

One-pot Synthesis and Surface Modification of Fe₃O₄ Nanoparticles Using Polyvinyl Alcohol by Coprecipitation and Ultrasonication Methods

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Abstract. Among the various substances developed through nanoparticles, iron oxide (Fe₃O₄) nanoparticle is one of the substances that have been widely used in various fields such as industry, agriculture, biotechnology and biomedicine. The synthesis of Fe₃O₄ nanoparticle can be carried out by two methods, consist of chemical and mechanical synthesis methods. Coprecipitation is one of the most commonly used methods for chemical synthesis. Fe₃O₄ compounds are easily oxidized because they are amphoteric. To avoid the continuous oxidation process, chemical modification process should be carried out with the addition of a solution of polyvinyl alcohol (PVA). In this study, PVA-coated Fe₃O₄ nanoparticles were synthesized by in-situ coprecipitation and ultrasonication methods through direct mixing (one-pot synthesis) of the iron (II) chloride tetrahydrate (FeCl₂·4H₂O), iron (III) chloride hexahydrate (FeCl₃·6H₂O), and PVA under alkaline condition. The effects of addition amount of NH₃ solution (by adjusting its flow rate using automated syringe pump) and PVA concentration were gently studied. Interaction of PVA with Fe₃O₄ nanoparticle was identified by infrared spectroscopy whereas lattice parameters and crystallite sizes of the synthesized Fe₃O₄ nanoparticles and PVA-coated Fe₃O₄ nanoparticles were assessed by X-ray diffraction (XRD).

1. Introduction

Nanoparticle is very small, invisible and microscopic with diameter ranging from 1 to 100 nm composed of both organic and inorganic chemical substances [1]. Among the various nanoparticles developed, iron oxide (Fe₃O₄) compound is one of the nanoparticle substances that have been widely used in various fields such as agricultural industry, biotechnology, and biomedicine [2].

In general, the synthesis of Fe₃O₄ nanoparticle can be done through two methods, namely chemical and mechanical syntheses methods, with coprecipitation method is one chemical synthesis method that is commonly used because the process is simple with lower cost [3]. One application of nanoparticles in the biomedical field is used as a drug delivery intermediate using Fe₃O₄ compounds. Fe₃O₄ compounds have several characteristics that are biocompatible, biodegradable, non-toxic, and containing magnetic properties [1].

On the other hand, Fe₃O₄ compounds also have some drawbacks that are easily oxidized and tend to agglomerate [4], so it is necessary to modify the surface chemically, of which is by the addition of polyvinyl alcohol (PVA) solution. Polyvinyl alcohol (PVA) is a polymer solution that has the properties to readily form a gel as it is reacted with water, so that the oxidation process in Fe₃O₄ compounds can be minimized [5].

In this study, the methods used in PVA-Fe₃O₄ syntheses are the combination of coprecipitation and sonochemical (ultrasonication) with the rationale is that the combination of these two methods tends to be easy to conduct, requiring relatively lower cost, and the final amount obtained is likely increase. In



addition, the combination of the two methods is expected to produce nanoparticles with the small size of distribution. Moreover, the ultrasonication synthesis method is believed to provide control over the more spherical forms/morphologically [6].

In this study, the surface of the modified Fe_3O_4 nanoparticles is PVA-based polymer which would be synthesized by a combination of coprecipitation-ultrasonication (co-precipitation assisted ultrasonication) method. The surface modification was carried out by addition of polyvinyl alcohol (PVA) solution at three concentration variations. In addition, the effect of time difference of sonication on the nanoparticle crystallite size was also studied in more detail. The effect of the addition of concentration of polyvinyl alcohol (PVA) solution and the duration of sonication on the crystallite size of Fe_3O_4 nanoparticles was analysed by using X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR).

2. Material and Method

2.1 Chemicals

The materials used in this study include ammonia 25% v/v in H_2O , and polyvinyl alcohol (PVA) purchased from Merck (Indonesia), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 99% (w/w), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 98% (w/w) solids purchased from Sigma-Aldrich (Singapore).

2.2 Synthesis of Fe_3O_4 nanoparticles and Fe_3O_4 -PVA Nanoparticles

In the process of synthesis of Fe_3O_4 bare nanoparticles, at first $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solids were consecutively weighed as much as 0.2 g and 0.5406 g (1:2 molar ratio), and then both solids were dissolved in a beaker glass with 20 mL deionized water. The Fe (II) and Fe (III) solutions were mixed and then placed on a sonicator device. Meanwhile, 2M of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution was prepared at the same time. Furthermore, 10 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution was flowed to Fe(II) and Fe(III) mixture with flow rate setting of 30 mL/h. During the process of addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$ into the mixture of Fe salt, a black precipitate was formed. The black precipitate indicates Fe_3O_4 has been formed. Next it was washed with distilled water to neutral pH. Before that, the characterised Fe_3O_4 nanoparticles were dried with freeze drying method.

The 2% of PVA solution was prepared by weighing 2 g of polyvinyl alcohol solids and dissolved into 100 mL of distilled water. The solution was stirred with magnetic stirrer on a hotplate at temperature of $\pm 82^\circ\text{C}$. The heating and stirring process was carried out for ± 15 minutes. Before further use, the PVA polymer solution was let cool to the room temperature.

The preparation of the Fe mixed solution between $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was carried out by weighing the two solids at 0.2 g and 0.5406 g respectively (Fe(II): Fe(III) molar ratio was 1:2). After Fe(II) and Fe(III) solids were weighed and then put into 100 mL beaker glass, and 10 mL PVA polymer solution was added. The mixture was stirred until both Fe solids were mixed with PVA polymer, and then the surface of the beaker glass was covered using an airtight plastic.

The next step was the beaker glass containing the mixture of Fe(II), Fe(III) and PVA solution was placed in a sonicator batch. A 10m L of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution was added to the mixture of Fe and PVA solution through a syringe pump. The addition of ammonia water is carried out by adjusting the flow rate at 30 mL/h.

During the addition process of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution to the mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, a black precipitate was formed. After the sonication process, the precipitate obtained was washed using distilled water until it reached a neutral pH (pH=7). Then the sample was dried with a freezing dryer before the characterisation process.

The same procedures as above were done for syntheses of Fe_3O_4 -PVA nanoparticles, but with different PVA concentrations of 3% and 4%. These three variations of PVA concentrations would be used to see how their effect on the size of the resulting crystallite nanoparticles.

2.3 Characterization of nanoparticles by FTIR and XRD

The characterization of Fe_3O_4 nanoparticles was employed by Fourier Transform Infrared (FTIR) (Shimadzu FTIR QP89500, KBr pellet in wavenumber range $4000\text{--}400\text{ cm}^{-1}$) and was performed to determine the presence of functional groups found in Fe_3O_4 bare nanoparticles and Fe_3O_4 -PVA

nanoparticles. While characterization of Fe_3O_4 nanoparticles using XRD was performed to determine the size of nanoparticle crystals as well as lattice parameters of the Fe_3O_4 bare nanoparticles and Fe_3O_4 -PVA nanoparticles. Measurements with X-ray diffraction (XRD-XPRT-PRO) were performed with Cu $K\alpha$ radiation (30 mA, 40 KV) with a range of 2θ 5-600. The X-ray diffraction pattern resulted from the characterization of each sample variant was then compared with Inorganic Crystal Structure Database (ICSD) #26410 data to confirm the existence of Fe_3O_4 of the sample variant of Fe_3O_4 -PVA nanoparticles. The size of the Fe_3O_4 -PVA crystals is determined by the modified Debye Scherer method with Equation as follows [1]:

$$\ln \beta = \ln \frac{K\lambda}{L \cdot \cos \theta} = \ln \frac{K\lambda}{L} + \ln \frac{1}{\cos \theta}$$

Where :

L : average size of crystallite (nm)

λ : wavelength of X-Ray (nm)

β : FWHM

K : crystallite shape constant

3. Result and Discussion

Prior to the addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution, a mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solids and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solids and polyvinyl alcohol (PVA) solution was bright yellow. After being added with $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution, the colour of the mixture would turn into solid black which indicates the formation of the Fe_3O_4 compound.

Precipitation occurs in Fe^{3+} ions because of the reaction to OH group of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution to form Fe(III) hydroxide in the pH range of 3-4. In addition Fe^{2+} ions will form Fe(II) hydroxide in the higher pH range (8-9) [7]. Fe(III) hydroxide decomposition process becomes FeOOH compound, and then FeOOH compound will react with $\text{Fe}(\text{OH})_2$ compound to form Fe_3O_4 compound. The use of 1:2 ratio in $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solids and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solids is intended to obtain higher purity magnetite compounds.

The samples of Fe_3O_4 nanoparticles were characterized using FT-IR. The result of the characterization using FT-IR was in the form of FT-IR spectra from the samples of Fe_3O_4 bare and Fe_3O_4 -PVA nanoparticles presented in Figure 1. The presence of Fe_3O_4 can be confirmed from the peak that appears in the wave number area between $3514\text{--}3334\text{ cm}^{-1}$. This peak indicates OH uptake on Fe_3O_4 surface.

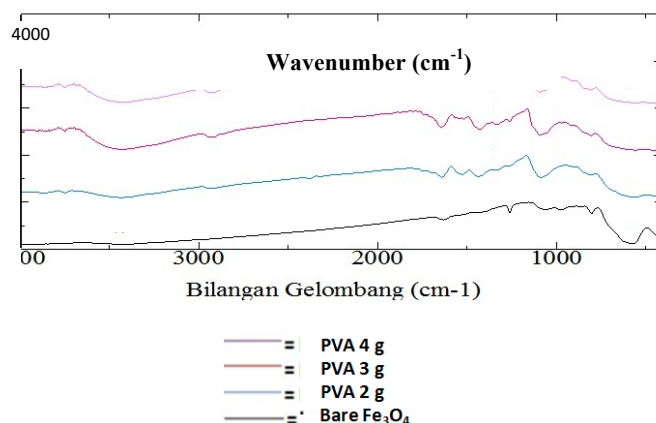


Figure 1. FT-IR spectra of Fe_3O_4 -PVA nanoparticles with the mass variations of PVA in ultrasonication time of 60 minutes

Based on the results of characterization using FTIR on the samples of Fe_3O_4 -PVA nanoparticles, 5 absorption peaks were obtained showing the functional groups indicating Fe_3O_4 and PVA. Adsorption peak at the 3400 cm^{-1} wave region is identified as OH group of Fe_3O_4 , while the C-H and C-C groups of PVA are identified respectively at the wavelength area of 2950 cm^{-1} and 1400 cm^{-1} . The interaction between PVA and Fe_3O_4 is known from the presence of absorption in the 1100 cm^{-1} wave area which is identical to the Fe-O-C group interactions. In the fingerprint area, there is absorption at the 560 cm^{-1} wave number which is confirmed as the interaction between Fe-O from Fe_3O_4 .

In the spectrum of Fe_3O_4 bare nanoparticles, it is observed that it does not contain C-C and C-O groups because there is no PVA content in this compound, while on the other three spectra, it is observed that the presence of C-C and C-O groups is because Fe_3O_4 compounds have been coated with PVA surface. As the PVA concentration increases, the intensity of the spectra of the Fe-O group formed becomes more evident, while the peaks obtained for the C-C and C-O groups even sharpen.

FTIR spectra showing the presence of Fe-O functional groups will be more evident with the increasing concentrations of PVA. Such condition will cause the PVA layer which coats Fe_3O_4 compounds to be more numerous, so the distance between Fe and O atoms produced is smaller. In the use of 2 to 3 g of PVA, there is a growing crystallite size due to the growing crystal of the Fe_3O_4 nanoparticles, while the use of mass of 3 to 4 grams of PV will cause the decrease of crystal size due to the ultrasonication process that will cause bonds between atoms increasingly tenuous. Ultrasonication process will provide energy that causes the breaking of the bonds so that the crystallite size resulted will be smaller.

The results of characterization with XRD are presented in Figure 2. Based on characterization using XRD, two identical peaks of Fe_3O_4 were obtained respectively at hkl (311) and (511). From Figure 2, we can get information that the decreasing diffractogram peaks due to the use of 2 to 3 grams of PVA, then sharp peaks reappear in the use of 3 to 4 grams of PVA at hkl position (311), while the peak of the diffractogram at hkl (511), the intensity decreases as the increasing mass usage of PVA.

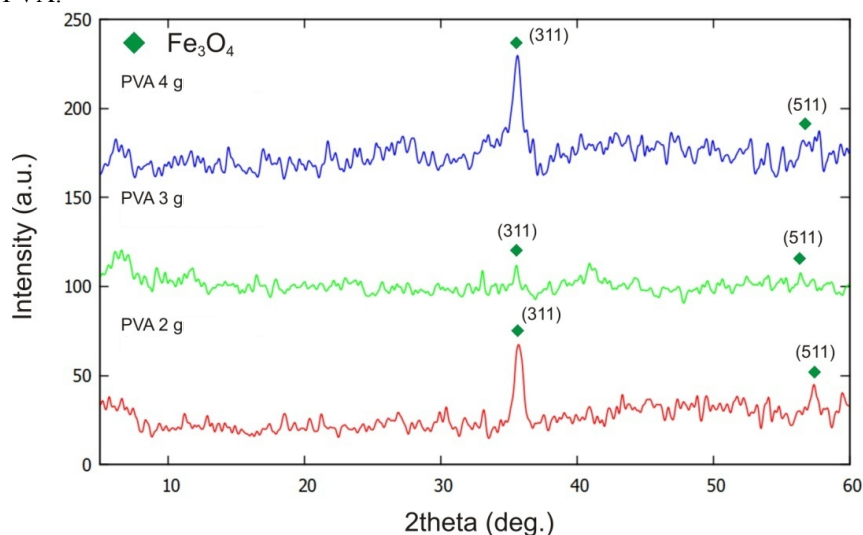


Figure 2. XRD pattern of PVA- Fe_3O_4 (2, 3 and 4 g PVA with ultrasonication time of 60 minutes)

The original large crystals will split and form smaller sizes. There is a comparable correlation between the size of the crystallite and the lattice parameter (Figure 3). Based on JCPDS file 19-629,

the lattice parameter for Fe_3O_4 is 8.396. The lattice parameter calculations show the values close to the lattice parameters for standard Fe_3O_4 .

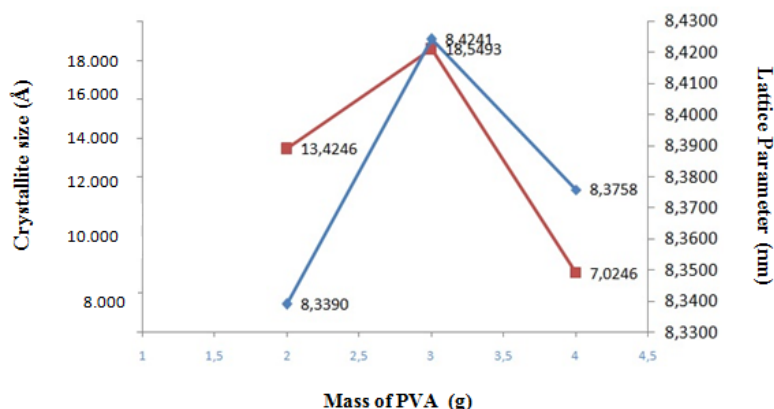


Figure 3. Graph of comparison between lattice parameter and the size of crystallite at PVA- Fe_3O_4 (2, 3 and 4 g in ultrasonication time of 60 minutes)

4. Conclusion

The Fe_3O_4 -PVA nanoparticles have been successfully synthesized by coprecipitation assisted ultrasonication methods. The effect of variation of concentration of PVA on Fe_3O_4 surface was studied from FTIR spectra. The decrease in the intensity of the absorption peaks from the OH group in the wavelength area $3514\text{--}3334\text{ cm}^{-1}$ correlates with an increase in PVA concentration. In addition, the concentration of PVA added on Fe_3O_4 surface affects the lattice parameter and the size of crystallite. The largest crystallite and lattice parameters were obtained in the addition of PVA with a concentration of 3%.

References

- [1]Wu, W., He Q and Jiang C 2008 Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies *Nanoscale Research Letters* **3** 397–415
- [2]Liu, X.D., Chen, H., Liu, S.S., Ye LQ and Li Y P2015 Hydrothermal Synthesis of Superparamagnetic Fe_3O_4 Nanoparticles with Ionic Liquids as Stabilize *Materials Research Bulletin* **62** 217-221
- [3]Hariani, P.L., Faizal, M., Ridwan, Marsi dan Setiabudidaya D 2013 Synthesis and Properties of Fe_3O_4 Nanoparticles by Co-precipitation Method to Removal Procion Dye *International Journal of Environmental Science and Development* **4** 336-340
- [4]Horak, D., Babic, M. Mackova Hand Benes M J 2007 Preparation and Properties Of Magnetic Nano And Microsized Particles For Biological And Environmental Separations *J. Sep. Sci.* **30** 1751-1772.
- [5]Ayyapan, S., Panneerselvam, G., Antony M P and Philip J 2011 High Temperature Stability of Surfactant Capped CoFe_2O_4 Nanoparticles *Materials Chemistry and Physics* **130** 1300-1306.

- [6] Monshi, A., Foroughi MR and Monshi MR 2012 Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD *World Journal of Nano Science and Engineering* **2** 154-160
- [7] Liang, X., Shi, H., Jia, X., Yang Y and Lin X 2011 Dispersibility, Shape and Magnetic Properties of Nano-Fe₃O₄ Particles *Materials Sciences and Application* **2** 1644-1653