

## The Ouw Natural Clay Impregnation Using Titanium Dioxide and Its Application as a Rhodamine B Dye Stuff Degradation

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### Abstract

This study aims to determine the effect of calcination temperature on Titanium dioxide impregnated Ouw Natural Clay (LAO) on the degradation of Rhodamine B dye. The calcination temperature used was 200, 300, and 400 °C. Their radiation was carried out with 3x8 watt UV lamps and sunlight. The degradation percentage of Rhodamine B dye produced by LAO-TiO<sub>2</sub> calcined at a temperature of 200, 300, and 400 °C with sunlight were 98.80%, 98.87%, and 96.07%, respectively. The degradation percentage of Rhodamine B dye produced by LAO-TiO<sub>2</sub> calcined at temperatures of 200, 300, and 400 °C with the help of UV light were 96.01%, 97.41 %, and 97.18%, respectively.

Keywords: *Photodegradation, Impregnation, Ouw natural clay, Rhodamine B, Titanium dioxide, Calcination Temperature*

### INTRODUCTION

Ouw Natural Clay (LAO) is a natural mineral from the silicate group with availability that is quite abundant in Indonesia, generally used in the ceramic industry, but can also be used as a catalyst, catalyst support, ion exchanger, and adsorbent. The distribution of clay in Maluku is on Ambon Island and Saparua Island (in Ouw Village to be precise). Based on previous research known that the main component of Ouw natural clay (LAO) is montmorillonite, a type of clay that is often used in various industrial fields, due to its superior properties (Catherina M. Bijang et al., 2019; Catherina M. Bijang, Sekewael, & Koritelu, 2014; Catherina M. Bijang, Tanasale, Kelrey, Mansur, & Azis, 2021).

Natural clay generally shows slow performance when used directly, so it is necessary to modify the clay structure (C. Bijang, Wahab, Maming, Ahmad, & Taba, 2015). By modifying its structure, clay can be used as a metal-supported catalyst. The method that can be used to improve the performance of clay as catalyst support is through the impregnation process on the clay structure using active metals (Suhernadi, Wardhani, & Purwonugroho, 2014). The active metal used has a dual role, namely as an impregnator and as a catalyst. In the impregnation method, the calcination process is an important step to activate the dispersed catalyst on the surface of the supporting material (A'yuni & Murwani, 2012). Thermal effects during

calcination also affect the structure of the clay (Catherina M. Bijang et al., 2015; Fatimah, 2009), can increase the acid site (Laili, Nurhayati, & Muhdarina, 2014), and the specific surface area caused by the loss of absorbed and hydrated water molecules. However, calcination at higher temperatures can change the physical and chemical properties of natural clay, so it is necessary to vary the calcination temperature to determine the thermal stability of the clay (Teddy, Bijang, Nurdin, & Kapelle, 2018).

Titanium dioxide is a material known as a catalyst material based on its semiconductor properties (Maulidiyah et al., 2017; Nurdin et al., 2018; Okoye et al., 2011). As a photocatalyst, TiO<sub>2</sub> is considered the most suitable material for a wide range of environmental applications, due to its chemical and biological inert nature, non-toxicity, stability to corrosion, and relatively cheap price. So far, TiO<sub>2</sub> has been used in water management in the form of a suspension. But it has the disadvantage which is the separation of TiO<sub>2</sub> particles takes a long time and is very expensive. The method that can be used to overcome the weakness of the TiO<sub>2</sub> suspension system is by dispersing TiO<sub>2</sub> on a stable and inert support material, such as Clay (Baizig, Khalfallah, & Jamoussi, 2015; Djellabi et al., 2014; Safni, Deliza, & Rahmayeni, 2014).

Rhodamine B is a toxic dye, when it enters to the human body it can cause various diseases such as kidney failure, cancer, and liver diseases. The presence

of Rhodamin B in the liquid waste originating from the waste of the industrial process needs to be handled properly so that it does not enter the water bodies that are used by the community. Without proper waste treatment, it will have the potential to become a cause of water pollution which reduces the quality of water consumed by living things. Waste management methods that are often used are adsorption, biodegradation, and chemical methods such as chlorination and ozonation. These methods are quite effective in dealing with waste but these methods require very large operational costs. Among the existing methods, photodegradation is an alternative method that is cheaper and easier to implement (Catherina M. Bijang et al., 2019; Kurian & Kavitha, 2016).

In this study, the calcination temperature of the TiO<sub>2</sub> impregnation process on Ouw natural clay (LAO) will be carried out which will then be used as a Rhodamine B dye degradation. A study of the light source is carried out by applying UV rays and sunlight.

## METHODOLOGY

### Materials and Instrumentals

The tools used include a set of glassware (Pyrex), electric heater (Cimarec), analytical balance (Ohaus), mortar and pestle, oven (Mettler), electric furnace (Barnstead Thermolyne 47900 Furnace), 100 mesh sieve, Spectrophotometer UV-Vis (Shimadzu UV-1201), Scanning Electron Microscopy (VEGA3 TESCAN SEM-EDS) and Photocatalytic Reactor.

The materials used include: Ouw natural clay (LAO), distilled water, NaCl (Merck), AgNO<sub>3</sub> p.a (Merck), H<sub>2</sub>SO<sub>4</sub> (Merck), BaCl<sub>2</sub> (Merck), TiO<sub>2</sub> (Technician), Whatman filter paper No. 42, Ethanol absolute (Merck), Rhodamin B (Merck), and H<sub>2</sub>O<sub>2</sub>.

### Methods

#### Sample preparation.

The extracted LAO was washed with distilled water several times, then filtered to obtain an LAO which completely free from impurities such as sand, gravel, and plant roots. After washing, LAO was dried for 2 hours in an oven at 120 °C.

#### Saturation Process

A total of 50 g of LAO was dispersed into 500 mL of 3 M NaCl solution while being stirred for 24 hours. LAO was then filtered and the residue obtained was washed with distilled water several

times until the filtrate did not produce a white precipitate with AgNO<sub>3</sub>.

#### Activation Process

As much as 25 grams of LAO which has been saturated, is dispersed into 100 mL of 2M H<sub>2</sub>SO<sub>4</sub> while being stirred. The activation process was carried out for 24 hours, then filtered and the residue obtained was washed with hot distilled water until the filtrate did not produce a precipitate with BaCl<sub>2</sub>. LAO dried in an oven at a temperature of 100-110 °C.

#### TiO impregnation.

As much as 25 g of activated LAO, 3.33 g of TiO<sub>2</sub>, and 25 mL of absolute ethanol were added while being stirred for 4 hours. The suspension was then dried in an oven at 110 °C for 2 hours. After that, it was ground and sieved using a 100-mesh sieve. Furthermore, calcination was carried out at various temperatures of 200, 300, and 400 °C for 5 hours. Characterization of the impregnated LAO structure was carried out using SEM.

#### Preparation of the Rhodamine B dye calibration curve

A total of 0.1 g of Rhodamine B dye was dissolved with distilled water. Then transferred to a 100 mL volumetric flask and diluted with distilled water until it reaches the mark. Furthermore, from a standard solution of 1000 ppm then diluted to 100 ppm with the volume of 100 mL and from 100 ppm then diluted to 25 ppm with the volume of 100 mL, and from 25 ppm it was then diluted to 5 ppm as with the volume of 100 mL and diluted again to 0.2; 0.4; 0.6; 0.8; and 1 ppm. After that, the absorbance was measured at max=554 nm using a UV-Vis spectrophotometer and a standard curve was made. A total of 0.1 g of Rhodamine B dye was dissolved with distilled water. Then transferred to a 100 mL volumetric flask and diluted with distilled water until it reaches the mark. Furthermore, from a standard solution of 1000 ppm then diluted to 100 ppm with the volume of 100 mL and from 100 ppm then diluted to 25 ppm with the volume of 100 mL, and from 25 ppm it was then diluted to 5 ppm as with the volume of 100 mL and diluted again to 0.2; 0.4; 0.6; 0.8; and 1 ppm. After that, the absorbance was measured at max=554 nm using a UV-Vis spectrophotometer and a standard curve was made.

#### Rhodamine B dye degradation

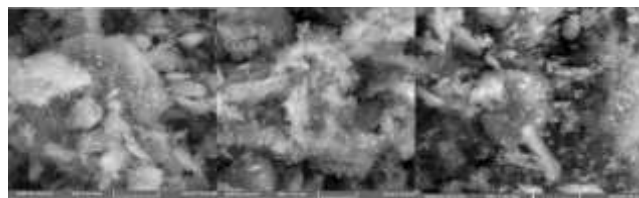
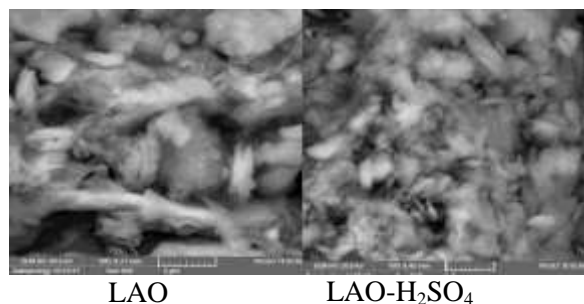
A total of 25 mL of Rhodamine B dye solution with a concentration of 10 mg/L was put into 9 Erlenmeyer and then added with 0.1 mL of H<sub>2</sub>O<sub>2</sub>.

Amount 50 mg of  $\text{TiO}_2$  was added to the first Erlenmeyer, 50 mg of prepared LAO was added to the second Erlenmeyer, 50 mg of LAO- $\text{TiO}_2$  added to the third Erlenmeyer, the fourth Erlenmeyer was added with 50 mg of LAO- $\text{TiO}_2$  200, the fifth Erlenmeyer was added with 50 mg of LAO- $\text{TiO}_2$  300, the sixth Erlenmeyer was added with 50 mg LAO- $\text{TiO}_2$  400, the seventh Erlenmeyer was added with 50 mg LAO- $\text{TiO}_2$  200, the eighth Erlenmeyer was added with 50 mg LAO- $\text{TiO}_2$  300, the ninth Erlenmeyer was added with 50 mg LAO- $\text{TiO}_2$  400 (samples were coded A, B, C, D, E, F, G, Hand successively). Before irradiation, the mixture was stirred for 1 hour, then 0.2 mL of 15%  $\text{H}_2\text{O}_2$  was added to each beaker. The degradation process was carried out for 30 minutes each using 3 UV lamps with 8 watts of power and direct sunlight at 08.55-09.25 am (320-420 nm). The suspension was then filtered and its absorbance was measured with a UV-Vis Spectrophotometer at  $\lambda_{\text{max}} = 554 \text{ nm}$ .

## RESULTS AND DISCUSSION

### Characterization

The results of characterization with SEM showed that LAO treatment with 2M sulfuric acid resulted in a more uniform crystal size and more pore formation. Calcination results at temperatures of 200, 300 and 400 °C showed the distribution of  $\text{TiO}_2$  particles on the clay surface. At a calcination temperature of 200 °C, it appears that the distribution of  $\text{TiO}_2$  particles is uneven and tends to accumulate at certain locations. The resulting pores also appear to be smaller than LAO- $\text{TiO}_2$  which was calcined at 300 and 400 °C. The distribution of  $\text{TiO}_2$  was most evenly distributed at a calcination temperature of 300 °C. The resulting pores are also more uniform in size than the results of calcination at 200 °C and 400 °C. The results of calcination at 400 °C showed that the resulting pore size was larger than calcination at 200 and 300 °C.



LAO- $\text{TiO}_2$  200 LAO- $\text{TiO}_2$  300 LAO- $\text{TiO}_2$  400

Figure 1. SEM results

Based on Figure 2, the higher the calcination temperature, the lower the characteristic reflection peak of montmorillonite. This of course is influenced by the thermal effect during calcination. From the data in Table 1, it can be seen that calcination at a temperature of 300 °C began to affect the stability of the montmorillonite structure with the loss of one reflection peak, even at a temperature of 400 °C, there were two reflection peaks of montmorillonite that had been lost (Azis, Bijang, Nurdin, Teddy, & Kapelle, 2020). This result is suitable with SEM characterization data which showed that the pore size at calcination 400 °C was larger than the pore size at calcination 200 °C and 300 °C.

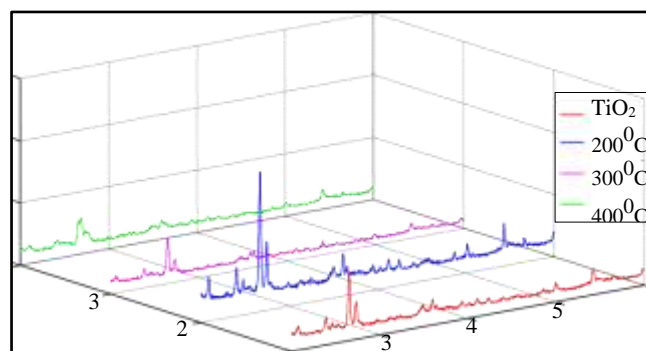


Figure 2. Sample Diffractogram

The success of the distribution of  $\text{TiO}_2$  on the clay surface can be seen from the appearance of specific  $\text{TiO}_2$  absorption, which can be seen in Table 2. The reflection peaks correspond to the crystal phases of rutile and anatase of  $\text{TiO}_2$ . This can explain the degradation ability of impregnated LAO- $\text{TiO}_2$  samples in degrading Rhodamine B dye.

The calcination process also plays a role in the distribution of  $\text{TiO}_2$  on the clay surface. This can be seen from the highest intensity of the overall  $\text{TiO}_2$  reflection peak in the calcined impregnated  $\text{TiO}_2$  clay at 200 °C (LT 200). The higher the calcination temperature, the intensity of the  $\text{TiO}_2$  reflection peak decreased. This shows that the calcination process affects the crystallinity of  $\text{TiO}_2$  (Azis et al., 2020).

Table 1. Data on the value of 2 $\theta$  clay before and after impregnation with TiO<sub>2</sub>

L	LT	LT 200	LT 300	LT 400
26.6142	26.5102	26.6325	26.4184	26.7380
23.9694	23.8752	23.9877	23.7779	-
34.9000	34.8200	34.9719	-	-

Note: Clay (L), TiO<sub>2</sub>impregnated clay (LT), TiO<sub>2</sub>impregnated clay calcined at 200 °C (LT 200) TiO<sub>2</sub>impregnated clay calcined at 300 °C (LT 300) TiO<sub>2</sub> impregnated clay calcined at 400 °C (LT 400)

Table 2. The arrangement of the crystal phase reflection peaks of TiO<sub>2</sub>

2 $\theta$	Note	2 $\theta$	Note	2 $\theta$	Note	2 $\theta$	Note	2 $\theta$	Note
25.281	A	25.260	A	25.220	A	25.240	A	25.600	A
48.376	A	48.535	A	48.691	A	48.404	A	48.562	A
55.296	A	55.000	A	55.160	A	55.060	A	55.160	A
27.234	R	27.300	R	27.419	R	27.212	R	27.460	R
36.100	R	36.380	R	36.068	R	36.207	R	36.167	R
41.225	R	41.059	R	41.223	R	40.933	R	41.170	R

Note: Anatase (A); Rutile (R)

The results of the measurement of the surface area of the samples are presented in Table 3. The data shows that the largest surface area was produced by the LAO-TiO<sub>2</sub> sample which was calcined at 400 °C. If it is connected with the data in Fig 2 and Table 1, the sample which was calcined at 400 °C indicates loss of montmorillonite peaks (meaning that there are some broken crystal lattices), it can be said that the damage to the lattice has an impact on the production of a large surface area.

This is supported by the results of SEM characterization which shows that there is a larger number of empty spaces. The decrease in surface area in the LAO-TiO<sub>2</sub> sample calcined at a temperature of 200 °C can be explained by the accumulation of TiO<sub>2</sub> distribution at certain locations as shown by the results of sample characterization using SEM.

Table 3. Surface Area of Sample

Sample	Surface Area (m <sup>2</sup> /g)
LT	161.800
LT 200	32.514
LT 300	146.477
LT 400	174.826

### Rhodamine B degradation

The degradation process of Rhodamine B dye using sunlight or UV light can be seen qualitatively with the loss of the initial color of the dye which indicates the destruction of the chromophore group of the dye. The degradation process lasts for 30 minutes. After the sample degradation process, the absorbance will be tested using a UV-Vis spectrophotometer at a wavelength of 554 nm. The results of the degradation of each sample are presented in Figure 3.

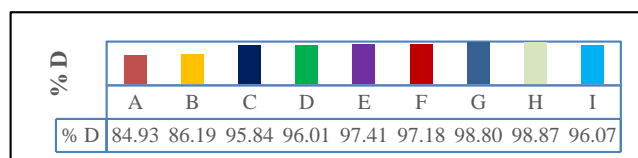


Figure 3. Rhodamine B dye degradation results by each sample

Figure 3 shows the highest percentage of each treatment, namely the type of treatment using a sunlight source and the use of a LAO-TiO<sub>2</sub> catalyst with a calcination temperature of 300 °C (sample H). While the lowest percentage of degradation was shown in the treatment with UV light source and the use of TiO<sub>2</sub> catalyst (sample A). The treatment with UV light and the use of LAO without TiO<sub>2</sub> (sample B) showed low results because only the adsorption process occurred.

Before the degradation process, each sample was added with H<sub>2</sub>O<sub>2</sub> solution with the aim of increasing the concentration of hydroxyl radicals in the degradation process so as to increase the amount of the substance being degraded. The addition of excess H<sub>2</sub>O<sub>2</sub> can result in the formation of H<sub>2</sub>O• radicals which are less reactive than •OH radicals, resulting in a decrease in the number of degraded dyes (C M Bijang et al., 2019; Kurian & Kavitha, 2016). Therefore, in this degradation process, only 0.2 ml of H<sub>2</sub>O<sub>2</sub> 15% was added in all treatments according to the optimum use (Suhernadi et al., 2014). Theoretically, photodegradation occurs because the TiO<sub>2</sub> impregnated clay contains titanium oxide which is a semiconductor material that has a filled valence band and an empty conduction band. When the photocatalyst is irradiated by light with an energy greater than the bandgap energy, a hole with the quality of a strong oxidizing agent will be produced to form the OH radicals and these radicals degrade the rhodamine B dye into simpler molecules. From the results of this study, it was

found that sunlight is a highly potential light source. Figure 3 shows the lowest percentage of degradation is in TiO<sub>2</sub> treatment (without LAO) added with H<sub>2</sub>O<sub>2</sub> (sample A). This is due to the lack of surface area of TiO<sub>2</sub> which is not imparted to porous materials such as LAO. The percentage of degradation using TiO<sub>2</sub>-LAO catalyst shows a high value, namely 95-98%. This shows that LAO that has been impregnated with TiO<sub>2</sub> has a combined adsorption function and photocatalytic function which is able to produce better degradation performance. The same thing was also shown other researcher which stated that the percentage of degradation of methylene blue dye using LAO-TiO<sub>2</sub> samples before and after calcination showed better performance, namely 96-98% (Teddy et al., 2018).

Calcination temperature study showed that calcination at 300°C showed the best performance both on UV light sources and sunlight. This can be explained by the XRD characterization results which stated that at 300°C only one montmorillonite area was damaged by heating, the surface area was also much larger than the 200°C temperature treatment and the SEM characterization results also showed a more even distribution of TiO<sub>2</sub>.

## CONCLUSION

Impregnation of TiO<sub>2</sub> on LAO can expand the surface of TiO<sub>2</sub> so that the photocatalytic-adsorption process can take place and produce a degradation percentage of 95 – 98%. LAO-TiO<sub>2</sub> composite calcined at 300 °C showed the greatest degradation using either UV light or sunlight. The use of sunlight is more effective than UV light in degrading Rhodamine B dye.

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