Ex-Situ Synthesis of Polyvinyl alcohol (PVA)-coated Fe$_3$O$_4$ Nanoparticles by Coprecipitation-Ultrasonication Method

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Abstract. In this study, the synthesis of Fe$_3$O$_4$ nanoparticles was done with surface modification using PVA with coprecipitation-ultrasonication method. Time variations and PVA concentrations were added to determine the effect on crystallite size and lattice parameters on the synthesis of Fe$_3$O$_4$-PVA nanoparticles. Fe$_3$O$_4$ characterization was done using X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) instruments. FTIR was employed to determine PVA coating on the surface of Fe$_3$O$_4$ nanoparticles. The crystallite size and lattice parameters were analyzed using XRD. From the FTIR data, it is known that the interaction between PVA and Fe$_3$O$_4$ nanoparticles is characterized by Fe-O-C group at 1100 cm$^{-1}$ region which is characteristic of Fe$_3$O$_4$-PVA nanoparticles, C-H groups of PVA in the range of 2950 cm$^{-1}$ wave number, C-C of PVA regions of wave number 1405 cm$^{-1}$, Fe$_3$O$_4$ and Fe$_3$O$_4$-PVA samples are in the range of 565 cm$^{-1}$. In addition, the variation of ultrasonication time and the addition of PVA concentration have an effect on the crystallite size change and the lattice parameter observed from the XRD data. The use of ultrasonication time will affect the size of the crystallite become smaller and the grating lattice parameters obtained are wider. The effect of addition of PVA showed that higher concentration of PVA resulted in smaller crystallite size and larger lattice parameters. These results indicated that ultrasonication time and addition of PVA concentration greatly affect the characteristics of nanoparticles.

1. Introduction
Nanoparticle has become rapidly growing field of study recently. Nanoparticle has an important role in various fields such as industry, healthcare, technology, and biology. It is divided into two types, nanocrystal and nanocarrier that have a wide variety of types such as quantum dot, liposomes, solid nano lipid particles, and metal nanoparticles [1]. Size of nanoparticles is about 1-100 nm [2]. It has unique magnetic characteristics such as super-paramagnetic, high coercivity, low temperature, and high magnetism. There are several methods for nanoparticle synthesis for instance thermal decomposition, hydrothermal synthesis, sonochemical, and co-precipitation [3]. Co-precipitation is a bottom-up synthesis step used to form a particle into certain size like nanometer-sized [4]. The principle of the co-precipitation method is to release a continuous bond metal in liquid form has without regard to the specific mechanism that occurs. From the method, a solid-shaped material from its liquid-shaped precipitates is obtained [5]. In general, this method can be applied to the synthesis process of zinc, titanium and iron [6]. Fe$_3$O$_4$ is a combined oxide metal of Fe$_2$O$_3$ and FeO. The oxide metal has amphoteric properties, and is easily oxidized by the environment, that is FeO becomes Fe$_2$O$_3$ after oxdation. Therefore, further treatment is needed to prevent Fe$_3$O$_4$ from oxidation. One method frequently used to prevent oxidation is a coating method with a polyvinyl alcohol (PVA) polymer [6,7,8].
PVA is a biocompatible polymer that can absorb moisture content for hydrogel formation [9]. Therefore, coating nanoparticle surfaces with modification using polyvinyl alcohol can prevent agglomeration resulting in monodisperse particles, coagulation, and stabilizing nanoparticles from oxidation [10]. PVA has a good film functioning as a shaper, emulsion, and adhesive properties. The surface layer of PVA particles can prevent agglomeration causing monodisperse particles. In the process, nanoparticles may be coated by PVA to prevent the coagulation of particles during bioapplication process [16].

Fe₃O₄ nanoparticle is commonly obtained by several chemical synthesis methods, for example coprecipitation, reverse micelle method, plasma microwave synthesis, sol-gel technique, freeze drying, ultrasound irradiation, hydrothermal methods, as well as laser pyrolysis techniques [11], [12]. Coprecipitation is the simplest, easiest and least expensive method, but it can produce Fe₃O₄ particles in the nanometer order. Surface modification of Fe₃O₄ nanoparticle can be done by ex-situ and in-situ. In surface modification, nanoparticles should have biocompatible properties and can be degraded by the body. Materials that can be used for surface modification are organic and inorganic materials. Some examples of the organic materials are poly (ethylene-co-vinyl acetate), polyvinylpyrolidone (PVP), poly-lactic-co-glycolic acid (PLGA), polyethylene glycol (PEG) or polyvinyl alcohol (PVA) which also functions as material for coating [11, 13].

Ultrasonication time affects crystal alteration size, lattice parameter and the morphology of a particle. Ultrasonication time also results in adsorption and desorption which indicate that extracting time is really fast [14]. The longer the sonication time is, particle size tends to be more homogeneous and shrink eventually leading to a stable nanoparticle size and less agglomeration. It occurs because shock wave in sonication method can separate agglomeration and there is a perfect dispersion with the addition of surfactant as stabilizer [15].

Based on all information aforementioned, in this work, Fe₃O₄-PVA nanoparticles were prepared by ex-situ synthesis using coprecipitation coupled with ultrasonication method. Some parameters influenced a crystal size as well as a lattice parameter were investigated through the optimization of ultrasonication time and PVA concentration.

2. Materials and Method

2.1 Chemicals and instrumentation

The materials used were (Iron (III) chloride hexahydrate, Iron (II) chloride tetrahydrate, PVA, Mw 3500 (Merck, Indonesia) and aqueous ammonium hydroxide.

The instruments were FTIR (Fourier Transform Infrared) spectrophotometer (Shimadzu FTIR QP89500, KBr pellet of which wavenumber ranges between 4000 and 400 cm⁻¹), Freeze Dry (35 XL Virtis SP Scientific with the temperature under -40°C and pressure up to ≤ 20 mT). XRD analysis was carried out using Diffractometer system XPERT-PRO with Cu-Kα λ= 1.5406 Å. The XRD data was recorded across a 2θ range of 5° to 60° using a step size of 0.001°.

2.2 Procedure reaction

The procedure for preparation of Fe₃O₄ nanoparticles was adopted from Ghanbari [17] with some modifications. The Fe₃O₄ nanoparticles were prepared first by mixing FeCl₂·4H₂O and FeCl₃·6H₂O with mol ratio of 1: 2 into 100 milliters of distilled water. In the following step, polyvinyl alcohol (5, 7, and 9 gram) was dissolved into100 mL of distilled water and stirred using a magnetic stirrer. Then, the Fe₃O₄ solution was placed on a sonicator, and an ammonia solution (2M) was added drop wise using a syringe pump at flow rate of 20 mL/h. These procedures resulted in the formation of black precipitates of Fe₃O₄-PVA5, Fe₃O₄-PVA7, and Fe₃O₄-PVA9 nanoparticles. The black precipitate was washed using distilled
water until it reached the neutral pH. The sample was dried using the freeze dryer and stored before being characterized.

3. Result and discussion
During initial preparation of Fe₃O₄ synthesis, along with the addition of distilled water, FeCl₃·6H₂O and FeCl₂·4H₂O salt solution turned into yellowish color. The addition of ammonia solution (2M) gradually turned yellowish solution into brownish yellow-brown, then brown-blackish and at the end of the process it became solid black. The formation of black color and the black precipitate indicated Fe₃O₄ nanoparticle formation. During the synthesis, the color of the solution changed several times due to the influence of the compound phase formed [17].

Ammonia solution, which was added into Fe(III) and Fe(II) solutions, caused OH to bind to Fe(III) and Fe(II) solution to form Fe₃O₄ nanoparticles. Furthermore, adding PVA solution to Fe₃O₄ nanoparticles resulted in coating Fe₃O₄ with PVA. It happened since the PVA compound has an O-H group, the H atom would be released and the C-H chain interacted with the Fe₃O₄ surface. Figure 1 described the Fe₃O₄-PVA interaction.

![Figure 1. Fe₃O₄-PVA Interaction Mechanisms](image)

**Figure 1. Fe₃O₄-PVA Interaction Mechanisms**

**Figure 2. IR Spectra of Fe₃O₄-PVA (5,7,9) Nanoparticles and Bare Fe₃O₄ in 60-minute Ultrasonification Time**
Figure 2 describes the Fe$_3$O$_4$-PVA and Fe$_3$O$_4$ nanoparticles spectra without coating. The spectra were obtained from Fe$_3$O$_4$-PVA samples with 60 minutes of ultrasonication time and the influence of (5, 7, and 9)%PVA concentrations. The absorption that appeared in the 3,600 cm$^{-1}$ range showed the presence of an O-H group and it was identified as OH on the Fe$_3$O$_4$ surface. The 2980 cm$^{-1}$ wave indicated the absorption of the C-H group of PVA and the absorption area of 1420 cm$^{-1}$ was the C-C group of PVA. However, the FTIR spectra did not appear on the bare Fe$_3$O$_4$. The Fe-O-C bond interaction may be identified from uptake in a range of about 1100 cm$^{-1}$ which indicated that Fe$_3$O$_4$ had been coated with PVA. The fingerprint range of 568 cm$^{-1}$[18] showed sharp uptake, indicating the presence of Fe-O bond in bare Fe$_3$O$_4$ and Fe$_3$O$_4$-PVA samples.

Table 1. Influence of Fe$_3$O$_4$-PVA Ultrasonification Time towards Crystallite Size and Lattice Parameter

| Samples       | Sonication time (min) | Crystallite size | Lattice parameter |
|---------------|-----------------------|------------------|-------------------|
| Bare Fe$_3$O$_4$ | 30                    | 14.6043          | 8.3260            |
|               | 60                    | 7.8547           | 8.3490            |
|               | 120                   | 7.3354           | 8.3900            |
| Fe$_3$O$_4$-PVA5 | 30                    | 5.3941           | 8.3900            |
|               | 60                    | 8.9134           | 8.3610            |
|               | 120                   | 6.3616           | 8.3660            |
| Fe$_3$O$_4$-PVA7 | 30                    | 9.8878           | 8.3710            |
|               | 60                    | 19.5592          | 8.3550            |
|               | 120                   | 7.2919           | 8.3740            |
| Fe$_3$O$_4$-PVA9 | 30                    | 6.4016           | 8.3870            |
|               | 60                    | 12.5494          | 8.3470            |
|               | 120                   | 6.7617           | 8.3840            |

Table 1 shows the changes in lattice parameters and crystallite size. Each variation had different trend or pattern. Generally the resulting pattern had similarities between each other making it easier to observe. It was also explained that lattice parameters with crystallite size were inversely proportional to the longer duration of ultrasonic usage time for the Fe$_3$O$_4$-PVA nanoparticle synthesis.

Figure 3. The effect of sonication time with crystallite size and Lattice parameter at 7% PVA of Fe$_3$O$_4$-PVA nanoparticles.

Figure 3 showed the smallest crystallite size is obtained at 7% PVA concentration and a 120-minute ultrasonication time. A 60-minute ultrasonication time resulted in crystallite with the largest size. Change in crystallite size obtained with 7% PVA concentration is similar to that when the PVA concentration was
5%. This may be due to the 30-minute ultrasonication time; during nucleation, the PVA polymer is immediately added to the nanoparticles. The PVA polymer could prevent formation of large sized Fe₃O₄ crystals. During the 60-minute ultrasonication, the nucleation took place and followed by growth of the nucleus after it was coated by PVA polymer. As an addition, the possibility of clustering nanoparticles also contributed larger-sized crystals. During the 120-minute ultrasonication, the size of the nanoparticle crystals decreased again since the Fe₃O₄ crystal clusters tended to interact with the PVA polymer and form the Fe₃O₄-PVA cluster. Yang (2005) stated that the longer the ultrasonication time would cause the isolation point (IEP) of Fe₃O₄ to lead to a more acidic condition (lower pH) [19]. In the pH conditions, the positive charge on the surface of Fe₃O₄ would increase. Consequently, the probability of a negatively charged PVA to interact with Fe₃O₄ positively charged would be greater. It would cause the crystallite size of Fe₃O₄-PVA with a 120-minute ultrasonication time became smaller. The lattice parameters of the 7% Fe₃O₄ nanoparticles with time the 30, 60 and 120 minute ultrasonication time were 8.3710 Å, 8.3550 Å and 8.3740 Å respectively. In the first 30 to 60 minutes, formation of Fe₃O₄ took place and after 60 minutes, deformation started taking place. Once the lattice narrowed down and the grid widened, deformation occurred and the bonds loosened.

![Figure 4](image-url). The effect of sonication time toward crystallite size and lattice parameter of bare Fe₃O₄ nanoparticles.

**Figure 4** stated that the lattice parameters of the bare Fe₃O₄ nanoparticles when ultrasonication times were 30, 60 and 120 minutes were 8.3260 Å, 8.3490 Å dan 8.3900 Å respectively. The smallest crystallite size of bare nanoparticles was obtained at 120-minute ultrasonication time. It indicated that Fe₃O₄ sonication process has taken place from the start. However, deformation took place causing larger and longer lattice parameter as well as smaller crystallite size.

**Table 2. Influence of PVA Concentration towards Crystallite Size and Lattice Parameter**

| Sonication Time (minutes) | PVA Mass (g) | Lattice Parameter | Crystallite Size |
|---------------------------|--------------|-------------------|-----------------|
| 30                        | 5            | 8.3900            | 5.3941          |
| 60                        | 7            | 8.3610            | 8.9134          |
| 120                       | 9            | 8.3660            | 6.3616          |
| 30                        | 5            | 8.3710            | 9.8878          |
| 60                        | 7            | 8.3550            | 19.5592         |
| 120                       | 9            | 8.3740            | 7.2919          |
| 30                        | 5            | 8.3870            | 6.4016          |
| 60                        | 7            | 8.3470            | 12.5894         |
| 120                       | 9            | 8.3840            | 6.7671          |
Based on Table 2 about the influence of PVA concentration on the crystallite size and lattice parameters, higher PVA concentration would result in smaller crystallite size and the larger lattice parameters.

**Figure 5.** The effect of PVA Concentrations towards Lattice parameter and Crystallite Size

Figure 5 described the analysis on the influence of (5, 7 and 9)% PVA concentration and 60-minute ultrasonication time towards the crystallite size and lattice parameter in Fe₃O₄-PVA nanoparticle formation. The (5, 7 and 9)% PVA concentration resulted in crystals of whose sizes were 9.8878, 19.5592 and 7.2919 nm while the lattice parameter was 8.3710 Å, 8.3550 Å and 8.3740 Å. When the lattice parameter was 8.396 Å (JCPDS File19-629), a crystal was identified as magnetite but when the lattice parameter was 8.346 Å(JCPDS File 39-1346), it was categorized as maghemite [18]. On the other hand, the XRD analysis is between magnetite and maghemite.

The addition of PVA polymers on the surface of Fe₃O₄ nanoparticles greatly affected the lattice parameters of the nanoparticles. Larger lattice parameters indicated wider gap between Fe and O atoms. Based on the findings, it may be concluded that there was correlation between the crystallite size and lattice parameters of the Fe₃O₄-PVA nanoparticles. In this case, the nanoparticle crystallite size was inversely proportional to the lattice parameter. The smaller the crystallite size resulted in the bigger lattice parameter. The 7% PVA concentration resulted in larger sized crystal compared to the 5% PVA concentration. However, the higher the PVA concentration (9%) was, the smaller the crystallite size would be. In 9% PVA concentration, smaller crystallite size would have larger lattice parameter.

The diffraction pattern generated from the characterization process indicated the formation of Fe₃O₄. Based on Figure 6 on one of the bare Fe₃O₄ variations, the diffraction peak at 2θ = 30°, 35.6°, 43.2° and 57.2°. The peak indicated that Fe₃O₄ nanoparticles had a cubic spinel structure based on the reference (JCPDS file, PDF No. 65-3107) [20].

**Figure 6.** Bare Fe₃O₄ Nanoparticle Difractogram
Based on Figure 7 on one of the 7% Fe$_3$O$_4$-PVA variations, the diffraction peak at 20 = 30.24°, 35.63°, 43.18° and 57.25°. The peak indicated that Fe$_3$O$_4$ nanoparticles had a cubic spinel structure based on the reference (JCPDS file, PDF No. 65-3107) [20].

![Figure 7. 7% Fe$_3$O$_4$-PVA Nanoparticle Difractogram](image)

4. Conclusion

Based on the findings of the research on the ex-situ Fe$_3$O$_4$ nanoparticles synthesis and surface modification using PVA with the coprecipitation-ultrasonication method with various time variations and the addition of variation of PVA concentration towards the influence of lattice parameter and crystallite size using the X-ray Diffraction (XRD) instrument, Fourier Transformation Infra-Red (FT-IR), it can be inferred the characterization of Fe$_3$O$_4$-PVA nanoparticles using FTIR can be seen from the peak of Fe-O-C group, that becomes characteristic of Fe$_3$O$_4$-PVA nanoparticles. The time of ultrasonication of Fe$_3$O$_4$-PVA nanoparticles greatly influences change of crystallite size and lattice parameter. Longer ultrasonication time results in smaller crystallite size and larger lattice parameter. Based on the XRD data, the optimum ultrasonication time was 60 minutes and the most suitable level of PVA is 7%.

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