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Photocatalytic Degradation of Lignin using TiO_2 from Ilmenite Prepared by Microwave Method

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Abstract

This study investigates the photocatalytic degradation of lignin using TiO_2 extracted from ilmenite through a microwave-assisted method. Characterization of the iron sand, which serves as the source of ilmenite, was conducted using X-ray fluorescence spectroscopy (XRF) and Energy Dispersive X-ray Spectroscopy (EDX). The XRF analysis revealed that the iron sand primarily consists of Fe and TiO_2, with minor impurities such as Al_2O_3, MgO, and SiO_2. After extraction, the iron mineral content increased significantly, while impurities decreased. EDX analysis confirmed the presence of Fe, O, and Ti elements in the iron sand sample, originating from various iron oxide phases. Subsequent degradation tests on lignin with varying microwave heating durations of ilmenite showed that a 90-minute heating duration achieved the highest lignin degradation percentage of 56.69%. This suggests that the optimum heating time for ilmenite is crucial for maximizing its photocatalytic activity. Overall, the findings highlight the potential of microwave-prepared TiO2 from ilmenite for efficient lignin degradation, with implications for environmental remediation and industrial applications.

Keywords: Photocatalyst; TiO_2; Ilmenite; lignin; degradation

Introduction

The abundance of iron sand as a crucial mineral resource on a global scale presents significant potential for various industrial applications. Iron sand deposits can be found in numerous locations worldwide, with notable major producers including Australia, Brazil, India, South Africa, and Indonesia. Within Indonesia itself, several regions boast substantial iron sand potential, such as Bangka Island, Central Kalimantan, and Southeast Sulawesi (1). Iron sand is composed of a mixture of magnetite, hematite, ilmenite, zircon, and monazite minerals. Ilmenite, a key mineral constituent of iron sand, serves as the primary source of titanium dioxide (TiO_2). Within iron sand, TiO_2 combines with iron to form a mineral called ilmenite ($FeTiO_3$).

The processing of ilmenite for TiO_2 production typically involves several stages, including magnetic separation, milling, chemical purification, and hydrometallurgical processing. These stages aim to remove impurities from the ilmenite mineral and increase the TiO_2 content to the required level for industrial applications. A common method used to isolate TiO_2 from iron sand is leaching using acidic solvents. The extraction and purification of TiO_2 have been developed by Nurdin et al. (2), employing sulfuric acid leaching through conventional heating (hot plate), yielding TiO_2 purities of 19.78% (1000 °C) and 8.97% (500 °C). However, the use of sulfuric acid leaching is deemed ineffective due to the production of complex by-products, including waste. Conversely, the hydrochloric acid leaching process has garnered attention from researchers for its advantages, including the effective removal of impurities, high leaching efficiency, reusability, and high-quality output.

The use of ilmenite as a raw material in the production of TiO_2 is relatively inexpensive and easily obtainable. Therefore, the utilization of TiO_2 derived from ilmenite for the photocatalytic degradation of lignin becomes an intriguing option (3,4). The application of TiO_2 photocatalysis for lignin degradation has been extensively studied in recent years (5–8). These studies indicate that TiO_2 can oxidize lignin into simpler and more easily decomposable compounds. Furthermore, utilizing TiO_2 from ilmenite can enhance photocatalysis efficiency and reduce production costs. Thus, employing TiO_2 photocatalysis from ilmenite for lignin degradation represents an innovative approach in the field of lignin waste processing (9). Moreover, it not only aids in addressing lignin waste issues but also contributes positively to the development of environmentally friendly and sustainable technologies.

Experimental Methods

The magnetic separation and pre-oxidation

The initial stage of TiO_2 extraction from iron sand begins with sampling and separating dried magnetic and non-magnetic sands under sunlight for one day. Subsequently, they are washed with water to reduce impurities, dried, and then subjected to grinding of the ilmenite concentrate using a mortar and pestle, followed by sieving through a 200 Mesh sieve. Furthermore, the oxidation process is conducted using a microwave heating reactor. Pre-oxidation is carried out by taking 5 grams of ilmenite each and placing it in a porcelain crucible, then calcination is performed using a furnace at a temperature of 900°C for 120 minutes followed by characterization using XRF.

Hydrochloric Acid (HCl) leaching process

The hydrochloric acid (HCl) leaching process is conducted on a laboratory scale using a relatively simple method. Initially, 100 mL of 8 M HCl is heated to approximately 105˚C. Subsequently, 5 g of iron sand is added to the solution. After thirty minutes, 0.7 g of Fe0 is introduced as a reducing agent. The mixture is continuously heated for varying durations for each sample: 50, 70, 90, 110, and 130 minutes. After completion of the leaching process, the solution is filtered using the Whatman No. 40 filter paper. The obtained residue is then washed, centrifuged, weighed, and calcined at approximately 550°C for 2 hours. Following this, characterization is carried out using Energy Dispersive X-ray (EDX) and X-ray Fluorescence (XRF) techniques.

Lignin degradation test

The determination of ilmenite percentage in lignin degradation is carried out by taking 5 ilmenite samples that have been degraded according to variations in microwave heating time, namely 50, 70, 90, 110, and 130 minutes. Subsequently, each sample is filtered using Whatman No. 40 filter paper. Next, the degraded lignin solution is obtained and its absorbance is measured, resulting in the percentage of degraded lignin. The most optimal lignin degradation result will be further developed for subsequent research.

Results and Discussion

Initial Characterization of Iron Sand

Characterization of iron sand by X-ray fluorescence spectroscopy (XRF) before chloride acid leaching extraction using microwaves is shown in **Figure 1**. Based on **Figure 1**, it can be observed that the content of lateritic iron ore is 92.16% Fe, 2.2% Si, 3% Al, and other mineral elements with percentages below 1%. One method employed to enhance the Fe content in the sample involves leaching processes to eliminate undesired minerals from the alcohol medium using an ultrasonic cleaner multiple times. On the other hand, XRF test results after extraction indicate an increase in iron mineral content from 92.16% to 98.51%. Meanwhile, other minerals significantly decrease as Si diminishes to 0.3%, and there are also some other elements lost with small percentages (10,11). Based on **Figure 1**, it can be observed that Fe and TiO_2 are the dominant compound elements contained in the iron sand powder sample, with percentages of 45.89% and 18.10% respectively. Hence, it can be inferred that the iron sand contains the mineral ilmenite. Additionally, the dominant impurity compounds are Al_2O_3, MgO, and SiO_2, with concentrations of 5.91%, 5.78%, and 5.53% respectively.

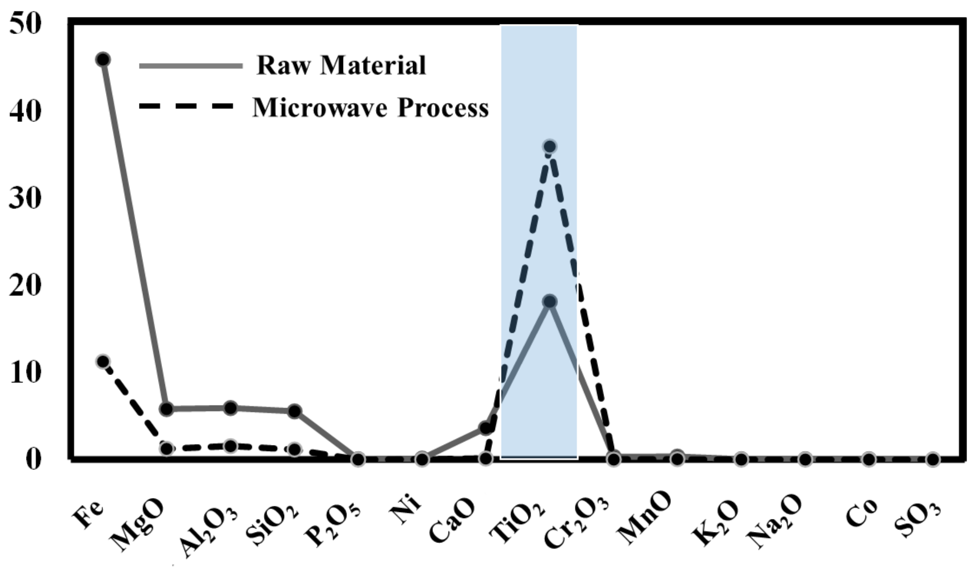
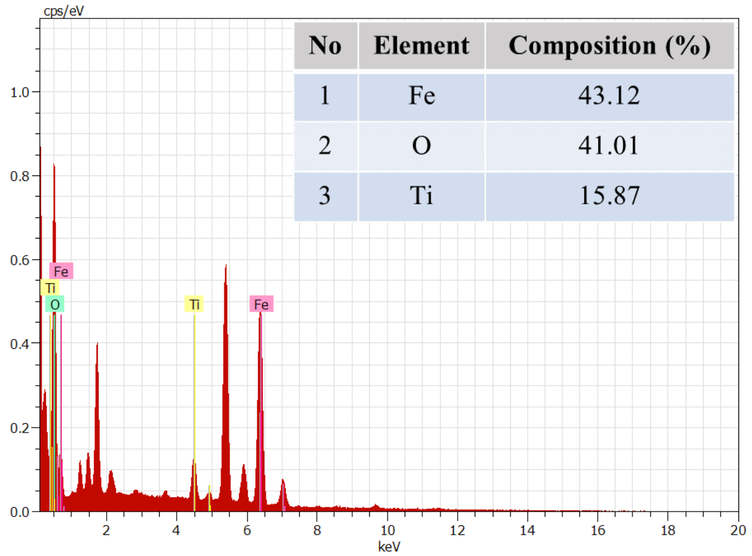


Figure 1. Characterization results of XRF analysis of iron sand before and after extraction

Energy Dispersive X-ray Spectroscopy (EDX) analysis

Based on the EDX characterization data, it is found that the iron sand sample contains Fe, O, and Ti elements (**Figure 2**). The content of Fe, O, and Ti elements are 43.12%, 41.01%, and 15.87% respectively. The Fe and O content originate from Magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) phases, which are iron oxides. The differences in physical characteristics of mineral content in the sand such as Fe, Ti, Mg, and Si are caused by differences in deposit locations.



No	Element	Composition (%)
1	Fe	43.12
2	O	41.01
3	Ti	15.87

Figure 2. Characterization of EDX

Degradation test of lignin

Degradation test of lignin with the influence of time aimed to determine the most effective time for a photocatalyst to generate •OH radicals (12,13). When the catalyst is irradiated with UV light with energy higher than the band gap energy, it will produce holes that act as strong oxidizers to form •OH radicals, which degrade lignin into simpler compounds (14,15). Based on **Figure 3**, it is known that the initial concentration of lignin is 500 ppm with variations in heating time of ilmenite using different microwave durations: 50, 70, 90, 110, and 130 minutes for a degradation period of 1 hour. The resulting degradation percentages are 26.71%, 42.75%, 56.69%, 40.46%, and 25.31%, respectively. These results indicate that heating ilmenite using a microwave for 90 minutes achieves the highest lignin degradation, reaching 56.69%. Thus, it can be assumed that the most effective duration for heating ilmenite using a microwave is 90 minutes, as indicated by the graph above, representing the optimum heating time. Consequently, it can be concluded that the longer the heating time of ilmenite, the lower its ability to degrade a compound.

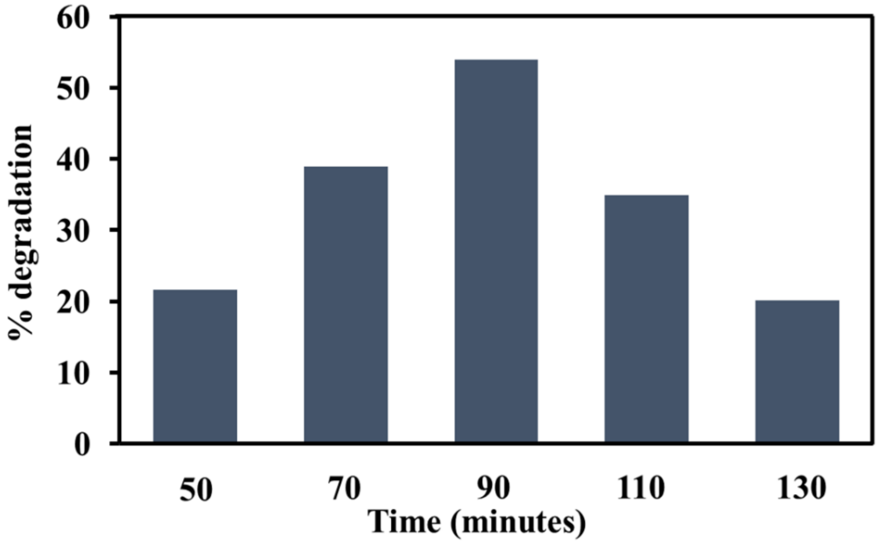


Figure 3. Graph of percentage of lignin degradation with time variation

Conclusions

Summarily, the study focused on the photocatalytic degradation of lignin using TiO_2 derived from ilmenite, prepared via a microwave method. Characterization of the iron sand sample before and after extraction revealed a significant increase in iron content, indicating the presence of ilmenite as the dominant compound. Energy Dispersive X-ray Spectroscopy (EDX) analysis confirmed the presence of Fe, O, and Ti elements in the iron sand sample, with varying concentrations attributable to differences in deposit locations. Moreover, results showed that heating ilmenite for 90 minutes achieved the highest lignin degradation percentage of 56.69%, suggesting an optimum heating time.

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Conflicts of Interest

The authors declare no conflict of interest.

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