

Photodegradation of Lignin by TiO₂-Ilmenite for Natural Pesticide Material

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The high lignin content in a waste of oil palm empty fruit bunch (OPEFB) can be utilized as an active compound in the preparation of natural pesticides. Lignin from OPEFB can be degraded into phenolic derivatives. The degradation of lignin was carried out by photooxidation using TiO₂, which was synthesized directly from the ilmenite minerals. The success of TiO₂-ilmenite synthesis was evidenced by the appearance of specific diffractogram peaks at $2\theta = 25.5^\circ$ for anatase TiO₂ and 27.65° for TiO₂ rutile. The ability of TiO₂-ilmenite in lignin degradation was analyzed using UV-visible spectroscopy. Based on the analysis, it was known that the use of TiO₂-ilmenite 0.3 g with radiation time of 20 to 30 min showed the highest degradation of 16.40-23.42 %. The degradation results were used to determine the antifungal activity of lignin from OPEFB. The results indicated that the high activity of lignin from OPEFB in inhibiting the growth of *Fusarium oxysporum* Schlecht with the highest clear zone diameter was 2.59 cm.

Keywords: Oil palm empty fruit bunch, TiO₂-ilmenite, Photooxidation, *Fusarium oxysporum*, Clear zone diameter.

INTRODUCTION

Lignin is an aromatic biopolymer of phenyl propane units with the second largest abundance after cellulose [1]. Lignin together with other lignocellulosic components form a complex chemical bond that forms the basis for the formation of plant cell walls. Lignin attracts a lot of attention due to its phenolic and non-phenolic compounds [2,3]. Lignin has been used in several applications in science such as antioxidant, asphalt, carbon fiber and related, board binder, polymers, dust control, paper, chemicals, battery, fuel, heat, grease, dispersants and agriculture [4]. In recent years lignin is widely developed as an environmentally friendly antifungal ingredient [2,5]. The high phenolic content of lignin is used to destroy cell membranes resulting in changes in cell permeability that would inhibit and impair the growth of fungal cells [6], denature cell proteins, wrinkle cell walls and disrupt the metabolic pathways of fungi [7,8].

Oil palm empty fruit bunch (OPEFB) are widely used as an alternative material for lignin isolation [9,10]. Oil palm empty fruit bunch is reported as a lignocellulosic material with a lignin content of about 18-35 %, so it is highly potential for the development of environmentally friendly antifungal

[11,12]. The complex chemical structure makes lignin difficult to degrade. In general, lignin degradation can be carried out thermally [13], but this degradation requires high temperatures so that the process is less effective for laboratory research.

Degradation of lignin by photocatalysis using TiO₂ is reported to effectively break the lignin bond resulting in phenolic derivatives such as *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [1,6]. The use of TiO₂ as a photocatalytic material due to low operational costs [14,15], high photocatalytic activity [16,17], rapid degradation time for organic compounds [18,19] and abundance of raw materials [20].

In this study, we reported on the lignin potential of OPEFB as an antifungal agent to be applied for the development of natural pesticide ingredients. The TiO₂-ilmenite mineral was used for lignin degradation of OPEFB and also tested for antifungal activity against *Fusarium oxysporum* Schlecht.

EXPERIMENTAL

TiO₂ catalyst preparation from ilmenite: The steps to obtain TiO₂ catalyst from ilmenite referred to the preparation step reported by Nurdin *et al.* [20]. Preparation consists of four important stages: magnetic separation, pre-oxidation,

silica reduction and leaching. The obtained TiO₂-ilmenite was further characterized using XRD. As a comparison, characterization of non-oxidation ilmenite was also performed.

Photooxidation of lignin from OPEFB and its bioactivity test: The photooxidation of lignin begun with a lignin extraction process of OPEFB by referring to the method reported Maulidiyah *et al.* [6]. The lignin extraction process was carried out with two repetitions. The initial stage of extraction was carried out using a benzene solvent: 96 % ethanol (2:1 v/v) for 6 h and continued using water at 100 °C for 1 h. Powdered OPEFB extraction results were then added in the digester containing a 96 % ethanol solution mixture: water (1:1). Into the digester, 20 % NaOH was added and cooked using a temperature of 170 °C for 2 h. The obtained filtrate was diluted using water by a ratio of 1:2 (v/v). The precipitation of lignin was carried out by titration method using 20 % H₂SO₄, separated by centrifugation at 4500 rpm for 20 min and analyzed using UV-visible spectrophotometer.

A total of 20 mL of solvent isolated lignin solution was inserted into 9 beaker glasses of 100 mL and every 3 beakers were added TiO₂-ilmenite of 0.1; 0.2; 0.3 g, respectively. Subsequently, the mixture was exposed to UV light and each time range 10, 20 and 30 min of mixture was taken and deposited for 12 h. The top layer formed was taken and centrifuged, then analyzed using UV-visible spectrophotometer and tested its bioactivity against *Fusarium oxysporum* Schlecht using the well diffusion method.

RESULTS AND DISCUSSION

Characterization of TiO₂-ilmenite: Fig. 1 shows the results of TiO₂-ilmenite characterization using XRD. The success of the extraction process is indicated by the specific diffractogram peak of the TiO₂. Both TiO₂-ilmenite from the pre-oxidation (Fig. 1d) and non-oxidation (Fig. 1c) results were demonstrated the success of the extraction process. The appearance of peaks at $2\theta = 25.5^\circ$ for preoxidation TiO₂ and 27.65° for non-oxidation TiO₂-ilmenite indicates that the phases formed for both TiO₂-ilmenite are anatase [21] and rutile [22], respectively. This is supported by appearing the same peak of TiO₂ anatase JCPDS 21-1271 (Fig. 1b) and TiO₂ rutile JCPDS 76-1940 (Fig. 1a). TiO₂ obtained from the ilmenite extract is further used in the OPEFB lignin photooxidation process.

Lignin extraction from OPEFB: Based on the extraction stage, the weight of lignin produced from 100 g of OPEFB sample is 15.52 g. These results explain that the effect of time on the amount of lignin, where the use of a long time will cause the degradation of lignin compounds. In addition, the use of high concentrations of sodium hydroxide is reported to cause lignin degradation to dissolve together with the solvent [6]. From UV-visible spectroscopic analysis results, it is known that the average rate of OPEFB lignin extracted is 86.37 % (Table-1).

Lignin photooxidation of OPEFB using TiO₂-ilmenite: The presence of TiO₂-ilmenite as a composite material causes lignin to be degraded to produce phenolic compounds. In general, TiO₂ is known as a semiconductor material whose surface is strong oxidizing when exposed to UV light so that

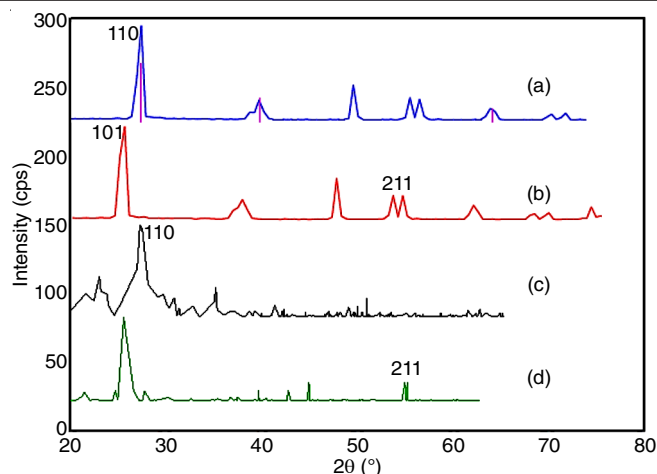


Fig. 1. Diffractogram pattern: (a) TiO₂ rutile JCPDS 76-1940; (b) TiO₂ anatase JCPDS 21-1272; (c) TiO₂-ilmenite non-oxidation; (d) TiO₂-ilmenite preoxidation

TABLE-1
PURITY TEST OF LIGNIN EXTRACTION RESULTS

Initial concentration (ppm)	Concentration of analysis results (ppm)	Average (ppm)	Lignin levels (%)
300	291.333	288.000	96.55
500	442.222	350.000	79.22
700	634.667	563.333	83.33
Average			86.37

it can be utilized to decompose lignin compounds. Fig. 2 shows the results of OPEFB lignin degradation with varying irradiation time and mass of TiO₂-ilmenite. Based on these figures, both the irradiation times and the mass of TiO₂-ilmenite affect the amount of degraded lignin. For lignin concentrations of 300 and 500 ppm, the mass of TiO₂-ilmenite 0.3 g with a 20 min exposure time (Fig. 2a) and 30 min (Fig. 2b) showed the highest degradation of 16.40 and 23.42 %, respectively.

Antifungal activity test against *Fusarium oxysporum* Schlecht: OPEFB lignin antifungal activity is observed based on clear zone areas around wells of solid media. Antifungal activity testing at 10, 20 and 30 min with TiO₂-ilmenite weight variation (0.1, 0.2 and 0.3 g) showed different activity in inhibiting the growth of *Fusarium oxysporum* Schlecht. The OPEFB lignin resistivity diameter in inhibiting the growth of *Fusarium oxysporum* Schlecht is shown in Table-2.

TABLE-2
DATA OF % DEGRADATION OPEFB LIGNIN WITH TiO₂-ILMENITE AND CLEAR ZONE TO INHIBIT *Fusarium oxysporum* SCHLECHT

Degradation time (min)	Weight TiO ₂ -ilmenite (g)	Degradation (%)	Diameter zone (mm)	Activity
0	0.0	0.000	0.00	Not active
10	0.1	23.504	0.00	Not active
20	0.1	25.600	0.00	Not active
30	0.1	32.383	17.66	Strong
10	0.2	13.925	0.00	Not active
20	0.2	20.841	0.00	Not active
30	0.2	28.598	9.30	Weakly
10	0.3	17.710	0.00	Not active
20	0.3	25.187	19.60	Strong
30	0.3	29.626	0.00	Not active

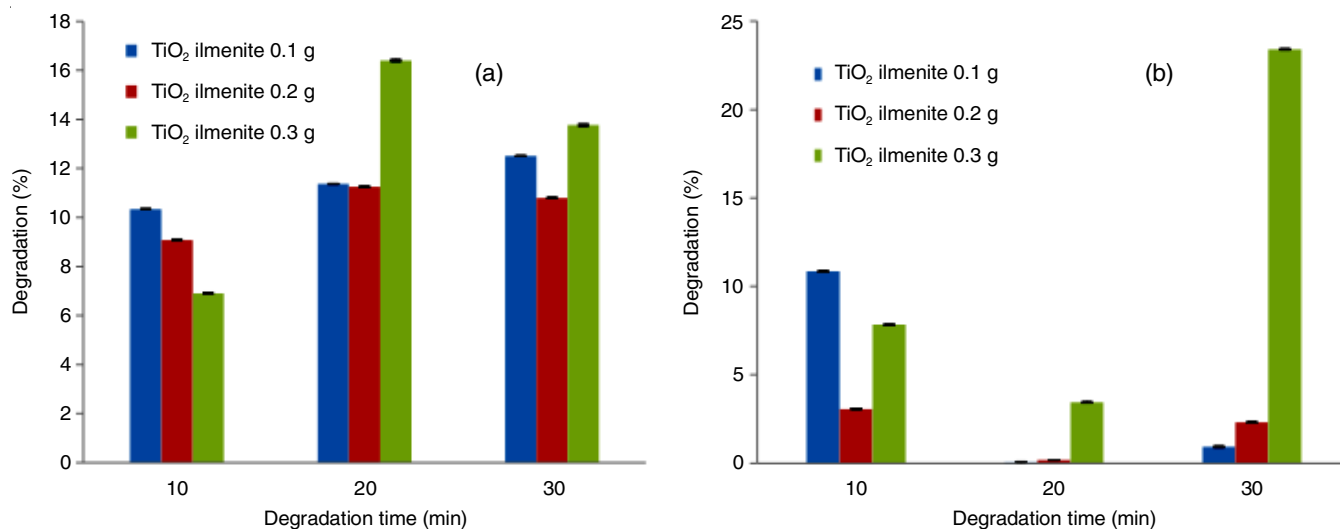


Fig. 2. Percentage of degraded lignin: (a) OPEFB lignin concentration of 300 ppm; (b) OPEFB lignin concentration of 500 ppm

Table-2 showed that the OPEFB lignin in degradation time of 30 min using 0.1 g TiO₂-ilmenite and 20 min using 0.3 g TiO₂-ilmenite indicated the highest activity with the diameter of the clear zone of 17.660 and 19.600 mm, respectively. Meanwhile, the OPEFB lignin in degradation time for 30 min using 0.2 g TiO₂-ilmenite was weakly to inhibit *Fusarium oxysporum* Schlecht. The resulting clear zone diameter approximates the diameter of the positive control. These results indicate that OPEFB lignin after degradation by using TiO₂-ilmenite has considered as an antifungal activity [23].

Conclusion

The photooxidation of lignin from OPEFB performed using TiO₂-ilmenite photocatalysts through UV light irradiation is influenced by photocatalyst mass and irradiation times. Long degradation time can cause damage to the lignin structure so that it will reduce the activity of antifungal. In general, lignin degradation compounds of OPEFB show the presence of antifungal activity in inhibiting the growth of *Fusarium oxysporum* Schlecht, so OPEFB waste can be an alternative active ingredient for the development of natural pesticides.

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