Ouw Natural Clay-Titanium Oksida (LaO-TiO$_2$) Composite Adsorption Ability On Lead (Pb) Metal

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Abstract. Research has been conducted to synthesize and characterize composite LAO-TiO$_2$ based on LAO mass variation and calcination temperature and its application as an adsorbent of lead metal (Pb). Characterization is done using X-Ray Diffraction (XRD) at an angle of 2θ: 5-60° of LAO mass variation for pillarization, which are 2, 3, and 5 with calcination temperature of 200, 250 and 300°C. The testing of the composite LAO-TiO$_2$ as lead (Pb) metal absorbent using Atomic Absorption Spectroscopy (AAS). The result shows the most significant basal spacing (d-spacing) is on mass variation 5 g (K5) after calcination with temperature 200 10.19 Å. Composite LAO-TiO$_2$ Application as lead (Pb) metal absorbent shows the adsorption capacity (Q) obtained ranges from 4.4-4.9 mg/g.

1. Introduction
Clay is the most common mineral on the surface of the earth, and its availability in Indonesia is quite abundant. Depending on their specific properties clays can be used as adsorbents, catalysts (including catalyst supports), ion exchangers, and color-removing agents [1–3]. The montmorillonite mineral is the most widely spread clay and can swell, high ion exchange capacity, and can be intercalated. In between montmorillonite sheets there is a space that can expand and be filled by water molecules and other interchangeable cations [4,5]. Based on the result of the researches shows the natural clay from Village of Ouw or known as Natural Ouw Clay, or abbreviated NOC (LAO in Indonesia) contains montmorillonite components [6,7].

In general, natural clay still has a weak performance if used directly, so it must be modified first to improve the performance of the clay. Some ways to improve clay performance are activation and pillarization. Activation with H$_2$SO$_4$ is the best way to improve the physical and chemical properties of montmorillonite [8]. The surface area of the bentonite will increase after activated by using H$_2$SO$_4$ concentrations of 0.5; 1; 1.5 and 2 M [7]. The structure of natural clay can modified through the pillarization method by using a metal polycation solution known as a pillar [9].

One of the factors that influence the success of the clay pillarization process is the calcination temperature. The calcination temperature affected the performance of biosensor that used bentonite pillarized as a matrix [7]. Ti pillared clay had increased basal spacing from 16.150 Å before calcined to 17.802 Å after calcined at 200 °C but decreased to 17.450 Å after calcined on 300 °C temperature. The manufacture of Titania pillared clay begins with the manufacture of a pillaring agent in the form of a solution of a Ti-polyhydroxy complex compound. The use of a polyhydroxy pillar...
agent is to obtain pillared clays with significant basal distance. With such a significant basal distance, pillared clay can be used for various purposes, for example as an adsorbent and catalyst [10].

The function of clay as an adsorbent can applied to heavy metals, one of which is Pb metal. Pb metal (Lead) is widely used in daily life but is also one of the metals that pollutes the environment and is harmful to health [11,12]. Such use results in Pb metal contamination, which can occur through consumption of contaminated food and beverages, air, and water. Pb metal poisoning in the body can affect the body's organs, including the nervous system, kidneys, reproductive system, endocrine system and heart, and disturbance to the brain that can result in intelligence and mental disorders [13]. Based on this background, the present study has been conducted synthesis Ouw Natural Clay-Titanium Oxide (LaO-TiO$_2$) Composite and utilization to absorb metal Pb ions.

2. Experimental

2.1 Materials and Instruments
Ouw Natural Clay, distilled water, NaCl 3 M (p.a. Merck), H$_2$SO$_4$ 2 M (p.a. Merck), TiCl$_4$ (p.a. Merck), Ethanol (p.a. Merck), AgNO$_3$ (p.a. Merck), BaCl$_2$ (p.a. Merck), Pb(NO$_3$)$_2$ 50 ppm (p.a. Merck), Whatman filter paper No. 42, a set of glassware (Pyrex), Analytical balance (Ohaus), Electric heaters (Cimarec), Magnetic stirrers, Vacuum pumps (Vacuubrand Gmbh + Co Kg), Ovens (Shel Lab), mortars and pestle, 100 mesh sieves, centrifuge (Centrifuge Heraeus Labofuge 200), Furnace (Electro Linn Therm), Shaker (GFL 3005), X-Ray Diffraction (Philips X’pert MPD), Atomic Absorption Spectroscopy (Thermo Fisher Scientific).

2.2 Sample Preparation
Ouw natural clay washed using distilled water several times, then filtered to obtain a clay that is completely free of impurities such as sand, gravel, and plant roots. After washing, the clay is dried for 2 hours in an oven at 120°C. The dried samples crushed and sieved using 100 mesh sieves.

2.3 Saturation Using NaCl
A total of 150 g of clay was dispersed into 300 mL of 3M NaCl solution while stirring with a magnetic stirrer for 24 hours. The clay is then filtered, and the residue obtained is washed with distilled water several times until the filtrate does not produce a white precipitate with AgNO$_3$ (chloride ion free). After washing, the precipitate is dried in an oven at 80°C Clay that has dried, then crushed until smooth and sieved using a 100 mesh sieve.

2.4 Activation with H$_2$SO$_4$
A total of 100 g of saturated clay was dispersed into 200 mL 2M H$_2$SO$_4$ while stirred with a magnetic stirrer. The activation process is carried out for 24 hours, then filtered and the residue obtained is washed with hot distilled water until the filtrate does not produce a precipitate with BaCl$_2$ (sulfate-free ion). The clay then dried in an oven at 80 °C Clay that has dried, then crushed until smooth and sieved using a 100 mesh sieve.

2.5 LAO-TiO$_2$ Composite Synthesis by Pillarization Method
The LAO-TiO$_2$ composite synthesis begins with the make of a pillar solution, a titanium polycation solution. The pillar solution prepared by mixing 5 mL of TiCl$_4$ with 10 mL of ethanol then stirred to a homogeneous solution. 5mL out of the solution formed was taken and mixed with 25 mL of distilled water and stirred for 3 hours. The prepared pillar solution was then added little by little to the suspensions of 2, 3 and 5 g of clay in 100 mL of water and stirred for 20 hours. The suspension is then centrifuged, put into a filter, and washed until the chloride ion disappears by testing using AgNO$_3$ solution. The obtained solids are then dried at 80 °C and crushed until smooth, then calcined at a temperature variation of 200, 250, and 300 °C for 4 hours and extracted with XRD [10].
2.6 Pb Metal Adsorption

0.25 g of LAO-TiO₂ composite added to 25 mL of Pb (II) solution with an initial concentration of 50 ppm. Then shaken with a shaker at a speed of 200 rpm. This treatment is carried out for 24 hours. Then filtered the LAO-TiO₂ composite and the filtrate measured by AAS.

2.7 Analysis of AAS Measurement Data

The adsorption capacity determined by using the equation:

\[ Qt = \frac{(C_0 - C_e) \times V}{m} \]

where:
- \( Qt \) = adsorption capacity (mg /g)
- \( C_0 \) = initial concentration of solution (ppm)
- \( C_e \) = final concentration of solution (ppm)
- \( V \) = volume of solution (L)
- \( m \) = mass of adsorbent (g)

3. Results and Discussion

3.1 Synthesis of LAO-TiO₂ Composite by Pillarization Method

The LAO-TiO₂ composites synthesis was done on LAO activated by H₂SO₄. The clay mass variations for the pillarization process 2, 3, and 5 g of clay. Pillarization process begins with the production of a pillarizing agent by mixing TiCl with ethanol to produce Ti(OEt)₄. The solution of Ti-polyhydroxy compound formed then mixed with ion free water to create hydrolysis and form Ti(OH)₄. Intercalation of the pillarizing agent into the montmorillonite silicate carried out by mixing the solution of the pillarizing agent with the clay dispersed in 100 mL of water. The next step is calcination on various temperature, 200, 250, 300 °C. Calcination is done to form stronger metal oxide pillars by converting the compound Ti(OH)₄ complexes into clay-TiO₂.

3.2 Determine the Basal Distance (d₀₀₁) with XRD

3.2.1 LAO Mass Variation

LAO-TiO₂ Composites analysis of X-Ray Diffraction (XRD) carried out at an angle of 2θ: 5 - 60°. The diffractogram produced in the area 2θ below 10° shows the size of the basal distance between the clay layers. In general, the central peak of montmorillonite is in the angle 2θ = 5° that corresponds to field d(001) [14,15]. The analysis results obtained in this study indicate montmorillonite have identified in the angle range of 2θ = 8.68-8.85° (Table 1). The statement corresponds to the results obtained (Table 1), which did not observe any peaks at an angle of 2θ: 5° but can observe at an angle of 2θ = 8°. The basal distance (d₀₀₁) observed in the region of 2θ = 8.3° (d: 10.65 Å) on montmorillonite after pillarization [16]. The shifting of the peak to the left that caused the central peak (2θ = 5°) not observed on the diffractogram or the peak disappears indicating a change in structure due to intercalation. The presence of montmorillonite also strengthened by the presence of a typical peak at an angle range of 2θ = 19° [17]. This result following the research that obtained a typical montmorillonite peak at 2θ = 19.9° (d = 4.45 Å) [16]. Overall, the intercalated LAO has the basal distance sequence from highest to lowest, i.e K5> K3> K2. It indicates that the LAO mass used in the pillarization process can influence the magnitude of the basal distance of montmorillonite itself. The results obtained show that the greater the LAO mass used, the higher the montmorillonite basal distance.
Table 1 LAO-TiO$_2$ composite basal distance (d-spacing) Data.

| Composite LAO-TiO$_2$ | Treatment | Calculation Temperature(°C) | Position(°) | d(001) (Å) |
|-----------------------|-----------|-----------------------------|-------------|------------|
|                       | *without calcination |                              |             |            |
| K2                    | *TK       | 200                         | 8.78        | 10.07      |
|                       |           | 250                         | 8.85        | 9.99       |
|                       |           | 300                         | 8.80        | 10.04      |
|                       | *TK       | 200                         | 8.75        | 10.10      |
|                       |           | 250                         | 8.83        | 10.01      |
|                       |           | 300                         | 8.79        | 10.05      |
| K3                    | *TK       | 200                         | 8.72        | 10.13      |
|                       |           | 250                         | 8.68        | 10.19      |
|                       |           | 300                         | 8.68        | 10.18      |
| K5                    | *TK       | 200                         | 8.81        | 10.03      |
|                       |           | 250                         | 8.81        |             |
|                       |           | 300                         | 8.81        |             |

3.2.2 Calcination Temperature Variations

Characterization carried out on the K2 sample (Fig. 1) shows the basal distance obtained for the sample without calcination is 10.07 Å. However, then it goes down after calcination at 200 °C, then rises again at 250 °C and drops again at 300 °C. In the K3 sample (Fig. 2), the basal distance obtained for the calcined sample is 10.10 Å. Nevertheless, then it goes down after Calcination at 200 °C and become 10.06 Å, and on the temperature of 250 and 350 °C 10.05 Å. The decrease in the basal distance at K2 and K3 after calcination (Table 1) caused by a change in the shape of the pillaring agent from the hydrated form to the oxide form due to dehydration.

Samples K2 and K3 experience a decrease in the basal distance after calcining with high calcination temperature except for K2 at calcination temperature of 200 °C, the basal distance obtained is smaller than at calcination temperatures of 250 and 300 °C. While, other study reported that Ti pillared clay at 200 °C experience an increase in the basal distance but then dropped at 300 °C due to high heating [10]. This result is possible because there has been delamination as one of the models of damage that occurs in laminate composites. One of the factors causing delamination is the separation of lamina (layers) from one another [16].

In the K5 sample (Fig. 3) the basal distance increased after calcining. These results are consistent with the study that reported that clay experienced an increase in basal distance after calcining at 200 °C but then dropped at 300 °C. Meanwhile the clay before calcined (intercalated) has a lower basal distance [10]. Overall, the results obtained indicate that the calcination temperature dramatically affects the distance of the layered montmorillonite structure resulting in its weak nature to the temperature treatment and can experience structural damage at high temperatures marked by decreasing in the montmorillonite basal distance.
Figure 1 LAO-TiO$_2$ composite diffractogram at calcination temperature variation for K2 sample (M: montmorillonite, A: anatase, R: rutile).
Figure 2 LAO-TiO$_2$ composite Diffractogram on calcination temperature variation for K3 sample (M: montmorillonite, A: anatase, R: Rutile).
3.2.3 TiO₂ Phase Analysis

The phase analysis of TiO₂ aims to know TiO₂ formed in LAO after being pillared. Through characterization, using XRD identified two phases of TiO₂ namely the anatase and rutile phases. An anatase phase is a metastable form so it can transform into rutile when given heat treatment. Most of the identified phases corresponding to the crystalline area at (101), (004), (200), and (211) for the anatase phase while the rutile phase corresponds to the crystal area in (101), (200), (111), (210), (211), and (220) [18].

**Figure 3** LAO-TiO₂ composite Diffractogram on calcination temperature variation for K5 sample (M: montmorillonite, A: anatase, R: rutile).
3.3 Lead Metal Adsorption (Pb)
In this study, LAO-TiO₂ composite have applied as Pb metal adsorbent. The results obtained through testing with AAS shown in Table 2. The AAS test results showed that the adsorption capacity obtained ranged from 4.4 - 4.9 mg/g. The percentage of Pb metal adsorption by LAO-TiO₂ composites previously activated with sulfuric acid higher than the percentage of LAO adsorption that was only activated by sulfuric acid. This result shows that LAO-TiO₂ composites synthesized by the pillization method using LAO have been activated by sulfuric acid increase the percentage of LAO-TiO₂ adsorption as Pb metal adsorbent. The adsorption capacity (Table 2) obtained shows the influence of basal distance (Table 1) of clay caused by calcination temperature and composition comparison in composites.

| Composite LAO-TiO₂ | Treatment Without Calcination | Calcination Temperature (°C) | Angle (°) h k l | Intensity | Relative. (%) |
|--------------------|-------------------------------|-------------------------------|----------------|-----------|---------------|
|                    |                               |                               | Anatase        | Rutile    |               |
| *TK                | 200                           | 37.79                         | 0 0 4          | 3.31      |               |
|                    |                               |                               | 2 0 0          | 5.23      |               |
| K2                 | 250                           | 37.72                         | 0 0 4          | 1.76      |               |
|                    |                               | 48.19                         | 2 1 1          | 0.69      |               |
|                    |                               | 54.90                         | 2 1 1          | 4.43      |               |
|                    |                               | 25.47                         | 1 0 1          | 2.56      |               |
|                    |                               | 37.71                         | 0 0 4          | 1.93      |               |
|                    |                               | 25.36                         | 1 0 1          | 5.29      |               |
|                    |                               | 37.65                         | 0 0 4          | 2.14      |               |
|                    |                               | 25.37                         | 1 0 1          | 3.90      |               |
| *TK                | 200                           | 37.74                         | 0 0 4          | 1.42      |               |
| K3                 | 250                           | 37.69                         | 0 0 4          | 1.39      |               |
|                    |                               | 55.26                         | 2 1 1          | 1.55      |               |
|                    |                               | 37.68                         | 0 0 4          | 1.93      |               |
|                    |                               | 54.87                         | 2 1 1          | 4.08      |               |
|                    |                               | 37.78                         | 0 0 4          | 1.92      |               |
|                    |                               | 54.90                         | 2 1 1          | 4.63      |               |
|                    |                               | 25.28                         | 1 0 1          | 3.47      |               |
| *TK                | 200                           | 39.26                         | 2 0 0          | 7.59      |               |
|                    |                               | 25.32                         | 1 0 1          | 3.70      |               |
|                    |                               | 36.29                         | 1 0 1          | 7.87      |               |
|                    |                               | 39.27                         | 2 0 0          | 7.45      |               |
|                    |                               | 41.05                         | 1 1 1          | 6.10      |               |
|                    |                               | 43.86                         | 2 1 0          | 1.74      |               |
|                    |                               | 54.10                         | 2 1 1          | 14.59     |               |
|                    |                               | 55.14                         | 2 1 1          | 2.79      |               |
|                    |                               | 56.44                         | 2 2 0          | 4.80      |               |
| K5                 | 200                           | 37.63                         | 0 0 4          | 1.48      |               |
|                    |                               | 48.09                         | 2 0 0          | 0.50      |               |

4. Conclusions
Based on the results obtained, it can conclude that LAO-TiO₂ composite with LAO mass variations of 2, 3, and 5 g and calcination temperatures of 200, 250, and 300 °C have been successfully synthesized
using the pillarization method. The results of characterization with XRD showed a reflection of d (001) montmorillonite at an angle range of $2\theta = 8.68-8.85^\circ$. The most considerable basal distance (d-spacing) obtained in the K5 sample (5 g LAO) after calcining at 200 °C which is 10.19Å. Application of LAO-TiO$_2$ composite as Pb metal adsorbent showed that the adsorption capacity ranged from 4.4 to 4.9 m/g.

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