

ALLOPHANE OF GAMALAMA VOLCANIC SOIL SURFACE MODIFICATION USING SULFURIC ACID: STUDY OF THE EFFECT OF SULFURIC ACID CONCENTRATION

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ABSTRACT: Allophane has an abundance of hydroxyl functional groups, making it suitable for catalytic conversion of different functional groups found in chemical products. It can help with the breakdown of cellulose, for example. An allophane clay variant has been discovered in Gamalama's volcanic soil. This clay has been used for a wide range of applications, including filtration and catalytic degradation of hemicellulose from diverse biomass plants. Although allophane has a wide range of applications, its structure and surface properties are by far its most important. Surfaces and structures can be altered using heat and chemicals such as sulfuric acid. The surface of allophane was altered with sulfuric acid in this experiment to assess the impact of applying varied amounts of sulfuric acid to the substance. Sulfonation entails immersing allophane obtained from Gamalama's volcanic soil in sulfuric acid solutions holding concentrations of 2, 4, and 6 M while maintaining a temperature of 60°C. The effect of sulfuric acid on the sulfonated allophane was then investigated using FTIR, XRD, and SEM. Sulfuric acid causes the allophane surface effect, which increases the surface area of a plate by 0.2 microns. The surface area of allophane decreases as the concentration of sulfuric acid increases.

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

1. INTRODUCTION

The eastern portion of Indonesia, and more specifically the North Maluku Province, is where allophane may be found in significantly high concentrations. The eruptions of five active volcanoes have resulted in the production of enormous quantities of volcanic sediment because of the volcanic activity. This demonstrates the adaptability of nanotechnology based on allophane. It can be applied to a large variety of different applications. The lengths of the allophane nanoparticles that are found in volcanic soil range from 3.5 to 5 nanometers. The specific surface area of this substance is greater than 300 m²g⁻¹, which is a very high figure. It would appear, at first glance, to have the potential to be a solid catalyst that is quite successful in a range of different sorts of processes. There are 8.6 1.9 nm⁻² of hydroxyl functional groups on the surface of allophane, which is a significantly lower number than the number of hydroxyl functional groups found on the surface of other mesopore silica materials. Allophane is an effective catalyst for modifying the functional groups of a wide variety of chemical compounds. This is due to the fact that it contains a large number of hydroxyl functional groups. Compounds that degrade cellulose are included in this category. The soil of the Gamalama volcano is composed of allophane particles consisting of four nanometers in diameter. These particles have a Si/Al ratio of 1.45 and a surface area per square meter of 125,158 grams. The type of clay in question is known as allophane, and it is

an incredibly uncommon variety. In biomass plants, it is utilized for a variety of reasons, including the removal of water and the degradation of hemicellulose. The molecular composition of allophane and the surface qualities of the material are the primary factors that determine its application. Sulfuric acid is one example of a chemical that can be used in conjunction with heat to modify surfaces and structural components. Bentonite, pillared clay, and kaolinite are only few of the clays that have been subjected to research by scientists regarding their transformation. The purpose of this research was to alter the surface properties of allophane by utilizing sulfuric acid, and then to investigate the effects of varying doses of sulfuric acid.

2. EXPERIMENTAL

The collection of the volcanic soil samples from Mount Gamalama took a total of three complete days. If you want to speed up the drying process, the only thing that can do so is air. The sample of soil is then broken down into particles that are no larger than 200 mesh after it has been dried. It was necessary to blend distilled water with a large number of dried samples in order to keep the acidity level between four and ten. To obtain a pH of 4, hydrochloric acid was applied. In order to attain a pH of 10, NaOH was utilized. After that, the material is let to rest at room temperature for ten to twenty hours before additional analysis is performed. Approximately ten centimeters below the surface of the fluid is where the colloidal layer makes its appearance. NaCl is also added in order to cause clumping.

The coagulation process results in the formation of precipitates as a possible outcome. After they have been extracted from the solution, these are then transferred to the membrane that is used for dialysis. The membrane is then washed with filtered water in order to eliminate the sodium chloride that is present in the silt. The use of AgNO₃ as a diagnostic tool ensured that there was no trace of sodium chloride present. In order to separate the fraction from the deposits, it is next subjected to centrifugation. Allophane is extracted from the soil by a series of steps, the last of which is drying. When heated at a temperature of sixty degrees Celsius for two hours, one gram of allophane and fifteen milliliters of hydrogen sulfide are produced. A total of 2, 4, and 6 M of sulfuric acid were utilized in this experiment. Throughout the course of this experiment, allophane, which was referred to as allo-2, allo-4, and allo-6 throughout, was sulfonated with solutions of 2, 4, and 6 M H₂SO₄. Following that, the acid content of allophane was investigated using FTIR, XRD, and SEM in order to determine how it impacted the surface of the material.

3. RESULTS AND DISCUSSION

According to the data obtained from the FTIR characterization (Figure 1), significant absorption takes place at the wavenumbers shown below: It is as follows: 316.33, 3448.72, 1635.64, 1033.85, 910.40, 532.35, and 439.77 are the coordinates for the cm⁻¹ coordinate system. In the past, FTIR spectroscopy has been utilized with great success in order to ascertain the composition of allophane and to locate an absorption peak. The signal at wave number 3448.72 cm⁻¹ may have originated from either aluminol or silanol, depending on the hydroxyl groups that were present. According to Bonelli et al. (2009), the revelation that the absorption peak in the 3800-3000 cm⁻¹ range is related with the stretching of the OH

hydroxyl group lends credence to this assertion. It has been discovered that the frequency of the Si-O-Si wave is somewhere in the range of 1000 to 1100 cm^{-1} respectively. An absorption peak for Si-O-Si may be seen in Figure 1 at a frequency of 1033.85 cm^{-1} . Studies conducted in the past have demonstrated that the presence of an absorption peak at a wave number of 1635 cm^{-1} is indicative of the bending of water molecules (Bonelli et al., 2013; Cipta et al., 2017). The peak at 910.40 cm^{-1} , which indicates that the Si-O-Al bonds are stretched, is one of the characteristics that help to distinguish aluminol or Al-allophane cemented aluminosilicate from other types of aluminosilicate. One of the characteristics of an alpha-octahedral material is the presence of an absorption peak with a wave number of 532.35 cm^{-1} .

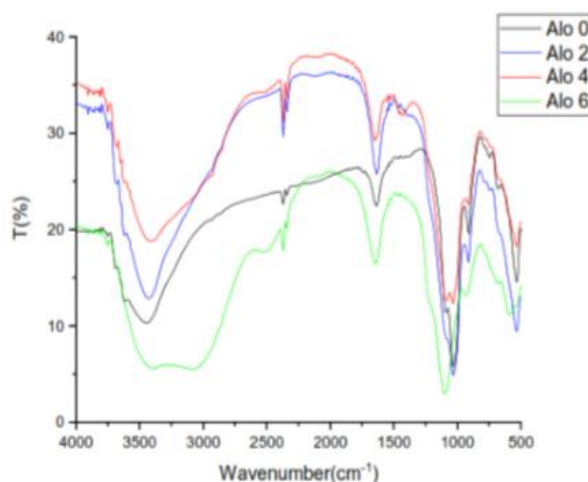


Fig.1. The FTIR patterns of Gamalama consisting of allophane and sulfonatedallophane are being explored.

The effect of varying sulfuric acid concentrations on the allophane structure of Gamalama was discovered after the plant was subjected to treatments with 4 M and 6 M H_2SO_4 . The signal that was produced by the sulfonate group was in the region of 1070 to 1200 cm^{-1} . When the sulfonatedallophane acid concentration was 2 M, the peak was not visible; nevertheless, it was there when the solvent concentration was 4 M and 6 M. The alo-4 FTIR spectrum has a wave number of 1087.85 cm^{-1} , which correlates to an absorption peak in the spectrum itself. A connection may be made between this and the stretching vibration of the functional group $\text{O}=\text{S}=\text{O}$. Within the alo-6 spectrum, this peak is subsequently shifted to 1103.28 cm^{-1} . This illustrates the connection that exists between the components of allophane, consisting of either aluminol or silanol, and the SO_3H component of sulfuric acid. When there is a higher concentration of H_2SO_4 , the absorption peak that occurs at wave number 1400 cm^{-1} becomes more pronounced and dispersed. There are two primary factors that have an impact on this outcome. In the beginning, hydrogen bonds were established between the sulfonate group and the allophane active group. Furthermore, the hydrophilic properties of SO_3H have the potential to increase the amount of water that is retained by allophane.

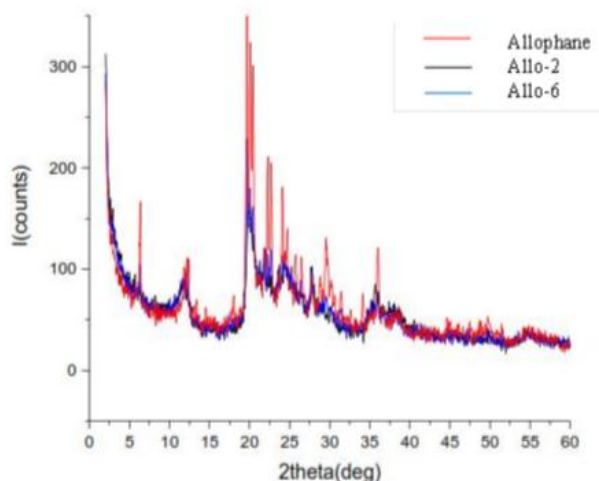


Fig.2. Samples of sulfonatedallophane and Gamalamaallophane were analyzed by X-ray diffraction (XRD), which is an experimental technique.

There is a decrease in the absorption efficiency of alo-4 and alo-6 compounds when the wave number is 513 cm^{-1} . With this information, it appears that sulfuric acid might be able to assist in the disintegration or breakdown of aluminum octahedral structures. However, the acid treatment did not completely destroy the allophane structure, despite the fact that the dealumination technique was successful. These findings are illustrated by the scanning electron micrographs (Figure 3) and the X-ray diffraction (Figure 2) images.

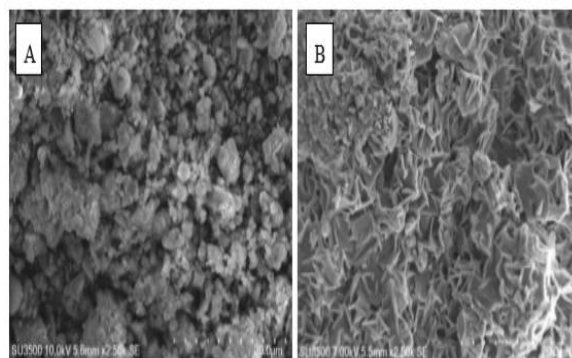


Fig.3. In this photograph taken using a scanning electron microscope (SEM), allophane (A) and allo-6 gamalama (B) are seen.

X-ray diffraction investigation revealed two distinct peaks at 2θ 7.8 $^\circ$ (corresponding to 3.09 $\text{\AA}$) and 19.38 $^\circ$ (corresponding to 6.7 $\text{\AA}$), as can be seen in Figure 2. These are the characteristics of crystals that are composed of low-order aluminosilicate. As demonstrated in Figure 3, the addition of H_2SO_4 6 M to sulfonatedallophane resulted in the displacement of two absorption peaks located at 2 (7.8 $^\circ$) and 19.38 $^\circ$, as well as a decrease in the intensity of those peaks. This leads one to believe that the conformation of the allophane molecule has undergone a change. There is a possibility that this is due to the octahedral layer being degraded by sulfuric acid. In order to provide evidence in support of this claim, the scanning electron microscopy (SEM) pictures of allophane are presented in Figure 3. Adding sulfuric acid at a concentration of 6M to allophane results in a change, as seen by surface photographs.

Table1 In order to determine the specific surface area of allophane and sulfonatedallophane that

were obtained from the Gamalama volcano, the SBET method was utilized.

Samples	Allo	Allo-2	Allo-4	Allo-6
SBET(m ² g ⁻¹)	125.158*	105.240	83.966	70.122

*From Cipta et.al (2017)

The previously observed asymmetrical spherule structure disappeared after being subjected to treatment with sulfuric acid at a concentration of 6M. Plates made of allophanegamalama have an average length of one micrometer and a morphology that is generally uniform throughout. It can be shown in Table 1 that the SBET surface area, also known as the allophane surface area, decreases. A decrease in surface area occurs whenever there is an increase in the concentration of sulfuric acid.

4. CONCLUSION

A plate-like surface that was more uniformly distributed was produced as a result of the combination of sulfuric acid at a concentration of 6M with allophane. In the process, it transforms from an uneven allophane spherule into a plate that is 0.2 meters long and flat and homogenous. It can be seen from the XRD diffractogram that the acid treatment did not entirely disrupt the structure of the allophanestructur.

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