

# Synthetic of Allophane-Like and Adsorption for Lead (Pb) Heavy Metals

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**Abstract.** A synthesis allophone-like had been done from aluminum nitrate nonahidrat ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and tetraethyl orthosilicate (TEOS). This study aims to determine synthesis of allophane-like based on variations in the ratio of Al/Si is applied as an adsorbent for the lead (Pb) metal. The study was conducted with ratio variation Al/Si 0.5; 0.75; 1; 1.25 and 1.5 from solution volume nonahidrat ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and TEOS at pH 3-4 calcined at temperature of 400°C. The adsorption type is determined by the adsorption isotherm. The results of the research shows that allophane-like can be synthesized from a solution of nonahidrat ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and TEOS with a variation of the ratio of Al/Si 0.5; 0.75; 1; 1.25 and 1.5. Allophane-like has function groups of -OH group; spanning asymmetrical form of O-Si-O/O-Al-O; Si-O/Al-O bending vibration and relatively weak absorption which strengthen their OH group. The results of allophane-like adsorption capacity of 1.61 mg/g in the ratio Al/Si of 1.5 at pH 4 with a contact time of 30 minutes with a percentage of 80.77% adsorption. The adsorptions of Pb heavy metals with allophane-like tend to follow the type of adsorption isotherms of Freundlich or physics.

## 1. Introduction

Indonesia is one of the most active volcanic regions in the world that has abundant resources of Andisol soil. Andisol soil contained mineral allophane aluminosilicate hydrate with a chemical composition that is not fixed and is shown in a ratio Al/Si which can vary 1-2. Allophane has diameter of 3-5 nm with high surface area and active function groups named silanol (Si-OH) and aluminol (Al-OH). Allophane has absorption and high cation exchange so that it can be used as an adsorbent, for example, the adsorbent of heavy metal ions in industrial waste [1].

In the previous research, allophane-like synthesis has been done using the ratio of Al/Si, nonahidrat solution of aluminum nitrate nonahidrat ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and tetraethyl orthosilicate (TEOS) with a ratio Al/Si 2; 1.5; 1 and 0.5 [2]. According to Denaix L *et al.* (1999) [3], allophane with a ratio Al/Si = 2 has similarities with imogolite with smaller pore diameter which is 2.4 nm. The Allophane heated at a temperature of 400°C is able to open the pores so it will increase the power to adsorb [4]. Therefore, the study was conducted synthetic allophane-like by using a solution of TEOS and nonahidrat ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) with the ratio Al/Si 0.5; 0.75; 1; 1.25 and 1.5 and then heated at a temperature of 400°C. Allophane-like can be used as an alternative of heavy metal adsorbent. Heavy metals are used in this study is a lead (Pb) heavy metal. Dispersion element Pb can also occur due to the disposal of waste from metal mining industry. This should be wary because it could pollute the environment that may lead to the emergence of various illness or death.



## 2. Experimental

### 2.1. The Synthetic and Characteristics of allophane-like

The conduction of allophane-like was started by adding TEOS solution to nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) 0.1 M solution. The ratio Al/Si was made according to the Table 1.

**Table 1.** Ratio Al/Si allophane-like

Ratio volume Al/Si	Ratio mol Al/Si	Volume $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Volume TEOS
0.5	0.006	50 mL	100 mL
0.75	0.009	50 mL	66.67 mL
1	0.012	50 mL	50 mL
1.25	0.015	50 mL	40 mL
1.5	0.018	50 mL	33.33 mL

150 mL NaOH solution put into the sample solution with the addition of 50 mL/hr with stirring and heating at room temperature. The pH of the solution set 3-4 with the addition of concentrated  $\text{H}_2\text{SO}_4$  in a state of agitation. The sample solution is kept overnight to form a gel. The gel was heated for 7 days at a temperature of  $100^\circ\text{C}$  [2]. The samples were dried calcined at a temperature of  $400^\circ\text{C}$ .

### 2.2. Characterization of allophane-like

In the characterization of allophane-like the activity process were done with function group analysis of allophane-like, crystallinity analysis of allophane-like, morphology analysis of allophane-like, surface analysis of allophane-like, acidity analysis of allophane-like.

### 2.3. Adsorption Capacity of allophane-like to Pb metal

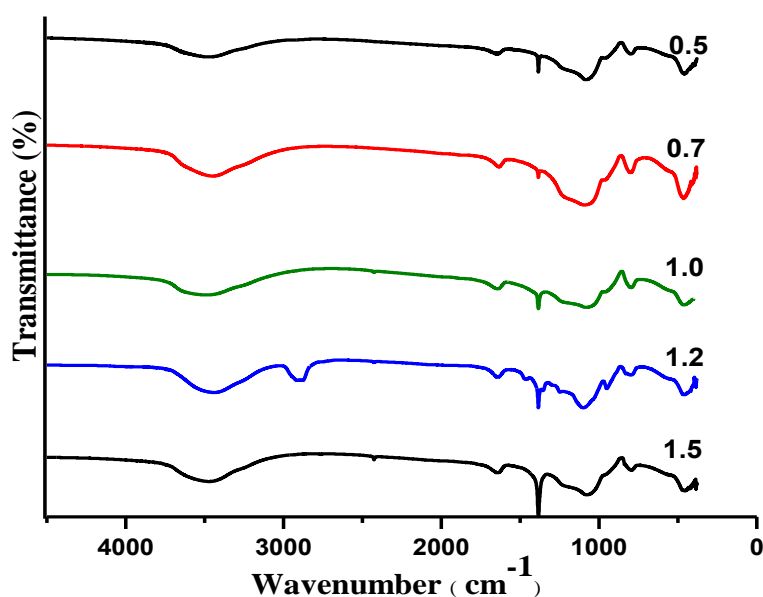
In the adsorption capacity of allophane-like for Pb ions metal were conducted solution of  $\text{HNO}_3$  0.05 M, and standard solution of Pb ions of 0 ppm; 1 ppm; 2 ppm; 3 ppm and 4 ppm. The determination of adsorption isotherms was done in optimum condition.

## 3. Result and Discussion

Allophane was synthesized from TEOS as silica source solution and nonahidrat ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) as a source of alumina. The ratio Al/Si used was 0.5; 0.75; 1; 1.25 and 1.5. The ratio of Al/Si was made using a volume ratio of nonahidrat ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) with volume variation of TEOS solution. The material made by using the ratio of the volume will produce a different mole ratio with natural allophane so that the material is called allophane-like or a material which has similarities with allophane. Allophane-like has shape and white turbid.

### 3.1. Analysis of functional groups allophane-like

IR analysis results for each ratio Al/Si allophane-like shown in Figure 1.



**Figure 1.** IR spectrum for allopahane-like ratio Al/Si = 0.5; Al/Si 0.75; Al/Si = 1; Al/Si = 1.25 and Al/Si = 1.5

Based on the results of FTIR analysis, each ratio of Al/Si has four main areas of infrared absorption. Functional areas shown in the wave number 3439; 3443; 3484; 3448 and 3463  $\text{cm}^{-1}$  which is -OH of  $\text{H}_2\text{O}$ . The wave number about 1600  $\text{cm}^{-1}$  indicates strengthen the absorption of H-OH group. Regional wave number of 962-1247  $\text{cm}^{-1}$  indicates the group O-Si-O or O-Al-O. Regional wave numbers 408-563  $\text{cm}^{-1}$  showed absorption of Si-O or Al-O. In the area of wave number of about 1400  $\text{cm}^{-1}$  which appears on each ratio Al/Si shows the area of Al-OH or Si-OH is often called the fingerprint region [5].

### 3.2. Analysis crystallinity of Allopahane-like

In diffractogram of allopahane-like do not show high crystallinity of allopahane-like at all ratios Al/Si. The allopahane-like sample showed an amorphous structure with a sloping peaks. According to [6] diffractogram allopahane have amorphous form. Allopahane-like has a low crystallinity because the calcination temperature treatment performed on samples at low temperatures [7]. The heating process at allopahane-like performed at a temperature of 400°C construct amorphous structure with high irregularity of crystalline allopahane.

In this study, it is also conducted the heating at a temperature of 600°C. The results of diffractogram of allopahane-like at the heating temperature of 600°C has a crystallinity higher than the heating temperature of 400°C. Diffractogram of allopahane-like with a heating temperature of 600°C has similarities with allopahane diffractogram according to the data JCPDS number 38-0449. Allopahane-like at the heating temperature of 600°C is not used as an adsorbent to heavy metals Pb due to have a small adsorption capacity as an adsorbent. According to Meima *et al.* (2002) [8], allopahane have no a high thermal resistance so that if it is done in a high-temperature heating, the surface area will decrease and cause the adsorption capacity decreases. According to Reinert *et al.* (2011) [4], the maximum adsorption capacity allopahane-like performed at a temperature of 400°C. Allopahane-like has a lower crystallinity compared with natural allopahane. Natural allopahane still contains several other minerals such as feldspar, gibbsit, kaolinite and montmorillonite.

### 3.3. Analysis of the surface morphology of the allophane-like

The results of SEM analysis can be seen that the allophane-like ratio Al/Si 0.5; 0.75; 1; 1.25 and 1.5 have morphology chunks shaped. Allophane has a surface morphology with irregular spherical granules with a rather dark color and spread evenly [8]. Allophane-like shaped chunk more than the natural allophane. This is because in the natural allophane still contains other minerals that may affect the structure of the surface morphology.

### 3.4. Allophane-like adsorption capacity to heavy metals Pb

Allophane synthesis adsorption capacity test of synthesized Allophane was conducted to determine allophane-like ability to absorb heavy metals lead (Pb). Allophane-like used are allophane-like composition of Al/Si 0.5; 0.75; 1; 1.25 and 1.5.

Factors that affect the adsorption of which is the contact time between the adsorbent and the adsorbate and the level of acidity (pH). In this study the variation of contact time and pH used to determine the optimum conditions of adsorption of heavy metal ions Pb by allophane-like. Variations contact time used is 30, 60, 90 and 120 minutes, while the pH variation is used 3-7. Fixed variables used are the number of adsorbent and adsorbate volume. Pb adsorption analysis is based on the concentration of the absorbed.

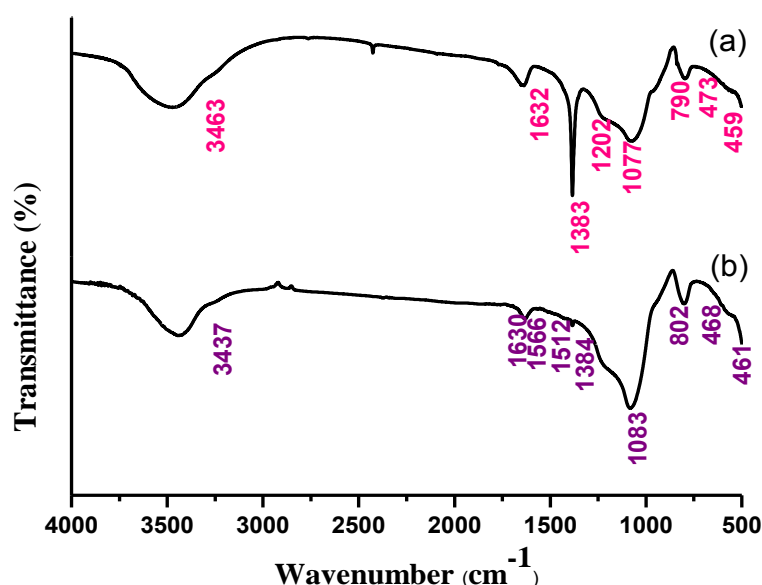
In the performance test diagram allophane-like, it can be seen that the higher the pH, the average adsorption capacity has increased to the optimum conditions and it will fall back. In each ratio Al/Si pH optimum adsorption of heavy metal ions Pb is at pH 4. This is supported which states that the adsorption of heavy metal ions Pb maximal at pH 4. At low pH ( $< 4$ ) there will be protonated resulting in the  $\text{H}_3\text{O}^+$ . This will lead to competition between  $\text{Pb}^{2+}$  with  $\text{H}_3\text{O}^+$  to bind to the negative sites adsorbent so that absorption of adsorbate will be disrupted. The resulting adsorption capacity has a smaller number. At high pH, there will be  $\text{Pb}(\text{OH})_2$  so that the absorption of the adsorbent will be reduced then the number of the adsorption capacity will decrease [9].

In this study, the respective ratios Al/Si has the optimum contact time at 30 minutes. Contact time is the time required by adsorbent to absorb heavy metal ions in the adsorbate. Pb metal ions will stick to the surface of the adsorbent until the optimum contact time. When the contact time was enough or superheated then Pb metal ions cannot be taken by the adsorbent surface and be released back into solution. This will result in reduced adsorption capacity value or decreased.

Adsorbent with the most optimum absorption is at ratio of Al/Si 1.5 to pH 4 and a contact time of 30 minutes. Adsorption capacity obtained was 1.6160 mg/g, which means as much as 1.6160 mg Pb ions are absorbed from 0.01 grams allophane-like are used. The concentration of metal ions Pb absorbed an average of 1.6160 ppm of 2 ppm concentration of the initial solution in 10 mL of solution with the percentage of metal ions Pb adsorbed is 80.77%. Percentage absorption of heavy metal ions Pb using allophane-like in optimum condition has better results when compared with the adsorption of metal ions Pb with natural allophane, which has a percentage of 46.90% [10]. This is because the presence of these minerals of natural allophane so the ability of adsorbent is less.

Allophane-like with optimum adsorption results were analyzed to determine the surface area. The surface area is showed in the number of total surface area of the sample in the form of powder in each sample mass. The larger of the surface area, the greater the absorption of heavy metal ions is. In this study, allophane-like with maximum adsorption results is in ratio Al/Si 1.5.

Allophane-like has a surface area of 201.558  $\text{m}^2/\text{g}$ . When compared with natural allophane, allophane-like has a greater surface area than the natural allophane has a surface area of 85.529  $\text{m}^2/\text{g}$ . The difference in the surface area of natural allophane and allophane-like is 116.029  $\text{m}^2/\text{g}$ . This is what causes adsorption of allophane-like is greater than the natural allophane.



**Figure 2.** Analysis of the function groups before (a) and after (b) adsorption

Allophane-like before and after the adsorption shifted in 1383 into 1384; 1427; 1512; 1586 and 802  $\text{cm}^{-1}$  which indicate a shift in the group O-Si-O or O-Al-O. The shift guessed because the hydrogen bonds between the silanol or aluminol with an adsorbent. Shifting absorption hydroxyl group (OH) was 3463  $\text{cm}^{-1}$  to 3437  $\text{cm}^{-1}$ . The formations of hydrogen bonds lead to the lower binding energy group O-H on Si-OH or Al-OH. The shift in the wave number of hydroxyl groups is also caused by the bonds between Pb metal with oxygen of the hydroxyl group. The metal that has been absorbed by the group Si-OH or Al-OH in the adsorbent will result in an increase of length and falling bond between the binding energy of the oxygen ions with hydrogen ions (O-H bonds) that causes the bond between them became weaker [11].

Active sites owned allophane Si-OH/ Al-OH, -O-Si-O-/O-Al-O- and Al-O-/Si-O-. Adsorption occurs when the allophane-like oxygen ions on the surface of Pb allophane binding so that it will form a bond Si-O-Pb or Al-O-Pb. Pb which acts as a Lewis acid will receive a free electron pair of O which acts as a base lewis. The electron paired by O and Pb will form a coordinate covalent bond. In the active group -O-Si-O-/O-Al-O- and Al-O-/ Si-O- will donate a lone pair on the Pb so that it will form a chemical bond well. The more oxygen ions on the surfaces, the more metal ions Pb absorbed by the adsorbent. This will make the adsorption capacity of greater number.

The determining of type of adsorption is done by determining the adsorption isotherm. The adsorption process according to the Langmuir showed that the interaction between Pb with allophane surface is limited to a single layer formation. Freundlich isotherm occurs in physics where the intermolecular force is greater than the force between molecules. In physics adsorption, heavy metals Pb is not strongly bound by allophane-like active sites that would cause re-release or desorption. Interactions occurred by heavy metals Pb enters through the pores of allophane-like and interacting with a weak binding energy van der Waals bonding. The weak force causes adsorbat can move from one surface to the other surface of the adsorbent. To find the equation corresponding to the Langmuir or Freundlich isotherm it can be seen from the correlation coefficient ( $R^2$ ) of the respective linear graph. The  $R^2$  score close to 1 means that the types of adsorption isotherms tend to follow them. Based on the results of linear regression in this study, Langmuir isotherm has a score of  $R^2$  0.544 with line equation  $y = 0.192x + 3.252$  while Freundlich isotherm has score of  $R^2$  0.974 with line equation  $y = 0.867x - 0.529$ . The  $R^2$  on Freundlich isotherm is close to 1 and higher when compared to the value

of R2 in the Langmuir isotherm that the adsorption type of research is likely to follow Freundlich isotherm or physics.

#### 4. Conclusion

The synthesis of allophane-like has successfully done with a solution of TEOS and nonahidrat ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) based on variations in the ratio of Al/Si 0.5; 0.75, 1, 1.25 and 1.5. Allophane-like characters have functional groups -OH, O-Si-O/O-Al-O and Si-O/Al-O. Allophane-like has a low crystallinity (amorphous). Allophane-like has active sites Si-OH/ Al-OH, -O-Si-O/-O-Al-O- and Al-O-/Si-O- which able to bind Pb metal ions. The adsorption capacity toward Pb heavy metals is shown with optimum adsorption capacity of 1.61 mg/g in the ratio Al/Si 1.5 at pH 4 with a contact time of 30 minutes. Allophane-like has isotherm types that tend to follow the type of Freundlich adsorption isotherm.

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