Factors Influence the Structural and Magnetic Properties of Ag-Fe₃O₄ Nanocomposites Synthesized by Reduction Method

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Abstract. Silver nanoparticles integrated with a magnetic matrix such as Fe₃O₄ to form Ag-Fe₃O₄ nanocomposites show some advantages in their applications as an antibacterial agent and heterogeneous catalyst. This material can be synthesized by a combination of electrochemical and reduction methods supported by ultrasonic route. The purposes of this study are to synthesize the nanocomposites by reduction method and to study the effect of synthesis parameters on the structural and magnetic properties of the generated nanocomposites. This research consisted of three main stages. The first step was the electrochemical synthesis of magnetite nanoparticles using electro-oxidation of iron in water. Second, adsorption of Ag⁺ on the surface of Fe₃O₄ carried out by sonication of a mixture of AgNO₃ solution and powder of Fe₃O₄ nanoparticles. The third stage was the reduction of Ag⁺ to Ag⁰ with glucose as reductant and NaOH as an accelerator, where it was conducted under a variation of AgNO₃ mole ratios to glucose and NaOH concentration. The characterizations of Ag-Fe₃O₄ nanocomposites were performed using XRD and VSM. The results of the characterizations showed that Ag-Fe₃O₄ nanocomposites have been successfully synthesized. There was an optimum concentration of NaOH at pH (11) and mole ratio of AgNO₃ to glucose (1 : 8) in the synthesis process producing the composite with the highest crystallinity.

Keywords: Ag, Fe₃O₄, nanocomposite, crystallinity, reduction method

1. Introduction

Composite is a combination of two or more materials to improve certain specific properties. The nanocomposite is a composite in nanometer dimensions. Nanocomposite has physical, chemical and mechanical properties which are better than the similar materials in macro scale [1]. The states of the nanocomposites in their applications can be colloids, powders, fibers, membranes or films. One of the nanocomposites is a composite between silver and magnetite, Ag-Fe₃O₄ which has many benefits, e.g. as a catalyst and an antibacterial [2-3]. The applications of Ag-Fe₃O₄ nanocomposite as an antibacterial agent related to the activity of silver that affect the metabolisms of cells and inhibit cell’s growth. Silver penetrates into the cell membrane and potent to prevent the synthesis of protein to further and ultimately lead the cell to die [4]. Due to the mentioned properties, the nanocomposite can be applied as an antibacterial in water treatment [5].

The methods for Ag-Fe₃O₄ nanocomposite synthesis include reduction method, sonochemical, solvothermal, sol-gel, and co-precipitation methods [6]. The synthesis of the composite in this study based on reduction method, started from the synthesis of Fe₃O₄ nanoparticles by electro-oxidation of iron in water [7], and then followed by synthesis of the Ag-Fe₃O₄ composite using a combination of
adsorption and reduction processes. The adsorption of Ag\(^+\) ion on the surface of magnetite was assisted by ultrasonic. Ultrasonic waves will make the agglomeration of magnetite rupture so that the size of the magnetite decreases and it creates greater surface area. A larger surface area of magnetite enhances its adsorption capacity. After the adsorption process, a reduction using sugar as a reducing agent and sodium hydroxide as an accelerator was conducted. Factors suspected to affect the characters of the resulting nanocomposite are the pH of the system and the mole ratio of AgNO\(_3\) to glucose. The purposes of this study was to synthesize the nanocomposite by using reduction method and study the effect of AgNO\(_3\) mole ratio to glucose and the concentration of NaOH or the pH system to the character of Ag-Fe\(_2\)O\(_4\) nanocomposite.

2. Experimental method
This research consisted of three main stages. The first step was the electrochemical synthesis of magnetite nanoparticles i.e. electro-oxidation of iron in water under DC 70V. The iron resulted via electroplating process using FeSO\(_4\).7H\(_2\)O (Merck) as the electrolyte. Second, adsorption of Ag\(^+\) on the surface of Fe\(_3\)O\(_4\) was carried out by sonication of a mixture of a solution of AgNO\(_3\) (Merck) and powder of Fe\(_3\)O\(_4\) nanoparticles under the frequency of 42 kHz. The third stage was the reduction of Ag\(^+\) to Ag\(^0\) with glucose as a reductant and NaOH (Merck) as an accelerator. The last step was conducted with a variation of AgNO\(_3\) mole ratios to glucose and the concentration of NaOH. Characterization of the Ag-Fe\(_2\)O\(_4\) nanocomposite was done using XRD (Panalytical Xpert Pro) and VSM (Type 1.2H VSM, Oxford). The XRD spectra of the composite were then confirmed by the XRD standard pattern of magnetite (JCPDS Card No. 19-629) and silver (AMCSD Code No. 0011135).

3. Results and Discussion
The synthesis of Ag-Fe\(_2\)O\(_4\) nanocomposite assisted by ultrasonic was conducted by dissolution of silver nitrate in demineralized water, so AgNO\(_3\) dissociates into Ag\(^+\) and NO\(_3^-\), and then they were mixed with Fe\(_3\)O\(_4\) and subsequently sonicated at room temperature. Glucose was used as a reducing agent to change silver (1) to silver (0). NaOH was added to the system for being the accelerator in the reduction process. The reaction equation of such process is described in the following equations.

\[
\text{Ag}^+ + \text{Fe}_3\text{O}_4 \rightarrow [\text{Ag(Fe}_3\text{O}_4)]^+ \tag{1}
\]

\[
2[\text{Ag(Fe}_3\text{O}_4)]^+ + 2 \text{OH}^- + \text{C}_3\text{H}_5\text{O}_2\text{CHO} \rightarrow 2 \text{Ag} + 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} + \text{C}_3\text{H}_5\text{O}_2\text{COOH} \tag{2}
\]

Theoretically, as shown in equation (2), the concentration of NaOH and the mole ratio between AgNO\(_3\) and Fe\(_3\)O\(_4\) will affect the process. The statement is confirmed by the results of the product’s characterization.

![Figure 1. XRD pattern of Ag-Fe\(_2\)O\(_4\) produced at the concentration of 0.04 NaOH M](attachment:image.png)
Figure 1 presents the result of XRD analysis of Ag-Fe₃O₄ produced in the concentration of 0.04 M NaOH. As shown in Figure 1, such spectrum presents two kinds of peaks belong to Fe₃O₄ and Ag, respectively, i.e. at 2θ 30.2°; 35.6°; 53.6°; 57.1°; 62.6°; and 38.1°, 44.3°, 64.4°, 77.5°, 81.5°. This diffraction data proved that a high purity of Ag-Fe₃O₄ has been successfully prepared. This conclusion was also supported by the corresponding magnetization curve that was produced by VSM analysis as shown in Figure 2. As described in Figure 2, the non-magnetic material of silver that was coated at magnetite’s surface reduced the magnetization saturation (Mₛ) of the particles. The same result was found by Jiang [2]. The SEM image of the particles is presented in Figure 3. After quantitative analysis, it can be seen that the average size of the particles is about 42.1 nm.

![Figure 2](image1.png)  
**Figure 2.** Magnetization curve of Ag-Fe₃O₄ produced at the concentration of 0.04 NaOH M

![Figure 3](image2.png)  
**Figure 3.** SEM image of Ag-Fe₃O₄ produced at the concentration of 0.04 NaOH M

The presence of silver on the surface of the magnetite particles improved its crystallinity. The XRD patterns presented in Figure 4 shows the highest intensity of the samples at 0.04 M concentration of NaOH that corresponds to pH = 11. Such pH is the optimal pH of the synthesis process. The crystallinity initially increased along with the increasing concentration of NaOH, until the optimum condition was reached, but an addition of a higher concentration of NaOH decreased the crystallinity. At a higher concentration of NaOH, the excess OH⁻ prevented the reduction of silver ions.

![Figure 4](image3.png)  
**Figure 4.** XRD patterns of Ag-Fe₃O₄ under a variation of NaOH concentration
As shown in Figure 5, in the synthesis of Ag-Fe$_3$O$_4$ with a variation of mole ratio of AgNO$_3$ to glucose, the highest intensity was obtained at the mole ratio of 1:8 as shown in Figure 5. However, NaOH had the more reductant inhibition performance as an accelerator.

![Figure 5. XRD pattern of the particles generated under various AgNO$_3$ mole ratios to glucose](image)

4. Conclusion
Ag-Fe$_3$O$_4$ nanocomposite has been successfully synthesized by a combination of electrochemical and reduction methods. The pH of the synthesis system and the mole ratio of reactants influence the character of the particles. There is an optimum pH = 11 and the mole ratio 1:8 of reactants in the formation of Ag-Fe$_3$O$_4$.

5. References
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