Effect of Polyethylene Glycol (PEG) on Particle Distribution of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 Nanoparticles

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Abstract. Mn$_{0.25}$Fe$_{2.75}$O$_4$ nanoparticles have been successfully synthesized using a coprecipitation method. PEG 6000 polymer was added on the synthesis of Mn$_{0.25}$Fe$_{2.75}$O$_4$, which aimed at decreasing and preventing the emergence of aggregation between particles. The characterization of the phase structure, absorption of functional groups, and distribution of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles have been successfully performed using the instruments of XRD, FTIR, and Small Angel X-Ray Scattering (SAXS) respectively. XRD characterization results showed that the phase structure formed was in the form of magnetite and corresponded to the Inorganic Crystal Structure Database (ICSD) number 9013529. The bond of Fe-O and Mn-O consecutively on the wave numbers of 430 and 482 cm$^{-1}$ which were the representation of Mn$_{0.25}$Fe$_{2.75}$O$_4$ material have been successfully confirmed through the characterization using FTIR, meanwhile the stretching vibrating on the wave numbers of 1251, 1352, 1472, and 1629 cm$^{-1}$ for functional groups C-H is the representation of PEG template which has the chemical structure of $-$OH$-$CH$_2$-$CH$_2$-$[n]$ OH. SAXS characterization showed that the primary and secondary particle sizes from the Mn$_{0.25}$Fe$_{2.75}$O$_4$–PEG 6000 nanoparticle were 3.08 and 11.4 nm respectively. The value is the optimum results of the PEG 6000 template influence on the synthesis of Mn$_{0.25}$Fe$_{2.75}$O$_4$–PEG 6000 nanoparticles which are potential to be a raw material of magnetic fluid and gel on hyperthermia therapy.

Keywords: Mn$_{0.25}$Fe$_{2.75}$O$_4$, PEG 6000, Template, SAXS
1. Introduction

Nowadays, a study on magnetic nanomaterial has been an interest of many researchers because the material ingredient has a wide potential to be applied on various fields such as in the fields of medical engineering, industry, and magnetic engineering. Among other magnetic materials, iron oxide (Fe₃O₄) is one of the interesting materials to be studied due to its unique magnetic property, chemical stability, and biocompatibility [1]. Magnetic materials based on Fe₃O₄ have been utilized in several applications including Magnetic Resonance Imaging (MRI) [2,3], anti-radar material [4], cancer therapy [5,6], drug delivery system [7] and et cetera.

In obtaining a magnetite nanoparticle, various ways and methods have been reported by researchers. Shahid et al. 2018 [8] synthesizing Fe₃O₄ particles with the materials of steel industry waste. Other researchers reported that Fe₃O₄ nanoparticles could be synthesized using a simple solvothermal method at 200 °C for 8 hours [9]. The method was using poly (vinyl) pyrrolidone (PVP) with a different concentration to gain unique nanoparticles with the average particle size of ~ 50–90 nm [9]. In addition, in the previous research [10], the researcher has successfully fabricated Fe₃O₄ nanoparticles using a coprecipitation method and obtained an average particle size of 15 nm.

To gain an optimum particle size and magnetization value from Fe₃O₄ nanoparticles, several ways and methods have been performed by the researchers, one of them is by performing a certain ion doping treatment such as Zn²⁺ [11], Ni²⁺ [12], and Mn²⁺ [13]. Specifically, on the ion doping on Mn²⁺, the distribution of Cation on metal ion can give an effect on the magnetic properties of Fe₃O₄ nanoparticles [14]. Taufi et al. 2015 also reported that the addition of Mn²⁺ ions to Fe₂O₃ which form Mn₂Fe₃O₄ can increase the saturation magnetization value of Fe₂O₃. This increase in magnetization is caused by Mn²⁺ ions which have a magnetic moment of 25% higher than Fe²⁺ ions, where the value of Mn²⁺ magnetic moment is recorded at 5μB while Fe²⁺ is 4μB [13]. This result showed that there is a significant effect of Fe₂O₃ nanoparticle doping process by Mn²⁺ ion, however, the synthesis and the characterization of PEG 6000 template effect on the synthesis process of Mn₀.2₅Fe₂.₇₅O₄-PEG 6000 nanoparticles is rarely reported. This research report also reviewed the PEG 6000 template effect on the structure and distribution of Mn₀.2₅Fe₂.₇₅O₄-PEG 6000 nanoparticles.

2. Materials and Methods

2.1. Synthesis of Mn₀.2₅Fe₂.₇₅O₄-PEG 6000 nanoparticles

The materials used in this research were iron sand from Tulungagung city Beach, hydrochloric acid (HCl), manganese (II) chloride tetrahydrate (MnCl₂·4H₂O), ammonium hydroxide (NH₄OH) and aquadest. The synthesis of Fe₃O₄ nanoparticles was begun by the separation process of iron sand using a permanent magnet to generate magnetic powder with a low impurity. Through a coprecipitation method, the magnetic powder obtained from the separation process was mixed with HCl on a certain concentration to generate FeCl₂ and FeCl₃ solutions. The solution was then added to MnCl₂·4H₂O with a concentration of x = 0.25. The next step is titration with an NH₄OH solution and processed using a hot plate magnetic stirrer. The titration result was washed with distilled water until it reached normal pH (pH 7) which was then filtered using filter paper with a certain mess scale. The obtained Mn₀.2₅Fe₂.₇₅O₄ nanoparticles were then mixed with 20 ml of PEG 6000 solution and processed on a hot plate magnetic stirrer for 1 hour at room temperature. The results of the mixture of nanoparticles Mn₀.2₅Fe₂.₇₅O₄ and PEG 6000 are then filtered again and in the oven for 1 hour. Finally, the formed Mn₀.2₅Fe₂.₇₅O₄-PEG 6000 nanoparticles were able to be XRD, FTIR, dan SAXS characterized.

2.2. Characterization

In order to find out the effect of PEG 6000 template on particle distribution of Mn₀.2₅Fe₂.₇₅O₄-PEG 6000 nanoparticles, the samples from this work were characterized using XRD, FTIR, and SAXS. The XRD instrument was used to find out the crystal structure of Mn₀.2₅Fe₂.₇₅O₄-PEG 6000 nanoparticles as phase composition, crystal size, and lattice parameter. FTIR characterization was conducted to know the
functional groups from Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles. While the SAXS was used to find out the particle distribution of primary and secondary particle sizes.

3. Results and Discussion

3.1. XRD Test Results
The XRD characterization of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles was performed at the range of 10$^0$ to 80$^0$. Figure 1 shows the diffraction pattern of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles in which the refinement was performed using Rietica software. From the analysis results, it was obtained that the phase of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles was magnetite phase which was identifies based on the database of Inorganic Crystal Structure Database (ICSD) number 9013529. The noted magnetite phase has the highest crystal peak at 35.4$^0$ in the field hkl (311) while the distribution of other crystal peaks is identified at the angles (2$\theta$) of 30.15$^0$, 43.05$^0$, 53.5$^0$, 56.97$^0$, 62.59$^0$, dan 74.28$^0$ and each corresponded to the Miller index position (111), (220), (400), (422), (511), dan (440). The lattice parameter and the comparison results of crystal grain size using a Rietica analysis and Debye Scherrer presented on Tabel 1. The lattice parameter results obtained between the data model with the refinement results showed the corresponding results. It can be concluded that the formed Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 is a magnetite phase representation.

![Figure 1. Refinement results of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles diffraction patterns](image_url)

Through a Rietica analysis, the crystal grain size of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles of 4.97 nm. This is in line with the average size of Mn-ferrites nanoparticles which is 5.1 nm as reported by Bahtiar et al. 2017 [15]. In addition to using Reitica analysis, Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles were also carried out particle size analysis using the Debye Scherrer method. In this method, the value of Full Width Half Maximum (FWHM) which is the reference is FWHM from the highest peak which is at the angle (2$\theta$) of 35.46$^0$ as shown in Figure 2. From the results of refinement, crystal grain size of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 nanoparticles is 6.29 nm. This result is slightly greater than the value obtained using Reitica analysis.
Table 1. The value of lattice parameter and crystal grain size Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000

| Sample                  | Lattice Parameter | Crystal Grain Size (nm) |
|-------------------------|-------------------|-------------------------|
|                         | $a = b = c$ (Å)   | Rietica     | Model     | Rietica     | Debye-Scherrer       |
| Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 | 8.38              | 8.40        | 4.97      | 6.29        |

3.2. FTIR Characterization Results

The FTIR characterization was conducted to find out the functional groups of Mn$_{0.25}$Fe$_{2.75}$O$_4$ nanoparticles after given the PEG 6000 template. PEG 6000 is the polymer that is easy to dissolve in water and non-toxic with the chemical structure of -OH[-CH$_2$-CH$_2$]-$_n$OH. The FTIR test result of Mn$_{0.25}$Fe$_{2.75}$O$_4$-PEG 6000 is shown in Figure 3.

Based on the results of the data obtained, the spectrum of Mn$_{0.25}$Fe$_{2.75}$O$_4$ nanoparticles was recorded on the functional groups of Fe-O and Mn-O were detected respectively at wave numbers 430 and 482 cm$^{-1}$. These results are consistent with the results of research conducted by previous researchers [16,17] that there is a bond of Fe-O dan Mn-O on the wavenumber below 700 cm$^{-1}$. There are also other studies reported that the functional groups of Fe-O dan Mn-O bond are at the wavenumber above 685 cm$^{-1}$ [18,19]. Furthermore, the analysis result of functional groups on nanoparticles was also supported by other research results, where the functional groups of Fe-O and Mn-O bound will face a stretching vibrating at the wavenumber of 430 – 580 cm$^{-1}$ [20–22].

Besides that, PEG polymer with the chemical structure of -OH[-CH$_2$-CH$_2$]-$_n$OH which becomes the template of Mn$_{0.25}$Fe$_{2.75}$O$_4$ experiences stretching vibrating at the wavenumbers of 1251, 1352, 1472, 1629, and 2879 cm$^{-1}$. The wavenumber is the representations of functional groups of C-H. The absorption of wave numbers also occurs at position 1300 cm$^{-1}$ which shows the representation of the functional group C=O. These results are consistent with previous research reports [23], functional group C=O vibrating is in the wavenumber of 1250 cm$^{-1}$ while the C-H functional group will experience stretching vibrating on the wavenumbers of 1298, 1350, 1456-1471, dan 2879-2791 cm$^{-1}$ [23]. The spectrum of nanoparticles was also observed in wave numbers 3346 cm$^{-1}$. The wavelength is a stretching of O-H functional groups from the sample. This is in line with research conducted by Vamvakidis et al.
[22,24,25]. They also report that the functional group of O-H Stretching is at a wavenumber of ~ 3439 nm⁻¹ or in the range of ~3500 cm⁻¹ [20].

![Figure 3](image)

**Figure 3.** FTIR characterization results for Mn₀.₂₅Fe₂.₇₅O₄-PEG 6000 nanoparticles

3.3. **The SAXS Test Results**

SAXS instrument is one of the sophisticated tools to be used to find out the structure distribution pattern of Mn₀.₂₅Fe₂.₇₅O₄-PEG 6000 nanoparticles. Figure 4 is the fitting result of SAXS characterization of Mn₀.₂₅Fe₂.₇₅O₄-PEG 6000 nanoparticles using global fitting performed by using a two-lognormal distribution pattern via SASfit software.

The global fitting results will obtain a fractal dimension (D), primary particle (r₁), and secondary particle (r₂). The global fitting pattern can be determined by matching the exponentials between the fractal area and the scattering intensity between the experimental data and the theoretical calculation as written in Equation 1 [26].

\[
I(q) \propto \int_0^\infty N_1(r_1) F_x(q,r_1) S(q, \zeta, D, r_1) dr_1 + \int_0^\infty N_2(r_2) F_y(q,r_2) S(q, \zeta, D, r_2) dr_2
\]  

Equation 1 is a theoretical calculation for global fitting using the two-lognormal size distribution with I(q) is intensity, \([F(q,r)]^2\) is the scattering amplitude from the information of electron density and variables \(S(q, \zeta, D, r)\) are structure factor.
Figure 4. Global fitting results of SAXS test on Mn0.25Fe2.75O4-PEG 6000 nanoparticles

A two-lognormal distribution that was used in SAXS analysis would generate a size distribution as a representation from structure factor and sphere as a representation from form factor. The global fitting analysis results generated red and black-colored curves. The red-colored curve is the result of global fitting based on theoretical calculation and the black-colored curve is the curve of experimental data results. From the global fitting analysis, it is found that the primary particle size from Mn0.25Fe2.75O4-PEG 6000 nanoparticles is 3.08 nm and the secondary particle size of Mn0.25Fe2.75O4-PEG 6000 nanoparticles is 11.4 nm. This result is not significantly different from the previous studies which stated that the primary and secondary particles of Mn0.25Fe2.75O4 nanoparticles are 3.8 and 9.6 nm respectively [27]. However, the secondary particle from Mn0.25Fe2.75O4-PEG 6000 showed a bigger value than nano Mn0.25Fe2.75O4 nanoparticles without PEG 6000 [27]. The difference in particle sizes between the Mn0.25Fe2.75O4 nanoparticles with and without PEG 6000 is caused by the PEG 6000 polymer template. The existence of PEG 6000 polymer template will cause Mn0.25Fe2.75O4 nanoparticles to be trapped inside the long PEG polymer network eventually raises an aggregation.

4. Conclusion
The synthesis of Mn0.25Fe2.75O4-PEG 6000 nanoparticles has been successfully performed using a coprecipitation method. Mn0.25Fe2.75O4-PEG 6000 nanoparticles have magnetite phase with the database of Inorganic Crystal Structure Database (ICSD) number 9013529 which can be observed from the XRD data analysis and has the average particle size of 4.97 nm. Through a global fitting analysis via two-lognormal distribution, SAXS characterization results showed that the primary and secondary particle sizes of Mn0.25Fe2.75O4-PEG 6000 are 3.08 and 11.4 nm respectively. The aggregation of Mn0.25Fe2.75O4-PEG 6000 nanoparticles occurred as an effect of the PEG 6000 polymer template existence. Mn0.25Fe2.75O4 nanoparticles were trapped in a long network of PEG 6000 polymer chains

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