Use of Sodium Silicate from Rice Husk Ash Basic Materials for Coating Electrolytes in the Synthesis of Magnetite Nanoparticles

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ABSTRACT
Magnetite nanoparticles had a measurement about 6.76 nm was synthesized through electrochemical technique in the synthetic sodium silicate solution which was gained through the extraction process of silica which content in the rice husk ash by using NaOH 1.5 M. Sodium silicate functions as electrolyte and simultaneously as a coated to maintain the size of the magnetite particle which was formed through electrolysis process. The synthesis of magnetite nanoparticles was implemented in the variation of voltage 1.5-12 V with the concentration of sodium silicate solution 100-800 ppm. The optimum synthesis condition was gained in the 7.5 voltage and 600 ppm which was detected based on the magnetite’s color of the magnetic toward the power of magnetite produced. The characterization of magnetite cluster was done through FTIR absorption data analysis, the description of particles topography and the content of magnetite element were founded out through SEM-EDX analysis, while the particles size and the characterization of magnetite by using XRD.

Keywords: Rice husk ash, sodiumsilicate, electrochemical, magnetite nanoparticles, characterization.

INTRODUCTION
Rice husk is one of Indonesia's agricultural waste utilization is still quite traditional. Indonesian rice production increase from year to year also resulted in increasing the amount of rice husk. Rice mill produces about 20-22% husk (Sriyanti et al, 2005). According to Houston (1972), in Laksmono (2000), the most common value of the burning of rice husk ash containing 86.7% -97.3% silica. Sodium silicate which is a direct precursor of silica, mostly made of melting quartz sand with sodium carbonate at a temperature of 1300 °C (Brinker and Scherer, 1990, in Sriyanti et al., 2005). Nuryono (2004) have managed to make sodium silicate is much easier and friendly environment by extracting silica from rice husk ash using 1.5 N NaOH solution at a lower temperature. Sodium silicate (Na2SiO3) has many benefits, one of which can be used as an electrolyte in the coating as well as synthesize magnetite nanoparticles (size below 15 nm) as done by Fajaroh et al. (2010). Fajaroh utilizing commercial sodium silicate because they are relatively inexpensive.

Nanoparticles of magnetite (Fe3O4) intensively developed today because it is interesting. 50-20 nm-sized particles of magnetite that possess the stronger (Thapa et al., 2004) that can be applied as, lymph node imaging, perfusion imaging, bone marrow imaging, and magnetite resonance angiography (unak, 2008). Particle size below 10 nm (ferrofluida) will be superparamagnetit (Thapa et al., 2004), can be found in the field of medical applications such as Drug Delivery System (DDS), Magnetite resonance imaging (MRI) and hypothermia (Kazeminezhad and Mosivand, 2011). Between 100-50 nm particle size tends to settle under the influence of gravity. Therefore, controlling the size becomes important in the synthesis of Fe3O4 nanoparticles for specific applications. Nanoparticles tend to aggregate to form large size back. Efforts to prevent aggregation is done by adding materials or molecular coating magnetite particles (Judge, 2008). Commercial sodium silicate and TEOS (Tetra Ethyl Ortho Silicate) is a source of silica compound that has been used by researchers as a coating material particles of magnetite.
Magnetite particle synthesis using electrolytes sodium silicate from rice husk ash base material be interesting to study as an alternative to the use of sodium silicate of low value materials ie rice husk. Using sodium silicate coating is expected to produce a particle size of magnetite nanoparticles smaller than 10 nm.

MATERIAL AND METHODS

Materials
The materials used in this study, among others, rice husk, a solution of 1.5 M NaOH, FeSO4 solution of 0.072 mol / L, water glass, 37% concentrated HCl, iron rods, sand paper, aluminum voil, plain filter paper, paper Whatman strain no. 42, and distilled water.

Tools
The tools used in this study include an adapter (DC Electrical Source 1.5 V-12 V), cables, power supply, platinum electrodes, bulb, hot plate, magnetite stirrer, Termolyne Barnstead Lab Furnace in 6000. Chemical Physics, Hasanuddin University, oven, analytical balance, balance arm (Ohaus), electric cooker, FTIR (IR Prestige-21 Fourier Transform Infrared Spectrophotometer Shimadzu) in the Lab. Integrated UNHAS, XRD (Rigaku MiniFlex X-Ray Diffraction) and SEM (VEGA3TESCAN SEM-EDX) in the Lab. UNM Physics and glass tools commonly used in the laboratory.

Methods

Preparation of Rice Husk Ash
Rice husk dried first, then burned in the open air to grayish black. Charcoal produced subsequently burned in a furnace to a white-gray at temperatures 705 °C for 4 hours.

Purification of SiO2 in Rice Husk Ash
Six grams of the burning of rice husk ash added 20 mL of concentrated HCl 37%. Mixture is boiled with stirring using a stirrer then magnetite settling for 1 night before filtered. After filtration, the precipitate obtained SiO2 dried for 1 night in an oven at a temperature of 110 oC.

Manufacture Sodium Silicate Solution
Five grams of SiO2 was treated with 1.5 M NaOH solution as much as 87 mL, then boil while stirring. Mixture has chilled, filtered using ordinary filter paper. The filtrate from the sodium silicate dried screening results were then tested solubility and characterized using FTIR.

synthesis of Fe3O4
Electroplating (coating) Iron
Iron rod that had been sanded used as cathode and platinum as the anode. Both electrodes mounted in an electrochemical cell as in Figure 2. Electroplating process is performed in 0.072 M FeSO4 solution at room temperature. Electric current flowed from the adapter with 1 A current density on voltage of 3 volts for 3 hours.

Voltage Determination of Optimum and Optimum Electrolyte Concentration

a. Determination of Optimum Voltage

a. Experimental apparatus assembled as shown in Figure 2. Water glass 400 ppm put in as many as 50 mL beaker. Results electroplating iron rod as anode, and a new iron rod (already sanded) as a cathode mounted in the electrochemical cell. Current of 1 A flows from the adapter voltage variations 1.5 V, 4.5 V, 7.5 V, and 12 V, for 12 hours. Products in the form of precipitate formed is separated using a filter paper No. Whatman 42, then dried. In the screening process, the funnel was closed using aluminum voil. Fe3O4 powders were then Diamanti and determined the optimum conditions of its formation.
Determination of Optimum Electrolyte Concentration

Experimental apparatus assembled as shown in Figure 2. Artificial Na2SiO3 solution (100 ppm, 300 ppm, 600 ppm, and 800 ppm) incorporated into the 50 mL beaker. Results electroplating iron rod as anode, and a new iron rod (already sanded) as a cathode mounted in the electrochemical cell. Current of 1 A flows from the adapter at the optimum voltage for 12 hours. The precipitate formed is separated using a filter paper No. Whatman. 42 then dried. In the screening process using aluminum foil funnel closed. Fe3O4 powders were obtained subsequently analyzed for the determination of optimum conditions. Follows (Figure 1) circuit simple equipment used to test the polarity of the Fe3O4 powders synthesized in determining the optimum electrolyte concentration.

Figure 1. Circuit analysis tool on the polarity of the 0.1 grams of powder Fe3O4: 1) Scale Ohaus mg on the balance sheet, 2) Expenses for calibration 3) Fe3O4 powder, 4) Magnets, 5) Balance Ohaus

b. Synthesis of Fe3O4 on Optimum Conditions

Experimental apparatus assembled as shown in Figure 2. Na2SiO3 solution made at the optimum concentration incorporated into the 50 mL beaker. Results electroplating iron rod as anode, and a new iron rod (already sanded) as a cathode mounted in the electrochemical cell current of 1 A supplied adapter on the optimum voltage for 12 hours. The precipitate formed is separated using a filter paper No. Whatman. 42, then dried. The screening process using aluminum foil closed.

Figure 2. Series of tools electrochemical cell: 1) DC Electrical Source 1.5 V-12 V, 2) electrolyte, 3) Electrodes, and 4) 100 mL beaker.

Product characterization

Dry powder synthesized at the optimum conditions were analyzed using FTIR and XRD for characterization and determination of particle size. Description of the morphology and determination of elemental powders were analyzed using SEM-EDX.
a. **XRD**

Working principle of x-ray diffractometer is as follows: the x-ray generator produces radiation ektromagnetik, who once controlled by the slit S1 perverts next fall on footage. Rays are scattered by the sample is centered on the slit S2 receiver and falls on the detector as well as transform it into the form of visible light (photons). XRD data like dhkl, Miller indices (hkl), and the FWHM is needed to determine the grain size of the sample (D) using the Scherrer formula (Sun et al., 2006):

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Dengan:
- $K = 0.89$ for magnetite
- $\lambda = 1.540562$ (radiation Cu-Kα)
- $\beta$ = score FWHM
- $\theta$ = apex angle

X-ray diffraction performed on the angle range $2\theta = 10^\circ$ - $90^\circ$ with the pace and step 20/menit 0.02 o.

b. **SEM-EDX**

SEM analysis aimed at determining the topology and morphology of the grains, and EDX for the determination of elemental composition (wt%) sample. SEM images were taken to a scale of 1 μm (or with magnification up to 25,000 times) with HV between 5-30 kV and Working Distance (WD) between 5 mm - 15 mm. WD = 15 mm specifically for elemental analysis by EDX (Sun et al., 2006).

In the data retrieval tool SEM-EDX, powder samples that had been placed on the specimen holder is inserted into the specimen chamber, then put in the SEM-EDX tools and equipment ready for operation. In the SEM-EDX measurements for each sample were analyzed using analysis area. Electron beam gun is derived from the area drained by the sample. Flow in the electron beam is then focused using electron optics Columb before the electron beam on the sample. After the electron beam on the sample, there will be some of the interactions in the irradiated samples. The interactions that take place will then be detected and transformed into an image by SEM analysis and also in the form of graphs by EDX analysis (Bambang, 2011).

**RESULT AND DISCUSSION**

At the anode, iron electrodes undergo oxidation to Fe 2 + ions and release electrons. Water at the anode surface will also be oxidized to O2, H + and release electrons (a). O2 gas bubbles identified with the small-geleelektrolit mbung INFERNAL SURFACE anode. Reduction reaction occurs on the cathode H2O into OH-and H2 gas (b). Formation of H2 gas can also be identified with the emergence of bubbles. H2 bubbles more visible than O2 bubbles because not react further so that they can be found at the end of synthesis. OH-ions formed at the cathode to the anode diffuses and reacts with Fe 2 + ions to form Fe (OH) 2. Because of the mobility of OH-faster than the Fe 2 +, the reaction forming Fe (OH) 2 occurs in the area around the anode (c). O2 source other than dissolved oxygen is also derived from the oxidation reaction occurs at the anode. Furthermore FeOOH and Fe (OH) 2 will react to form Fe3O4 (d) (Januarita et al, 2010). Reactions that occur in the synthesis process can be seen in Figure3:
Figure 3. Mechanism of formation of magnetite nanoparticles in an electrochemical cell (Januarita et al, 2010).
Voltage variations affect the physical properties of the resulting product. The lower voltage resulting precipitate magnetite produced the brown brick. This is due to electron transfer in solution resulting in the slow formation of magnetite particles in the anode region is also getting slower, a result which had originally formed magnetite is oxidized again characterized by the formation of sludge brown brick. The optimum voltage is determined by the form of the product is black (color magnetite) (Fajaroh et al, 2010). In Figure 4 it can be seen that the products formed in the solid black working voltage of 7.5 volts and 12 (first and second from the right). However, to save energy, then selected the most low voltage of 7.5 volts. Physical form of magnetite particles was synthesized as shown in Figure 4.

Figure 4. Magnetite powder synthesized at different voltages (from left to right respectively 1.5, 4.5, 7.5, 12 volt) which takes place in an electrolyte solution of commercial sodium silicate (water glass) 400 ppm.
Synthesis of magnetite nanoparticles at various concentration of sodium silicate coating gives the product a fine black powder. Not physically visible difference between magnetite powder synthesized at certain concentrations with others. Magnetite particles were obtained at a concentration of sodium silicate made 100, 300, 600 and 800 ppm can be seen in Figure 5:
Figure 5. Fe₃O₄ powders synthesized using sodium silicate as an electrolyte made at various concentrations. Testing the magnetic attraction of the Fe₃O₄ powders made using simple equipment. This test is based on the style that has 0.1 grams of powdered magnetite regardless of the pull of the magnet (magnitude = 91.78 mT). Test result data obtained by magnetic attraction as in Figure 6.

![Artificial Sodium Silicate Electrolyte concentration curve](image)

**Artificial Sodium Silicate Electrolyte concentration (ppm)**

Figure 6. Na₂SiO₃ electrolyte concentration curve made with a magnetic attraction to pollen Fe₃O₄. The greater the concentration of sodium silicate electrolyte used, the nature of magnetic attraction towards the stronger Fe₃O₄ powder until a certain concentration. Based on the graph in Figure 6, it is known that the magnetic attraction of the Fe₃O₄ optimum concentration of 600 ppm. According to Thapa et al., 2008, the Fe₃O₄ particles will reach the peak magnetitnya when the particle size reaches 10 nm. After descending through the 10 nm, then kemagnetannya gradually declined. Identify the types of bonds and functional groups contained in the Fe₃O₄ particles synthesized using FTIR analysis. FTIR spectra patterns of silica-coated Fe₃O₄ compounds can be seen in Figure 7.

![FTIR spectra patterns](image)

Figure 7. a) Pola FTIR Fe₃O₄@SiO₂ yang diperoleh Yunqiang dkk., (2011), b) Pola FTIR Fe₃O₄ yang diintesis dalam larutan elektolit natrium silikat komersial 600 ppm pada voltase 7,5 volt. Vibration bonds Fe₃O₄ in Figure 7b is shown in wave numbers 451.3 cm⁻¹ and 570.9 cm⁻¹. Vibrations of OH functional groups at 3419.79 cm⁻¹ indicate the presence of an impurity compound FeOOH. Wave numbers at 1001.06 cm⁻¹ indicate the presence of Si-O groups of bond Si-O-Si. Peak pattern is the one who raised Yunqiang et al., (2011) in Figure 7a.

Table 1. Wave numbers that appear in the FTIR analysis of synthesized Fe₃O₄ powders in commercial Na₂SiO₃ (water glass) 600 ppm at 7.5 V.

<table>
<thead>
<tr>
<th>No</th>
<th>Wave numbers (σ)</th>
<th>Clusters Indication</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>451.3 cm⁻¹ dan 570.9 cm⁻¹</td>
<td>Vibration bonds Fe₃O₄</td>
</tr>
<tr>
<td>2</td>
<td>3419.79 cm⁻¹</td>
<td>Vibrations of functional groups O-H dari FeOOH.</td>
</tr>
<tr>
<td>3</td>
<td>1631.78 cm⁻¹</td>
<td>Bending vibration –OH at the water molecules</td>
</tr>
<tr>
<td>4</td>
<td>1001.06 cm⁻¹</td>
<td>Vibration bonds Si-O of bonding Si-O-Si.</td>
</tr>
</tbody>
</table>

FTIR spectra patterns of Fe₃O₄ synthesized compounds in artificial Na₂SiO₃ electrolyte solution (hereinafter referred to as Fe₃O₄ @ Na₂SiO₃ artificial) (Figure 8) is similar to the pattern shown Fe₃O₄ FTIR spectrum synthesis results in a solution of sodium silicate electrolyte commercial (hereinafter referred to as the commercial Fe₃O₄ @ Na₂SiO₃) (Figure 7b).

Figure 8. FTIR analysis results Na₂SiO₃ artificial Fe₃O₄ @ 600 ppm at rated voltage of 7.5 volts. Broad and sharp peaks of Figure 8 appears at wavenumber 887.26 cm⁻¹ and 925 cm⁻¹ indicating the presence of Si-O group of the bond Si-O-Si. Short absorption peak at the wave number indicates the amount of silica attached to the magnetite particles are very small.

Deposits obtained black powder form and can be pulled by a magnet. Deposit filtered using filter paper and then dried at 42 Whatman oven to reduce the moisture content. Furthermore precipitate obtained was analyzed using X-Ray Diffraction (XRD) and SEM. Figure 10a shows the diffraction pattern of magnetite particles synthesized in accordance with the standard diffraction pattern JCPDS No. Fe₃O₄. 19-0629 (Figure 9).

Sodium silicate is used as an electrolyte artificial coating in this case produce magnetite particles are monodisperse. Peaks indicate a clear and sharp crystal Fe₃O₄ particles has been well established. Not found peaks No. JCPDN standard diffraction pattern. 44-1415 of FeOOH which is usually the impurity magnetite. FeOOH characteristic absorption peak usually appears at 13, 27.5, 47 20.
**Figure 9.** XRD pattern standard Fe$_3$O$_4$ (JCPDS Card No. 19-629)

**Figure 10.** XRD pattern of Fe$_3$O$_4$ powder were synthesized at the optimum conditions a) XRD pattern artificial Fe$_3$O$_4$@Na$_2$SiO$_3$, b) XRD pattern of Fe$_3$O$_4$@Na$_2$SiO$_3$ commercial compound.

Pattern powder XRD of Fe$_3$O$_4$ @ Na$_2$SiO$_3$ commercial (water glass) as electrolyte (see Figure 10b) produces peaks and less obvious enough. Only two peaks that appear pretty sharp at 35 and 63. Unfavorable diffractogram pattern depicts the crystal structure of magnetite produced unfavorable. In addition, other peaks that are not in accordance with the standards of the Fe$_3$O$_4$ peak also appeared at diffractogram pattern.
Based on calculations using the Scherrer formula, derived grain size Fe3O4 synthesized using water glass electrolyte was 6.82 nm, while the electrolytes sodium silicate synthesis using artificial produce grain sizes are slightly smaller at 6.76 nm.

SEM analysis aimed at determining the topology and morphology of the grains, and EDX for the determination of elemental composition (wt%) sample. Because of the resulting magnetite grain size smaller than 10 nm (beyond the resolution SEM), the grain size of the sample being tested can not be obtained by using SEM. Grain size of it can only be detected using TEM (Transmission Electron Microscope). The EDX analysis performed on 5 different positions on the sample as shown in Figure 11 below.

Figure 11. EDX analysis of the position of the elemental composition determination (box): a) Fe3O4 @ Na2SiO3 (water glass) at magnification 50 lm commercial. b) Fe3O4 @ Na2SiO3 artificial enlargement of 20 lm.

The fifth point in the analysis of each sample has a wt% different. The data analysis results can be seen in Table 2 and Table 3.

Table 2. Tabulation of Elemental Composition (wt%) samples Fe3O4 @ Na2SiO3 Commercial

<table>
<thead>
<tr>
<th>Posisi</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
<th>Si</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44.3</td>
<td>39.5</td>
<td>11.4</td>
<td>3.8</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>48.1</td>
<td>39.2</td>
<td>8.9</td>
<td>3.8</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>68.5</td>
<td>20.4</td>
<td>7.5</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>41.7</td>
<td>43.4</td>
<td>10.7</td>
<td>4.2</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>51.9</td>
<td>36.9</td>
<td>8.4</td>
<td>2.8</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3. Tabulation of Elemental Composition (wt%) Sample Fe3O4 @ Na2SiO3 Artificial

<table>
<thead>
<tr>
<th>Posisi</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
<th>Si</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53.7</td>
<td>37.3</td>
<td>8.3</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>58.8</td>
<td>33.5</td>
<td>7.0</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>61.6</td>
<td>31.6</td>
<td>6.5</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>47.4</td>
<td>37.6</td>
<td>14.4</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>61.2</td>
<td>30.4</td>
<td>7.6</td>
<td>0.8</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2, shows the presence of Na elements were detected as 1.0%. This indicates that there are elements of the residual Na commercial solution of sodium silicate (water glass). While in Table 3, the rest of the elements Na was not detected as in Table 2. The following sample SEM morphology
commercial Fe3O4 @ Na2SiO3 (water glass) and Fe3O4 @ Na2SiO3 artificial obtained on such a scale.

![SEM patterns](image1)

Figure 12. SEM patterns of the samples Fe3O4 @ Na2SiO3 made on a scale of 1 lm (a) and Fe3O4 @ Na2SiO3 commercial samples (water glass) on a scale of 20 lm (b)

SEM patterns of the samples that have been enlarged to a scale of 1 lm still has not given the expected results topography granular Fe3O4 samples. However, it can be seen that the resulting grain samples Fe3O4 @ NaSiO3 made on a scale of 1 lm (Fig. 12a) is more clearly visible than a grain of Fe3O4 @ NaSiO3 commercial samples (water glass) on a scale of 20 lm (Fig. 12b).

CONCLUSIONS

The results showed that 5 grams of rice husk ash were extracted using 1.5 M NaOH solution, obtained about 5.4 grams of sodium silicate which is subsequently used as the electrolyte in the coating as well as the synthesis of magnetite nanoparticles. Synthesis is performed by electrochemical methods produce Fe3O4 powders with grain sizes of 6.76 nm. The smaller the voltage synthesis produce Fe3O4 powder brown brick, while the electrolyte concentration resulted in a greater coating magnetic attraction towards the stronger Fe3O4 powder until a certain concentration. Voltage and concentration obtained optimum synthesis respectively at 7.5 volts and 600 ppm.

REFERENCES