Analyses of magnetic properties and crystal size on Fe$_3$O$_4$ nanoparticle from local iron sand using PEG as soft template

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Abstract. Nano-sized Fe$_3$O$_4$ has been considered prominent in material science research due to its potential applications in multi-layered aspects. One of the simple and inexpensive methods of nanosized Fe$_3$O$_4$ synthesis is co-precipitation. However, this method has not provided a uniform size. Therefore, this study carried out a few modifications by using PEG-200 and PEG-1000 as a soft template with a volume ratio of 1:1, 1:3, and 1:5. The Fe precursors used in this study are iron sand from the Brantas River, Kediri-East Java, Indonesia. The XRD results showed that the use of PEG in the synthesis of Fe$_3$O$_4$ did not affect the Fe$_3$O$_4$ phase, and this study obtained a crystal size with a range of 6-12 nm. Based on morphological observations using SEM, the use of soft templates in Fe$_3$O$_4$ synthesis can reduce agglomeration rather than without using a PEG template. All Fe$_3$O$_4$ powder samples showed ferrimagnetic behavior with a saturation magnetization of 39.5-70 emu/g.

1. Introduction

One of the most widely scattered materials in Indonesia for the synthesis of Fe$_3$O$_4$ is iron sand. The iron sand consists of magnetite (Fe$_3$O$_4$) elements with high levels (<85%) [1]. Many researchers develop nano-sized material because it encompasses excellent physical and chemical properties. The superiority of nanomaterial is influenced by mesoscopic, surface, and quantum size effects [2]. The characteristic of magnetic material depends on the particle size [3]. Magnetic particles with a size of 10 nm are superparamagnetic at room temperature [4].

Research on iron sand as a magnetic nanoparticle material has been carried out by many researchers because it has broad potential in a variety of applications such as Ferrofluids [5], humidity sensor [6], magnetic field sensor [7], catalyst [8], Magnetic Resonance Imaging (MRI) [9], Drug Delivery Systems [10], and many more. Many potential applications of Fe$_3$O$_4$ and their synthesis process using natural materials are very interesting to develop. However, the synthesis of Fe$_3$O$_4$ nanoparticles still encounters a problem, such as a tendency for agglomeration and inhomogeneity. In response to these constraints, an alternative solution is of paramount importance in the synthesis of Fe$_3$O$_4$ nanoparticles such as employing a template which aims to form nano-sized particles [11].

Polyethylene Glycol (PEG) is one of the templates which can control the particle size and reduce the occurrence of interactions between particles, which can lead to agglomeration [12]. However, the use
of PEG and its function are under-explored. Thereby, in this study, we investigated the effect of the PEG volume ratio on the particle size distribution and magnetic properties.

2. Methods
The Fe$_3$O$_4$ powder was synthesized using the co-precipitation method using iron sand from Brantas river, Kediri-East Java, Indonesia. In this study, we used PEG-1000 and PEG-200 for synthesizing Fe$_3$O$_4$ powder as a soft template. The iron sand was extracted by a permanent magnet and dissolved in HCl (12 M, PA) at 70 °C. The homogeneous solution was filtered to remove the impurity and obtained the FeCl$_3$ + FeCl$_2$ solution. The PEG solution and FeCl$_3$ + FeCl$_2$ solution was stirred at 40 °C for 15 minutes, called solution A. The volume ratio of PEG and FeCl$_3$ + FeCl$_2$ solution was varied in 1:1, 1:3, and 1:5. Then, solution A was titrated with NH$_4$OH and stirred at 70 °C for 30 minutes. The obtained precipitate was washed with distilled water. Therefore, the precipitate was dried up at 70 °C for 2 hours. All samples were characterized by using XRD for phase identification, SEM (Scanning Electron Microscopy) for recognizing the morphology, and VSM for classifying the magnetic properties.

3. Results and Discussion
Figure 1 presents the results of the XRD characterization of Fe$_3$O$_4$ using PEG 200 in Fig. 1a and using PEG 1000 in Fig 1b, which matches the Fe$_3$O$_4$ model data (ICSD model no. 96012) and corresponds with the literature [13]. The diffraction patterns in Fig. 1a and 1b have the same pattern and verify that there is no peak other than the peak of the magnetite phase. This shows that the variation of PEG template volume does not affect the phase in Fe$_3$O$_4$ particles. The broad peaks of XRD in all samples indicate a small crystal size [14].

Calculation of crystal size is achieved using the Scherer equation shown in Eq. 1. The FWHM (Full Width at Half Maximum) value that is obtained from the results of X-ray diffraction peak fittings using the Gaussian function. The calculation results of crystal size are shown in Table 1 for Fe$_3$O$_4$ using PEG-200 and Table 2 for Fe$_3$O$_4$ using PEG-1000.

$$D = \frac{k \lambda}{B \cos \theta}$$  \hspace{1cm} (1)

where $k$ is the Scherrer constant of 0.9, $\lambda$ is Cu wavelength of 0.154056 (Å), $B$ is FWHM of X-ray diffraction peaks, and $\theta$ is the Bragg angle.

The average Fe$_3$O$_4$ crystal size without using PEG was 8.31 nm. The use of PEG-200 in Fe$_3$O$_4$ with the volume ratio of 1:1, 1:3, and 1:5 shows that the size tends to increase as the volume of PEG-200 increases, as shown in Table 1. This result is also seen from the diffraction peak pattern (311) in Fig. 1a that the greater the PEG-200 volume, the narrower the diffraction peak is (311). Meanwhile, Fe$_3$O$_4$ using PEG 1000 is effective at a volume ratio of 1:1 obtained by a crystal size of 6.56 nm as shown in Table 2.

| Sample                  | Crystallite Size (nm) | Difference (nm) |
|-------------------------|-----------------------|-----------------|
| Fe$_3$O$_4$              | 8.31                  | -               |
| Fe$_3$O$_4$ + PEG 200 (1:1) | 9.04                  | 0.73            |
| Fe$_3$O$_4$ + PEG 200 (1:3) | 12.66                 | 4.35            |
| Fe$_3$O$_4$ + PEG 200 (1:5) | 12.37                 | 4.06            |

| Sample                  | Crystallite Size (nm) | Difference (nm) |
|-------------------------|-----------------------|-----------------|
| Fe$_3$O$_4$              | 8.31                  | -               |
| Fe$_3$O$_4$ + PEG 1000 (1:1) | 6.56                  | 1.75            |
| Fe$_3$O$_4$ + PEG 1000 (1:3) | 9.91                  | 1.60            |
| Fe$_3$O$_4$ + PEG 1000 (1:5) | 9.62                  | 1.31            |
Figure 1. XRD Patterns of Fe$_3$O$_4$ using (a) PEG-200, and (b) PEG-1000

The morphology of Fe$_3$O$_4$, Fe$_3$O$_4$ using PEG 200 (1:1), and Fe$_3$O$_4$ using PEG 1000 (1:1) are displayed in Fig 2a, 2b, and 2c, respectively. All samples have the same morphology in the form of a sphere. In the Fe$_3$O$_4$ sample without PEG, it was seen that there was decreased agglomeration in the addition of PEG-200 and PEG-1000. This indicates that the use of PEG as a template has been successful. PEG layers cause limited growth of Fe$_3$O$_4$ particles in all directions, thereby reducing interactions between particles and reducing the agglomeration, which corresponds with the previous work [12].

Figure 2. The morphology of (a) Fe$_3$O$_4$ without PEG, (b) Fe$_3$O$_4$ using PEG 200 (1:1), (c) Fe$_3$O$_4$ using PEG 1000 (1:1)

Based on the results of the VSM characterization in Fig. 3, the magnetic properties of powder Fe$_3$O$_4$ without and using PEG as a template is classified in a soft magnet (Ferrimagnetic). It is found that the hysteresis curves are almost symmetrical, which corresponds with the previous study done by Wei et al. [2]. However, based on the particle size mechanism in magnetic materials, when particles are below the critical size (less than 15 nm for certain materials), the material has a single domain. In the context of magnetic materials that have a single domain, the smaller the particle size, the smaller the value of the coercivity field ($H_c$) is [14]. Meanwhile, the value of $H_c$ in this study is still quite large.

From hysteresis curves in Fig. 3, we can acquire the value of saturation magnetization, remanent magnetization, and coercivity field, which is presented in Table 3. The magnetization value was obtained from the fitting using the modified Langevin equation shown in Eq. 2. The saturation magnetization values of Fe$_3$O$_4$ without PEG, using PEG-200, and PEG-1000 are 39.5, 70, and 51.2 emu/g, respectively. These results are similar to the research conducted by Rashdan et al. [15]. The hysteresis curve of the Fe$_3$O$_4$ sample using PEG-200 has a higher susceptibility. This finding is consistent with the results of the magnetization obtained, which is also higher. These results are following the theoretical framework written in Eq. 4. These results are similar to previous studies conducted by Taufiq et al. [16], contending that a magnetic sample that has a high susceptibility produces greater magnetization.
In Figure 3, it shows when the magnetic field was increased from -1.5 T to 1.5 T, the magnetization increased sharply and formed a curve S, creating a hysterical loop with a nearly zero coercivity field. The sample of Fe₃O₄ using PEG-200 (1:1) has greater saturation magnetization than the sample of Fe₃O₄ using PEG-1000 (1:1), which has smaller crystal sizes in this study. This is possible because the Fe₃O₄ sample using PEG-1000 (1:1) has a non-homogeneous morphology that affects the saturation magnetization value to decrease.

$$M = M_s \left[ \coth \left( \frac{k_B T}{\mu H} - \frac{k_B T}{\mu H} \right) \right] = M_s L \left( \frac{\mu_H}{k_B T} \right) + \chi H$$

(2)

$$M = \chi H$$

(3)

where $M$ is the magnetization of Fe₃O₄ samples (emu/g), $M_s$ is saturation magnetization (emu/g), $\mu$ is the average of the magnetic moment, $k$ is Boltzmann constant, and $H$ is the magnetic field, $T$ is temperature, and $\chi$ is the susceptibility [17].

| Sample                | Fe₃O₄ | Fe₃O₄ using PEG 200 | Fe₃O₄ using PEG 1000 |
|-----------------------|-------|---------------------|----------------------|
| Crystallite Size (nm) | 8.31  | 9.04                | 6.56                 |
| $M_s$ (emu/g)         | 39.5  | 70                  | 51.2                 |
| Bold $M_s$ (emu/g)    | 17.54 | 13.1                | 12.3                 |
| $H_c$ (Tesla)         | -0.031| -0.020              | -0.020               |

4. Conclusion
The soft template based on PEG-200 and PEG-1000 was successfully applied to synthesizing nano-sized Fe₃O₄. The crystal size of Fe₃O₄ without a template is obtained at 8.31 nm. The use of PEG-200 affects the greater addition of PEG volume and the greater crystal size with a value range of 9-12 nm. However, the addition of PEG-1000 with ratio volume 1:1 gained the smallest size, which is 6.56 nm. Moreover, the data SEM confirmed that the role of PEG could reduce agglomeration. In terms of magnetic characteristics, all samples have ferrimagnetic properties. The Fe₃O₄ sample using PEG 200 (1:1) has the highest coercivity field compared to other samples, which is 70 emu/g.
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