The Role of Na$_2$SiO$_3$ Loading in the Synthesis of Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$ Composite

S Aini$^{1,*}$, F Azra$^1$, N Rahma$^1$ and A Cahyadi$^1$

$^1$Chemistry Department, Faculty of Science, Universitas Negeri Padang (Padang State University), Jln. Prof. Dr. Hamka, Air Tawar, Padang Post Cod 25131, west Sumatera, Indonesia.

*syamsiaini@fmipa.unp.ac.id

Abstract. Mesoporous silica on the surface of nanoparticles' magnetic Fe$_3$O$_4$-Fe$_2$O$_3$ has been synthesized in one pot reaction method by using Sijunjung iron sand and Na$_2$SiO$_3$ as raw materials. The influence of Na$_2$SiO$_3$ mole as raw materials on the existence of silica pore size on the surface of Fe$_3$O$_4$-Fe$_2$O$_3$ composite product has been studied. The product were characterized by X-ray diffraction. The results showed that mesoporous silica start to form on the surface of the Fe$_3$O$_4$-Fe$_2$O$_3$ composite when Na$_2$SiO$_3$ was used 8 times moles of iron sand. The increasing of Na$_2$SiO$_3$ mole lead to increase of OH$^-$ concentration and transformed some Fe$_3$O$_4$ into Fe$_2$O$_3$.

1. Introduction

The Fe$_3$O$_4$ nanoparticles of iron sand are magnetic particle that has interesting characteristics including optical and catalytic properties and are widely used in various applications including Drug Delivery Systems (DDS), Magnetic Resonance Imaging (MRI), heavy metal separators for water purification and hyperthermia therapy systems, and as heterogeneous catalyst [3, 9, 10]. S. Aini (2019) [2] stated that Sijunjuang iron sand has the highest percentage of Fe and magnetic susceptibility of the four iron sand in West Sumatra and can be used as raw material to synthesize magnetic nanoparticles. However, iron nanoparticles are unstable in an acidic medium when used as catalysts directly. Therefore, they need stabilizers that are resistant to acid and high temperature, such as mesoporous silica [5].

The research about mesoporous silica synthesis on the surface of Fe$_3$O$_4$-Fe$_2$O$_3$ magnetic nanoparticles has been a concern due to its characteristics and high potency. The previous research about synthesis and characterization of the core-shell structure of nanoparticles composite Fe$_3$O$_4$@SiO$_2$ had been performed by Gao et al, (2011)[7]. His product was a superparamagnetic material, and the product was synthesized by varying the mole amount of the TEOS raw material. The results showed that the increasing mole of TEOS used will cause the intensity of SiO$_2$ to be increased as well. Thaib, S. (2015)[15] synthesizes mesoporous silica on the surface of Fe$_3$O$_4$ by using inexpensive commercial Na$_2$SiO$_3$ as a source of silica.

Sodium silicate from silica sand that was synthesized by S Aini et al. (2018) [1] has different Na$_2$O/SiO$_2$ mole ratio compared to commercial Na$_2$SiO$_3$, to produce mesoporous silica layers on the surface of Fe$_3$O$_4$-Fe$_2$O$_3$ nanoparticles composite require different reaction conditions with commercial Na$_2$SiO$_3$. 

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Therefore, in this study the effect of the mole ratio of Na$_2$SiO$_3$/ iron sand as raw material for coating a mixture of Fe$_3$O$_4$-Fe$_2$O$_3$ nanoparticles using XRD, SEM,TEM data was studied as follows:

2. Experimental Section

2.1. Reagents and materials
Sodium silicate (Na$_2$SiO$_3$) from the Nyalo River silica sand, nanoparticles magnetic Fe$_3$O$_4$ and Fe$_2$O$_3$ from Sijunung iron sand, Cetyl Trimethyl Ammonium Bromide (CTAB) Merck, Ethanol Pa, Ammonia 28% Merck, NaOH p.a 99% Merck, HCl p.a Merck, aquades.

2.2. Apparatus
We use X-ray diffractometer (XRD) to identify the presence of Fe$_3$O$_4$-Fe$_2$O$_3$ and SiO$_2$ particles, the existence of mesoporous silica and to measure the average size of Fe$_3$O$_4$, Fe$_2$O$_3$ and SiO$_2$ particles. The magnetic susceptibility have been measured by using Magnetic susceptibility Motor Bartington type MS2B dual Frequency Sensor. The morphology and particle size of the Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m8) composite was characterize using a scanning electron microscope SEM JEOL JSM-6510, and transmission Electron Microscopy (TEM) JEOL JEM-1400.

2.3. The synthesis of Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$ Composite
Synthesis and surface coating of Fe$_3$O$_4$-Fe$_2$O$_3$ composites with mesoporous silica were carried out using the one-pot method by applying the method discovered by L Zhang (2016), [16], N Z Knezevic, (2014)[11], and S Aini, (2018)[1] as follows:

Stage 1). 0.5 gram of iron sand (Fe$_3$O$_4$) dissolved in 5 ml of HCl Pa 12 M while sonicated for 1 hour and then decantation. The filtrate (solution of FeCl$_2$, FeCl$_3$) was diluted by 20 ml H$_2$O, and dropped into a mixture of 20 ml NH$_3$OH p.a and 5 ml NaOH 8 M while stirring with ultrasonic until a colloidal brownish-black Fe$_3$O$_4$-Fe$_2$O$_3$ formed.

Stage 2). A mixture of Fe$_3$O$_4$ and Fe$_2$O$_3$ added dropwise to the solution containing 0.5 g CTAB, 3.5 ml of ethanol Pa in 230 ml of water while stirring with a magnetic stirrer for ± 1 hour on speed of 400 rpm. Stage 3). Sodium silicate (8.78 grams; 10.92 grams; 13.05 grams. Mole ratio of Na$_2$SiO$_3$/Iron sand are 8, 10 and 12 dissolved in 25 ml H$_2$O, add 2M HCl until the solution pH was 12-13. The solution added by dropwise to a solution containing nanoparticles magnetic of Fe$_3$O$_4$, Fe$_2$O$_3$, CTAB, ethanol, H2O while stirring and heating at 85 °C for 2 hours, then at 90 °C for 2 hours. The solid was washed with aquades. Finally, the surfactant was removed by calcinations at 3000C for ± 1 hour and at 5500C for 6 hours. The Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$ composite was synthesized by varying mol ratio of sodium silicate/Iron Sand (8, 10 and 12) and the product labeled as a). Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m8), b). Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m10), and c). Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$ (m12).

3. Results and Discussion
The phase identification of Fe$_3$O$_4$ and Fe$_2$O$_3$ nanoparticles in a brownish-black Fe$_3$O$_4$-Fe$_2$O$_3$ colloid was carried out using the X-ray diffraction pattern data in Fig. 1a. and Table 1. The identification results show that the product has a main peak of 2θ Fe$_3$O$_4$ standard, and a main peak of 2θ Fe$_2$O$_3$ standard.

| Table 1. The 2θ peak list of nanoparticles in a brownish-black Fe$_3$O$_4$-Fe$_2$O$_3$ colloid product |
|--------------------------------------------------|
| Fe$_3$O$_4$ (JCPDS No. 01-090-12.2) | 18.09 | 29.75 | 35.039 | 42.57 | 56.279 | 61.785 |
| Fe$_2$O$_3$ (JCPDS no.00-002-0915) | 24.099 | 33.280 | 35.744 | 49.498 | 54.233 | 64.179 |

The existence of Fe$_3$O$_4$, Fe$_2$O$_3$, and SiO$_2$ in each Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$ composite can be seen in Fig. 1b, 1c, and 1d. In general, there are major peaks of Fe$_3$O$_4$, Fe$_2$O$_3$, and SiO$_2$ on each diffractogram (1b,
1c, 1d), but with different patterns and intensities. The intensity of the main peak of SiO\textsubscript{2} (at 2\(\Theta\) 26) increases with the increase of Na\textsubscript{2}SiO\textsubscript{3} used, as well as the main peak of Fe\textsubscript{3}O\textsubscript{4} (at 2\(\Theta\) 33, 28) and in contrast to the main peak of Fe\textsubscript{2}O\textsubscript{4} (at 2\(\Theta\) 35,039) decreases.

![Figure 1](image)

**Figure 1.** The X-ray Diffractogram Pattern of the a). Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} nanoparticles, b). Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m8), c. Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m10), and d). Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m12).

The SiO\textsubscript{2} diffractogram peak of the Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m8) sample lower than the Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m10) and Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m12) sample. The main diffractogram peak of Fe\textsubscript{3}O\textsubscript{4} is very clear, the magnetic pull is strong, and susceptibility for the sample of Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m8) is higher (Table 2).

The Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m10) sample had more main peak diffractogram of SiO\textsubscript{2} than Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m8) and lower than Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m12), the peak diffractogram Fe\textsubscript{3}O\textsubscript{4} began to appear. However, Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m10) had high peak diffractogram of silica but had weak magnetic attraction and low susceptibility.

The Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m12) sample had wide and weak peak of Fe\textsubscript{3}O\textsubscript{4} and lower susceptibility compared to Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m8) and Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m10). The diffractogram peak at 2\(\Theta\) 26 increase with a rise of Na\textsubscript{2}SiO\textsubscript{3} as raw material. The particle size of Fe\textsubscript{3}O\textsubscript{4} decrease for some various Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2} products with the increasing of Na\textsubscript{2}SiO\textsubscript{3} amount, in contrast to the Fe\textsubscript{2}O\textsubscript{3} size. It was estimated that the more Na\textsubscript{2}SiO\textsubscript{3} was added, the higher the pH, and the easier Fe\textsuperscript{2+} oxidized to form Fe\textsubscript{3}O\textsubscript{4}. This tendency was similar to that obtained by Shah (2015)[13]. In other case, the oxidation of some Fe\textsubscript{2}O\textsubscript{3} became Fe\textsubscript{3}O\textsubscript{4} produce brown Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2}(m12).

The intensity and pattern of this diffractogram are in line with the changes in particle size of Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, and SiO\textsubscript{2}. The particle size of Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} in NH\textsubscript{4}OH solvent and for different Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} @SiO\textsubscript{2} product has been calculated from XRD data using the Scherer’s formula for the main peaks of Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} at 2\(\Theta\) 35.039, 33.280, and 26.430 respectively. The X-ray diffraction pattern of the Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} each particle in the solvent of NH\textsubscript{4}OH has an average size about 20 nm and 30 nm. From the X-ray diffraction data, it can be concluded that the particles synthesized from iron sand in NH\textsubscript{4}OH solution are in nano-sized mixtures of Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} particles. This is supported by the physical characteristic of the brownish-black mixture and the product can be pulled by magnet even in wet condition as shown in Fig. 2 below.
Table 2. The Color and the Magnetic Susceptibility of Fe$_3$O$_4$-Fe$_2$O$_3$SiO$_2$ product

| Product                              | Magnetic susceptibility (10$^{-8}$ m$^3$/kg) | Color of sample |
|--------------------------------------|--------------------------------------------|-----------------|
| Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m8)  | 966.5                                      |                 |
| Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m10) | 790.5                                      |                 |
| Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m13) | 491.5                                      |                 |
| Sijunjuang iron sand                 | 1998.7                                     |                 |

Table 3. The particle size of Fe$_3$O$_4$, Fe$_2$O$_3$ and SiO$_2$

| No. | Sample                                      | SiO$_2$ | Fe$_3$O$_4$ | Fe$_2$O$_3$ |
|-----|---------------------------------------------|---------|-------------|-------------|
| 1.  | Fe$_3$O$_4$-Fe$_2$O$_3$ in NH$_4$OH          | -       | 20          | 3           |
| 2.  | Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m8)         | 5.18    | 20          | 5           |
| 3.  | Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m10)        | 20.06   | 15          | 7           |
| 4.  | Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$(m12)        | 40.58   | 8           | 10          |

Figure 2. Withdrawal of Fe$_3$O$_4$ and Fe$_2$O$_3$ nanoparticles in NH$_4$OH solvents

Table 3 shows that, in general, particle sizes of Fe$_3$O$_4$, Fe$_2$O$_3$, and silica shells on the surface of Fe$_3$O$_4$-Fe$_2$O$_3$ in nanometers. Table 3 and Table 2 show that the greater mole of addition of sodium silicate to the mixture of Fe$_3$O$_4$ and Fe$_2$O$_3$ caused the size of silica particles on the surface of Fe$_3$O$_4$-Fe$_2$O$_3$ composites and the particle size of Fe$_2$O$_3$ increase. On the other hand, Fe$_3$O$_4$ particle size decrease and magnetic susceptibility are reduced. These results were similar to those found by C Azmiyawti et al. (2018)[4] and associated with the results of the study of H, Setyawan et al (2012)[12] and B Li, et al (2019)[8], that OH- ions are an important medium for forming Ferro hydroxide, while at the same time, some Ferro hydroxides oxidize to produce ferries hydroxide. The susceptibility greater than 0.1 SI or greater than 0.001 X 10$^{-6}$ m$^3$/kg indicates the product with a high magnetic field, while the decrease in
susceptibility was caused by the formation of brown Fe₂O₃ minerals[6]. The presence of silica pores in Fe₃O₄-Fe₂O₃@SiO₂(m8) nanoparticles was characterized using small-angles X-Ray diffractogram and the results are shown in Fig. 3,

**Figure 3.** The Small Angle X-Ray Diffractogram Pattern of Fe₃O₄-Fe₂O₃@SiO₂(m8), Fe₃O₄-Fe₂O₃@SiO₂(m10) and Fe₃O₄-Fe₂O₃@SiO₂(m12) sample.

According to Fig. 3, Fe₃O₄-Fe₂O₃@SiO₂(m8) sample had a high peak of 20 at a small-angle 2.21, 2.95, and 3.91, which indicated that mesoporous silica on the surface of nanoparticles of Fe₃O₄-Fe₂O₃ had pore size in the range meso (2-50 nm). It is similar to the results of the study of Solemi Golezani et al. (2016)[14] The small-angle X-ray diffractogram pattern for Fe₃O₄-Fe₂O₃@SiO₂(m10) samples and Fe₃O₄-Fe₂O₃@SiO₂(m12) is the same as Fe₃O₄-Fe₂O₃@SiO₂(m8) samples, with the intensity not too much different. There are no regularity in the amount of Na₂SiO₃ to the peak intensity of small-angle X-ray diffractogram because the amount of surfactant as a pore mold used is the same for all three samples.

The presence of Fe₃O₄, Fe₂O₃ nanoparticles before and after being coated with silica was characterized by using a transmission electron microscope (TEM). The obtained TEM images of Fe₃O₄, Fe₂O₃ and Fe₃O₄-Fe₂O₃@SiO₂(m8) particles clearly showed a Fe₃O₄-Fe₂O₃ particles in nanoscale, and nanoparticles Fe₃O₄-Fe₂O₃ were coated with silica shell with the size smaller than 50 nm. SEM image also shows that the size of the Fe₃O₄-Fe₂O₃@SiO₂(m8) composite was below 0.1 micrometers (< 100 nm) or in nanometer size.
4. Conclusion

The study of the effect of mole ratio of Na$_2$SiO$_3$ iron sand to coat the surface of the mixture of Fe$_3$O$_4$ and Fe$_2$O$_3$ nanoparticles using x-ray diffractogram data and supported by SEM, TEM and Magnetic susceptibility data show that the optimal mole ratio of Na$_2$SiO$_3$/iron sand used for the mesoporous silica synthesis on the surface of Fe$_3$O$_4$-Fe$_2$O$_3$ nanoparticles magnetic was 8. The Fe$_3$O$_4$-Fe$_2$O$_3$@SiO$_2$ has pore in the mesoporous size area and high magnetic susceptibility.

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