Hydrothermal Synthesis of Hematite (α-Fe₂O₃) from Indonesia Iron Sand

Furqonul Hadin Al Hadi [a], Tanti Haryati [a], Novita Andarini [a], Suwardiyanto [a], Yudi Aris Sulistiyo [a]

Abstract: High potency of Indonesian iron sand can be optimized by transforming to valuable iron oxide product namely Hematite (α-Fe₂O₃). Hydrothermal synthesis was carried out to transform iron oxide phase to hematite that can be analyzed by x-ray diffraction method. Utilization of iron sand that extracted from iron sand) was carried out to attain the high purity of hematite. The heating temperature and time hydrothermal reaction were also evaluated to understand the oxide iron crystal transformation.

Keywords: Iron sand, hematite, α-Fe₂O₃, hydrothermal synthesis.

INTRODUCTION

Indonesia’s Iron sand abundancy is deposited in several areas such as Sumatra, South of Jawa, Sulawesi, Maluku, and Papua that possibly produced from volcanic eruption and erosion of older rock [1]. In 2020, Ministry of Energy and Mineral Resources of the Republic of Indonesia reported the amount of Iron sand resources in Indonesia is 2.9 Billion tons and supply 1.7% of world Iron sand that the iron content was less than 12% [2]. However, Zulhan et al. (2021) reported the mined and concentrated iron sand deposits in some areas contained more than 54% iron and 7% titanium [3]. Iron sand can be utilized in various applications namely steel manufacturing, pigment Sources [4], titanium feedstock [5], adsorbent for water purification [6-8].

In particularly, iron oxides have large potential applications in data storage, biotechnology, biomedicine, catalyst, sensors, and environmental remediation due to its unique physical and chemical properties [9]. Regarding the most oxidation state of iron (Fe²⁺ and Fe³⁺), iron oxides have three common form that is Hematite (α-Fe₂O₃), maghemite (Fe₂O₃), and magnetite (γ-Fe₃O₄) [10]. Among these, the hematite is most environmentally friendly as a semiconductor materials (e.g., 2.1 eV) [11-12]. The stability of Hematite was determined from the rombohedral structure with the latice oxygen close packing and two third of the lattice was occupy with the Fe³⁺ ions [13].

Among various synthesis methods of hematite, the hydrothermal method is one of the most common and the least expensive routes of synthesizing nanoparticles with different morphologies. Recently, hematite was synthesized by the bottom-up model using iron ion (Fe³⁺) under supercritical condition [14-15]. To the best of our knowledge, few scientific paper reported the top-down model from the iron sand using hydrothermal synthesis technique. The challenge of top-down model is the iron sand has several iron oxide phase and also other oxide that possibly interfere the production of α-Fe₂O₃. Since the transformation of iron sand to hematite can be conducted by hydrothermal synthesis, It can improve the economic value of iron sand.

This study was aimed to evaluate the transformation of crystal structure of iron sand using hydrothermal synthesis. Moreover, evaluation the best raw material (iron sand or Fe(OH)₃ as raw material produced multyphase in product reaction, while the usage of Fe(OH)₃ that extracted from iron sand attained high purity of hematite. The best conditions of reaction were at 160 °C for 24 h. Higher temperature and longer time reaction transformed α- α-Fe₂O₃ to be γ-Al₂O₃ and Fe₃O₄ as more stable phase.

EXPERIMENTAL PROCEDURE

Iron sand taken by magnet of 10 mg was added with 100 mL of concetrated Hydrochloric acid (37%, merck). The mixture was heated at 70 °C in constant stirring for 1 h. Then, the mixture was filtered and the filtrate was added with 4 M of NaOH (Merck) in mole rasio 1:3. The obtained product was dark chocolate coloid Fe(OH)₃. Afterwards, the coloid was transferred to teflon lined stainless steel autoclave reactor, added with NaOH 2M of 30 mL, firmly sealed and heated. The hydrothermal reaction condition following Table 1. After the hydrothermal reaction, autoclaves were cooled at room temperature. Then, the samples were filtered and washed with deionized water. The solid product were dried at 60 °C for 12 h. Finally, the powder can be used for further analysis.

RESULT AND DISCUSSION

Effect of Hydrothermal Reaction Temperature

Iron sand from Paseban Beach, Jember, Indonesia has identified the crystal structure following X-Ray diffraction analysis. Figure 1.a - 1.d showed the diffractogram of the consecutive standard for α-Fe₂O₃, γ-Fe₂O₃, Fe₃O₄, and SiO₂ that was used as a comparison for the diffractogram of the sample product. Following the diffractiongram of standard, iron sand has compounds such as SiO₂ (silica/quartz), α-Fe₂O₃, γ-Fe₂O₃, Fe₃O₄, and unidentified crystal structure (Figure 1.e). After separation using a magnet, the peaks of SiO₂ in Figure 1.f were absent (2θ = 26.65° and 39.52°), and remaining the iron oxides compounds (Fe₂O₃, and Fe₃O₄). All of the materials product obtained were analyzed the crystallinity by X-Ray diffraction technique (MPD X’pert PANalytical) using CuKα radiation 1.5405 Å. The samples were scanned in the diffraction angle 20 = 10° - 60°.

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Table 1. reaction conditions and chemical used in the hydrothermal synthesis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basic Resistance (Ohm)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1 g iron sand, 30 mL of NaOH 2M</td>
<td>160</td>
<td>24</td>
</tr>
<tr>
<td>S2</td>
<td>1 g iron sand, 30 mL of NaOH 2M</td>
<td>185</td>
<td>24</td>
</tr>
<tr>
<td>S3</td>
<td>1 g iron sand, 30 mL of NaOH 2M</td>
<td>210</td>
<td>24</td>
</tr>
<tr>
<td>S4</td>
<td>100 mL of colloid Fe(OH)₃, 30 mL of NaOH 2M</td>
<td>160</td>
<td>24</td>
</tr>
<tr>
<td>S5</td>
<td>100 mL of colloid Fe(OH)₃, 30 mL of NaOH 2M</td>
<td>185</td>
<td>24</td>
</tr>
<tr>
<td>S6</td>
<td>100 mL of colloid Fe(OH)₃, 30 mL of NaOH 2M</td>
<td>210</td>
<td>24</td>
</tr>
<tr>
<td>S7</td>
<td>100 mL of colloid Fe(OH)₃, 30 mL of NaOH 2M</td>
<td>160</td>
<td>36</td>
</tr>
<tr>
<td>S8</td>
<td>100 mL of colloid Fe(OH)₃, 30 mL of NaOH 2M</td>
<td>160</td>
<td>48</td>
</tr>
</tbody>
</table>

α-Fe₂O₃ was transformed to a more stable structure namely Fe₂O₃ which can be seen by arising peaks at 2θ = 18.21, 30.20, 35.81, 36.76, 42.94, and 56.87 following ruff.info/magnetite. Zhang et al. (2013) also reported that γ-Fe₂O₃ was a more stable phase than α-Fe₂O₃ possibly form at the higher reaction temperature [16].

The transformation of the crystal phase that was identified by diffractogram x-ray was studied using different raw materials namely iron sand and Fe(OH)₃ from extracted iron sand in the thermal influence on the hydrothermal reaction. Figure 2 showed the polymorph crystal structures obtained using Fe(OH)₃ as a hydrothermal reaction source such as α-Fe₂O₃ and Fe₂O₃. The characteristic peaks of α-Fe₂O₃ can be identified at 2θ = 24.73, 33.18, 35.72, 38.23, 41.1, 49.63, and 54.24 which were similar to the database from ruff.info/hematite. Increasing of hydrothermal temperature (160 to 180°C) reduced the peak intensity of α-Fe₂O₃ due to increasing the nucleation rate and decreasing the crystal size obtained. Increasing the temperature to 210 °C, the crystal of α-Fe₂O₃ was transformed to a more stable structure namely Fe₂O₃ which can be seen by arising peaks at 2θ = 18.21, 30.20, 35.81, 36.76, 42.94, and 56.87 following ruff.info/magnetite. Zhang et al. (2013) also reported that γ-Fe₂O₃ was a more stable phase than α-Fe₂O₃ possibly form at the higher reaction temperature [16].

On the other hand, Figure 3 showed that the utilization of iron sand as raw materials for hydrothermal reaction produced more crystal structure compared to Fe(OH)₃ such as α-Fe₂O₃, γ-Fe₂O₃, Fe₂O₃, and silica (SiO₂). An additional crystal structure of γ-Fe₂O₃ was formed by increasing the reaction temperature. Meanwhile, a strong peak at 2θ = 27.90 can be addressed to silica that can be produced from the decomposition of Fe₂SiO₅ (Fayalite) by NaOH during the hydrothermal. During the hydrothermal, sodium silicate from the reaction of fayalite and NaOH was hydrolyzed and condensed producing a small amount of amorphous SiO₂. Sun et al (2018) reported that Fayalite is a product of the burning process in the magma chamber that is released in the eruption process [17]. Increasing the reaction temperature decreased the peak intensity of SiO₂ due to increasing the solubility of fayalite on NaOH that can be discharged in the filtration process.

**Effect of Time Hydrothermal Reaction**

The transformation of crystal structures was also evaluated by the various hydrothermal time reaction. The raw material usage was Fe(OH)₃ from the extracted iron sand which has the better result to produce α-Fe₂O₃ in the previous study compared to iron sand. Figure 4.c showed that high purity of α-Fe₂O₃ was obtained in 24 h of hydrothermal time reaction. It was indicated
from the characteristic peaks of α-Fe₂O₃ at 2θ = 31.75, 35.53, 45.52, dan 56.60. Increasing time reaction to 36 h was maintained of the α-Fe₂O₃ structure with the lower intensity of those peaks. Moreover, arising characteristic peaks of the crystal of γ-Fe₂O₃ and Fe₃O₄ that were followed by the absence of peaks α-Fe₂O₃ were observed in 48 h of time reaction. It was caused that the γ-Fe₂O₃ and Fe₃O₄ were the more stable phase than α-Fe₂O₃ [16].

![Figure 4](image_url)

Figure 4. Diffractogram x-ray of (a) α-Fe₂O₃ standart (R110013), (b) γ-Fe₂O₃ standart, (c) Fe₃O₄ standart (R061111), sample at time reaction (d) 24 h, (e) 36 h, f). 48 h, using raw material Fe(OH)₃ extracted from iron sand at 160 °C of hydrothermal temperature.

Decreasing α-Fe₂O₃ peaks and appearing γ-Fe₂O₃ and Fe₃O₄ phases was in line with Mikio et al., (2013) that reported the increasing hydrothermal time obtained the optimum condition at 32 h, meanwhile. the longer time reaction appearing the oxidation reaction to transform α-Fe₂O₃ to be γ-Fe₂O₃ phase [18]. Juliansyah et al. (2015) also reported that increasing time reaction increased the energy that accelerated the nucleation and crystal growth during the reaction to form a smaller crystal size. It also had a high possibility to transform the obtained crystal to be the more stable phase at the end of the reaction process [19].

CONCLUSION

The ideal condition to attain the α-Fe₂O₃ phase by the hydrothermal reaction was using Fe(OH)₃ which was a product of the extraction of iron sand. The utilization of iron sand itself was triggered in producing multiphase in the reaction product. Increasing the temperature and time of hydrothermal reaction accelerates the transformation of α-Fe₂O₃ to γ-Fe₂O₃ and Fe₃O₄ phase. The best condition to attain high purity of α-Fe₂O₃ was at temperature reaction 160 °C for 24 h of time reaction.

REFERENCES


