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Synthesis of Titanium Oxysulfate from Ilmenite through Hydrothermal, Water Leaching and Sulfuric Acid Leaching Routes

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Abstract. Ilmenite ($FeTiO_3$) is a mineral that abundantly available in nature. Its extraction process can provide titanium dioxide (TiO_2) which is useful for various strategic applications including dye-sensitized solar cells, photocatalysts, and water splitting. To obtain TiO_2, ilmenite has to be converted first into titanium oxysulfate ($TiOSO_4$) precursor. This procedure needs optimization in processing parameters. Therefore, this research focuses on the preparing $TiOSO_4$ precursor by ilmenite extraction. The process involved hydrothermal reaction with the time variation of 1 to 5 hours, water leaching at 40 ^oC and sulfuric acid leaching with two different concentration of 3 and 18 M at 90 ^oC. The residues from ilmenite extraction were characterized using scanning electron microscope (SEM), x-ray diffraction (XRD), x-ray fluorescence (XRF), while the filtrate was characterized using inductively coupled plasma-optical emission spectrometry (ICP-OES). The results showed that the ilmenite granules derived from hydrothermal process residue was still existed in the large grains. As the grain size became smaller after water and acid leaching, the effectiveness of the two treatments was noticeable. Upon hydrothermal process, increasing the reaction time from 1 to 5 hours decreased the concentration of titanium element in the filtrate from 400.39 to 18.31 ppm. However, the process of water and acid leaching successfully increased the titanium content in $TiOSO_4$ from 4394.32 to 7868.82 ppm. It was also found that by increasing the sulfuric acid concentration up to 18 M has provided a more stable $TiOSO_4$ solution for the purpose of TiO_2 formation.

INTRODUCTION

Ilmenite is a natural material that contains iron, titanium and other minerals in which the percentage of titanium dioxide (TiO_2) can reach about ~35-65% [1,2]. Ilmenite can also be found in lead processing waste [3]. Natural ilmenite has been strongly considered as an important basic material for producing TiO_2 [4]. In addition, TiO_2 has been well-known as one of the strategic semiconductor materials that can be used for various important applications including photocatalysts [5], dye-sensitized solar cells [6], and water splitting [7]. To extract titanium dioxide from ilmenite, the synthesis process can be carried out through pyrometallurgy [8] or hydrometallurgy [9] routes. The pyrometallurgy extraction process is limited with the fact that it requires high temperature and thus expensive costs [10]. By contrast, hydrometallurgical extraction process is more feasible due to its low temperature condition [11]. This technique involves acid chemical solution, for example hydrochloric acid [12] or sulfuric acid [13] pathways. Hydrochloric acid pathway is more volatile whereas the sulfuric acid one is non-volatile and relatively cheap [14]. Previous studies have successfully synthesized titanium oxysulfate from ilmenite minerals (black sands of Puerto Colombia, Atlántico, Colombia) and ilmenite Bangka Indonesia using the sol-gel[3], leaching [15], and hydrothermal methods [13]. However, the final product produced from each of these methods still contains impurities. Therefore,

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for optimization by reducing the impurities, a combination of the aforementioned synthesis methods such as hydrothermal, water leaching and acid leaching was carried out in this study

One of the steps in the decomposition of ilmenite is known as hydrothermal process[3]. In the step, prior to acid leaching, the decomposition process of ilmenite needs to be carried out with dissolution in NaOH solution inside a pressurized autoclave under a certain temperature and time duration. The purpose of self-decomposition is to change the chemical characteristics of ilmenite so that it can be easily dissolved in further leaching steps with water and acid. Sulfuric acid leaching results a $TiOSO_4$ solution as the precursor for TiO_2 production. In the hydrothermal process, the applied temperature and time are the key factors that affect the solubility of titanium in the filtrate. In addition, upon sulfuric acid leaching step, the concentration of acid also influences the solubility of titanium in $TiOSO_4$ solution.

Based on the aforementioned background, in this study we investigated the effect of variation in the hydrothermal reaction time from 1 to 5 hours, and the concentration of sulfuric acid of 3 and 18 M upon leaching process on the levels of dissolved titanium in the $TiOSO_4$ solution.

MATERIALS AND METHODS

The synthesis was started first by preparing the hydrothermal solution in which 12 grams of sodium hydroxide (NaOH pellet, Merck) were dissolved in 30 ml of distilled water and then stirred homogeneously. Furthermore, 20 grams of ilmenite ($FeTiO_{3,}$ Bangka Indonesia) powder were dispersed into ethanol solution of NaOH 10 M. The mixture solution was stirred for 3 hours to obtain a homogeneous dispersion, prior to hydrothermal treatment. This step was carried out by putting the mixture solution into in a Teflon lined autoclave, and heated at 150^0 C in oven for different time of 1 to 5 hours. This resulted in a residue which was further subjected to water leaching with the ratio of residue to water was kept at 1:4. This dispersion was stirred at 40^0C for 3 hours. Finally, the residue was leached in sulfuric acid ($H_2SO_{4,}$ Merck) media with a ratio of residue and acid of 1:5. For investigation purposes, the concentration of sulfuric acid was varied as 3 and 18 M and the mixtures were stirred at 90^0 C for 1.5 hours. For the whole processes the resulting products were filtrate and residue. For characterizing the filtrate, inductively coupled plasma-optical emission spectrometry (ICP-OES) was used, while for the residue a field-emission scanning electron microscopy (FESEM JEOL JIB 4610F) was used to check its morphology, x-ray diffraction (XRD) (Shimadzu X-Ray Diffractometer 7000; Cu Kα radiation λ = 1.5418) to study the crystal structure, the average crystallite size was estimated using Scherrer's formula [16] and x-ray fluorescence (XRF) for composition checking.

RESULTS AND DISCUSSIONS

Particle Morphology of Ilmenite

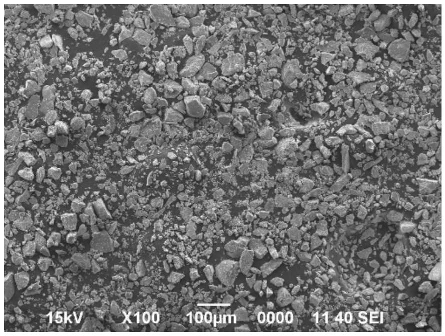
Figure 1a shows the result of SEM observation on the raw ilmenite which appeared as small granules like lumps of clay stone having average sizes of 50.35 μm. Upon hydrothermal process at 150 °C for 3 hours, the granules grew into bigger size of 143.19 μm in average (Figure 1.b). The size increased in ilmenite granules as a result of thermal driving force at 150 °C under pressurized alkaline media inside the autoclave, which resulted in restructuring of titanium and iron elements. These big granules turned back into much smaller particles after water acid leaching at about 31.89 μm, as shown by Figure 1c, as a consequence of titanium and iron elements were scraped off.

Chemical Composition of Ilmenite

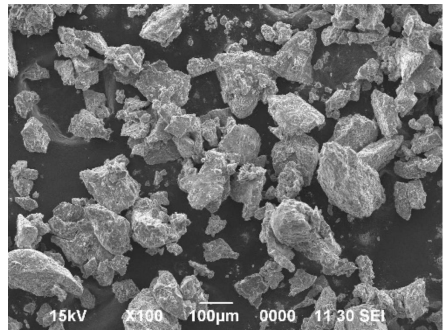
Table 1 shows the chemical composition from XRF for the raw ilmenite and those after hydrothermal, water leaching and sulfuric acid leaching process. It shows that the chemical composition of TiO_2 has increased from 24.436 to 50.632%. This also applied for the case of Fe_2O_3 which has increased from 17.784 to 26,107 %. On the other hand, the concentration of several other impurities such as SiO_2 and SnO_2 were decreased significantly, from 2.677 to 0.968% and from 31.782 to 5.721%, respectively. And also impurities such as Al_2O_3 were decreased significantly from 1,599 to 0% due to the element was dissolved and reacted with sodium hydroxide in the hydrothermal process and the reaction produced sodium aluminate ($NaAl(OH)_4$). The formation of ($NaAl(OH)_4$) follows the reaction below:

$$Al_2O_3\,(s) + 3H_2O(l) + 2NaOH\,(aq) + Heat \rightarrow 2NaAl(OH)_4\,(aq) \quad (1)$$

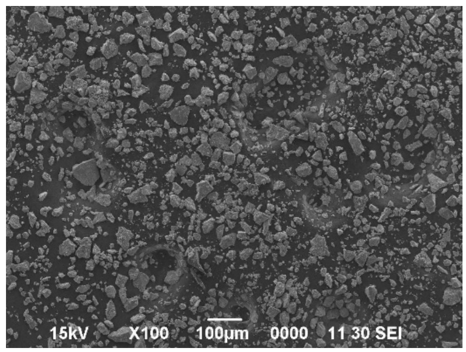
These results confirmed the effectiveness of water and sulfuric acid leaching in removing out the impurities.



(a)



(b)



(c)

FIGURE 1. SEM images of ilmenite: (a) before treatment, (b) after 3 hours' hydrothermal process, and (c) after water leaching

TABLE 1. Chemical composition of ilmenite as raw mineral and after treatments (hydrothermal, water and acid leaching)

Compound	TiO_2	Fe_2O_3	Al_2O_3	SiO_2	SnO_2	Cr_2O_3
Raw ilmenite (%)	24.436	17.784	1.599	2.677	31.782	0.129
After hydrothermal (%)	47.152	28.096	-	0.389	6.841	0.154
After water leaching (%)	49.120	24.886	-	1.273	5.396	0.144
After sulfuric acid leaching (%)	50.632	26.107	-	0.968	5.721	0.111

Crystal Structural of Ilmenite

Figure 2 is XRD diffractogram of raw ilmenite and those of after the treatments, i.e. hydrothermal and water leaching. For raw ilmenite as shown in Fig. 2a the crystalline structure was demonstrated with three peaks at the diffraction angle 2θ of 27.58, 34,66, 54,29^o. The first sharp peak belongs to SnO_2 phase, while the other two with relatively lower intensities are associated with $FeTiO_3$ phase. This result was consistent as shown in Table 1 that SnO_2 phase was more dominant than the TiO_2 as indicated with its chemical composition of 31.782% compared to that of TiO_2 which was only 24.436%. Furthermore, after the hydrothermal process (Figure 2b), on top of the existing $FeTiO_3$ phase, the XRD diffractogram shown that the new peaks belong to rutile phase appeared at 2θ of 28,01, 38,02, 48,04 and 62,05 ^{o}. All the peaks matched with ICDD card no 21-1272 with lattice fields (101), (004), (200) and (204) [13]. In addition, the existence of $NaTiO_3$ phase was also observed as a consequence of titanate cation in ilmenite with sodium solution. Figure 2c provide the result of XRD on the ilmenite sample after water leaching with the increase in TiO_2 rutile, $NaTiO_3$ and Fe_2O_3 peaks was obviously seen. On the other hand, the diffraction peak of SnO_2 was significantly decreased confirming the effectiveness of water to get rid of the impurity of ilmenite. Further analysis on the crystallite growth was performed on the obtained XRD diffractograms by using Scherrer's equation [16]. The results of crystallite size estimation are presented in Table 2.

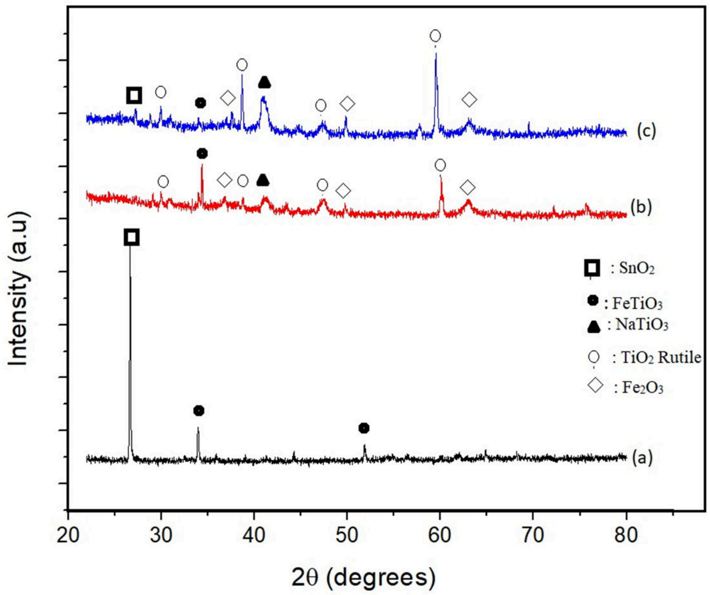


FIGURE 2. XRD spectra of ilmenite: (a) before treatment (raw), (b) after hydrothermal process, and (c) after water leaching

TABLE 2. Estimated crystallite sizes of ilmenite: (a) before treatment, (b) after hydrothermal process, and (c) after water leaching

Compound	Average crystallite size (nm)
Raw Ilmenite	61.96
After hydrothermal	68.01
After water Leaching	60.07

Table 2 shows that the estimated average crystallite size of ilmenite increased when its raw mineral was subjected to hydrothermal process from 61.96 to 68.01 nm. However, with the application of water leaching the crystallite size decreased to 60.07 nm. This finding is in accordance with what has been analyzed with SEM from Figures 1 with the increase and the decrease in the particle or granule sizes of ilmenite following the sequence of treatments.

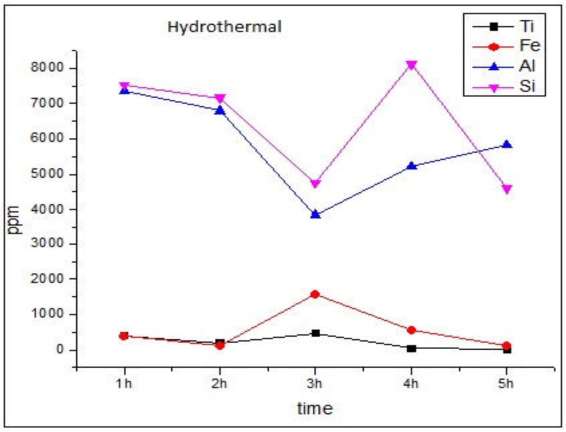
Inductively Coupled Plasma-Optical Emission Spectrometry of Ilmenite Filtrate

The previous obtained results of the hydrothermal process, water leaching and acid leaching were ilmenite residues as solid. However, it should be noted that the filtrate is also of importance to be analyzed for checking the effectiveness of each steps. In addition, the filtrate became the primary concern because in the form of $TiOSO_4$ solution as the final product it is the expected precursor for synthesizing TiO_2 material. The formation of $TiOSO_4$ follows the reaction below:

$$FeTiO_3\,(s) + 2HSO_4\,(aq) \rightarrow FeSO_4\,(aq) + TiOSO_4\,(aq) + 2H_2O(l) \qquad (2)$$

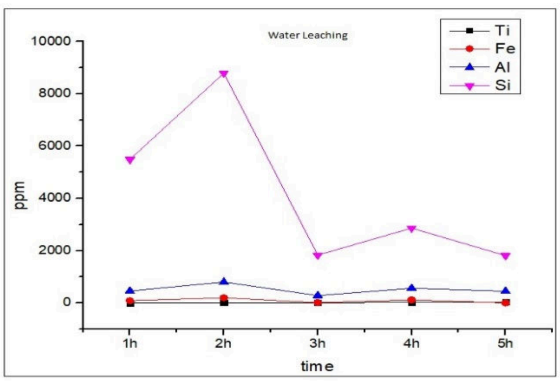
In this investigation, the characterization of the resulting filtrate was performed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and the results was presented in Figures 3 to 5. Upon hydrothermal process with various duration from 1 to 5 hours, the titanium element in the filtrate decreased from 400.39 to 18.31 ppm (Figure 3). However, upon being subjected to water leaching, the filtrate provided an increase of titanium element from 0.72 to 31.37 when the duration time of process was prolonged from 1 to 5 hours (Figure 4). Further leaching with sulfuric acid (Figure 5) with the same increase in duration time, the content of titanium element was dramatically enhanced from 4394.32 to 7868.82 ppm. This shows that the sequential steps taken in this work has been able to improve the content of titanium element in the targeted filtrate as the $TiOSO_4$ solution.

For further investigation purposes, the solid residues obtained from the hydrothermal process, water leaching and sulfuric acid leaching were dissolved in aqua regia. It should be noted that upon the acid leaching for this residue, the concentration of sulfuric acid was varied as 3 M and 18 M. All resulting solutions after dissolution with aqua regia were re-characterized with ICP-OS. The results are presented in Figure 6.



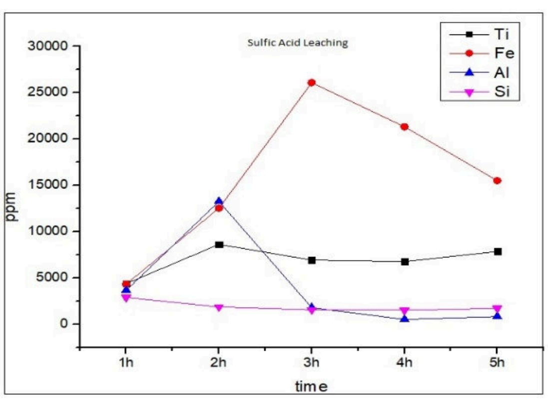
Hydrothermal	Ti (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
1 h	400.39	403.22	7368.68	7529,04
2 h	185.69	108.48	6795.58	7166,52
3 h	475.48	1579.81	3849.05	4748,54
4 h	46.38	572.97	5227.79	8119,42
5 h	18.31	124.74	5830.78	4604,16
Average	225,26	558.05	5839.78	6433,54

FIGURE 3. ICP-OS results of the filtrate after hydrothermal process



Water Leaching	Ti (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
1 h	0.72	88.31	458.89	5490.64
2 h	8.79	197.25	802.16	8791.44
3 h	12.39	14.08	280.66	1829.34
4 h	15.94	117.59	563.13	2865.56
5 h	31.37	0.11	447.45	1810.58
Average	13.85	83.47	510.46	4157.51

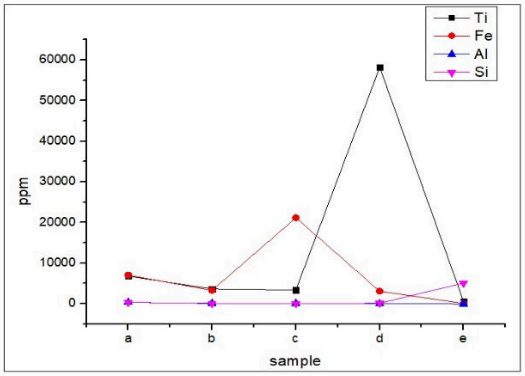
FIGURE 4. ICP-OS results of the filtrate after water leaching



Sulfuric acid leaching	Ti (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
1 h	4394.32	4345.00	3663.5	2904.80
2 h	8635.14	12535.50	13274.8	1881.37
3 h	6938.05	26092.30	1797.45	1566.75
4 h	6772.45	21325.70	534.53	1516.46
5 h	7868.82	15507.00	827.22	1733.44
Average	6921,76	15961,10	4019.50	1920.56

FIGURE 5. ICP-OS results of the filtrate after sulfuric acid leaching

It can be seen that titanium element obtained through dissolution with low concentrations of 3 M can provide much higher result (58194.13 ppm) compared to that of high concentration of 18 M, which is only 606.52 ppm. For the purpose of TiO_2 phase formation, the former can provide faster hydrolysis and thus bigger granules/aggregates, while the latter tends to facilitate a more stable condition towards hydrolysis and thus smaller particles [13]. In this sense, the $TiOSO_4$ solution



Hydrothermal	Ti (ppm)	Fe (ppm)	Al n)	Si (ppm)
• Raw ilmenite	6790.86	7062.40	343.58	352.38
• After hydrothermal	3660.56	3300.95	113.40	42.17
• After water leaching	3367.95	21170.20	89.24	16.03
• After acid leaching 3 M	58194.13	3081.15	9.28	127.11
• After acid leaching 18 M	606.52	62.89	-73.25	5082.80

FIGURE 6. ICP-OS results of the ilmenite residue dissolved in aqua regia after being subjected to various process.

CONCLUSIONS

In this study, $TiOSO_4$ precursors has been successfully synthesized through the hydrometallurgy route involving hydrothermal process, water leaching and sulfuric acid leaching. With longer hydrothermal process time from 1 to 5 hours the level of dissolved Ti element in the filtrate decreased from 400.39 ppm to 18.31 ppm. Upon subsequent water leaching with the similar time duration, an increase of titanium element was obtained from 0.72 to 31.37. A more significant enhancement from 4394.32 to 7868.82 ppm was finally achieved with the sulfuric acid leaching.

A variation in sulfuric acid concentration with 3 and 18 M provided useful clue for TiO_2 nanoparticle synthesis. With a low concentration of 3 M sulfuric acid, it was obtained that a high titanium element level of 58194.13 ppm can be achieved, while with that of high concentration 18 M sulfuric acid the dissolved titanium level only reached a value of 606.52 ppm. A higher titanium level in $TiOSO_4$ filtrate as TiO_2 precursor will provide faster hydrolysis and thus bigger aggregates, while $TiOSO_4$ filtrate with low level of titanium element is more stable and thus facilitate slower rate of hydrolysis.

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