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EXTRACTION OF TITANIUM DIOXIDE (TiO_2) FROM THE IRON SAND OF MANDIRI BEACH, WEST COAST AS NANOPARTICLES USING THE PYROMETALLURGICAL METHOD

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ABSTRAK
Pasir besi di Indonesia tersebar di berbagai pantai salah satunya adalah Pantai Mandiri yang terletak di Pesisir Barat menggunakan metode *random sampling*. Preparasi pasir besi dilakukan dengan cara separasi magnetik menggunakan magnet batang untuk memisahkan pasir besi dari pengotornya. Pasir besi Pantai Mandiri mengandung beberapa unsur dominan yaitu Fe, Si, Ti, Al, Ca, K, dan Mn. Ekstraksi TiO_2 dari pasir besi dilakukan menggunakan metode pirometalurgi dengan variasi suhu *roasting* 600, 700, dan 800 °C. Sampel hasil ekstraksi, dikarakterisasi menggunakan XRF dan menunjukkan kandungan TiO_2 dalam sampel meningkat seiring dengan peningkatan suhu *roasting* yaitu 6,970; 8,436; dan 8,659%. Sampel hasil ekstraksi dengan suhu *roasting* 800 °C dikarakterisasi menggunakan XRD dan menunjukkan bahwa TiO_2 yang diperoleh memiliki fase anatase berstruktur kristal tetragonal dengan a = b = 3,7840 Å dan c = 9,5150 Å, memiliki nilai sudut $\alpha = \beta = \gamma = 90°$, serta memiliki ukuran yang tergolong nanopartikel yaitu 55,16 nm.

Kata kunci: nanopartikel, pasir besi, pirometalurgi, dan TiO_2.

ABSTRACT
Iron sand in Indonesia is spread on various beaches, one of which is Mandiri Beach located on the West Coast using the random sampling method. Iron sand preparation is carried out by magnetic separation using rod magnets to separate iron sand from impurities. Pantai Mandiri iron sand contains several dominant elements, namely Fe, Si, Ti, Al, Ca, K, and Mn. TiO_2 extraction from iron sand is carried out using the pyrometallurgical method with roasting

temperature variations of 600, 700, and 800 °C. The extracted sample was characterized using XRF and showed that the TiO_2 content in the sample increased with an increase in roasting temperature of 6.970; 8.436; and 8.659%. The extracted sample with a roasting temperature of 800 °C was characterized using XRD and showed that the TiO_2 obtained had an anatase phase with a tetragonal crystal structure with a = b = 3.7840 Å and c = 9.5150 Å, had an angular value of $\alpha = \beta = \gamma = 90°$, and had a nanoparticle size of 55.16 nm.

Keywords: nanoparticles, iron sand, pyrometallurgy, and TiO_2.

INTRODUCTION

Iron sand in Indonesia is spread across various coasts such as the west coast of Sumatra, the south coast of Java, Kalimantan, Sulawesi, Nusa Tenggara and the Maluku Islands (Elsafitri *et al*., 2020). In Lampung, iron sand is often found on West Coast beaches. On the west coast of Pesisir Barat Regency there are mountains, namely Mount Pugung, Mount Sebayan, Mount Telalawan and Mount Tampak Tunggak, apart from that there are several rivers that cross the coast. This is what causes the abundance of iron sand along the West Coast beaches (Giovano *et al*., 2021). Iron sand contains magnetite or iron oxide compounds which consist of a mixture of iron and oxygen including hematite (Fe_2O_3), magnetite (Fe_3O_4) and ilmenite ($FeTiO_3$) (Indrawati *et al*., 2013).

The ilmenite compound ($FeTiO_3$) in iron sand can be extracted into titanium dioxide (TiO_2). TiO_2 can be used for photocatalysis because it is chemically stable and safe, and it is used as a semiconductor in Dye-Sensitized Solar Cells (DSSC) because TiO_2 is inert, harmless, cheap, corrosion resistant, and has good optical characteristics (Astuti dan Ningsi, 2017). Apart from that, TiO_2 is also widely used in the aviation industry because it is light, strong and better than stainless steel at resisting corrosion (Lu *and* Chen, 2009).

Currently, iron sand with nanoparticle size is being intensively developed because nano-sized iron sand has greater opportunities for application (Rianna *et al*., 2022). Nanomaterials are materials that have sizes ranging from 1 to 100 nm. Nanometer-sized materials have several chemical and physical properties that are superior to those of large-sized materials, such as magnetic, optical, catalytic and mechanical properties (Hosokawa *et al*., 2007).

Several methods have been used to extract TiO_2 from iron sand, including pyrometallurgical and hydrometallurgical methods. The pyrometallurgical method is a method of burning iron sand with the help of carbon as a reducing agent at high temperatures so that the iron in ilmenite can be reduced and produce slag rich in TiO_2. Meanwhile, the hydrometallurgical process is the process of dissolving iron sand using a solution of hydrochloric acid or sulfuric acid, but the presence of iron which is also dissolved in the acid requires further processing (Setiawati *et al*., 2013). In addition, the extraction of TiO_2 from iron sand using the hydrometallurgical method takes a very long time because it requires a calcination process at a fairly high temperature (Istiqomah *et al*., 2019).

In the research of Najihah *et al*. (2018), TiO_2 was extracted from Tulungagung iron sand using the hydrometallurgical method with a sulfuric acid solvent with a concentration of 8 M accompanied by heating. In this research, the material obtained is nanocrystalline TiO_2 in the rutile phase which is formed when heated to a temperature of 1000 °C for 7 hours. The size of the nanocrystalline obtained was 2.01 nm. In the research of Indrawati *et al*. (2013), TiO_2 was extracted from iron sand using the pyrometallurgical method. Iron sand reacts with sodium carbonate (Na_2CO_3). The material obtained was TiO_2 of 17.26% at a temperature of 600 °C, 76.54% at a temperature of 700 °C, and 51.5% at a temperature of 800 °C.

Based on the description above, research will be carried out regarding the extraction of TiO_2 nanoparticles from the iron sand of Mandiri Beach, located in Pesisir Barat Regency, Lampung Province using the pyrometallurgical method with temperature variations of 600, 700 and 800 °C. The TiO_2 that has been obtained will be characterized using XRD to determine the phases formed and XRF to determine the minerals contained therein.

METHOD

Tools and materials

The tools used in this research include glassware (measuring glass, beaker, measuring flask, Erlenmeyer, glass funnel and dropper), bar magnet, PQ-N2 planetary

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ball mill, 325 mesh sieve, AS200Tap sieve shaker, spatula, reagent bottle, Nabertherm furnace, porcelain cup, hot plate, magnetic stirrer, thermometer, oven, filter paper, X-ray Diffraction (XRD) Brand Panalytical Xpert 3 Powder, X-ray Fluorescence (XRF) Brand Panalytical Epsilon 3 XLE, and Scanning Electron Microscope (SEM) Brand Thermo Scienticis Quatro S. The materials used in this research include Pantai Mandiri iron sand, sodium carbonate, 8 M sulfuric acid, and distilled water.

Procedure

Iron sand originating from Mandiri Beach, West Coast is physically separated from impurities using a bar magnet. The iron sand will stick to the magnet while the non-magnetic impurities will remain behind. Then, the iron sand obtained was ground using a PQ-N2 planetary ball mill at a speed of 300 rpm for 50 minutes and sifted using a 325 mesh sieve on an AS200Tap sieve shaker. Then, characterization was carried out using XRF to determine the initial content of the sample.

The iron sand sample measuring 325 mesh was mixed with sodium carbonate (Na_2CO_3) in a ratio of 1:2 and the total weight was 60 grams. Next, the roasting process is carried out in a furnace with temperature variations of 600, 700, and 800 ℃ for 1 hour. The roasted samples were washed (leached) using distilled water and 8 M H_2SO_4 with a solid to liquid ratio of 1:3 over an electric heater at a temperature of 90 ℃ and stirred using a magnetic stirrer for 30 minutes at a rate of 300 rpm. Then, the precipitate obtained was washed again using distilled water to remove any residual acid contained in the sample. Next, the samples were dried in an oven at a temperature of 105 ℃. Then, the dried samples were characterized using XRF and XRD.

RESULTS AND DISCUSSION

Sample Preparation

Iron sand samples were obtained from Mandiri Beach which is located in Pekon Mandiri, South Krui District, Pesisir Barat Regency, Lampung. Sampling was carried out using the random sampling method, namely simple random sampling. The samples that have been obtained are separated from impurities by means of magnetic separation using a magnet. From this magnetic separation, two types of samples will be obtained, including concentrate samples, namely black magnetic minerals and tailings samples, namely white nonmagnetic minerals. In this research, the sample used was a concentrate sample (Bahfie *et al*., 2022). The iron sand samples were ground using a PQ-N2 planetary ball mill at a speed of 300 rpm for 50 minutes and sieved using a 325 mesh sieve on an AS200Tap sieve shaker. The sample passed through the 325 mesh sieve was gray in color.

XRF Characterization of Iron Sand

The prepared iron sand was characterized using XRF to determine the content of the iron sand. The characterization results can be seen in Table 1.

Table 1. Results of XRF characterization of Mandiri Beach iron sand preparation results

No	Element	Concentration (%)	Oxide	Concentration (%)
1	Fe	52.854	Fe_2O_3	42.084
2	Si	20.553	SiO_2	30.335
3	Ti	7.600	TiO_2	7.808
4	Al	7.449	Al_2O_3	9.970
5	Ca	6.873	CaO	5.990
6	K	2.076	K_2O	1.588
7	Mn	0.556	MnO	0.406
8	Other elements	<0.5	Other oxide	<0.5

From the results of XRF characterization, it is known that the most dominant elements found in the Mandiri Beach iron sand are Fe, Si, Ti, Al, Ca, K, and Mn with the respective content percentages being 52.854; 20,553; 7,600; 7,449; 6,873; 2,076; and 0.556%. Apart from that, Mandiri Beach iron sand also contains other elements with a content percentage of less than 0.5%.

TiO_2 Extraction from Iron Sand

Iron sand that has been ground using a PQ-N2 planetary ball mill is added with sodium carbonate (Na_2CO_3) to help the compound decomposition process and make the compound quite porous so that the sample leaching process runs more easily. According to Lasheen (2008), the optimal ratio between iron sand and Na2CO3 in the

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roasting process is 0.55:1. The roasting process is carried out with temperature variations of 600, 700, and 800°C and a holding time of 1 hour. The reactions that occur in the roasting process are as follows:

$$FeTiO_{3(s)} + Na_2CO_{3(s)} \rightarrow Na_2TiO_{3(s)} + FeO_{(s)} + CO_{2(g)} \quad (1)$$

Ilmenite ($FeTiO_3$) decomposes into Na_2TiO_3 and FeO due to the breaking of oxygen bonds between Fe and Ti atoms in the presence of sodium ions (Na^+) (Indrawati *et al*., 2013). From the roasting results, 56.23 grams of brown powder were obtained at a roasting temperature of 600 °C; 56.08 grams at a roasting temperature of 700°C; and 54.11 grams at a roasting temperature of 800 °C.

(a) (b) (c)

Figure 1. Samples from roasting at (a) 600 °C, (b) 700 °C, and (c) 800 °C.

The leaching process was carried out on the roasted samples using distilled water with the following reaction:

$$Na_2TiO_{3(s)} + FeO_{(s)} + 3H_2O_{(l)} \rightarrow H_2TiO_{3(s)} + Fe(OH)_{2(l)} + 2NaOH_{(l)} \quad (2)$$

When leaching distilled water, the Na^+ ions in Na_2TiO_3 are easily replaced by H^+ ions (Chen *et al*., 2022), so that Na_2TiO_3 is decomposed into H_2TiO_3. In the leaching process, a yellow filtrate is obtained which indicates the formation of $Fe(OH)_2$ due to the dissolution of Fe^{2+} ions in distilled water (Indrawati *et al*., 2013).

The acid leaching process was carried out using 8 M H_2SO_4. Leaching using H_2SO_4 8 M aims to increase the purity of the sample by dissolving Fe metal, the dissolved Fe metal forms $FeSO_4$. After acid leaching, the sample was washed using distilled water to remove residual acid. Washing is carried out until the filtrate obtained is colorless.

During the washing process, the first filtrate obtained was green which indicated the presence of $FeSO_4$, so it could be said that the Fe in the sample was reduced (Indrawati *et al*., 2013).

The samples obtained from washing were dried using an oven at a temperature of 105 °C until a constant weight was used to remove the water content from the samples with the following reaction:

$$TiO.H_2O_{(s)} \rightarrow TiO_{2(s)} + H_2O_{(g)} \quad (3)$$

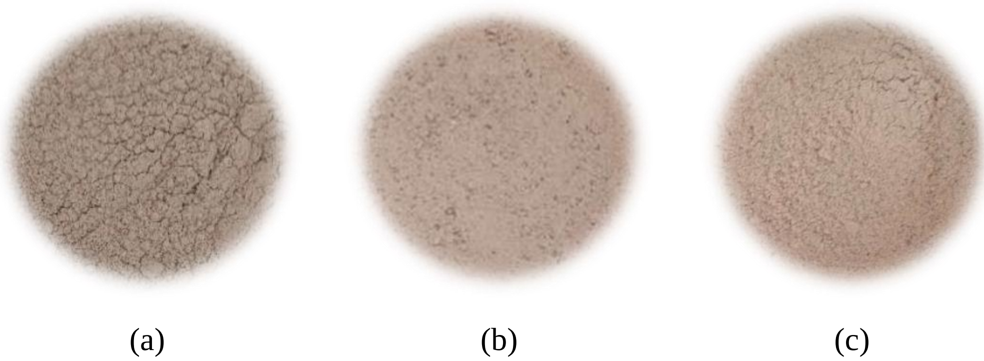

Figure 2. TiO_2 extraction results at (a) 600 °C, (b) 700 °C, and (c) 800 °C

The final result of this extraction was a gray powder with a yield of 24.29% at a roasting temperature of 600 °C; 23.27% at a roasting temperature of 700 °C; and 16.74% at a roasting temperature of 800 °C.

XRF characterization

The extraction results obtained were characterized using XRF to determine the content of the sample and the results are shown in Table 2.

Table 2. Results of the oxide component characterization of extraction samples

No	Oxide	Concentration (%)		
		600 °C	700 °C	800 °C
1	SiO_2	42.748	47.687	48.135
2	Fe_2O_3	32.482	33.650	31.029
3	TiO_2	6.970	8.436	8.659
4	CaO	4.950	3.589	4.394
5	SO_3	4.722	2.708	5.409

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6	Al_2O_3	3.908	2.194	0.943
7	K_2O	0.710	0.351	0.100
8	Other oxide	<0.5	<0.5	<0.5

From the XRF characterization results obtained, it shows that the TiO_2 content in the extracted samples increases with increasing roasting temperature, namely 6.970; 8,436; and 8.659%. This shows that increasing the roasting temperature will increase the reaction between iron sand and Na_2CO_3. Apart from that, increasing the roasting temperature also affects the reactivity of iron oxide compounds where iron becomes easier to remove through the leaching process, so that the Fe content in the sample decreases (Setiawati *et al*., 2013). At raosting temperatures of 600 and 700 °C, the TiO_2 obtained is less than optimal because Na_2CO_3 has not reacted optimally with $FeTiO_3$, so the decomposition process has not gone well (Indrawati *et al*., 2013). At a rising temperature of 800 °C, the decomposition process runs optimally and forms porous sodium titanate, making it easier for the sample leaching process using distilled water and H_2SO_4 (Lasheen, 2008). Based on the results obtained, the optimal roasting temperature for TiO_2 extraction from Pantai Mandiri iron sand is 800 °C.

XRD Characterization

Samples extracted at a roasting temperature of 800 °C were characterized using XRD. The results obtained were analyzed using High-Score Plus which is equipped with COD and the following results were obtained:

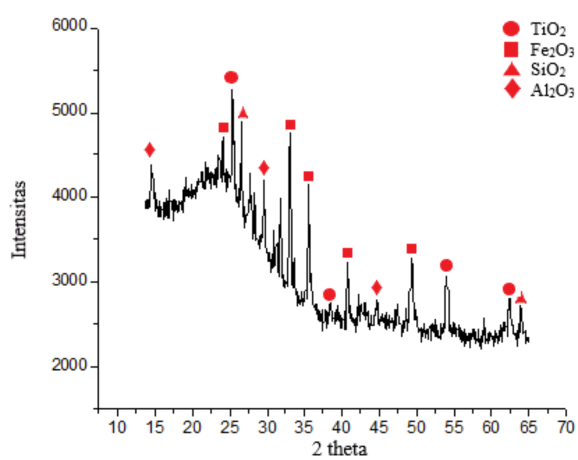

Figure 3. Sample diffraction patterns from high-score plus analysis

Based on the analysis obtained, the sample extracted from a roasting temperature of 800 ℃ contains three dominant compounds, namely TiO_2, Fe_2O_3, SiO_2, and Al_2O_3. The TiO_2 formed has four peaks located at the diffraction angle 2θ of 25.34; 38.51; 54.01; and 62.38° with crystal orientation. From this diffractogram, it is known that TiO_2 has been formed in the anatase phase and the lattice parameters of the sample are obtained, namely a = b = 3.7840 Å and c = 9.5150 Å, and it has an angle value of α = β = γ = 90° which indicates that the anatase formed has a tetragonal crystal structure.

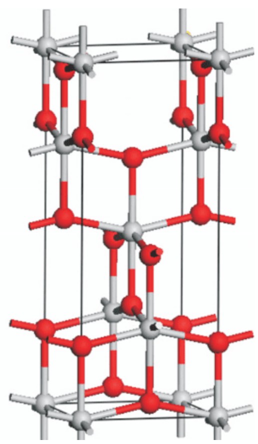

Figure 4. Anatase crystal structure (Yin *et al*., 2010)

In Figure 4, Ti atoms are shown in white and oxygen atoms are shown in red. An anatase crystal consists of 4 atoms per unit cell with a volume of 0.1363 nm^3 and a density value of 3894 kg/m^3 (Hanaor *and* Sorrell, 2011).

The highest peak of TiO_2 is located at the diffraction angle 2θ of 25.34° with the hkl (101) plane. This peak can be used to determine the size of the crystals formed using the Scherrer equation, namely:

$$D = \frac{k\lambda}{\beta Cos\theta} \quad (4)$$

From the calculation results, the TiO_2 crystal size is 55.16 nm. This crystal size shows that the anatase obtained has nano-sized particles so it is classified as a nanocrystal.

TiO_2 which is classified as nanocrystals or nanoparticles can be used in various fields because it is light, strong, non-flammable, does not cause toxic effects, has high biocompatibility, is resistant to high temperatures and corrosion, and has bactericidal and fungicide functions (Supriyatna *et al*., 2020). TiO_2 can be used as an antibacterial for *Escherichia coli* (Ahmad *and* Meryam, 2013), as a polymer composite (Huang *et al*., 2014), and as a semiconductors in Dye-Sensitized Solar Cell (DSSC) (Astuti and Ningsi, 2017).

CONCLUSION

The iron sand of Pantai Mandiri Pesisir Barat consists of various elements, the most dominant elements are Fe, Si, Ti, Al, Ca, K, and Mn with the respective content percentages being 52.854; 20,553; 7,600; 7,449; 6,873; 2,076; and 0.556%. The result of TiO_2 extraction is a gray powder with a yield of 24.29% at a roasting temperature of 600 ℃; 23.27% at a roasting temperature of 700 ℃; and 16.74% at a roasting temperature of 800 ℃. TiO_2 obtained from the extraction of Pantai Mandiri Pesisir Barat iron sand using the pyrometallurgical method has a content percentage of 6.970% at a roasting temperature of 600 ℃; 8.436 % at a roasting temperature of 700 ℃; and 8.659% at a roasting temperature of 800 ℃. The optimal roasting temperature for TiO_2 extraction from Pantai Mandiri iron sand is 800 ℃. The results of characterization by γ are 90°. Based on the Scherrer equation, the TiO_2 crystal size is 55.16 nm, this size shows that the TiO_2 obtained is classified as a nanocrystal.

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