UV-Ilmenite based photo-catalysis in lignin based black liquor

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Abstract. Ilmenite can be found abundantly in iron sand from sea shore along Wolowo beach in Button district, Southeast Sulawesi, Indonesia. The ability of ilmenite in degrading lignin in black liquor has been investigated. The results of lignin degradation process in black liquor are supposed to be the potential resources for fungicide such as coniferyl, sinapyl, and p-coumaryl alcohol. The process was conducted in 10 watt ultraviolet (UV) light chamber with two parameters applying include exposure time and ilmenite composition. Two scheme of process are used by differentiating the feed, raw black liquor (scheme 1) and the liquor after adding of 1% sodium hydroxide into lignin-based sludge (scheme 2). Decolourization and lignin degradation analysis after the process were conducted by using UV-Vis spectrophotometer and LCMS, respectively. The results showed that the treatment from the scheme 1 was better than the scheme 2. Both lignin degradation and decolourization can effectively result in more than 31% by using 0.3 g ilmenite for 10 minutes UV exposure. The interim analysis by liquid chromatography-mass spectrophotometer (LCMS) exhibits the suspected target in range 309.4 to 311.39 g/mol as p-coumaryl alcohol while two other targets did not found in chromatogram. Thus, this research requires further evaluation and development to maximise the degradation result so the final goal can be achieved successfully.

1. Introduction
Iron sand based ilmenite has already been investigated regarding its content of TiO₂ which is well known as a potentially used catalyst [1-2]. As a facile material which has valuable content, the investigations are announced relating its preparation and application. The preparation of ilmenite is related with the characteristic of material that influences its performance [3 ]. The calcination by applying high temperature in a furnace is one of potential methods to be conducted as it may reduce the use of chemicals. At high temperature (800 °C and above), the TiO₂ is separated from Fe₂O₃. 2TiO₂ that composed during the increasing of temperature up to 800 °C [4]. TiO₂ is the most used catalyst material that works well under light exposure. Ultraviolet (UV) and other kinds of light can be used to enhance the TiO₂ work in ilmenite. This method is considered as the safest way process since it is easy to tackle even though electricity based light is not available at a place [5]. In addition, TiO₂ is the most stable chemical compound but has high reactivity under UV or other kinds of light exposure so it opens a wide application [5]. One example of its application refers to wastewater treatment that mostly can degrade the recalcitrant dissolving compounds up to 90% [3, 6].
Another commonly found wastewater problem in pulp and paper industry or lignocellulosic biomass-based bioethanol is lignin-based black liquor (LBBL). A high amount of LBBL is usually obtained during the pretreatment process as a delignification method of lignocellulosic biomass. LBBL can be further utilized at a time of its treatment process. Lignin in LBBL can be acquired by neutralization process that result in lignin based sludge [7]. Lignin is valuable compound that can be converted into another high-added product which potentially developed for industry needs [8, 9]. Lignin is structured by several aromatic hydrocarbon compounds, such as p-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol in which they are potentially utilized as fungicide [10]. However, to result in the monomer of lignin, materials are needed in decomposing the lignin into simple monomer. Natural-based materials are favorable for establishing green environmental research.

This work aimed to investigate local ilmenite capability as potential-natural resources for catalyst in wastewater treatment and also evaluate the resource recovery of lignin degradation result in black liquor which can be used as biopesticide namely coniferyl, sinapyl, and p-coumaryl alcohol.

2. Materials and Method
2.1 Black liquor and ilmenite
The black liquor as lignin containing wastewater was collected from bioethanol second generation pilot plant at Research Center for Chemistry, Indonesian Institute of Sciences (LIPI). The sample was then used as the lignin source in this experimental study.

Ilmenite containing TiO$_2$ was given by Department of Chemistry, University of Haluoleo Kendari. It was procured from the beach shore in Wolowa, Button District, Southeast Sulawesi, Indonesia. The enhancement of TiO$_2$ performance in ilmenite was conducted by employing a mechanism of ilmenite preparation, i.e calcination at 800 °C for 5 hours to reduce Fe content. The calcination was performed twice and the magnet was used to eliminate Fe content from the calcinated ilmenite.

Figure 1. The procedures of lignin based liquor degradation and decolorization
2.2 Experimental set up
Two schemes were carried out (Figure 1) to extract the lignin based pesticide compound from the samples. The scheme was conducted to investigate alkaline condition of black liquor that may influence catalyst work in lignin degradation as well as black liquor decolorization. Black liquor from the first scheme was conditioned at the pH up to 10, meanwhile black liquor pH from the second scheme was set below 10.

The photocatalytic process was conducted following the chart with UV exposure process in a handmade chamber as shown in Figure 2. All experiments were performed at room temperature.

![Figure 2. UV chamber for lignin based black liquor processs](image)

2.3 Analysis
The ilmenite content was characterized by using X-Ray Fluorescence (XRF) (Torontech Tt-Edxpert, Canada) and X-Ray Diffraction (XRD) (Rigaku, Japan). Meanwhile, black liquor decolourization results were measured by spectrophotometer UV-Vis at 280 nm (maximum wave length) to measure concentration of lignin dissolved in black liquor by assistance of standard curve from commercial lignin (Sigma Aldrich, Singapore), then the decolorization percentage is calculated by following the equation [11]:

\[
\% \text{ decolourization} = 100 \times \frac{(C_0 - C_t)}{C_0}
\]

Liquid chromatograph mass spectrophotometer (LCMS) was used to confirm and find the molecular weight of the targeted samples. Lignin can be degraded into its three main compound i.e synaphyl alcohol (molecular weight/MW : 210.23 g.mol⁻¹), p-coumaryl alcohol 4-O-Glucoside (molecular weight/MW : 311.32 g.mol⁻¹), and coniferyl alcohol (molecular weight/MW : 180.2 g.mol⁻¹).

3. Results and Discussion
3.1 Ilmenite characterization
The ilmenite results before and after calcination processes are shown in Table 1. It can be seen that the increasing of Ti content occurs though it still has lower content than Fe content in ilmenite before and after the calcination process.

Although the ilmenite still has low Ti content, but it cannot be assumed affecting the performance of ilmenite. Presenting high content of iron in ilmenite, the ilmenite work is considered getting a positive support from the iron in ilmenite which roles doping catalyst that is able to enhance the TiO₂ work. However, the number of doping catalyst shall be estimated in an adequate amount, therefore, the effective performance of ilmenite can be well achieved [12]. The right combination between metal based doping catalyst and TiO₂ allows reduction-oxidation mechanism and improves the performance
of photocatalysis process that can degrade the recalcitrant compound such as dyes in textile industry wastewater [13, 14].

| Table 1. Quantitative content of ilmenite before and after calcination process. |
|---------------------------------|-----------------|-----------------|
|                                | Ilmenite content before calcination process (% w/w) | Ilmenite content after calcination process (% w/w) |
|                                | Fe               | Cr              | Ti              | Si              | Al              | Mn              | Ni              | V               |
| Fe                             | 62.17 ± 0.22     | 26.69 ± 0.21    | 3.64 ± 0.10     | 4.02 ± 0.12     | 2.14 ± 0.13     | 0.76 ± 0.04     | 0.43 ± 0.03     | 0.14 ± 0.03     |
| Cr                             |                 |                 |                 |                 |                 |                 |                 |                 |
| Ti                             |                 |                 |                 |                 |                 |                 |                 |                 |
| Si                             |                 |                 |                 |                 |                 |                 |                 |                 |
| Al                             |                 |                 |                 |                 |                 |                 |                 |                 |
| Mn                             |                 |                 |                 |                 |                 | 0.74 ± 0.03     |                 |                 |
| Ni                             |                 |                 |                 |                 |                 |                 | 0.42 ± 0.02     |                 |
| V                              |                 |                 |                 |                 |                 |                 |                 | 0.03 ± 0.01     |
| Mn                             |                 |                 |                 |                 |                 |                 | 0.74 ± 0.03     |                 |
| Ni                             |                 |                 |                 |                 |                 |                 | 0.42 ± 0.02     |                 |
| V                              |                 |                 |                 |                 |                 |                 | 0.03 ± 0.01     |                 |

The XRD result translates the form of structure of ilmenite as illustrated in Figure 3. The figure shows the XRD result depicted the distribution peaks at 27°, 36°, and 55° [3]. These indicated that the structure of ilmenite after the calcination was rutile with micro powder. In addition, the pattern is quite similar to standard as explained in elsewhere report. Rutile is one of the structure of catalyst that has stable performance at different temperature and pressure [15]. This property is important in deciding a suitable process by considering time and also pressure to achieve the best result.

![XRD result of ilmenite after the calcination process](image)

**Figure 3.** XRD result of ilmenite after the calcination process

### 3.2 Decolorization and Degradation Process

Investigating the condition of sample which may influence the process is important work to do. Nevertheless, the process was not only relying on the sample’s condition but also the catalyst ability that was assisted by photo or light. This is a basic reason for present experiment where ilmenite performance as TiO₂ sources can be increased by the assistance of light either UV or visible light (VL).
Figure 4 illustrates that the decolorization result was linear to the ilmenite addition. The more ilmenite added in lignin-based black liquor, the bigger result of decolorization. It may be caused by the light aid that has greater energy than the catalyst material, then induce the creation of electron-hole pairs which may form/degrade a compound due to the reduction-oxidation method [3]. Although, fluctuated result is shown in the process which use higher concentration (5000 ppm) of raw black liquor. At a fixed time of 30 minutes, the addition of 0.2 and 0.3 g ilmenite resulted in a dramatically decrease if compared to the 0.1 g ilmenite addition result. The overloading of ilmenite affects the degradation where the reduction of surface area happened due to forming clump of ilmenite in black liquor [16].

The findings also confirmed that the UV exposure time of 10 minutes was effective, indicated by less lignin was degraded in decolorization process. The selected best treatment was the addition of ilmenite 0.3 g, 10 minutes with 3000 ppm of lignin-based black liquor concentration.

The trends in the second scheme process was similar to that of the first scheme (Figure 5). It can be concluded that the condition of samples does not influence the ilmenite performance. This study is in agreement with the previous report which found that the performance of catalyst in degrading lignin or other organic-dissolved compounds shows better performance at the range of pH up to 10 [17]. These can be explained that the number of ilmenite added provides more active surface that can work effectively in decolorization, therefore the higher concentration will cause an inhibitory effect for catalyst/ilmenite work because it will reduce the irradiation field[18]. In addition, the higher pH support catalyst work as the hydroxyl groups induced the enhancement of reduction-oxidation mechanism that will lead to an effective decolorization as well as degradation result [19].

Figure 6 shows that both schemes have almost similar peaks as the results of degradation process. It is found that p-coumaryl alcohol molecular weight (MW) emerge in both LCMS result, meanwhile other two compounds (sinapyl and coniferyl alcohol) MW are not found in the chromatograph. Previous work also has revealed the lignin depolymerization that occurs as the increasing of time. The longer time of process, the more the obtained MW that will boost the reaction of involving-radical intermediate and polymerize the dissolving lignin in black liquor [20].
Figure 5. The second scheme process, decolorization and degradation process of lignin based black liquor: a) 300 ppm, b) 500 ppm, and c) 700 ppm.

Figure 6. the LC MS results of a) first scheme, b) second scheme
4. Conclusions
The photocatalysis has not succeeded enough in decolorizing lignin-based black liquor since the ilmenite can only decolorize about 31% by using 0.3 g ilmenite for 10 minutes, but it can decompose lignin into its monomer compound, \( p \)-coumaryl alcohol. Therefore, further research is suggested, particularly on the process and evaluation, to enhance the interim analysis and also the isolation of the degrading compound.

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