

## Determination of Surface Acidity on The Natural and Synthetic Montmorillonite Clays by Titration Method

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### Abstract

Determination of surface acidity on the natural and synthetic montmorillonite clays has been carried out using the acid-base titration method to count the number of bound acid sites per gram of clay. The total acidity of natural and synthetic montmorillonite surfaces obtained was 4.67 and 5.33 mmol/g, respectively. FTIR analysis results indicate the presence of functional groups from the tetrahedral and octahedral constituents. Both samples have similar absorption patterns. A decrease followed the similarity of absorption patterns in intensity and shift in some absorption bands and the appearance of new absorption bands.

*Keywords:* Acidity, natural montmorillonite, synthetic montmorillonite, clays, acid-base titration

### INTRODUCTION

The solid acid derived from clays are widely used to catalyze various reaction. In order to comprehend the mechanism of their catalytic action and predict their activity and selectivity, information on the nature, amount and strenght of the acid sites exposed on their surfaces is needed.

One of the potentials of natural clay in Maluku is in Ouw Village (Sekewael, Tehubijuluw, & Reawaruw, 2013). Bijang, Tanasale, Kelrey, Mansur, & Azis, (2021) reported that the clay from Ouw Village contains montmorillonite-type minerals. Apart from natural clay, it is also known as synthetic clay, which is clay produced by a particular industry for a specific purpose, for example, for drilling or as a catalyst (Bijang, Tanasale, Kelrey, Mansur, & Azis, 2021). One example of synthetic Montmorillonite is Montmorillonite K10, or acid activated Montmorillonite. Natural and synthetic montmorillonite have Brønsted and Lewis acid sites, respectively. The Lewis acid site comes from the incomplete coordination of the  $Al^{3+}$  and  $Fe^{3+}$  cations in the crystal defect type. These cations can be modified through the exchange of  $Na^+$ ,  $Ca^+$ , or other cations. Bronsted acid sites are in the Si-OH-Si, Al-OH-Al, Si-OH-Al groups, and water molecules coordinated with  $Mn^+$  (Sekewael, Wijaya, Triyono & Budiman, 2017).

The acidity of the Montmorillonite clay is one of the material's chemicals properties, which plays an essential role in the catalysis of a reaction. Several researchers have reported the effect of acidity on the

montmorillonite type clays' catalytic activity (Sekewael, Wijaya, Triono & Budiman, 2017).

This research was determined the number of bonded acid sites per gram of natural and synthetic montmorillonite clays used the acid-base titration method and the amount of base bound to the Brønsted or Lowry acid site was determined qualitatively, using FTIR instrument. Previous researchers have never done this research. The acid sites of the clay had reacted with excess base (NaOH), and the excess has titrated with acid (HCl) (Widihati & Ratnayani, 2010). Suarya (2012) reported that the surface acidity of the clay is 0.4665 mmol/g. Several bases will neutralize the acid groups on the clay surface (Suarya, 2012).

### METHODOLOGY

#### Materials and Instruments

The materials were used: Ouw natural clay, montmorillonite K10, HCl, NaOH, phenolphthalein (pp), Universal pH paper, Whatman filter paper No. 42, aquades, aquabides. The instrument were used: a set of glassware, analytical balance, sieve, oven, desiccator, hotplate stirrer, pH meter, mortar, burette, clamp, stative, volumetric flask, volume pipette, drop pipette, and FTIR spectrophotometer.

#### Methods

##### Sample Preparation

Amount 350 g of natural clay samples were taken and then washed three times and filtered with distilled

water. The pure clays are dried in an oven at 120 °C. The clay is crushed until smooth, then sieved with a 100-mesh sieve, then stored in a desiccator. The prepared natural clay and the K10 montmorillonite samples were heated for 1 hour at 90 °C each and then used to determine surface acidity.

### Surface acidity determination using the acid-base titration method

Amount 0.50 g of natural clay and montmorillonite K10 samples were added to three of 100 mL Erlenmeyer, then 25.0 mL of 1 M NaOH solution was added to each Erlenmeyer. The mixture was left at room temperature for 2 hours and stirred with a magnetic stirrer. The reaction product is then centrifuged and filtered using filter paper. Each filtrate is added 2-3 drops of phenolphthalein (pp) indicator, which is indicated by the appearance of pink color. The filtrate was titrated with 1 M HCl solution until the color changed, changing to the initial filtrate color. The same treatment was carried out for a blank containing only 25.0 mL of 1 M NaOH solution. The volume of the HCl solution used was measured titrimetrically.

The filtered clay silt was then washed with aquabides twice, then dried at room temperature. The dried precipitate was then analyzed using an FTIR spectrophotometer.

## RESULTS AND DISCUSSION

The results of the sample preparation stage are shown in Figure 1. Physically, it can be observed that the color changes are quite different. Natural montmorillonite has a brownish-gray color, while synthetic montmorillonite has a whitish-gray color because it has undergone an acid bleaching process.



Figure 1. Natural Montmorillonite clay (MA) and synthetic Montmorillonite clay (MK)

Both montmorillonite samples physically feel soft and smooth when held due to the small particle size of

montmorillonite  $\pm 1$  nm. Information about the functional groups contained in the MA and MK samples is shown by infrared spectra in the region of the wavenumber 4000-400  $\text{cm}^{-1}$ , which is divided into two groups of frequency regions, namely: the area between 4000-3000  $\text{cm}^{-1}$ , which is the stretching vibration area of water that is adsorbed or OH-octahedral groups and the area between 1400-800  $\text{cm}^{-1}$  caused by bending vibrations from Al-OH or Si-O is called the fingerprint region.

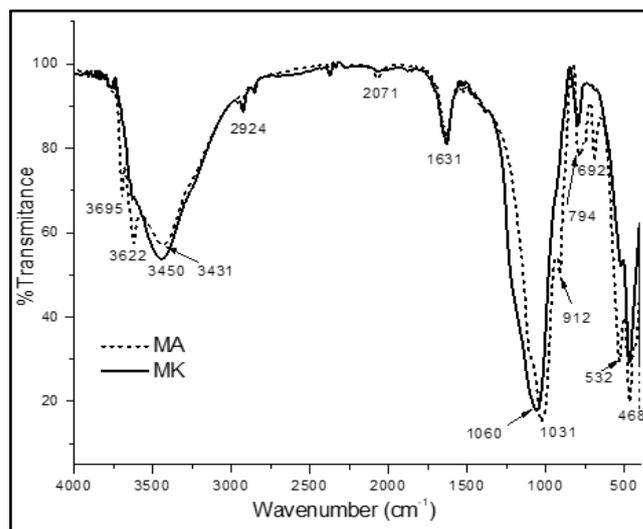


Figure 2. FTIR spektra before titration: natural Montmorillonite (MA), synthetic Montmorillonite (MK)

The important peaks for the identification of MA and MK are shown in Figure 2. The absorption peaks at wavenumbers 3695  $\text{cm}^{-1}$ ; 3431  $\text{cm}^{-1}$ ; 1631  $\text{cm}^{-1}$ ; 1031  $\text{cm}^{-1}$ ; 794  $\text{cm}^{-1}$ ; 532  $\text{cm}^{-1}$ ; and 468  $\text{cm}^{-1}$  are similar to those reported in the literature (Sekewael, Wijaya, & Triyono, 2018). The absorption band at wave number 3695  $\text{cm}^{-1}$  was identified as the octahedral structural stretch-OH band (Al-OH). This peak was not appeared for MK due to the acid effect of synthetic montmorillonite. The sharp peak at 3622  $\text{cm}^{-1}$  belongs to MA indicate isomorphous substitution of octahedral  $\text{Al}^{3+}$  by  $\text{Fe}^{2+}$  or  $\text{Mg}^{2+}$  cations in the montmorillonite structure (Hayati-Ashtiani, 2012).

The bending vibrations of the hydroxyl group at 912  $\text{cm}^{-1}$  (Al-Al-OH) also proved this partially isomorphous substitution of  $\text{Al}^{3+}$  in the octahedral layer, similar to what was reported by (Hayati-Ashtiani, 2012). Broadband with medium acid intensity at 3431  $\text{cm}^{-1}$  and 3450  $\text{cm}^{-1}$ , belonging to MA and MK, was identified as stretching vibration-OH water molecules. An absorption band strengthened this band at the wavenumber 1631  $\text{cm}^{-1}$ , the bending vibration band of water molecules. The presence of these bands is an

indication that montmorillonite has water-absorbing properties.

The absorption band at  $1031\text{ cm}^{-1}$  is the typical stretching vibration of Si-O in the tetrahedral layer, while the bending vibration of Si-O-Si appears at  $468\text{ cm}^{-1}$ . The bending vibration characteristic of the Al(IV) tetrahedral appeared at  $794\text{ cm}^{-1}$  and was strengthened by an absorption band at  $532\text{ cm}^{-1}$  which corresponded to the bending vibration of Al-Si-O.

The sharp absorption at wave number  $692\text{ cm}^{-1}$  shown by natural montmorillonite is an asymmetric O-Si-O range (Molu & Yurdakoç, 2010). Yuan *et al.* (2008) explained that this absorption is the absorption of Al-O and Si-O pairs outside the plane. Meanwhile, according to Tyagi, Chudasama, & Jasra, (2006), the absorption at  $692\text{ cm}^{-1}$  is the functional group absorption belonging to the quartz component. This uptake does not appear in synthetic montmorillonite. Synthetic montmorillonite is acid-activated montmorillonite, where the Al metal in the octahedral structure undergoes a dealumination. The above evidence is strengthened by the absence of absorption at wavenumbers  $3622\text{ cm}^{-1}$  and  $912\text{ cm}^{-1}$ , which according to Tyagi, Chudasama, & Jasra, (2006) is a hydroxyl group absorption that binds to  $\text{Al}^{3+}$  cations. This absorption occurs in natural montmorillonite, where the  $\text{Al}^{3+}$  cation is still attached to the hydroxyl group in the octahedral position. Furthermore, to analyze the acidity of montmorillonite clay, titration is carried out with the base NaOH. Shifts or the emergence of new absorption can be studied from the FTIR analysis result, as shown in Figure 3.

In general, there is no significant change from natural montmorillonite absorption, as shown in Figure 2. The absorption in the central vibration region and the fingerprint area is still observed. The interaction between the NaOH base and the Brønsted montmorillonite acid group was evidenced by weak absorption at the  $1382\text{ cm}^{-1}$  region, marked as the Brønsted acid site (Figure 3). The conclusion obtained from the FTIR analysis result is that, overall, infrared spectroscopic data show functional groups from tetrahedral and octahedral sheets that compose natural montmorillonite and synthetic montmorillonite minerals. The samples, both MA and MK as well as MA-T and MK-T, have similar absorption patterns. The similarity of absorption patterns is followed by a decrease in intensity and a shift in several absorption bands and new absorption bands.

Determination of the total surface acidity was carried out by acid-base titration. The acidic site of montmorillonite will react with the base NaOH. The remaining -OH, which does not react with the acid site,

will be titrated with HCl acid. The end-point of the titration was detected using the phenolphthalein indicator.

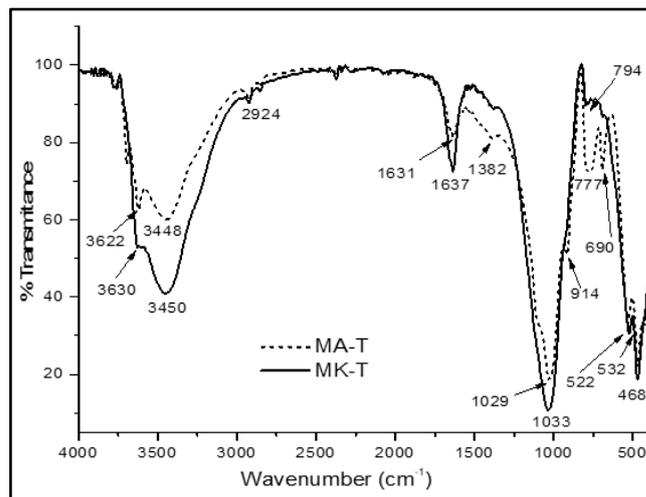


Figure 3. FTIR spektra after titration: natural Montmorillonite (MA-T), synthetic Montmorillonite (MK-T)

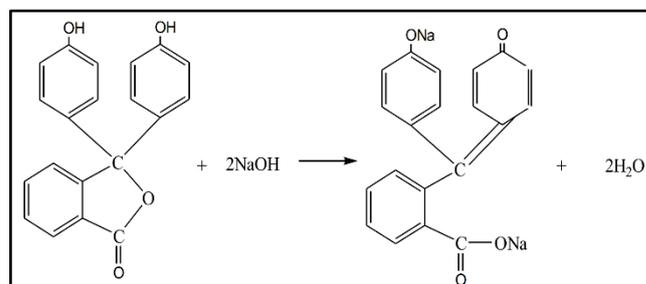
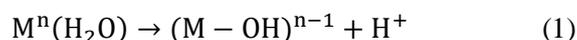


Figure 4. The reaction of pp indicator with NaOH

After the sample absorbs the NaOH base, the montmorillonite acid site is calculated based on the acid-base titration result. The acid-base titration of the test sample solution using sodium hydroxide solution with pp indicator shows a pink color change in the test sample solution (Figure 4), which indicates that the test sample is acidic. The calculation of the total acidity solid is presented in Table 1.

The acid strength of a solid surface (the surface acidity) is defined as its proton-donating ability. The total surface acidity value of natural clay from Ouv village is 10 times higher than the clay reported by Suarya (2012). It seems, therefore, that the hydration water of the exchangeable cations is acidic, donating protons according to the scheme (Equation 1).



The calculation results in Table 1 show that the total acidity of synthetic montmorillonite is higher than natural montmorillonite. Synthetic montmorillonite K10 itself is called montmorillonite acid because it has been through an activation with acid. These results are not much different, as reported by (Sekewael, Wijaya, Triyono, & Budiman, 2016). The acidity of montmorillonite K10 of 4.83 mmol/g was measured using the gravimetric method (Sekewael, Wijaya, Triyono, & Budiman, 2016). Montmorillonite K10 was used as a good acid catalyst for lauric acid esterification (Sekewael, Wijaya, & Triyono, 2020).

Table 1. Total surface acidity value ( $K_a$ )

Sample	$K_a$ (mmol/g)			
	Simplo	Duplo	Triplo	Average
MA	4.00	6.00	4.00	4.67
MK	6.00	4.00	6.00	5.33

The total acidity value ( $K_a$ ) is calculated based on Equation 1.

$$K_a = \frac{(V_1 - V_2) M \text{ HCl}}{\text{Sample weight}} \quad (1)$$

(Note  $V_1$  = volume of titrant for blank titration;  $V_2$  = volume of titrant for titration of residual NaOH; M HCl = molarity of HCl).

Additional information about the surface acidity of solids was obtained from the sample's IR spectra after absorbing the NaOH base, as described in Figure 3. The presence of two types of acid sites, namely Brønsted and Lewis, can be determined. If the solid absorbs the ammonia base, there will be a transfer of protons from the Brønsted acid site to the base to form  $\text{NH}_4^+$ , while  $\text{NH}_3$  undergoes chemisorption and forms a coordination bond between the Lewis base ( $\text{NH}_3$ ) and the surface of the Lewis acid site (Sekewael, Wijaya, & Triyono, 2020).

## CONCLUSION

The acid-base titration method can be used to determine the total surface acidity of natural and synthetic montmorillonite. The total surface acidity of natural and synthetic montmorillonite was 4.67 and 5.33 mmol/g, respectively.

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