

Allophane of Gamalama Volcanic Soil Surface Modification Using Sulfuric Acid: Study of the Effect of Sulfuric Acid Concentration

**Nur A. Limatahu*¹, Nur Jannah Baturante¹,
St. Hayatun Nur Abu¹, Nurul Aulia Rahman¹**

*¹Department of Chemistry Education,
Faculty of Teacher Training and Education, Khairun University,
Ternate, Indonesia*

Abstract

A large number of hydroxyl functional groups makes allophane very suitable to be applied as a catalyst in the modification of various functional groups of chemical compounds, such as cellulose hydrolysis reactions. The presence of allophane in Gamalama volcanic soil has been identified and characterized that is one type of clay that has been used for various things such as adsorbents and catalyst support materials for hemicellulose decomposition from various biomass plants. The structure and surface properties of allophane are very important in determining the application. Modification of structures and surfaces can be done with the help of heating and chemical agents such as sulfuric acid. In this study, the surface of allophane was modified using sulfuric acid and figured out the effect of sulfuric acid concentration on it. Allophane that already separated from Gamalama volcanic soil are sulfonated by immerse with sulfuric acid 2,4, and 6 M with 60°C temperature maintain. Sulfonated allophane then characterized with FTIR, XRD, and SEM to figured out the effect of sulfuric acid. Sulfuric acid has an effect to allophane surface that is make more uniform the surface in plate form with length 0.2 μm . Higher sulfuric acid concentration reduce the surface area of allophane.

Keywords : Sulfuric acid, sulfonation, allophane, Gamalama volcanic soil.

INTRODUCTION

North Maluku Province is one of the eastern regions of Indonesia that is rich in allophane potential. The existence of five active volcanoes that have erupted and produced millions of tons of volcanic soil has become a great potential in the development of allophane-based nanotechnology for various applications. Allophane is a nanomaterial contained in volcanic soil having a size of 3.5-5.0 nm with a very large specific surface area of around $300 \text{ m}^2\text{g}^{-1}$ [1]–[3], theoretically has a high ability as a solid catalyst for various reactions. The number of hydroxyl functional groups on the surface of the allophane is far more than the various other mesopore silica materials which are around $8.6 \pm 1.9 \text{ nm}^{-2}$. A large number of hydroxyl functional groups makes allophane very suitable to be applied as a catalyst in the modification of various functional groups of chemical compounds, such as cellulose hydrolysis reactions [3]. In Gamalama volcanic soil has been identified and characterized by the presence of allophane with a diameter of 4 nm, Si / Al ratio 1.45, and a surface area of $125,158 \text{ g m}^{-2}$ [4][5]. Allophane is one type of clay that has been used for various things such as adsorbents and catalyst support materials for hemicellulose decomposition from various biomass plants [3][6]. The structure and surface properties of allophane are very important in determining the application. Modification of structures and surfaces can be done with the help of heating and chemical agents such as sulfuric acid. Some researchers have carried out sulfonation studies using sulfuric acid in several other types of clay such as bentonite [7], kaolinite [8], and pillared clay [9]. In this study, the surface of allophane was modified using sulfuric acid and figured out the effect of sulfuric acid concentration on it.

EXPERIMENTAL

Volcanic soil samples from Mount Gamalama were first reduced for 3 days. The drying process is carried out only with air help. After drying, the soil sample is further crushed to 200 mesh size. A number of dry samples were added with distilled water to then condition the acidity level with a pH range of 4 and 10. The addition of HCl was done to condition pH 4, and for pH 10 was done by addition of NaOH. The sample is then poured for 10-20 hours in room temperature. The colloidal layer at a distance of about 10 cm from the surface of the solution is taken and then coagulated with the addition of NaCl.

The deposits produced from the coagulation process are separated from the solution to then be inserted into the dialysis membrane. The membrane is then immersed in distilled water to remove NaCl from the sediment. As an indicator, AgNO_3 was used to ensure the precipitate was free of NaCl. After that, the fraction is then centrifuged to separate the deposits. The final step in the allophane extraction stage is drying the sediment. As much as 1 gram of allophane and 15 mL of H_2SO_4 are stirred for 2 hours and heating 60°C . The concentration of sulfuric acid used was 2, 4, and 6 M. Allophane sulfonated by H_2SO_4 2, 4, 6 M, in this article denoted as allo-2, allo-4, and

allo-6. To determine the effect of acid concentration on the surface of allophane, then characterized using FTIR, XRD, and SEM.

RESULTS AND DISCUSSION

The FTIR characterization results (Fig.1) show high absorption at wavenumbers 3448.72 cm^{-1} , 1635.64 cm^{-1} , 1033.85 cm^{-1} , 910.40 cm^{-1} , 532.35 cm^{-1} , 439.77 cm^{-1} , and 316.33 cm^{-1} . Some previous researchers have successfully characterized the allophane structure using FTIR spectroscopy and found an absorbing peak that was obtained in this study. The peak at wave number 3448.72 cm^{-1} indicates the presence of hydroxyl groups which may be derived from silanol or aluminol. This statement is consistent with Bonelli *et al.* (2009), which states that absorption of the peak in the range $3800\text{--}3000\text{ cm}^{-1}$ is the absorption area for stretching of the OH hydroxyl group [10]. The existence of Si-O-Si vibration is 1000 cm^{-1} - 1100 cm^{-1} [11]. Figure 1 shows the absorption peak for an indication of Si-O-Si presence at wave number 1033.85 cm^{-1} . The absorption peak at 1635 cm^{-1} wave number is an indication of water molecular bending which has also been proposed by (Bonelli *et al.*, 2013; Cipta *et al.*, 2017). The peak at 910.40 cm^{-1} indication of Si-O-Al stretching which is characteristic of aluminol or Al-allophane mineralized aluminosilicate [13]. The absorption peak at 532.35 cm^{-1} wave number is an indication of Al octahedral [14].

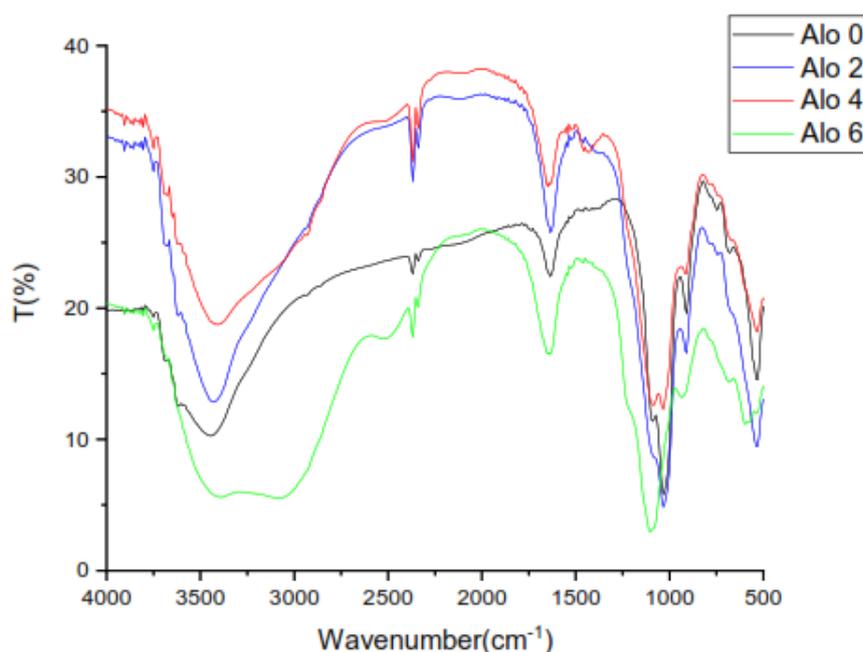


Fig. 1. FTIR Spectra of allophane and sulfonated allophane Gamalama

The effect of the concentration of sulfuric acid on the allophane structure of Gamalama, began to be seen in the treatment of H_2SO_4 4 M and 6 M. The characteristics of the sulfonate group were found at wave numbers around $1070\text{-}1200\text{ cm}^{-1}$. The peak 2 M sulfonated allophane acid did not appear, but it appeared on sulfonated allophane 4 M and 6 M. The absorption peak at wave number 1087.85 cm^{-1} was a stretching vibration character $\text{O} = \text{S} = \text{O}$ found in alo-4 FTIR spectra then shifted to 1103.28 cm^{-1} on alo-6. This shows an indication of the binding of the SO_3H group from sulfuric acid to aluminol or silanol groups of allophane. With increasing concentrations of H_2SO_4 , the absorption peak at wave number 1400 cm^{-1} increases and widens. This might be caused by two things, namely, the first formation of hydrogen bonding interactions between the sulfonate group and the allophane active group. Second, perhaps due to the hydrophilic nature of SO_3H it causes an increase in allophane retention of water.

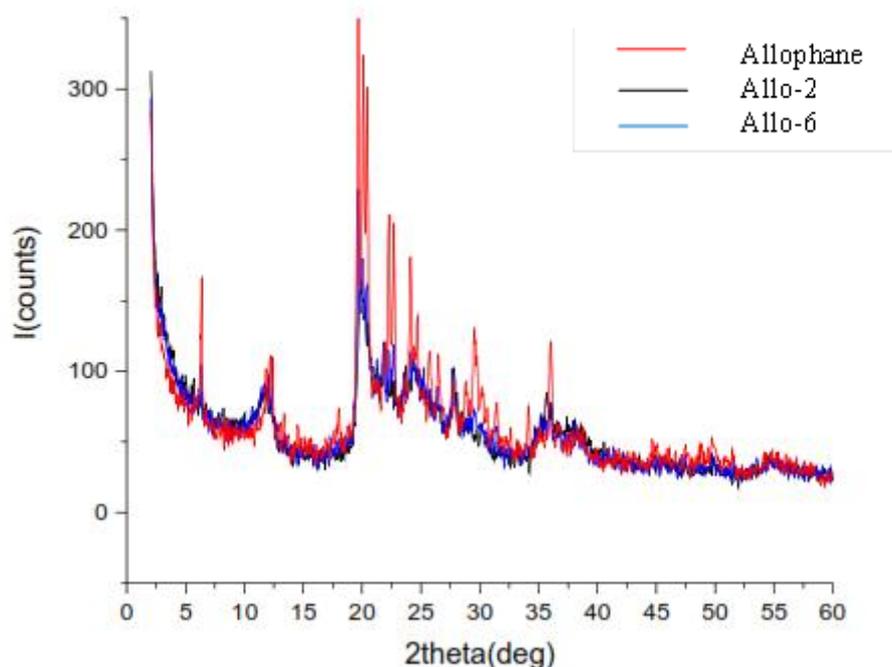


Fig. 2. XRD of Allophane and Sulfonated allophane Gamalama

The decrease in absorption intensity at wave numbers 513 cm^{-1} is shown by alo-4 and alo-6 which indicate the possibility of increasing the dealumination or dissolution of al octahedral by sulfuric acid. Although the dealumination process occurs, the acid treatment has not yet reached the stage of destruction of the allophane structure. This is indicated by the XRD diffractogram (Figure 2) and SEM photos (Figure 3).

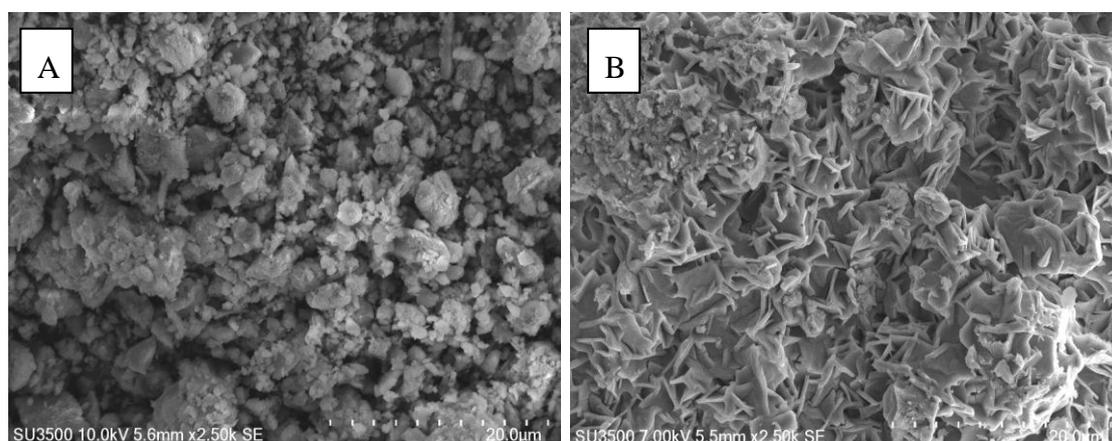


Fig. 3. SEM images of (A) allophane and (B) Allo-6 Gamalama

Figure 2, which is the result of XRD characterization shows a high peak at 2θ 7.8° (3.09 \AA) and 19.38° (6.7 \AA) commonly found for low order regular aluminosilicate minerals. Based on Figure 3, after sulfonated allophane using H_2SO_4 6 M there was a shift and a decrease in intensity of 2 absorption peaks at 2θ (7.8°) and 19.38° . This indicates a change in the composition of allophane structure which may be caused by the dissolution of the octahedral layer by sulfuric acid. This statement is supported by SEM photos of allophane shown in Figure 3. From SEM images, it appears that allophane surface changes after sulfonated by sulfuric acid 6M.

Table 1. S_{BET} of allophane and sulfonated allophane Gamalama

Samples	Allo	Allo-2	Allo-4	Allo-6
$S_{\text{BET}}(\text{m}^2\text{g}^{-1})$	125.158*	105.240	83.966	70.122

*From Cipta et.al (2017)

The structure in the form of irregular spherule which initially dominated before sulfuric acid treatment, disappeared after being given 6 M sulfuric acid. Allophane Gamalama becomes dominated by a more uniform plate shape with a length of about $0.2 \mu\text{m}$. This causes a decrease in S_{BET} surface area of allophane as presented in table 1. The surface area decreases with increasing concentration of sulfuric acid.

CONCLUSION

Sulfuric acid 6 M make allophane surface became more uniform in plate shape. The irregular spherule that dominated allophane change into uniform plate shape with a length of about $0.2 \mu\text{m}$. This acid treatment has not yet reached the stage of destruction of the allophane structure which is confirmed by XRD diffractogram.

ACKNOWLEDGEMENTS

The authors acknowledge to Indonesian Ministry of Research and Higher Education for funding this study through grant PDUPT No.056/PEN-PDUPT/PL/2018.

REFERENCES

- [1] P. Du, P. Yuan, D. Liu, S. Wang, H. Song, And H. Guo, "Calcination-Induced Changes In Structure, Morphology, And Porosity Of Allophane," *Appl. Clay Sci.*, Vol. 158, Pp. 211–218, Jun. 2018.
- [2] T. Henmi And K. Wada, "Morphology And Composition Of Allophane," *Am. Mineral.*, Vol. 61, Pp. 379–390, 1976.
- [3] Y. Ogaki, Y. Shinozuka, T. Hara, N. Ichikuni, And S. Shimazu, "Hemicellulose Decomposition And Saccharides Production From Various Plant Biomass By Sulfonated Allophane Catalyst," *Catal. Today*, Vol. 164, No. 1, Pp. 415–418, Apr. 2011.
- [4] I. Cipta, N. A. Limatahu, N. A. St. Hayatun, I. Kartini, And Y. Arryanto, "Effect Of Allophane From Gamalama Volcanic Soil On Properties Of Bio-Allophane Composite," *Asian J. Chem.*, Vol. 29, No. 5, Pp. 1042–1044, 2017.
- [5] I. Cipta, N. A. Limatahu, S. H. Nur Abu, I. Kartini, And Y. Arryanto, "Characterization Of Allophane From Gamalama Volcanic Soil, North Maluku, Indonesia," *Asian J. Chem.*, Vol. 29, No. 8, Pp. 1702–1704, 2017.
- [6] J. Silva-Yumi, M. Escudey, M. Gacitua, And C. Pizarro, "Kinetics, Adsorption And Desorption Of Cd(II) And Cu(II) On Natural Allophane: Effect Of Iron Oxide Coating," *Geoderma*, Vol. 319, Pp. 70–79, 2018.
- [7] N. Yildiz, Z. Aktas, And A. Calimli, "Sulphuric Acid Activation Of A Calcium Bentonite Sulphuric Acid Activation Of A Calcium Bentonite," *Part. Sci. Technol.*, Vol. 22, No. January 2004, Pp. 21–33, 2015.
- [8] O. A. Saputra, D. A. Saputra, K. S. Rini, And E. Pramono, "Influence Of Sulfonated-Kaolin On Cationic Exchange Capacity Swelling Degree And Morphology Of Chitosan / Kaolin Composites," Vol. 5, No. June, Pp. 85–94, 2016.
- [9] P. A. Caldeira, M. Goncalves, F. C. A. Figueiredo, S. Maria Dal Bosco, D. Mandelli, And W. A. Carvalho, "Sulfonated Niobia And Pillared Clay As Catalyst In Etherification Reaction Of Glycerol," *Appl. Catal. A Gen.*, Vol. 478, Pp. 98–106, 2014.
- [10] B. Bonelli, I. Bottero, N. Ballarini, S. Passeri, F. Cavani, And E. Garrone, "Ir Spectroscopic And Catalytic Characterization Of The Acidity Of Imogolite-Based Systems," *J. Catal.*, Vol. 264, No. 1, Pp. 15–30, May 2009.
- [11] T. Henmi, K. Tange, T. Minagawa, And N. Yoshinaga, "Effect Of SiO₂/Al₂O₃

- Ratio On The Thermal Reactions Of Allophane. Ii. Infrared And X-Ray Powder Diffraction Data,” *Clays Clay Miner.*, Vol. 29, No. 2, Pp. 124–128, 1981.
- [12] B. Bonelli, C. Zanzottera, M. Armandi, S. Esposito, And E. Garrone, “Ir Spectroscopic Study Of The Acidic Properties Of Alumino-Silicate Single-Walled Nanotubes Of The Imogolite Type,” *Catal. Today*, Vol. 218–219, Pp. 3–9, Dec. 2013.
- [13] E. J. Kim And J. E. Herrera, “Characteristics Of Lead Corrosion Scales Formed During Drinking Water Distribution And Their Potential Influence On The Release Of Lead And Other Contaminants,” *Environ. Sci. Technol.*, Vol. 44, No. 16, Pp. 6054–6061, 2010.
- [14] R. L. Parfitt And R. J. Furkert, “Identification And Structure Of Two Types Of Allophane From Volcanic Ash Soils And Tephra,” *Clays Clay Miner.*, Vol. 28, No. 5, Pp. 328–334, 1980.

