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Research Article

NATURAL BIOPESTICIDE PREPARATION AS ANTIMICROBIAL MATERIAL BASED ON LIGNIN PHOTODEGRADATION USING MINERAL ILMENITE ($FeO.TiO_2$)

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ABSTRACT

Natural biopesticide has been prepared by lignin photodegradation for antimicrobial activity on *Fusarium oxysporum* and *Xanthomonas* sp. The photodegradation process in UV reactor was performed by $FeO.TiO_2$ mass and lignin concentration variations. The results showed that lignin concentration on 500 ppm and 700 ppm with 0.2 g $FeO.TiO_2$ as an optimum mass to degrade lignin were 20.63% and 27.17%. Based on antimicrobial activity test against *Fusarium oxysporum* showed that the lignin degradation compound in 300 ppm, 500 ppm, and 700 ppm were 11.67 mm, 13 mm, and 21 mm diameter zone. Meanwhile, the results of lignin degradation compound have a good activity test of *Xanthomonas* sp. for 300 ppm, 500 ppm, and 700 ppm with inhibitory zone were 17.6 mm, 18.33 mm, and 19.66 mm, respectively. These results indicated that the lignin photodegradation for 700 ppm using $FeO.TiO_2$ has produced activity with a strong inhibitory zone against *Fusarium oxysporum* and *Xanthomonas* sp.

Keywords: Lignin, $FeO.TiO_2$, *Fusarium oxysporum*, *Xanthomonas* sp., photodegradation

INTRODUCTION

Degradation of photocatalytic organic compounds is an alternative method which many researchers have been widely reported in recent years. Utilization of photocatalyst material such as Titanium dioxide (TiO_2) has an advantage i.e. the abundance of raw materials, friendly used (green chemistry), non-toxic, and high degradation activity cause faster for efficiency degradation time[1,2]. In otherhand, it is high for oxidation reaction with the potential charge is ± 3.5 V. It is high oxidation to produce hole (h^+) of TiO_2 photocatalyst under UV light irradiation[3]. Meanwhile, the h^+ could be not active where the electron back to the hole, this phenomenon namely recombination process[4]. This condition needed to modificate TiO_2 material to reduce the occurrence of electron recombination[5,6].

$FeO.TiO_2$ material is a modification between TiO_2 material and Fe dopan which can be synthesized by using a sol-gel method[7]. In last year, $FeO.TiO_2$ was many applicable to degrade the organic compounds such as Rhodamin B, Methyl Orange, and Methylene Blue[8,9]. It is the high physicochemical activity because of inert materials, high-efficiency photocatalysis, friendly used, and abundance materials in Southeast Sulawesi-Indonesia[10]. This material facilitates the separation of electron-hole pairs to prevent the occurrence of rapid recombination process. Moreover, the $FeO.TiO_2$ can be obtained by using extraction method from mineral sands[11]. Nurdin et al. reported that $FeO.TiO_2$ mineral containing much metal distribution for applicable to the catalyst materials. The complex mineral in mineral sands due to high density for photocatalyst material to degrade organic compounds in wastewater pollution[12].

In this study, we are reporting the $FeO.TiO_2$ activity to degrade lignin compound in photocatalysis system. This results, we used for antimicrobial activity test which potentially as the natural pesticide[13,14]. Lignin was many used for industries such as pulp, biodiesel, and bioethanol[15,16]. It is advantages in agriculture field as the natural pesticide due to the lignin have a complex structure that containing a hydroxyl group (-OH) which affect for bacterial life[17,18]. An approach of this study provides $FeO.TiO_2$ effective to degrade lignin compound from empty palm oil fruit bunches (EPOFB) to produce the derivates of lignin compound such as *p*-coumaryl alcohol, sinapyl alcohol, and coumaryl alcohol[19,20]. The degradation of lignin using photodegradation showed a good effective compared with the other method likes enzymatic and thermal.

MATERIAL AND METHODS

Apparatus and chemical

UV reactor used to degrade lignin solution, 10-watt UV lamp (Black Light Blue (blb/uv-a)) as UV light sources, reflux equipment for synthesis $FeO.TiO_2$, glasses apparatus, analytic balance, UV-Vis spectrophotometer (JASCO V-730 UV-Vis Spectrophotometer) used for absorbance analysis of lignin degradation. Titanium tetraisopropoxide (TTIP) (Sigma-Aldrich) as precursor $FeO.TiO_2$, $Fe(NO_3)_3$ dopant Fe sources (Sigma-

Aldrich), Acetyl Acetonate (Sigma-Aldrich), 99% ethanol (Sigma-Aldrich), and distilled water as the solvent casting. Natural strain *Fusarium oxysporum* and X*anthomonas* sp., and Potato Dextrose Agar (PDA) (Sigma-Aldrich).

Synthesis of FeO.TiO_2

The FeO.TiO_2 synthesis is performed referring to the method reported by Wibowo et al. and Maulidiyah et al. that the synthesis of FeO.TiO_2 by mixing two solutions in the reflux flask. The first solution is a colloidal solution of TiO_2 prepared by hydrolysis of 4.0 mL TTIP in 0.50 mL acetyl acetone, and 15.0 mL of 99% ethanol. The second solution was prepared by mixing 15.0 mL of 99% ethanol, 2.0 mL of distilled water and addition 1.0 mL of 0.1 M acetic acid. The two solutions were mixed and stirred using a magnetic stirrer for 3 h at 50°C and continued with the addition of $Fe(NO_3)_3$ as Fe dopant to give FeO.TiO_2 in the form of sol. The remaining solvent was evaporated in an open space and continued with heating at 80°C[9,21].

Lignin Degradation

The degradation of lignin was carried out in a UV reactor which was reportedly performed by Nurdin et al. that the 20 mL lignin solution with a concentration of 500 ppm was filled in 3 chemical glass and added FeO.TiO_2 with a mass of 0.1 g, 0.2 g, and 0.3 g, respectively. The chemical glass containing the lignin-FeO.TiO_2 mixture is added in the reactor and exposed to UV light with a wavelength of 365 nm for 40 minutes. The lignin solution was taken and filtered. Then this solution was measured the absorbance value using a UV-Vis spectrophotometer, while the degradation result was stored for the antimicrobial activity test[22].

Antimicrobial Activity Test

The method of wells was carried out by using 2 layers of solid medium and semisolid medium of PDA. The resulting wells were then filled with a solution of lignin degradation as a test compound, distilled water as a negative control, and 2% benomyl as a positive control of 15 µL. Subsequently, it was incubated for 24 hours at 37°C to obtain an inhibitory zone which was formed to determine the antimicrobial inhibition test results.

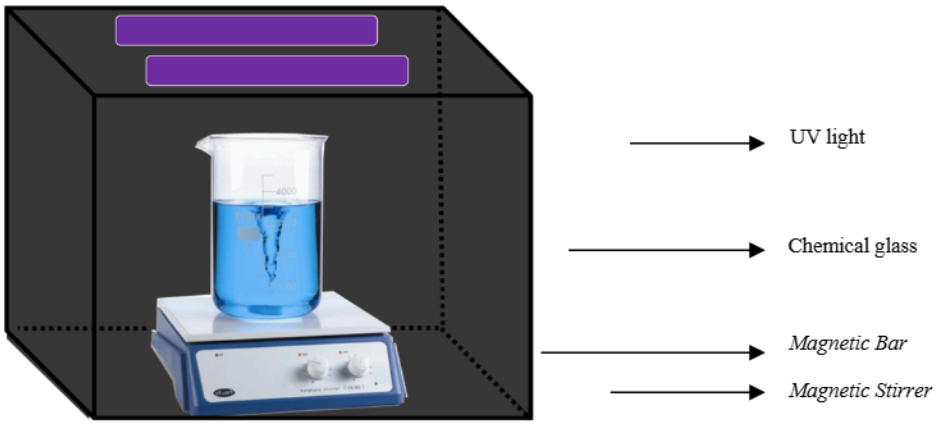


Figure 1: Lignin degradation scheme in the UV Reactor in the presence of FeO.TiO_2.

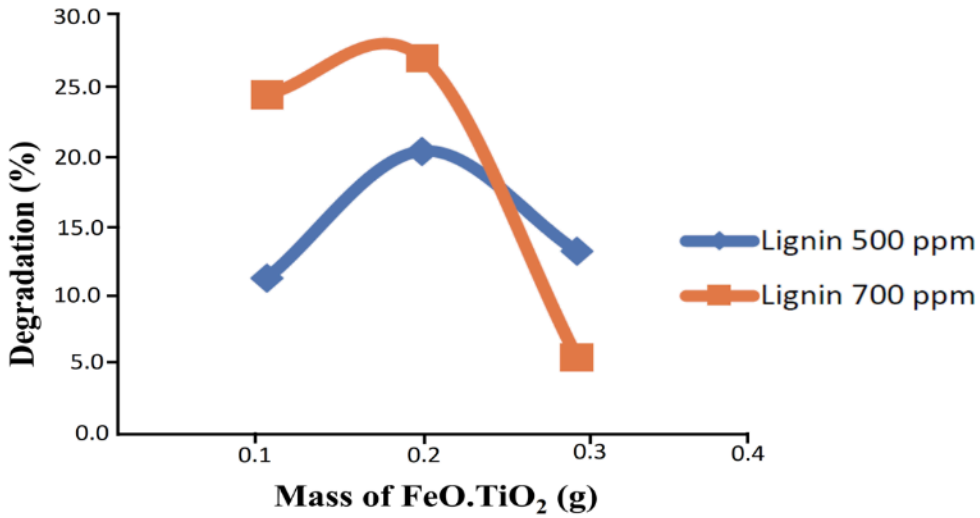
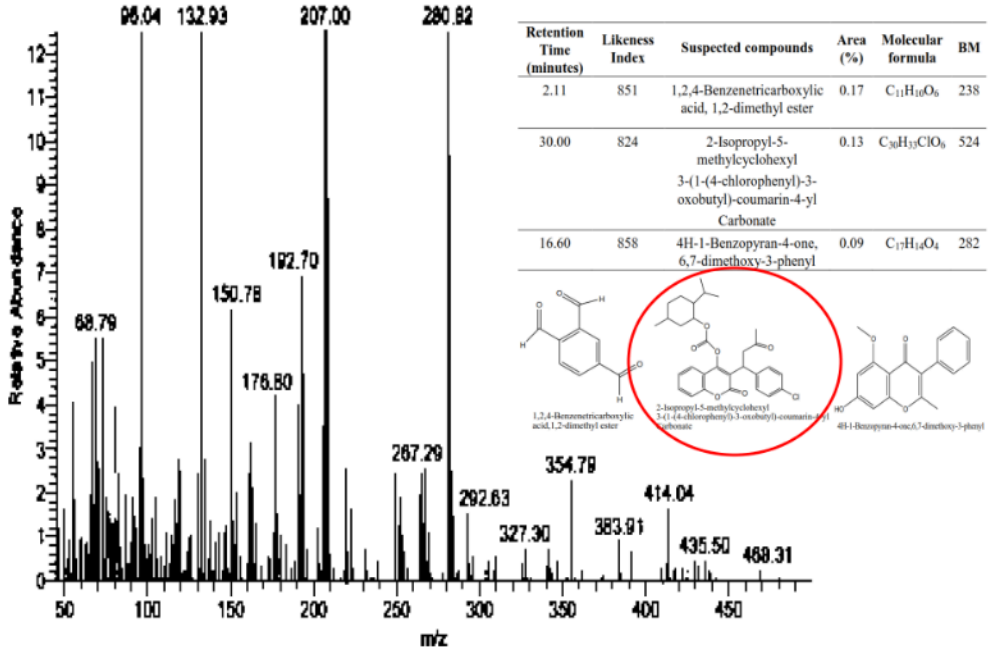


Figure 2: Effectivity of FeO.TiO_2 mass in lignin degradation.



Retention Time (minutes)	Likeness Index	Suspected compounds	Area (%)	Molecular formula	BM
2.11	851	1,2,4-Benzenetricarboxylic acid, 1,2-dimethyl ester	0.17	$C_{11}H_{10}O_6$	238
30.00	824	2-Isopropyl-5-methylcyclohexyl 3-(1-(4-chlorophenyl)-3-oxobutyl)-coumarin-4-yl Carbonate	0.13	$C_{30}H_{33}ClO_6$	524
16.60	858	4H-1-Benzopyran-4-one, 6,7-dimethoxy-3-phenyl	0.09	$C_{17}H_{14}O_4$	282

Figure 3. The result of GC-MS analysis as lignin-derived.

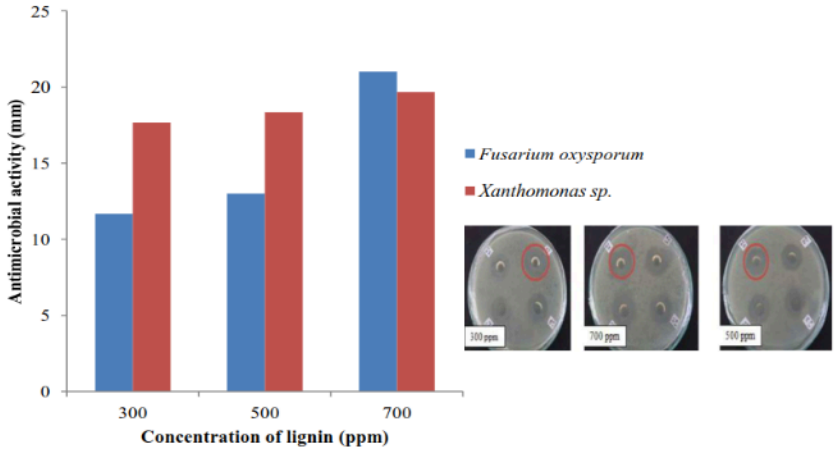


Figure 4: The antimicrobial activity of lignin degradation compound against *Fusarium oxysporum* and *Xanthomonas* sp.

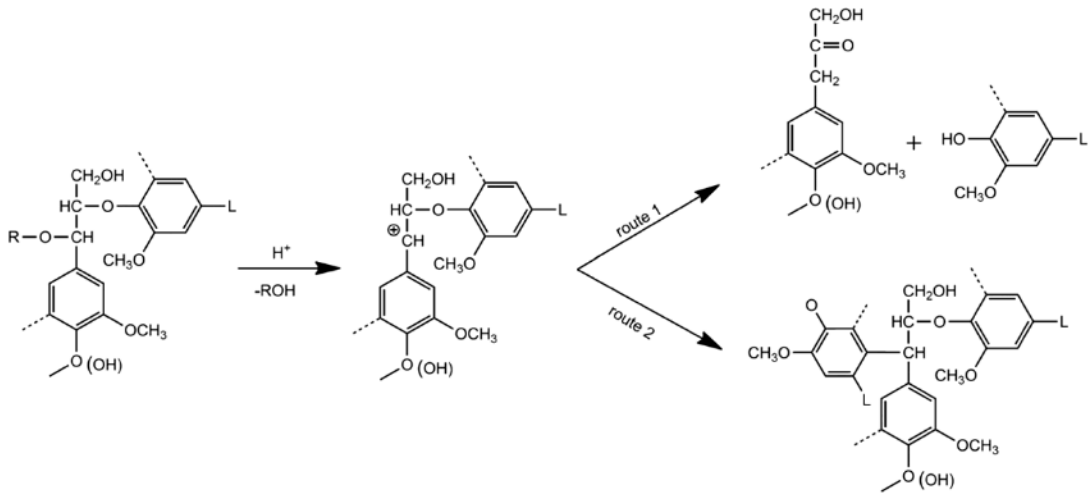


Figure 5. Depolymerization and rearrangement of lignin degraded polymer structures[24]

RESULTS

Photodegradation of Lignin

Based on photodegradation results against 500 ppm lignin solution, it can be seen that $FeO.TiO_2$ mass of 0.2 g has a high degradation of 20.63% compared with 0.1 g and 0.3 g which has percentage degradation of 11.71% and 13.6% (Figure 2). The presence of $FeO.TiO_2$ effectively for accelerating lignin degradation. According to Wibowo et al. reported that $FeO.TiO_2$ has good photodegradation activity to degrade organic compounds[8]. In this work, we also studied the effectiveness of $FeO.TiO_2$ mass by a testing performance at higher lignin concentration of 700 ppm. Based on $FeO.TiO_2$ mass variation, the results showed that $FeO.TiO_2$ with 0.2 g mass still a high percent degradation of 27.17% compared with 0.1 g and 0.3 g.

Based on GC-MS data from lignin degradation for 40 minutes (Figure 3) indicated that lignin derivate has obtained as phenol group compounds such as 2-Isopropyl-5-methylcyclohexyl-3-(1-phenyl-3-oxobutyl)-coumarin-4-yl carbonate. Furthermore, the other phenol compounds indicated provides degradation result s of 4H-1-Benzopyran-4-one,6,7-dimethoxy-3-phenyl, and 1,2,4-Benzenetricarboxylic acid, 1,2-dimethyl ester. This compounds also have an antimicrobial activity.

Antimicrobial activity of Lignin degradation compounds

The antimicrobial activity test by using well diffusion method which aimed to find out the high inhibitory of lignin degraded compound on the growth of *Fusarium oxysporum* and *Xanthomonas* sp. by observing the clear zone size formed around the medium containing the fungus.

Based on the results of *Fusarium oxysporum* that lignin compound of 700 ppm degraded for 40 minutes showed a high inhibitory activity compared to lignin 300 ppm and 500 ppm namely 21 nm. The same results of *Xanthomonas* sp. Activity test (Figure 4) that the lignin degradation compound of 700 ppm provides a high inhibitory activity of 19.66 mm. The amount of lignin compound 700 ppm degraded becomes the reason for the high inhibitory power activity to *Fusarium oxysporum* and *Xanthomonas* sp.

The inhibitory activity results from lignin photodegradation of 700 ppm is a relatively strong inhibitory, based on Mulyadi et al. that the mushroom or microbial growth resistance response is less effective when the clear zone diameter is <10 mm, weak if it ranges from 10-15 mm, medium between 16-20 mm, and strong above equal to 20 mm[23].

DISCUSSION

The increase of degradation result caused by the lignin depolymerization which is the cleavage of ester and ether bonds into a simpler structure (Figure 5). There was also to rearrange the condensed lignin polymer structure to form a new complex[24].

Furthermore, the lignin degraded was tested against *Fusarium oxysporum* and *Xanthomonas* sp. antimicrobial. The selection of *Fusarium oxysporum* as a model of pathogenic fungus is caused it is reportedly attaced leading crops that trigger wilts, blights, bots, and cancer. Meanwhile, *Xanthomonas* sp. reported can affect wilt disease in plants[12]. These results indicated that the lignin photodegradation for 700 ppm using $FeO.TiO_2$ has produced activity with a strong inhibitory zone against *Fusarium oxysporum* and *Xanthomonas* sp.

Maulidiyah et al. reported that photocatalytic lignin degradation compounds contain phenolic derivatives which have high activity in damaging fungal activity. In addition, the use of a long photocatalytic degradation time will result in perfect lignin degradation resulting in H_2O molecules. While the rapid degradation time causes ineffective degradation. Both of these will have an impact on the decrease in antimicrobial activity[13].

The antimicrobial activity of the lignin photodegradation compound can occur that the lipid destruction process on *Fusarium oxysporum* and *Xanthomonas* sp. plasma membrane. In addition, the occurrence of protein denaturation by lignin degradation compounds that lysis cell wall so that it can damage the microbial cell walls[12].

CONCLUSION

The effectiveness of $FeO.TiO_2$ in degrading lignin is influenced by mass and degradation time. The $FeO.TiO_2$ mass of 0.2 g is the optimum mass in this study, while the optimum degradation time lasts for 40 minutes. The time factor showed the high antimicrobial activity for the inactivation of *Fusarium oxysporum* and *Xanthomonas* sp. with inhibitory power generated of 21 mm and 19.66 mm. This inhibitory power is classified as a strong inhibitory category.

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