Modification of photocatalyst Ti-Pillared clay by Zn metal addition for decolorization process of organic liquid waste

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Abstract. Black liquor produced from a pretreatment process of bioethanol using the lignocellulose material, such as an empty palm bunch. Black liquor is organic liquid waste and should be treated before release to the environment. One of the degradation processes of black liquor is by the photocatalytic reaction using the Ti-Pillared Clay (Ti-PiLC) catalyst. However, there is a limitation of process condition if using a Ti-PiLC catalyst; the degradation process should be conducted under a UV light source. This study is focused on the modification of photocatalytic catalyst Ti-PiLC by adding Zn metal (Ti-Zn/PiLC), thus the degradation process of black liquor could be conducted on a visible light source. Characterizations of the prepared photocatalysts were obtained using XRD, BET, TPD, TGA, SEM, TEM and UV-Vis spectrophotometer for the degradation degree. Although the degradation process of black liquor could be conducted on the visible light source, the degradation degree was still minor compared with only using Ti-PiLC photocatalyst. It is assumed that combination Ti and Zn as the active metals of the photocatalyst was not good enough to enhance the degradation process of black liquor even on the visible light source, perhaps using other metal, such as cerium (Ce).

Keywords: photocatalyst; black liquor; Ti-PiLC; Zn metal; visible light

1. Introduction

Industrial growth in Indonesia has a major influence on society and the country. Industries that produce black liquor from bioethanol processing from Palm Oil Empty Bunches can pollute the environment. Black liquor is a threat to human health through contamination of drinking water supplies or edible organic species [1].

Petruzzelli et al. and Cortez et al. have used black liquor processing methods using advanced oxidation processes (AOPs) that used Fenton reagents by Fe2+/H2O2/UV and H2O2/UV systems [2,3]. The Fenton system, besides being modified with the help of UV light, can also be combined with TiO2 photocatalyst. The combination of the TiO2 photocatalyst (UV/TiO2 system) and the Fenton system can cause a high increase in ⋅OH production. This system is called the Photo-Fenton system [2,3].

TiO2 was easily agglomerated and lose its stability, to overcome this problem natural porous solid such as zeolite and bentonite can be utilized. In contrast to zeolite, cation exchange in bentonite increases the pore volume that can affect its absorption capacity. According to Beiser [4], the band gap of TiO2 is around 3.2 - 3.8 eV. Although has a wide bandgap (3.2 eV), TiO2 can only utilize 5 % of the solar light on the UV region. This problem can be solved by doping Zn to reduce the bandgap of TiO2 [5].
The present study will prepare Ti-pillared and a mixture of TiO$_2$-ZnO pillared bentonite (Ti/PilLC and Ti-Zn/PilLC) as a substitute for commercial TiO$_2$ photocatalyst. The prepared catalysts will be used in the decolorization process of black liquor through the Photo-Fenton system.

2. Experimental

2.1. Materials
Black liquor is the side product/waste liquid from the alkali pretreatment process of bioethanol production using a lignocellulosic material, in this case from an empty fruit bunch. Mostly black liquor is a very base waste liquid that contains many lignin compounds. Another materials were used in this study such as titanium (IV) ethoxide (TEOT, Aldrich) as precursors of titanium dioxide (TiO$_2$), Zinc chloride (ZnCl$_2$, Merck), bentonite (Aldrich), sodium hydroxide (NaOH, Merck), hydrochloride acid solution (Merck), iron (II) sulfate (FeSO$_4$•7H$_2$O, Merck), hydrogen peroxide 30 % (H$_2$O$_2$, Merck), and commercial TiO$_2$ P25 (Aldrich).

2.2. Preparation of TiO$_2$/PilLC and TiO$_2$-ZnO/PilLC Catalysts
Photocatalyst TiO$_2$ in this study was prepared by the pillariation method [6,7]. About 1% bentonite suspension (5 gr) was mixed with a Ti$^{4+}$ polycation solution with a ratio of 10 mmol.g$^{-1}$ bentonites. The Ti$^{4+}$ polycation solution was prepared by dissolving TEOT in 5M HCl under vigorous stirring with an H/Ti molar ratio of two was obtained. Bentonite suspension was mixed with a polycation solution, stirred for 12 hours, and then washed with distilled water until it was free from Cl$^{-}$ ion using the AgCl$_2$ solution. Bentonite suspension was dried for 12 hours at 100 °C, and then calcined at 400 °C for 4 hours. The resulting catalyst was labelled as TiO$_2$/PilLC.

Similar preparation steps were performed to prepare TiO$_2$-ZnO/PilLC catalysts. However, the polycation solution is a mixture of 5M TEOT solution in HCl and 0.4M ZnCl$_2$ solution in CH$_3$OH. Several mole ratio of Ti$^{4+}$:Zn$^{2+}$ was about of 0.1; 0.5; 0.7; and 1 were utilized to prepare TiO$_2$-ZnO/PilLC photocatalysts.

2.3. Characterization catalysis
The prepared catalysts were characterized using various methods to determine their physical and chemical properties. The crystal structures were analyzed with X-Ray Diffractometer (XRD) using the Rigaku diffractometer, with Cu Ka radiation at 40 kV and 30 mA, and a secondary graphite monochromator XRD. The specific surface area of the samples was analysed using Tristar II 3020 Micromeritics Instrument by Brunauer-Emmett-Teller (BET) adsorption method through nitrogen adsorption-desorption isotherms, performing at 77.3 K on liquid nitrogen, and the surface morphology was analyzed using a scanning electron microscope (SEM).

2.4. Decolorization process of black liquor
About 20 mL of black liquor solution (pH 4) was put into the reactor. Before being degraded, 0.03 gr of TiO$_2$/PilLC catalyst, 0.06 g, and 0.01 g Fenton (H$_2$O$_2$ + Fe$_2$O$_3$) were added into black liquor solution. The reaction was carried out in the photocatalytic reactor for some time (10 to 60 min) with different conditions which were dark (no light), visible light, UV-C (253.7 nm) and UV-A (365 nm). Later, the solution was centrifuged at 5000 rpm for 60 min and analyzed using a spectrophotometer with absorbance was measured at 250 nm wavelength to determine lignin concentration and decolorization efficiency of the black liquor.

3. Results and Discussions
The X-ray diffraction (XRD) patterns of the catalyst samples are shown in Figure 1. Patterns a and b are observed for the prepared catalysts of TiO$_2$/PilLC and TiO$_2$-ZnO/PilLC, while pattern c was for the original bentonite.
The main characteristic peaks of bentonite (Figure 1.c) was observed as the montmorillonite (JCPDS card no 29-1499) [8]. After the pillarization process with TiO₂, there are some intensity peaks of bentonite decreased or shrank which was indicated that the interaction between bentonite and TiO₂ occurred. Moreover, new peaks were also observed for the XRD patterns of TiO₂/PiLC and TiO₂-ZnO/PiLC (Figure 1.a and b), especially at around 2θ of 25° and 47° which is obtained as TiO₂ anatase peaks (JCPDS card no 21-1272).

![XRD patterns results](image)

**Figure 1.** XRD patterns results of (a) TiO₂-ZnO/PiLC (0,5), (b) TiO₂/PiLC, (c) bentonite, (d) TiO₂ anatase standard, and (e) ZnO standard

![XRD patterns results](image)

**Figure 2.** XRD patterns results of TiO₂-ZnO/PiLC with several ratios of TiO₂:ZnO. (a) ZnO/PiLC, (b) 0.7, (c) 0.5, (d) 0.1, and (e) ZnO standard.

Figure 2 shown the XRD results of the prepared catalysts of TiO₂-ZnO/PiLC with several ratios of TiO₂:ZnO. The characteristic of ZnO peaks on the bentonite after pillarization seems could not fully be observed. Peaks appeared around 2θ of 18°, 28°, and 50° after the concentration of ZnO was increased which is suggested as bentonite peaks (JCPDS card no 29-1499), and there is no peaks of ZnO (JCPDS card no 79-2205) was observed of Figure 2. It is suggested that ZnO was well be dispersed on the bentonite after the pillarization, or ZnO crystal was very small and thus difficult to be detected by XRD [9]. Mostly, the change of peaks in Figure 2 was due to the effect of the TiO₂ crystalline. The peak 2θ around 25° will be diminished with increasing of ZnO concentration. This peak clearly showed fitting to the TiO₂ anatase crystalline. The prepared catalysts were also characterized to calculate the specific surface area, pore-volume, and average pore size distribution. Those results were shown in Table 1.
After the pillarization process, the surface area of the original bentonite was significantly increased from 25.66 m²·g⁻¹ to 210.90 m²·g⁻¹ using Ti metal as the pillared. However, the surface area of TiO₂/PiLC prepared catalyst will be declined with increasing concentration of Zn metal on the TiO₂-ZnO/PiLC catalysts. A surface area slightly enhanced with the TiO₂-ZnO around 0.1, then gradually decreased with more addition of ZnO. It is suggested that the maximum ratio of TiO₂-ZnO as the pillared is around 0.1. Besides surface area, the pore volume of TiO₂-ZnO/PiLC 0.1 catalyst also obtains a higher value compared to the others, which is describing become a porous catalyst after the pillarization.

With the addition of ZnO on the TiO₂-ZnO/PiLC prepared catalyst, the surface area and pore volume also become decrease. It is suggested that Ti metal was substituted with Zn metal as the pillared at ratio TiO₂:ZnO more than 0.1. Due to the size of the ZnO molecule which is smaller than TiO₂, therefore, not only the size of TiO₂-ZnO pillared become smaller, but also the quantity of the pillared also reduced, thus diminished the surface area and pore volume, as observed in Table 1. This information is also supported by the XRD results in Figure 2 shows that the peak at 2θ round of 25°, which is belonging to TiO₂ crystalline, becomes diminished with increasing the ZnO concentration on the TiO₂-ZnO/PiLC prepared catalysts. Moreover, it seems that the size of pillared ZnO not only smaller than the TiO₂ pillared but also was wider thus also increased the pore diameter of prepared catalysts, especially at ZnO/PiLC catalyst. Based on the results of XRD and surface area measurements, it is suggested that the pillarization process was successfully obtained.

| Table 1. Specific surface area, pore volume and pore diameter of the prepared catalysts. |
| --- | --- | --- | --- |
| No | Catalysts | Surface Area (m²·g⁻¹) | Pore volume (cm³·g⁻¹) | Average Pore diameter (nm) |
| 1 | Bentonite | 25.66 | 0.025 | 4.90 |
| 2 | TiO₂/PiLC | 210.90 | 0.168 | 3.74 |
| 3 | TiO₂-ZnO/PiLC 0.1 | 230.10 | 0.220 | 4.07 |
| 4 | TiO₂-ZnO/PiLC 0.5 | 192.51 | 0.181 | 4.16 |
| 5 | TiO₂-ZnO/PiLC 0.7 | 100.54 | 0.180 | 7.26 |
| 6 | ZnO/PiLC | 18.08 | 0.079 | 17.61 |
| 7 | TiO₂ (P25) | 50.95 | 0.259 | 20.36 |

Figure 3. SEM image of (a) original bentonite and (b) TiO₂/PiLC catalyst

The morphology of bentonite before and after the pillarization process with TiO₂ using SEM analysis is shown in Figure 3. Both morphology structures of original bentonite and TiO₂/PiLC catalyst were almost the same that compose of the layers structure material. However, the particle size of material
became smaller after the pillari zation with Ti metals; especially the layer structure is smaller of the TiO\(_2\)/PiLC catalyst compare with the original bentonite.

Moreover, the SEM analysis results for several ratios of TiO\(_2\)-ZnO/PiLC prepared catalysts were detail described in Figure 4. Generally, the morphology of all TiO\(_2\)-ZnO/PiLC prepared catalysts was composed of layers structure, due to the started material is formed the original bentonite. However, the detailed distinctions of morphology for the prepared catalyst at several ratio of TiO\(_2\):ZnO could not fully be obtained or clarified from the SEM analysis as shown in Figure 4, although the nitrogen adsorption measurement results (Table 1) described that the surface area of the TiO\(_2\)-ZnO/PiLC prepared catalysts decreased with the addition ratio of ZnO. All of TiO\(_2\)-ZnO/PiLC prepared catalysts are described as the porous layer materials, which contain many pores on the surface.

![SEM image of TiO\(_2\)-ZnO/PiLC prepared catalysts at ratios of (a) 0.1, (b) 0.5, and (c) 0.7](image)

**Figure 4.** SEM image of TiO\(_2\)-ZnO/PiLC prepared catalysts at ratios of (a) 0.1, (b) 0.5, and (c) 0.7

Based on the nitrogen adsorption measurement (Table 1), the TiO\(_2\)-ZnO/PiLC ratio of 0.1 has a higher value of surface area compared to the others, therefore this catalyst as a starting material that will be used for the decolorization process of black liquor as the photocatalyst. For the first steps, TiO\(_2\)-ZnO/PiLC 0.1 catalyst was carried out at the decolorization process in UV-C light with various time reactions (10, 20, 30 and 60 min). The results of the decolorization process with various time reactions are described in Figure 5. The percent decolorization process was significantly enhanced at a time reaction of 10 until 30 min. It almost becomes unchanging with the addition of time reaction of decolorization until 60 min (less than 10 % different). It is suggested that the capacity of the decolorization process was very high at the beginning of the process due to the availability of a large amount of radical \(\bullet OH\) from Fenton and TiO\(_2\)-ZnO/PiLC catalyst, which reacted directly to the lignin compound [10]. Therefore, the optimum time process of decolorization in this study could be concluded around 30 min.
The addition of ZnO on TiO$_2$/PiLC catalysts is as doping to improve the performance of the photocatalyst, due to could reduce the bandgap distance between the valence band and conduction band [5]. The effect of the addition of ZnO on the TiO$_2$/PiLC catalyst for the decolorization process of black liquor also conducted, and the result is shown in Figure 6. The TiO$_2$-ZnO/PiLC catalyst with a ratio of 0.1 mol shows a predominant performance to decolorize of black liquor with using UV-C light for 60 min with percent decolorization around of 90.93 % obtained. The capability of the decolorization process on the TiO$_2$-ZnO/PiLC catalyst with a ratio of 0.1 also establishes a higher value compared to a commercial photocatalyst such as TiO$_2$ P25. The TiO$_2$-ZnO/PiLC catalyst with a ratio of 0.1 mol together with Fenton has optimally enhanced the formation of radical •OH which was used for the decolorization process.

More addition ratio of ZnO constructed a decline in the decolorization performance of black liquor from the alkali pretreatment process of bioethanol production using empty fruit bunch oil palm bunches (TKS). Declining the decolorization performance is affected by decreasing in surface area. More addition of ZnO on TiO$_2$/PiLC catalysts is suggested generates the pillars size shape become shorter as the results of the surface area analysis in Table 1.

Black liquor was utilized in this study contain lignin concentration around 6400 ppm. The use of concentrations that are not too high is to provide access to the light source to contact the photocatalyst. The light source is very important in the photocatalytic process. Radical OH is formed by TiO$_2$ photocatalyst depends on the TiO$_2$ capacity to produce electron pairs and hole when absorbing photon energy from a beam of light, which causes electron excitation from the valence band to conduction band. The photo-electronic transition efficiency is low due to ultraviolet light is only 4% in the sun's spectrum.
Photocatalyst which response to visible light is required to increase the use of sunlight for hydrogen energy production by separating water from the degradation of organic pollutants and other applications [11]. This study also investigates several light sources such as UV-A, UV-C, visible light, and no light (dark) for a capability comparison of TiO$_2$-ZnO/PiLC catalysts with a ratio of 0.1 in the decolorization process of black liquor. The result of source light affected the capability of the decolorization process is detailed described in Figure 7.

![Figure 7](image)

**Figure 7.** Effect of light source for the decolorization process on TiO$_2$-ZnO/PiLC 0.1 catalyst

Figure 7 shows that the maximum decolorization process is obtained when used UV-C as the light source, while other light sources such as UV-A and even visible light were minor than UV-C. Although, the capability of the decolorization process using UV-A and visible light sources was above 80%. Furthermore, the percent decolorization process at UV-C light source is around of 90.98%. It is suggested that TiO$_2$-ZnO/PiLC catalyst contact with UV-C light obtained higher the capability to decompose H$_2$O$_2$ and reduces the Ferro compound compare to other the light source. During the process of reducing Fe$^{3+}$ to Fe$^{2+}$, two radicals OH are generated for each H$_2$O$_2$. The Ferro complex compounds that are constructed in the photochemical reaction process are also able to produce free radical OH and some organic material can be decomposed directly under UV irradiation [11]. Yuningrat *et al.* also observed that radical OH was produced together with oxygen, they will be oxidized the organic pollutants and produce simpler compounds such as CO$_2$ and H$_2$O [12], as is shown this reaction below.

\[
\text{HO} + \text{O}_2 + \text{CnOmH}(2n-2m+2) \rightarrow n \text{CO}_2 + (n-m+1) \text{H}_2\text{O}
\]  

(1)

The effect of ZnO addition on TiO$_2$-ZnO/PiLC catalysts to the capability of the decolorization process at a visible light source was also investigated in this study, and the results are shown in Figure 8.

![Figure 8](image)

**Figure 8.** The decolorization process with a visible light source for the TiO$_2$-ZnO prepared catalysts
It shows that the effect of the ZnO addition on the TiO2/PiLC catalysts was not significantly enhanced the capability of the decolorization process at visible light. Although TiO2-ZnO/PiLC catalysts with a ratio of 0.5 illustrated a superior value of percent decolorization compared to the other catalysts, the increase of percent decolorization process, not more than 5% compared to TiO2/PiLC and TiO2-ZnO/PiLC with a ratio of 0.1 catalysts. It is assumed that the addition of ZnO on TiO2/PiLC catalyst in this study, is not expanding the capability of the decolorization process in visible light. El-Bahy et al. disclosed that the addition of ZnO as doping to improve the photocatalyst performance, by collapse the bandgap distance between the valence band and conduction band [5]. However, this phenomenon of ZnO addition on TiO2/PiLC catalysts is not observed in this study.

It is suggested that not only ZnO particle size is too small, but also the quantity of ZnO concentration is still deficient to construct the pillars in bentonite, therefore increasing the TiO2:ZnO ratio on TiO2-ZnO/PiLC catalyst affected to decline the surface area as confirmed in Table 1.

4. Conclusion
Based on the characterization results, it is concluded that the pillarization using Ti metal as the pillared is successfully obtained, as shown in the XRD analysis and nitrogen adsorption measurement results. The addition of ZnO on the TiO2/PiLC catalysts with several ratios of 0.1, 0.5, 0.7, and 1.0 exhibits a significant effect on the decline of surface area, pores volume, except the TiO2-ZnO/PiLC catalyst with a ratio of 0.1 obtained a higher surface area and pore volume. The SEM analysis also displayed that all of TiO2-ZnO/PiLC catalysts are porous material. Moreover, the significant capability of the decolorization process was obtained on the TiO2-ZnO/PiLC with a ratio of 0.1, and even higher than commercial TiO2 photocatalysts. However, the effect of ZnO on the TiO2/PiLC catalyst as doping in this study revealed that there is no significant enhancement of the decolorization process capability, especially at a visible light source. It is suggested that not only ZnO particle size is too small, but also the quantity of ZnO concentration is still deficient to construct the pillars in bentonite, or perhaps using other metal for the pillared, such as cerium (Ce).

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