

Preparation of Fe₂O₃-TiO₂ composite from Sukabumi iron sand through magnetic separation, pyrometallurgy, and hydrometallurgy

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Abstract. Preparation of Fe₂O₃/TiO₂ composite from Sukabumi iron sand by magnetic separation, roasting, leaching and precipitation treatment has been carried out. Magnetic separation can separate magnetic particles and non-magnetic particles of iron sand content, while the non-magnetic particles (wustite (FeO), hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃) and magnetite (Fe₃O₄)) was washing with oxalic acid 1 M. The result product then was roasted at 800 °C treated by sodium carbonate (Na₂CO₃) addition of 1:1; 2:1 and 1:2 (w/w) of iron sand to Na₂CO₃ weight ratio, respectively. The X-Ray Fluorescence (XRF) analysis result shown that Sukabumi iron sand have hematite (Fe₂O₃) and titanium dioxide (TiO₂) content about 72.17% dan 14.42%. XRD analysis of roasted iron sand shown the rutile (TiO₂), Hematite (Fe₂O₃), NaFeO₂, FeO, and Na₂TiO₃. Leaching of roasted iron sand using sulphuric acid (H₂SO₄) have influenced by concentrations of the H₂SO₄ solution. The optimum iron sand dissolution occurred in H₂SO₄ 9 M, which condensation product of the leachant have a weight ratio of Fe:Ti = 1:1 (w/w). Meanwhile, the settling back-filtrate result of second condensation was obtained a ratio of Fe₂O₃: TiO₂ of 3: 1 (w/w).

1. Introduction

Titanium dioxide (TiO₂) has a great potential application in water purification [1–3]. Because this semiconductor be able to degrade the organic compounds through the photocatalytic activity. This photocatalyst also has high chemical stability and low toxicity. However, the major drawback of TiO₂ is that, TiO₂ alone can only photodegrade organics under ultraviolet light and has large band gap (3.2 eV) that absorbs only 4% of sunlight from solar spectrum [4]. Accordingly, many efforts have been made to extend the absorbance of TiO₂ to visible light by doping the transition metal or composites [5].

Futhermore, Fe₂O₃–TiO₂ composites as a photocatalyst can respond to visible light due to the narrow band-gap of Fe₂O₃. It has also been found that another kind of iron oxide, Fe₃O₄, reacted with TiO₂ powders and produced iron titanium oxide compounds, such as FeTiO₃ [6].



Commonly, the $\text{Fe}_2\text{O}_3\text{--TiO}_2$ composite was prepared from different precursor like Titanyl acetylacetonate (TiAcAc) [7], titanium (IV) isopropoxide and Fe(III) acetylacetonate [8], $\text{Ti(SO}_4)_2$ and $\text{Fe}_2(\text{SO}_4)_3$ [9]. Here we report the preparation of $\text{Fe}_2\text{O}_3\text{--TiO}_2$ in 1:1 ratio (w/w) from Sukabumi iron sand through magnetic separation, pyrometallurgy, and hydrometallurgy.

2. Experimental section

1.1. Materials and equipment

The materials used was iron sand from Sukabumi (Indonesia), acetone, methanol p.a (Merck), sodium carbonate (Merck), and oxalic acid (Merck). The equipment that require in this research was ultrasonic cleaner (DSA50 GL₁), planetary ball miller, oven (Memmert), sulphuric acid 96% (Merck), thermometer (Futaba, 0 °C-220 °C), and water. The materials characterization both before and after treatment were carried out by X-Ray Diffraction (XRD Bruker D8 Advance), X-Ray fluorescence (XRF Bruker S2 Ranger), and Scanning Electron Microscopy (SEM Quanta 250). Roasting process was carried out by Furnace Thermolyne 4800.

1.2. Preparation of Iron Sand

The Sukabumi iron sand was analyzed by X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). The magnetic and non magnetic particles was then separated by magnet. Subsequently the separated particles were milled by planetary ball milling (1000 rpm) for 2 hours. Milling process was conducted in w/w ratio, ball milling:material = 10:1 (130 gram:13 gram).

1.3. Fabrication of $\text{Fe}_2\text{O}_3/\text{TiO}_2$

1.3.1. Washing Non Magnetic Particles under Ultrasonic Irradiation

A 50 gram iron sand powder was washed with 150 mL oxalic acid (1 M) for 2 hours under ultrasonic irradiation. Precipitate and filtrate were separated and subsequently characterized by XRF.

1.3.2. Pyrometallurgy

Sukabumi iron sand was added Na_2CO_3 in ratio 1:2 (w/w) and afterwards roasted 800 °C for 2 hours. The roasted iron sand was analysed by XRF. A 20 gram iron sand was washed by 300 ml water in 90 °C for 2 hours. The precipitation was characterized by XRD and SEM.

1.3.3. Hydrometallurgy using Sulphuric Acid

Sukabumi iron sand was leached under reflux (90 °C) with an addition of 100 mL H_2SO_4 (9 M) for 2 hours. Subsequently the filtrate and precipitate were separated. The precipitate was analyzed by XRF. Whereas, the co-precipitation process from filtrate was washed by water and ethanol. The obtained precipitate was analyzed by XRF.

3. Result and Discussion

Firstly, the pretreatment Sukabumi iron sand was analysed qualitative and quantitative by XRF instrument. The result in Figure 1 and Table 1 shows that Sukabumi iron sand contains Fe 50.48%, Ti 8.65%, and other elements under 5%.

Table 1. Quantitative analysis of pretreatment Sukabumi iron sand (w/w)

Element	Concentration
Fe	50,48%
Ti	8,65%
Si	3,07%
Al	1,16%
Ca	0,78%
Mn	0,57%

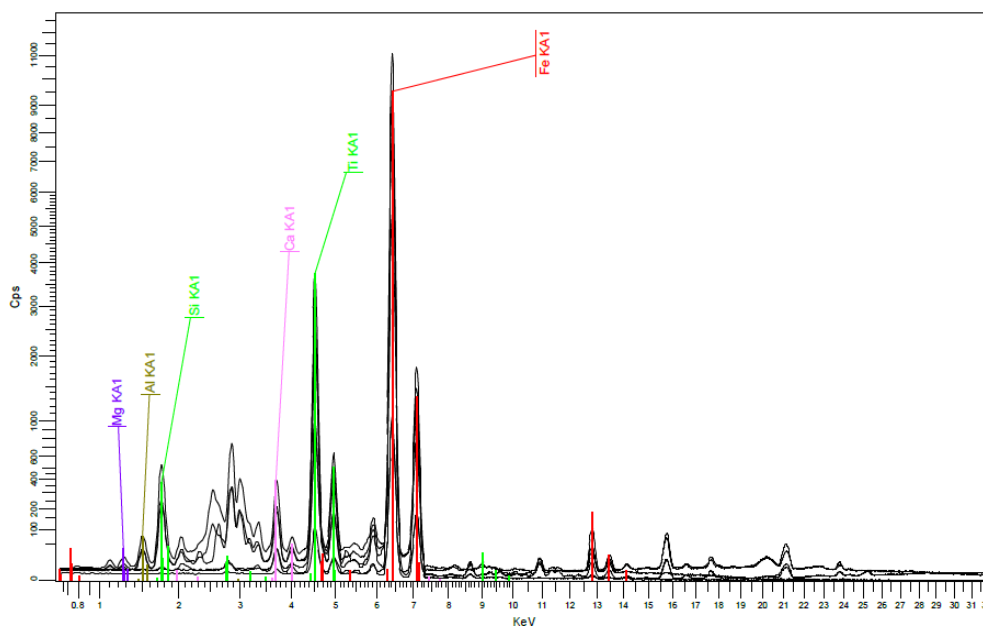


Figure 1. XRF analysis of pretreatment Sukabumi iron sand

Morphology of iron sand in Figure 2, shows that material have a rock shape. While the size particle is about 122,7 μm .

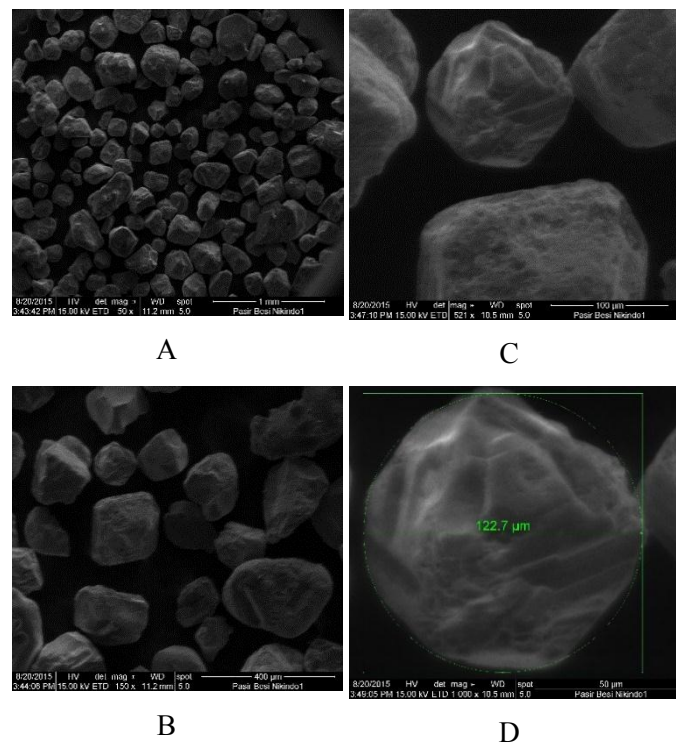


Figure 2. SEM results of Sukabumi iron sand a) 50x, b) 150x, c) 500x, and d) 1000x magnification

Magnetic separation of iron sand be able to reduce the magnetic particles such as wustite (FeO), hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and magnetite (Fe_3O_4). The XRF result (Table 2) have been proof this statement. Fe content in non magnetic particles reduce from 50.48% to 38.81%.

Table 2. XRF result from iron sand after magnetic separation

Element	Concentration
Fe	38,81%
Ti	13,18%
Si	5,47%
Ca	1,55%
Al	1,45%
Mn	0,68%

Washing the iron sand with oxalic acid under ultrasonic radiation has been done for reducing the impurities. The XRF result (Table 3) indicates that Fe and Ti content were decrease. It possibly because of dissolution of such amount Fe and Ti in oxalic acid, while Si content increase due to low solubility of this element in oxalic acid solvent.

The roasting treatment with an addition of sodium carbonate was done for decomposition of materials in iron sand such as Fe_2TiO_5 (pseudobrookite) to form hematite (Fe_2O_3) and TiO_2 . This is have a deal with the XRD result in Figure 3. The high peaks were corresponds to JCPDS No. 20-1115 (Na_2CO_3) in $2\theta = 38.177^\circ$ ($d_{hkl} = 002$) and $2\theta = 43.379^\circ$ ($d_{hkl} = 020$), JCPDS No. 89-1633 (TiO_2 rutile) in $2\theta =$

30.46° (hkl = 222), 2θ = 35.316° (hkl = 400) and 2θ = 38.604° (hkl = 331), JCPDS No. 88-2359 (Fe₂O₃) in 2θ = 23.851° (hkl = 012), 2θ = 32.856° (hkl = 104) and 2θ = 35.080° (hkl = 110), FeO also show in 2θ = 35.927° (hkl = 111) and 2θ = 41.725° (hkl = 200) according to JCPDS No. 89 – 0687.

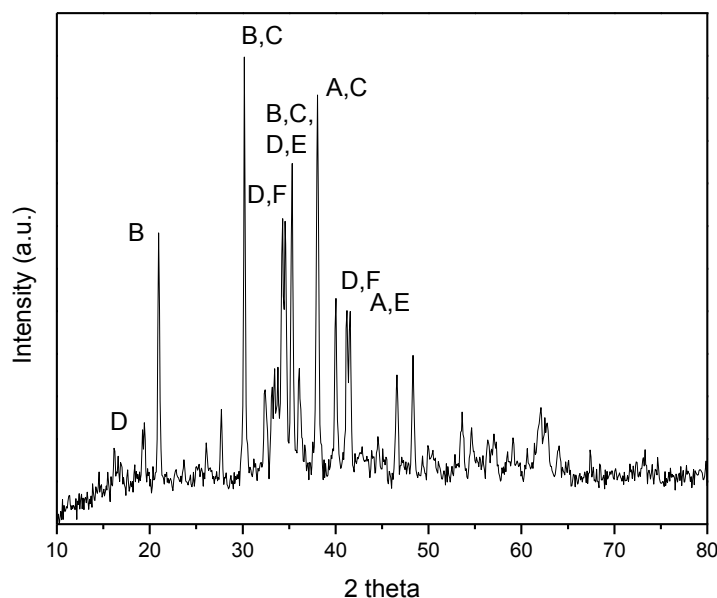
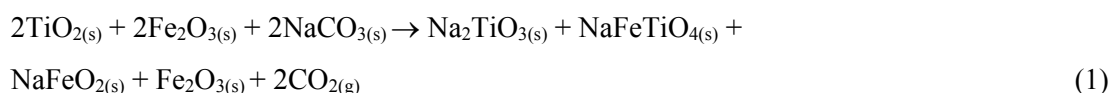


Figure 3. Diffractogram XRD of roasted iron sand (A = sodium carbonate, B = hematite , C = rutile, D= NaFeO₂, E = FeO, F = Na₂TiO₃)

The mechanism reaction that may occur during the roasting process is in equation 1.



Iron sand and Na₂CO₃ in roasting process were conducted in several ratio of 1:2 (A) ; 1:1 (B) ; 2:1 (C) (w/w), and the XRF result shows that (Table 3), those different ratio are be able to influence the obtained Fe and Ti.

Table 3. XRF result of roasted iron sand with an addition of Na₂CO₃ in ratio (w/w) 1:2 (A) ; 1:1 (B) ; 2:1 (C)

A		B		C	
Element	Concentration	Element	Concentration	Element	Concentration
Fe	32.75%	Fe	21.93%	Fe	22.14%
Ti	10.40%	Na	14.59%	Si	11.64%
Na	8.24%	Si	9.68%	Na	10.21%
Si	6.76%	Ti	5.89%	Ti	6.42%
Ca	1.57%	Ca	3.93%	Ca	4.06%
Al	1.24%	Al	2.73%	Al	3.25%
Mn	0.58%	Mn	0.39%	Mn	0.37%

Not only the content of Fe and Ti that changes through the treatment, but also the morphology of iron sand (Figure 4). The materials was leached under reflux with an addition of strong acid H_2SO_4 9 M. This process could dissolve the iron sand reach 86.70%. The possible reaction in leaching process is in equation 2-4. While XRF results can be seen in Table 4.

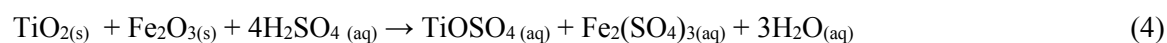
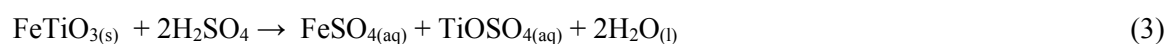
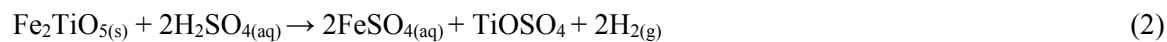


Table 4. XRF result of first precipitate and co-precipitate (w/w)

First precipitate		Co-precipitate	
Element	Concentrations	Element	Concentrations
Si	35.71%	Fe	32.42%
Fe	5.96%	Na	11.69%
Ti	4.23%	Ti	8.09%
S	1.80%	S	4.28%
Ca	1.01%	Al	1.04%
Al	0.38%	Ca	0.83%

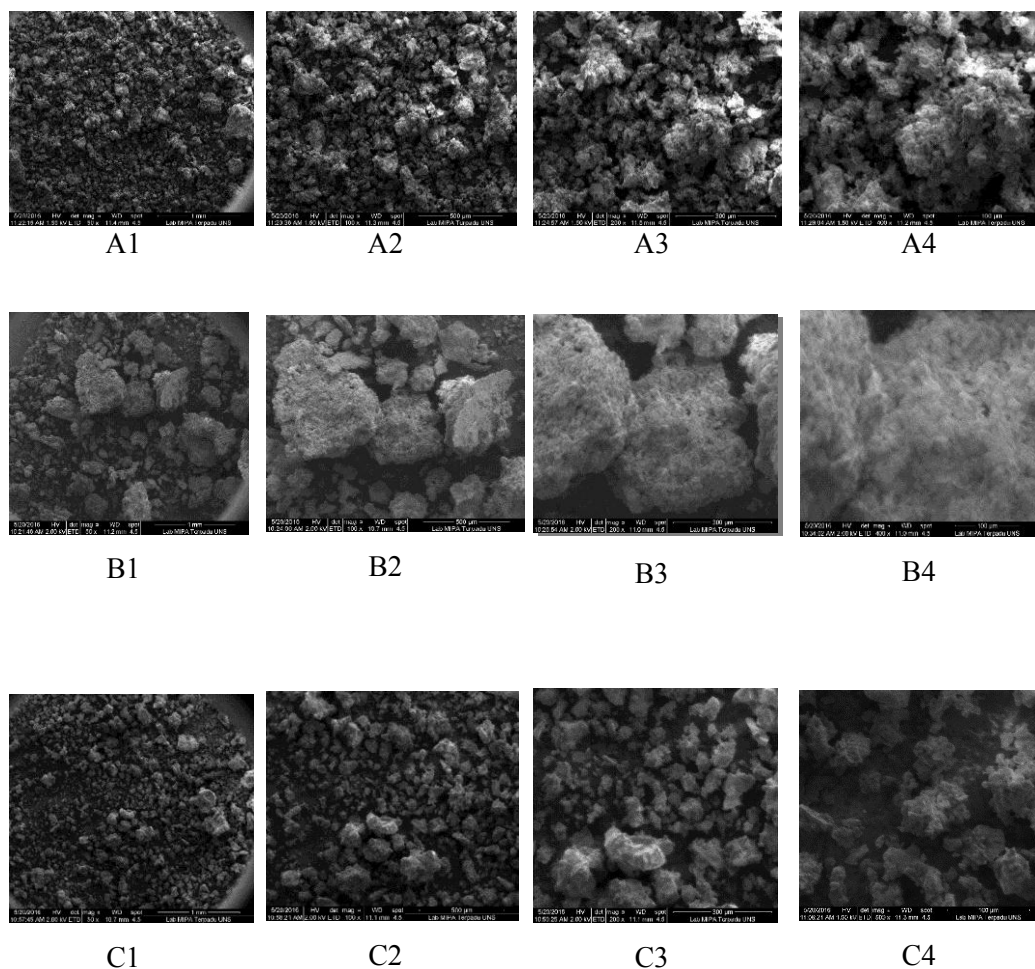


Figure 4. Morphology of roasted iron sand with an addition of Na_2CO_3 in ratio (w/w) 1:2 (A); 1:1 (B); 2:1 (C)

In conclusion, preparation of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite through magnetic separation, pyrometallurgy, and hydrometallurgy be able to yield Fe 5.96%, Ti 4.23% from precipitate. Then from coprecipitation process produce Fe 32.42% and Ti 8.09%. The more addition of Na_2CO_3 the more decomposition can occurred. While addition of sodium carbonate with ratio iron sand: Na_2CO_3 = 1:2 was the optimum condition for obtained Fe:Ti (1:1).

4. Acknowledgment

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5. References

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