of 1000 times. Figure 3 shows a typical SEM of Fe$_3$O$_4$ magnetic nanoparticles and Fe$_3$O$_4$@PEG nanoparticles, which 0.3 gram of PEG. The magnetic Fe$_3$O$_4$ nanoparticles that were not covered by PEG appeared to be agglomerated, while the Fe$_3$O$_4$ nanoparticles additional by PEG were spherical in shape, better dispersed, and the grain boundaries were clearer. The grain size of Fe$_3$O$_4$ 11.86 nm Fe$_3$O$_4$@PEG was measured and calculated using imageJ, are obtained 13.83 nm, which correspond to the crystallite size.
Figure 4 shows the energy dispersive X-ray (EDX) in magnetic nanoparticles. The results show that the dominant phase is in O, Cl, and Fe with energies of 0.525 keV, 2.621 keV, and 6.398 keV, respectively, with a K wavelength. The presence of the Cl phase in the final product indicates contamination during the suspension process. Fe₃O₄ nanoparticles that have been synthesized have wt% of Fe: 70.57% and O: 29.43%, while Fe₃O₄ nanoparticles with the addition of PEG have wt% of Fe: 65.91% and O: 34.09%. EDX analysis shows that iron (Fe) has successfully synthesized and released its impurity [20].

4. Conclusion
The magnetic nanoparticles Fe₃O₄ and Fe₃O₄ with the addition of PEG have been successfully synthesized using the co-precipitation method. The crystallite size of the nanoparticles were 11-13 nm and dispersed better with additional PEG. Fe₃O₄ and Fe₃O₄@PEG nanoparticles have dominant phases of Fe and O, with the phase of Fe about 65% and O about 35%. The crystallite size of Fe₃O₄ nanoparticles decreased with increasing PEG amount, except for the addition of 0.3 grams of PEG.

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