ORGANOMETALLIC $[\text{Fe}_2\text{O} (\text{OOCC}_3\text{H}_5)\text{H}_2\text{O}] (\text{NO}_3)$ AS INTERCALANT OF BENTONITE

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ABSTRACT

Intercalation of organometallic compounds $[\text{Fe}_2\text{O} (\text{OOCC}_3\text{H}_5)\text{H}_2\text{O}] (\text{NO}_3)$-$\text{nH}_2\text{O}$ on bentonite by weight ratio of bentonite:organometallic $(1 : 1); (1 : 2); (1 : 3)$; and $(1 : 4)$ has been carried out. The intercalation bentonite was characterized using FT-IR spectrophotometer, XRD and XRF analyses. Characterization using FT-IR spectrophotometer showed higher intensity of peak wavenumber at 470.6 cm$^{-1}$ for Fe-$\text{O}$ vibration on the ratio $(1 : 3)$. While XRD characterization showed the shift of diffraction angle of 20 was 5.24° and has basal spacing of 16.8 Å. In the XRF characterization, the intercalation process of organometallic compounds $[\text{Fe}_2\text{O} (\text{OOCC}_3\text{H}_5)\text{H}_2\text{O}] (\text{NO}_3)$-$\text{nH}_2\text{O}$ on bentonite was occurred optimally with percentage of metal oxide reached 71.75 %.

Keywords: intercalation, bentonite, organometallic, $[\text{Fe}_2\text{O} (\text{OOCC}_3\text{H}_5)\text{H}_2\text{O}] (\text{NO}_3)$-$\text{nH}_2\text{O}$.

INTRODUCTION

Bentonite is a layered material contain inorganic minerals who can find easily in natural (Abderrazek et al, 2016). Bentonite are used as adsorbent, catalyst, ion exchange, and various industrial applications (Santos et al, 2016). In the application of bentonite as adsorbent have some weakness, due to impurities of some minerals that can make the adsorption is not optimal. Therefore, to optimize the adsorption process then bentonite should be activated. The process activation of bentonite is intended to separate the impurities naturally from bentonite. In general, there are two step of activation process for activation including physically and chemically processes. On physical processes is needed to combustion in a high temperature causes water molecules from crystal and other inorganic constituents, so that two cluster OH who bounded each other, they have to detach one water molecule (Scoonheydt et al, 2008), while on chemical processes by using acid mineral such as sulfuric acid is intended to omit the metals that be found in bentonite and chemical processes by using acid mineral such as sulfuric acid is intended to omit the metals that be found in bentonite and banded in ion H$^+$ which is originated from acid. therefore the layer who as an insertion entry will be larger. The modification of bentonite is expected to produce bentonite which can be conducted by insertion of molecules, compounds, and organic/inorganic complexes.

The research of layer materials intercalation including bentonite using metal oxides shows distance between layer is a little small (Yang et al, 2005). Thus higher compound with positive charge is needed as intercalant of bentonite. This research was conducted an intercalation process of bentonite using a organometallic compound as insertion. Organometallic compound $[\text{Fe}_2\text{O} (\text{OOCC}_3\text{H}_5)\text{H}_2\text{O}] (\text{NO}_3)$-$\text{nH}_2\text{O}$ have advantage such as high reactivity, high cation size, and also easy to synthesis. In this research, various weight of organometallic compound has been used to know the optimal intercalation process. The ratio of bentonite:organometallic complex was $(1:1); (1:2); (1:3)$; and $(1:4)$. Product of insertion was characterized by spectrofotometer FT-IR, XRD, and XRF analyses in order to know the optimal insertion process.

EXPERIMENTAL SECTION

Materials

Natural bentonite was obtained from Jambi Province, Indonesia. Sulfuric acid, Iron(III) nitrate, sodium benzoate, and sodium hydroxide was obtained from Merck and directly used after purchased. Deionized water was supplied from Purite®.

Preparation of Bentonite (Ozcan, 2016)

The nature bentonite is prepared by physically and chemically processes. 100 g of natural bentonite was heated using furnace at 400 °C for two hours then the material was kept at room temperature over night. The bentonite then was acidified using sulfuric acid for two hours. Bentonite after treatment was characterized using FT-IR spectrophotometer, XRD, and XRF.

Synthesis of Organometallic Compunds $[\text{Fe}_2\text{O} (\text{OOCC}_3\text{H}_5)\text{H}_2\text{O}] (\text{NO}_3)$-$\text{nH}_2\text{O}$ (Uchida et al, 2008)

Synthesis of organometallic compounds was carried out by mixing a 32 g of iron(III)nitrate that has been dissolved in 100 mL of water. In the solution was added 24 g sodium benzoate and the mixtures were stirred by magnetic stirrer for 15 minutes. The brown orange solution will be formed, filtered, washed by water to obtain $[\text{Fe}_2\text{O} (\text{OOCC}_3\text{H}_5)\text{H}_2\text{O}] (\text{NO}_3)$-$\text{nH}_2\text{O}$. Organometallic compound was characterized using FT-IR spectrophotometer.

Intercalation of Bentonite with Organometallic Compound $[\text{Fe}_2\text{O} (\text{OOCC}_3\text{H}_5)\text{H}_2\text{O}] (\text{NO}_3)$-$\text{nH}_2\text{O}$ (Gil et al, 2009)

Bentonite was mixed with 200 mL water to form white suspension (reactant A). Organometallic compound as intercalant compound was prepared by adding 100 mL sodium hydroxide (NaOH) 1 M into 15 g of organometallic compound (reactant B). Reactant A and B was mixed and the mixtures was...
refluxed with gentle stirring for 24 hours at room temperature under nitrogen gas. The product intercalation of bentonite with organometallic compounds was washed with water and dried at 90°C. In order to know the optimum intercalation process, the ratio of bentonite:organometallic compound was applied (1:1); (1:2); (1:3); and (1:4). The bentonite intercalated organometallic compounds were characterized using FT-IR spectrophotometer, XRD and XRF analysis.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of Organometallic Compounds** [Fe₃O(OOCC₆H₄)₆(H₂O)₃][NO₃]·nH₂O

Synthesis of organometallic compounds [Fe₃O(OOCC₆H₄)₆(H₂O)₃][NO₃]·nH₂O was carried out under air conditions without protection of an inert gas, which has different from almost synthesis of organometallic complexes (Szafran et al., 1991). Organometallic compounds [Fe₃O(OOCC₆H₄)₆(H₂O)₃][NO₃]·nH₂O has light brown crystals. The organometallic compounds were then characterized using FT-IR spectrophotometer aimed at identifying functional groups. FT-IR spectra of natural organometallic compounds were characterized using FT-IR spectrophotometer aimed to identifying functional groups. FT-IR spectra of natural organometallic compounds, which has also strongly appeared by vibration at 3410.1 cm⁻¹. The data of wavenumbers of organometallic compounds [Fe₃O(OOCC₆H₄)₆(H₂O)₃][NO₃]·nH₂O are summarized in Table 1.

**Identification of Natural Bentonite and Bentonite Intercalated Organometallic Compounds** [Fe₃O(OOCC₆H₄)₆(H₂O)₃][NO₃]·nH₂O using FT-IR Spectrophotometer

Before the intercalation process, natural bentonite was characterized using FT-IR spectrophotometer aimed at identifying functional groups. FT-IR spectra of natural bentonite at Figure 2(A) shows vibration of Al-OH-Al vibration in wavenumber 3626.1 cm⁻¹ and vibration of Al-OH-Al at wavenumber 910.4 cm⁻¹. The water content that acts as an interlayer molecule on bentonite appears as a stretch vibration of H-O-H observed at the wavenumber 3448.7 cm⁻¹ while the H-O-H bend vibration appears at 1635.6 cm⁻¹. The absorption at 1038.3 cm⁻¹ indicate the bend vibration of Si-O-Si (Derrick et al., 1999).

There are two stages to remove impurities on bentonite i.e. heating at 400°C and acidification using sulfuric acid (H₂SO₄). On bentonite with heating at 400°C causes a change in deformation of the H₂O bond, since the existing H₂O is released, therefore the bentonite peak becomes widened and expanded so that it eventually collapses at 400°C. The success of this process are characterized by changes in functional groups with the shift in the wavenumbers as seen in Figure 2 (B). The absorption bands in Figure 2 (B) of the Al-OH-Al vibration are shifted at 3695.6 cm⁻¹ and quartz minerals are shifted at 694.3 cm⁻¹ wavenumbers. Vibration of stretch and bend of H-O-H appear on the same wavenumber in natural bentonite, i.e at 3448.7 cm⁻¹ and at 1635.6 cm⁻¹. The stretching and bending vibration of Si-O-Si are shown in the 1033.8 cm⁻¹ and 532 cm⁻¹ and the Al-OH-Al bending vibrations remain at the 910.4 cm⁻¹.

The second activation process of natural bentonite is acidification using sulfuric acid. Acidification using sulfuric acid aims to remove small metals as impurities attached to bentonite. This activation will open interlayer of bentonite. FT-IR spectrum in Figure 2 (C) shows the shift of wavenumbers of bentonite after acid activation. The absorption band for Al-OH-Al stretching vibration shifts to wavenumber 3672.4 cm⁻¹. The H-O-H stretching vibration shifts to wavenumber 3425.5 cm⁻¹ and the Si-O-Si stretching vibration stay at the wavenumber 1041.5 cm⁻¹. The bending vibrations of Al-OH-Al appearing at 910.4 cm⁻¹ and the H-O-H bending vibrations appear at 1635.6 cm⁻¹. Similar to natural bentonite and bentonite heating at 400°C there is no shift in wavenumbers, stretching and bending vibrations of Si-O-Si stay at wavenumber 532 cm⁻¹.

Intercalation process of bentonite with organometallic compound was completely conducted by adding water to bentonite which is continued with addition of sodium oxide (NaOH). This goal is to build a suspension for easy intercalation process. In the process of intercalation, there is no contact of oxygen form the air, which has protected by introducing N₂ gas. The process of intercalation of bentonite with these

| Wavenumber (cm⁻¹) | Functional groups |
|-------------------|-------------------|
| 3410.1            | ν(O-H)            |
| 3070.6            | ν(Als-H)          |
| 1419.6-1612.4     | ν(C-H), ν(C-O), ν(C=C) |
| 709.8             | ν(N-O)            |
| 469.0             | ν(Fe-O)           |

Figure 1. shows the peaks of functional groups of organometallic compounds appearing at wavenumbers 400-4000 cm⁻¹. The main peaks of the organometallic compound appear at the 469 cm⁻¹ for Fe-O vibration (Hasegawa et al., 2007). At the wavenumber 709.8 cm⁻¹ for the N-O vibration as the counter ion of the benzoate ligand. [Fe₃O(OOCC₆H₄)₆(H₂O)₃][NO₃]·nH₂O has a C-H vibration, the C-O vibration, and the C-H vibration, which appears at the wavenumbers 1419.6 cm⁻¹, 1612.4 cm⁻¹ (Lesbani et al., 2008). Wavenumber 3070.6 cm⁻¹ is indicated for Ar-H bend vibration. The absorption band at 1689.6 cm⁻¹ for O-H vibration indicating the presence of water ligands in organometallic compounds, which has also strongly appeared by vibration at 3410.1 cm⁻¹. The data of wavenumbers of organometallic compounds [Fe₃O(OOCC₆H₄)₆(H₂O)₃][NO₃]·nH₂O are summarized in Table 1.
organometallic compounds is carried out by varying the weight ratio, between the weight of the bentonite and the organometallic weight: (1: 1), (1: 2), (1: 3) and (1: 4). This experiment was carried out in order to know the optimum intercalation process.

The results of intercalation of organometallic compounds with the weight ratio of (1: 1), (1: 2), (1: 3) and (1: 4) were characterized using FT-IR spectrophotometer to see functional groups formed as in Figure 3. In Figure 3 (D), it is seen that the vibration of the Fe-O organometallic compound appears at a wavenumber of 462.5 cm\(^{-1}\). The strong of absorption bands for Al-OH-Al stretch vibrations shifted to 3618.4 cm\(^{-1}\). The O-H stretching vibration widened at 3448.7 cm\(^{-1}\). This indicates the presence of an O-H group on benzoate as well as a benzoate ligand in the form of C-C vibration, C = C vibration, C = O vibration appearing at wavenumbers 1388.7 - 1635 cm\(^{-1}\). Si-O-Si stretch vibration at wavenumber 1018.4 cm\(^{-1}\) and Al-OH-Al bending vibrations that appear at wavenumbers 910.4. Stretching and bending vibrations of Al-O-Si are seen at 524.6 cm\(^{-1}\).

In the result of bentonite intercalation of organometallic compound Figure 3 (F) (1: 3) it is appeared that the emergence of strong absorption at wavenumber 470.6 cm\(^{-1}\) for vibration of Fe-O organometallic compound. The presence of absorbing bands for the OH vibration is widened in the wavenumber 3448.7 cm\(^{-1}\). The vibration of the C=C, the vibration C = O occurs at the wavenumbers 1388.7 – 1635 cm\(^{-1}\), Si-O-Si at 1033.8 cm\(^{-1}\), Al-OH-Al buckling vibrations that appear at 910.4 cm\(^{-1}\) wavenumbers, whereas, stretching vibration of Al-O-Si bends are appeared at 524.6 cm\(^{-1}\). These vibrations are almost similar with vibration in Figure 3G.

The FT-IR spectra of Figure 3 show that the variation in the weight ratio of intercalated bentonite did not differ significantly. In order to know the optimal intercalation process, characterization using XRD was conducted for further analysis.

![Figure 2. FT-IR spectrum of A) natural bentonite. B) bentonite with heating at 400 °C. C) bentonite with acidification](image)

![Figure 3. FT-IR spectrum of Intecalated Bentonite, D) 1:1, E) 1:2, F) 1:3, G) 1:4.](image)

**Identification of Natural Bentonite and Bentonite Intercalated Organometallic Compounds**

**[Fe_3O(OOC_{6}H_{5})_{6}(H_{2}O)]_{3} (NO_{3})_{n}H_{2}O using X-Ray Diffraction**

The objectives analysis using XRD is to look at the structural changes that occur in bentonite after intercalation by observing the diffraction angle change (2θ). Bentonite is a class of minerals that contain montmorillonite as main fraction. (Brindley et al, 1990.). Bentonite shows the observed montmorillonite at 2θ from 3 - 6°. This is evident from the diffraction angle (2θ) of natural bentonite, bentonite with heating at 400°C and bentonite with acidification using sulfuric acid i.e the shifting angle of montmorillonite diffraction at 4.1°, 3.3° and 4.1°.

The existence of diffraction at the 2θ angle of 20° and 26° as shown in Figure 4 (A), (B), and (C) indicates the existence of
other minerals like quartz and illite. If bentonite is intercalated by molecules and compounds, there will be XRD diffraction patterns shift of montmorillonite, quartz, and illite (Bertella et al., 2011). In Figure 4 (D) shows the weight ratio (1:1), there is a shift in the diffraction angle of 2θ montmorillonite in bentonite of 5.2° with basal spacing of 16.7 Å.

In comparison (1:2) presented in Figure 4 (E) also seen shift angle of diffraction 2θ montmorillonite at 5.3° with basal spacing 16.4 Å. In Figure 4 (F), the ratio (1:3) also shows a shift in the angle of diffraction of 2θ montmorillonite at bentonite of 5.2° with basal spacing 16.8 Å. The shift of the diffraction angle 2θ in the ratio of the weight of bentonite to the organometallic compound [FeO(OOCC6H5)3(H2O)]3(NO3)2nH2O can be seen in Figure 4 (D), (E), (F), and (G).

Figure 4 Diffraction patterns of A) natural bentonite, B) bentonite with heating at 400 °C, C) bentonite with acidification D) bentonite:organometallic 1:1, E) 1:2, F) 1:3, and G) 1:4.

In the ratio (1:4) shown in Figure 4 (G) it does not have a 2θ montmorillonite diffraction angle shift in bentonite but has a basal spacing of 24 Å. This cannot be said to be optimal because there is no shift in the diffraction angles of 2θ montmorillonite. The success of bentonite intercalation of organometallic compounds can be seen from the shifting angle of 2θ montmorillonite from 3 - 6°. In Figure 4 (G) the entry of organometallic compound is not only in 1 layer, but in other layers as well.

Therefore, the results of the XRD characterization data can be stated that in the weight ratio of bentonite: organometallic compound (1:3) is more optimally intercalated. To be able to demonstrate the optimal intercalation results, another process of characterization was conducted using XRF analysis (X-ray Fluorescence).

Identification of Natural Bentonite and Bentonite Intercalated Organometallic Compounds [FeO(OOCC6H5)3(H2O)]3(NO3)2nH2O using X-Ray Fluorescence Sinar-X (XRF)

Characterization using XRF aims to look at the metal oxide compositions contained in natural bentonite, activated bentonite and intercalated bentonite with organometallic compound in the ratio (1:1), (1:2), (1:3) and (1:4). The results data of XRF analysis is presented in Table 3. In Table 3 it is seen that natural bentonite is composed of montmorillonite mineral containing silica and alumina which yield percentage amount of Al2O3 and SiO2 metal oxides of 17% and 43.6%. Other measured metal oxides are P2O5 with a percentage of 0.71%, K2O with a percentage of 0.2%. Composition of CaO with percentage as much as 0.99%, TiO2 with percentage 1.87%, V2O5 with percentage 0.11%, Cr2O3 with percentage 33.39%, NiO with percentage 0.87%, CuO with percentage 0.15% ZnO with a percentage of 0.09%, Re2O7 with 0.11% percentage, and Eu3O4 with 0.2%.

With the activation of natural bentonite causes the value of metal oxide content decreases. This is in accordance with the activation purpose of removing impurities on bentonite in the form of small metals. Activation of the first bentonite by heating at 400 °C indicates that some oxides are decreased, as CaO decreases its percentage to 0.92%, V2O5 to 0.07%. While other metal oxides have the same percentage as natural bentonite despite the presence of binding metal oxides, such as TiO2 to 1.91%, Cr2O3 to 0.11%, Mn to 0.19%, Fe2O3 to 33.57%. This reduction in metal oxide content due to metal oxides on the bentonite is already lost oxide activation due to heating to form other inorganic substances.

Tabel 2. Metal oxide composition using XRF

| Sample | Al2O3 (%) | SiO2 (%) | Fe2O3 (%) | P2O5 (%) | K2O (%) | CaO (%) | TiO2 (%) | V2O5 (%) | Cr2O3 (%) | NiO (%) | CuO (%) | ZnO (%) | Re2O7 (%) | Eu3O4 (%) |
|--------|-----------|----------|-----------|----------|--------|---------|----------|---------|----------|--------|---------|---------|-----------|----------|
| BAO    | 17        | 43.6     | 33.7      | 0.7      | 0.2    | 0.07    | 1.3      | 0.1     | 0.07     | 0.02   | 0.12    |
| B400   | 17        | 43.7     | 33.5      | 0.7      | 0.2    | 0.07    | 1.3      | 0.1     | 0.07     | 0.02   | 0.12    |
| BAA    | 11        | 28.8     | 39.2      | 0.1      | 0.4    | 1.7     | 0.52     | 0.08    | 0.17     |
| HA1    | 10        | 20.7     | 55.2      | 0.67     | 0.67   | 7.45    | 0.18     | 0.15    |
| HD2    | 5.2       | 23.5     | 62.9      | 0.43     | 0.10   | 1.07    | 0.03     | 0.31    |
| HD3    | 6         | 28.7     | 71.7      | 0.42     | 0.084  | 0.064   | 0.31     | 0.02    |
| HD4    | 0.11      | 19       | 70.12     | 0.45     | 0.004  | 0.025   | 0.072    | 0.01    | 0.060 |

AO: natural bentonite ; B400: physical activation at 400 °C; BAA: chemical activation using sulfuric acid; HA1: (1:1); HB2: (1:2); HC3: (1:3); HD4: (1:4).

The second activation of natural bentonite by adding sulfuric acid. This causes a decrease in the percentage of metal oxide. The decrease in the percentage of metal oxide on the acidified bentonite is shown in Table 2. The decrease of metal oxide is Al2O3 to 11%, SiO2 to 28.8%, K2O to 0.19%, TiO2 to 1.73%, V2O5 to 0.06%, Cr2O3 becomes 0.06%, Mn to 0.17%, Fe2O3 to 29.2%, NiO to 0.88%, and CuO to 0.15%.

Furthermore, to determine the results of intercalation of bentonite with organometallic compound [FeO(OOCC6H5)3(H2O)]3(NO3)2nH2O in the ratio (1:2), (1:3) and (1:4) are performed by observing the oxide content, especially the Al2O3 and SiO2 metal oxides located on the intercalation layer. Then the intercalation compound content of organometallic compound causes the metal oxide of Fe2O3 to increase. The result of XRF analysis in Table 2 shows that the ratio of weight (1:2) and (1:3) has significant decrease of Al2O3, Al2O3 has a percentage of 8.2%,
SiO₂ has a percentage of 23.9% and an increase of Fe₂O₃ to 63, 89%.

However, in the weight ratio (1: 3) the metal oxide decreased Al₂O₃ to 6.2%, SiO₂ had a percentage of 18.7% and the increase of Fe₂O₃ to 71.75%. Therefore, the result of bentonite intercalation of the optimal organometallic compound is shown in the ratio (1: 3) because it contains a lot of Fe₂O₃ composition as well as decreasing the good percentage of each treatment.

**CONCLUSION**

Bentonite intercalated organometallic compounds [Fe₃O(OOCC₆H₅)₆(H₂O)₃](NO₃) showed optimal intercalation process in the weight ratio (1: 3). Characterization using XRD showed an diffraction at 5.2 ° having a basal spacing of 16.8 Å. Further characterization using XRF showed the intercalation (1: 3) has percentage 12.75% of metal oxide.

**ACKNOWLEDGEMENT**

We thank to Prof. Aldes Lesbani for fruitful discussion related with this research. HPU and DMS thanks to Integrated Research Laboratory, Graduate School, Sriwijaya University for laboratory equipment and support.

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