

Characterization of Montmorillonite Clay from Naturally Occurring Clay Deposits in Murunkan Area

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Abstract— Engineering fields widely use montmorillonite(MMT) nano clay for wide range of applications. Identify the presence of MMT and other minerals in naturally occurred clay deposits in Murunkan region and discussing the possibilities to extract MMT for commercial purpose was the objective of this research. In this research, naturally occurring clay deposits in Murunkan region was considered. Non-clay particles were removed in order to enhance the clay content and to prepare the samples. Selected samples were undergone characterizations method such as Fourier transform infrared spectroscopy (FTIR), Differential thermal analysis (DTA), linear shrinkage test, X-ray diffraction (XRD). Then MMT was isolated through the process of ultrasonic treatment and sedimentation. Presence of MMT in higher percentage is ensured through X-ray diffraction analysis on Murunkan clay. The ultrasonic method and sedimentation method has improved the amount of finer particles and removed coarse particles.

Keywords— clay, Murunkan, montmorillonite

I. INTRODUCTION

Clay soil is a group of soil, determined by the classification system by soil scientists. Generally, clay particles are very small compared to other types of soil and having a high to very high specific surface value.

In terms of their physical locations, clay minerals can be divided into two categories: Residual clay and clay transported or sedimentary clay. The residual clays derived from the weathering of surface rocks or shale such a dark fine-grained sedimentary rock composed of layers of compressed clay, mud, or mud by various means, and generally found the place of origin. Residual clays could be produced by the chemical decomposition of rock that is granite containing silica and alumina from the dissolution of rocks, namely limestone and the dissolution and termination of the shale. The transported clay, the second type is removed from the initial filing through erosion and deposited in a distant place.

Montmorillonite is a few members of the larger group smectite clay. The general formula for the chemical

structure of this group is $(Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si,Al)_4O_{10}(OH)_2 \cdot XH_2O$. The significant difference between the members of this group seem to chemical characteristics. The structure contains a layer silicate layers sandwich a layer of aluminum oxide / hydroxide $(Al_2(OH)_4)$. These are used as fillers in paints, rubber, as plasticizer in sand casting, in drilling muds, and electrical, heat, and acid resistant porcelain.

The basic raw material of montmorillonite is a 2:1 foil layers smectite clay mineral with platelayer structure. Chemically, this can be described as calcium hydroxide, hydrated magnesium aluminum silicate, sodium, $(NaCa)_{0.33}(AlMg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. The particle size, surface area, and aspect ratio are particularly important characteristics desired in nanoclays. The length and width of the particles may range from 1.5 μm a few tenths of a micron. The third dimension of a particle has been described in the literature as the thickness, width, or diameter. However, diameter seems to be more appropriate. The diameter of a particle is extremely smaller than its length, counting only billionth of a meter (1 nm). Therefore, an extremely high average aspect ratio (length to diameter) 200 to 500 is possible. A small amount of nanoclay exhibits a high surface, that is, a product known as nanoclay are an over 750 m^2/g (F.Uddin, Mar 2008), which is a rough equivalent to the area occupied by nine football fields.

The swelling response of montmorillonite, and the corresponding development of swelling pressure when swelling is restrained, is a result of complex montmorillonite-water interactions between particles and within the particle itself. Montmorillonite is hydrophilic like most other clay minerals. It swells with the absorption of water, which greatly increases its volume. Water penetrates the interlayer molecular spaces, and the variation in the level of swelling is possible in various grades. Montmorillonite typically exhibits a gradual dehydration and phase change to stronger non expendable clay, illite, under increasing temperature and pressure.

The temperature and pressure at which the transition begins depends upon several factors, namely,

montmorillonite initial composition, chemistry of the available fluid, porosity and geological environment (C. Morrow, June 1990). The interlayer cations are exchangeable, and amount of expansion as a result of absorption of water depends largely on the type of exchangeable cation. When present as the dominant exchangeable sodium cation, the increase in volume montmorillonite is several times the original amount. This feature was sodium montmorillonite become an important ingredient in the non-explosive agents for splitting rocks with reduced waste.

Moreover, the cation substitution creates a charge imbalance that allows the chemical composition to vary. The exact theoretical formula is never seen in nature (Anon., n.d.) Therefore, it is also shown without the structural substitution as $(OH)_4Si_8Al_4O_{20} \cdot nH_2O$ (Anon., n.d.). However, the occurrence in nature in any form consists of water molecules. Commercially available nano clays with over 98 % montmorillonite have variable colors, which are the result of substitution of interlayer cations by iron, titanium, and manganese within the lattice structure and depend upon the level of substitution and valence state of captions. Because the metals have central coordination positions in the layer structure, they cannot be economically removed.

An interesting aspect of the clay montmorillonite, leading to the application as a catalyst, the structure of the catalytic sites offering Bronsted acid and Lewis (D.D.Eberi, n.d.). The interchangeability of the interlayer cations helps in changing the nature of the acid with the use of ion exchange procedures. In organic chemistry, montmorillonite and modified species that are listed as produced by firing of montmorillonite, as found effective catalysts. Cation exchange produces more effective montmorillonite species, including Fe^+ montmorillonite and clay (Jang, n.d.).

III. METHODOLOGY

A. Clay Source

Naturally-occurring clay exists in many areas of Srilanka. With curiosity and ingenuity and weather condition one can find out where nature has deposited it for natural use. At the end of our survey two places Murunkan in Mannar district were identified as MMT clay enriched places. More than one sample were collected at Murunkan from different location like Giant’s tank at Murunkan, Madawachchiya – Talaimannar High way road construction dig at Murunkan, MavilankaiKulam Tank at Palampiddi and Allavangai Lake at Allavangai in the Mannar district.

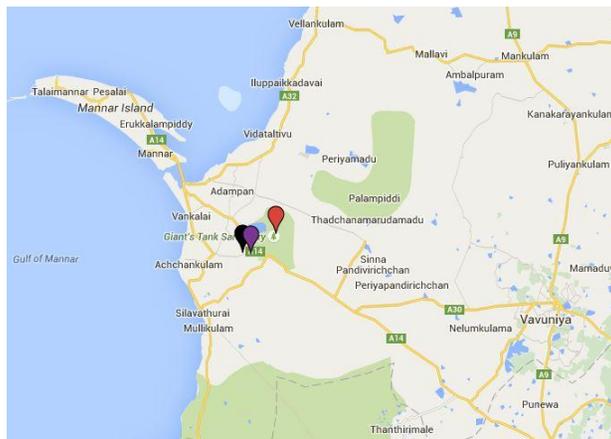
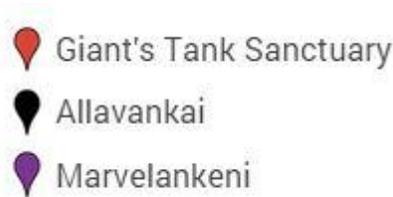


Figure 1: Map of Mannar district where clay was extracted

Table 1: Coordinates of extracted place.

Place	Latitude	Longitude
Giant’s tank	8.869796	80.018452
Marvilankeni	8.839128	80.025766
Allavankai	8.840497	80.013900

1) Sample preparation;

Samples were collected from Giant’s tank, Allavankai and Mavilankeni in Murunkan. The collected samples were wet sieved by using 53-micron sieve. Then it was placed into oven at about 120⁰ C until it getting dried. The dried sample was milled using mortar and pestle and sieved again by the same sieve (53micron dry sieve). Finally, it was placed into the oven at about 300⁰ C for one hour for the purpose of removal of organic materials from the clay samples.

B. Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR analysis was done using BRUKER ALPHA-T with mechanism of identifying the absorption peaks. Infrared instruments measure the vibrational spectrum of a sample by passing infrared radiation through it and recording which wavelengths have been absorbed and to what extent. Since the amount of energy absorbed is a function of the number of molecules present, the infrared instrument provides both qualitative and quantitative information. The recorded spectrum is a plot of the transmittance of the sample versus the frequency (or wavelength) of the radiation. This spectrum is a fundamental property of the molecule and can be used

both to characterize the sample and to determine its concentration. FTIR test was carried out by using KBr pellet method for frequency range of 4000-500cm⁻¹.

C. Thermal analysis of the samples

Thermal analysis generally covers two different experimental techniques:

- Thermo Gravimetric Analysis (TGA)
- Differential Thermal Analysis (DTA)

The basic principle in TGA is to measure the mass of a sample as a function of temperature. In principle, this simple measurement is an important and powerful tool in solid state chemistry and materials science. The method can be used to determine water of crystallization, follow degradation of materials, reaction kinetics, study oxidation and reduction, and teach the principles of stoichiometry formula and analysis.

The prepared samples were analysed by using DTA and TGA testing instrument which name is RIGAKU THERMOFLEX with the mechanism of Spectrum (Endo or Exo thermic peaks). The test was carried out from room temperature to 990°C with temperature increment rate of 10°C per min.

D. Liner shrinkage test

Linear shrinkage is the decrease in length of a soil sample when oven-dried, starting with a moisture content of the sample at the liquid limit. By riffling or quartering, a sample was obtained of at least 300 g of the clay passing the No 36 British Standard (B.S) sieve (425 microns) prepared according with the procedure for the preparation of disturbed clay samples for testing. This sample was placed in the mixing bowl and thoroughly mixed with de-ionized water using the spatula, until the mass becomes a thick homogeneous paste. Sufficient water was added to bring it to a consistency equal to or slightly wetter than the liquid limit. When the sample was tested in the liquid limit machine, the groove would close with between 15 and 25 blows.

The mold was cleaned and the inside of the mold was greased. The prepared wet clay was placed in the mold, taking care to thoroughly remove all air bubbles from each layer by lightly tapping the base of the mold. Slightly overfilled the mold and then excess clay was levelled off with the spatula and all soil adhering to the rim of the mold was removed.

The entire experiment was allowed to dry at room temperature for about 24 hours until a distinct change in colour can be noticed and then transferred into an oven and dry at between 105 °C and 110 °C.

The specimen was allowed to cool and then measure its longitudinal shrinkage length to the nearest millimetre. The specimen was cracks into pieces, so firmly held the separate parts together and measured the shrinkage length and some part of the specimen curls in the mould carefully removed it and measure the length of the top and bottom surfaces. The shrinkage was obtained through subtract the mean of these two lengths from the internal length of the mould.

Calculate the percentage linear shrinkage (LS) of the specimen by this equation

$$LS=L_S/L*100\%$$

Where:

L = Length of the mold (mm)

Ls = Longitudinal shrinkage of the specimen (mm)

E. Isolation of clay samples

Isolation of clay fraction of the specimens was carried out by combinational method of sedimentation and centrifuging. Because the coarse particles to remove and to get easy to identify. About 5g of raw clay with particle size less than 53 microns was dispersed in 1liter of deionized water and stirring 15 minutes. Then specimen was sonicated for 20 minutes without changing beaker because obstructs the dispersion particles of the solution. The procedure was repeated two more times for the same sample with the sonication time 10 min and 15 min respectively. The upper fraction of the dispersion was collected about 50 ml using pipette after 24 hours settlement of particles. Centrifugation was carried out for 10 minutes at 900 rpm. The fine fraction of dispersion or upper part was collected. The final supernatant solution was collected and dried at 80° C until the water evaporation completely

F. X- Ray Diffraction

The isolated clay sample was prepared to powder specimen of a size less than 53microns. The specimen was then prepared by placing the powder in the recess of the glass plate compacting it with enough pressure to cause adhesion between the powder and the glass plate. Then the surface was smoothed off. The slide was then fixed on the sample holder of the X ray diffractometer and the scanning unit was moved continuously over a circular scale and the variation of intensity was obtained against the changing angle on a strip chart.

The following parameters were set up for the test

Start angle: 03°

Stop angle: 70°

Scan speed: 2°/min

X-ray wave length: 1.54 °A

III. RESULTS AND DISCUSSION

A. Fourier Transform Infrared Spectroscopy

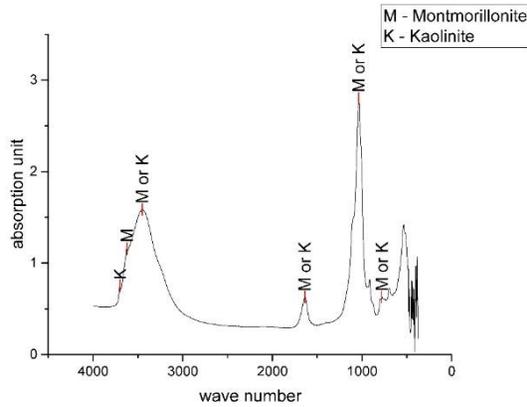


Figure 2: FTIR spectrum of Murunkan 1 clay samples

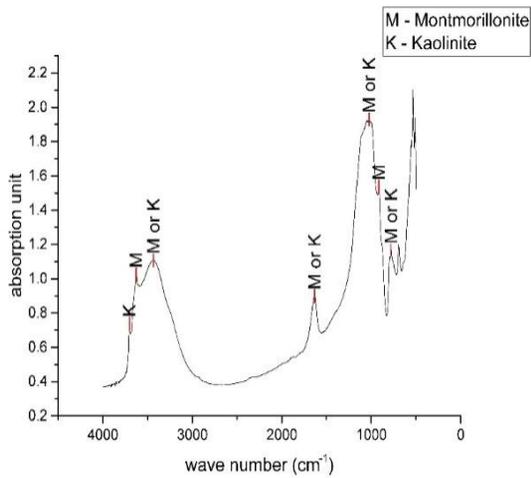


Figure 3: FTIR spectrum of Murunkan 2 clay samples

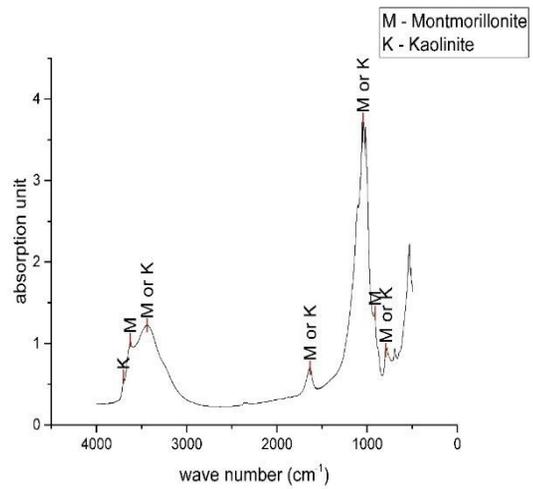


Figure 4: FTIR spectrum of Allavankai clay samples

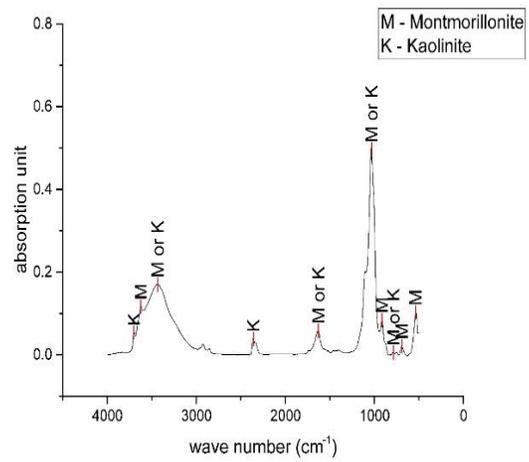


Figure 5: FTIR spectrum of Marvelankeni clay samples

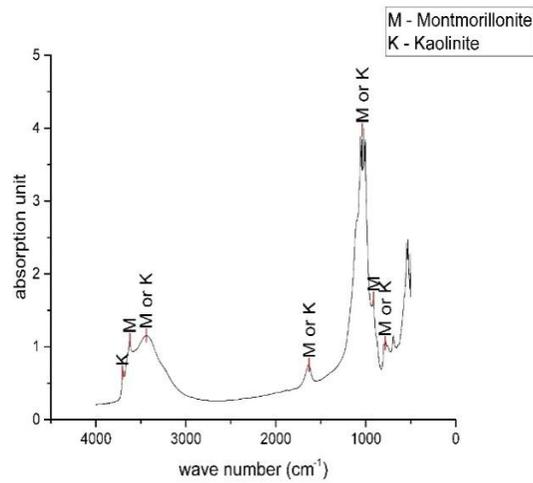


Figure 6: FTIR spectrum of Murunkan construction pit clay samples

The splitting of the band indicates presence of more than one type of hydroxyl bonds, due to their different absorption frequencies. The absorption bands present in the spectrum those are relevant to each bond types and necessary for the identification of the clay minerals.

When we consider a spectroscopy of commercial montmorillonite, which are absorbed the energy at particular wave numbers. The band included spectral bands of montmorillonite only: stretching bands of structural hydroxyl groups (3640 cm⁻¹), broad stretching band of water (3440 cm⁻¹), deformation band of water (1650 cm⁻¹), band of Si-O stretching (1040 cm⁻¹), deformation bands of Al-Al-OH vibration (915 cm⁻¹), deformation bands of Al-Mg-OH vibration (840 cm⁻¹), Si-O stretching band of silica (800 cm⁻¹), coupled out-of-plane vibration band of Al-O and Si-O (625 cm⁻¹) and deformation bands Al-O-Si, Si-O-Si, respectively (525 cm⁻¹ and 470 cm⁻¹). These peaks were illustrated in Table 2: absorption bands of clay samples.

According to the commercial montmorillonite characteristic peak wave number, clays' peak wave numbers were also similar to that. In the result we have concluded the montmorillonite particles are in the samples (D.D.Wanasinghe, 2012), (S.U.Adikary, 2012).

Table 2: absorption bands of clay samples

Absorption Peak No	Murunkan Clay (cm ⁻¹)	Allavankai Clay (cm ⁻¹)	Mavilankeni Clay (cm ⁻¹)	Montmorillonite (cm ⁻¹)	Kaolinite (cm ⁻¹)
1	3711	3711	3711		3755
2	3632	3631	3632	3626	
3	3447	3447	3447	3450	3451
4		2357			
5	1632	1632	1632	1637	1633
6		1107	1035		
7		1077		1067	
8		1054			
9	987	1026			
10		919	919	918	
11		803			805
12	763	785	785	797	
13	684	696	696		
14		553	553		568
15	526	536	535	529	

- 1 -OH stretching of structural hydroxyl groups
- 2 -OH stretching of structural free hydroxyl groups
- 3 -OH stretching of water
- 4 -----
- 5 -OH deformation of water
- 6 -Si-O stretching of cristobalite
- 7 - Si-O stretching
- 8 - Si-O stretching
- 9 - Si-O stretching
- 10 - Al-Al-OH deformation
- 11 -Si-O stretching of silica
- 12 -Si-O stretching of quartz
- 13 Coupled Al-O & Si-O out of the plane
- 14 -Al-O-Si deformation
- 15 Al-O-Si deformation

B. Thermal Analysis of Samples

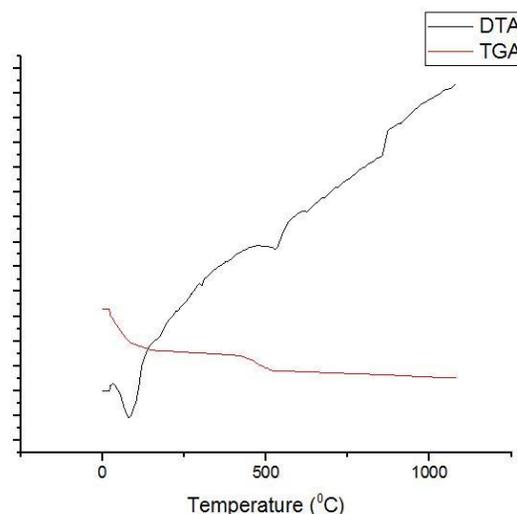


Figure 7XI: DTA and TGA curve of Allavankai sample

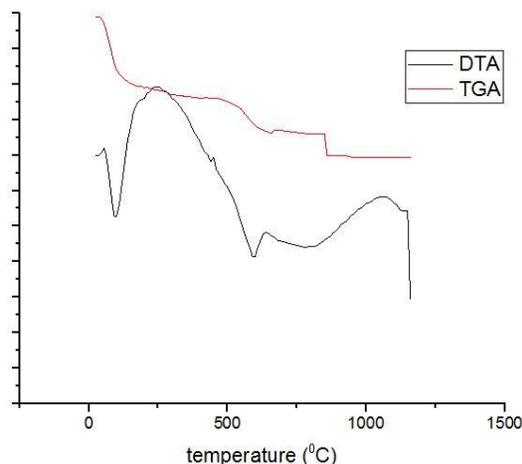


Figure 8: DTA and TGA curve of Murunkan sample

The clay sample was undergone DTA and TGA tests by heating the samples from room temperature to 990°C at 10°C increment per minute. Peaks found in these tests are tabulated in Table 3. Three peaks, endo, endo and exo respectively, were observed for DTA curve of sample. The first and second endothermic peak observed was occurred due to dehydration and dehydroxilation respectively. Dehydration occurred at 87°C and dehydroxilation which is known as releasing of OH groups from the octahedral layer of the lattice water in MMT occurred at 534°C. The exothermic peak was occurred due of the breakdown of crystal structure of the dehydrated MMT and happened at 914°C to the sample. When considering the peaks of the DTA curves of MMT, it was observed that the first peak was occurred within range but there was a small difference in the second endothermic positions. The endothermic peak in the range of 525-575 °c is due to the loss of hydroxy is in kaolinite. Endothermic peaks in the range of 650-700°C are as a result of hydroxyl of Montmorillonite. The reason, for the difference occurred at second peak, was due to different interlay cation and different other minerals present in the sample (S.U. Adikary, 2012).

Table 4 DTA & TGA results of clay samples

Clay type	DTA		TGA	
	Peak	Temp erature	Weight lost%	Weight lost %
Giant's tank	Endo	87	4.37	16.51
	Endo	534	2.09	7.90
	Exo	914	-	-
Allavankai	Endo	80	3.87	14.79
	Endo	510	2.27	8.68
Montmorillonite	Endo	120		10.99
	Endo	680		3.90

C. Liner Shrinkage Test

Measurement of soil shrinkage characteristics can help to identify the naturally occurring clay deposits such as montmorillonite, kaolinite and contraction expansion potential of Geological deposits. Linear shrinkage test is used to calculate the one-dimensional shrinkage, although the volume shrinkage can be calculated. Linear shrinkage is a ratio between the average length of oven dry sample after shrinking and the wet sample with initial water content equal to or higher than the liquid limit original length.

Table 5. shrinkage percentage of each sample

Clay	Shrinkage %
Murunkan	17.84
Mavilankeni	23.94
Soil	9.13
Bentonite	8.5-15

These three samples are showing more expansion than the soil sample hence we can decide that the clay samples having the expected clay minerals.

D. X-RAY DIFFRACTION

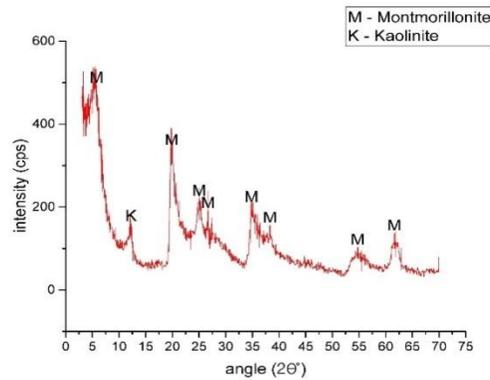


Figure 9: XRD spectrums of purified Giant's tank clay samples

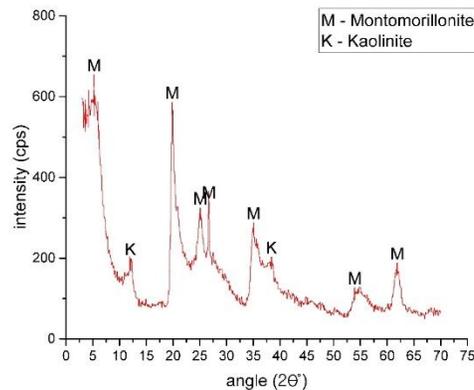


Figure10: XRD spectrums of purified Marvelankeni clay samples

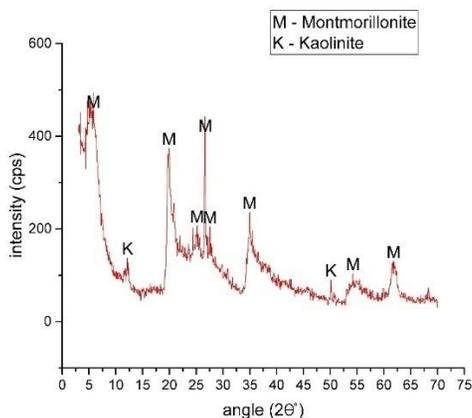


Figure 11: XRD spectrums of purified Allavankai clay samples

The XRD analysis results clearly show that the isolated clay samples were concentrated by montmorillonite and the specimens have been removed the impurities such as Quartz and kaolinite to in small level. The analysis also shows the presence of Montmorillonite in all the samples; very sharp peaks in some samples while relatively small peaks in others. For the extraction process the specimens with distinctive Montmorillonite peaks in the XRD analysis would be chosen as they would yield greater amount of Montmorillonite when being extracted.

IV. CONCLUSION

All the characterizations method such as Fourier transform infrared spectroscopy (FTIR), Differential thermal analysis (DTA), linear shrinkage test, X-ray diffraction (XRD) are ensure that all the samples having the required clay mineral of Montmorillonite.

The extraction process was mainly focused in Ultrasonic method with Sedimentation. After the sedimentation the samples were subjected to XRD analysis. The XRD spectrums ensured the presence of Montmorillonite significantly. Hence this would be the easiest method to extract the Montmorillonite from naturally occurring clay deposits and also the reach conformed that the Montmorillonite mineral significantly available in Murunkan area.

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