Extraction of Montmorillonite nano Particles from Clay Deposits in Nachchaduwa Area

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Abstract— *Clay deposits in Nachchaduwa, located in the Anuradhapura district, have been used for generations in brick, tile, and traditional cookware manufacturing industries. In modern industries Montmorillonite clay has applications mainly in the field of polymer-clay nano composites. The Composites synthesised by infusing Montmorillonite nano particles into the polymer are known to show superior mechanical properties, which are difficult to achieve otherwise. Currently Montmorillonite needed for the local industries are being imported. If Montmorillonite can be extracted from these deposits as nano particles they can be used in the manufacturing industry. This research was mainly focused on the extraction of these Montmorillonite nano particles from the clay deposits located in the Nachchaduwa area, which can be used in the fabrication of polymer-clay nano composite. The extraction technique was based on sedimentation and centrifuging techniques. The initial stage of the extraction process consisted of removing impurities. After this purification the clay fraction of the samples were isolated and were subjected to several centrifuging steps to isolate the Montmorillonite. Characterization of the resultants after major steps in the process were carried using X-Ray diffraction and laser particle size analysis.*

The results of these analysis revealed that these clay specimens in this region was mainly consisting of Kaolinite and Montmorillonite, which conforms with previous research findings, and the main impurity being quartz. The impurities were removed to a great deal by initial sieving and then the clay fraction was isolated by the initial sedimentation. The final resultant which was subjected to centrifuging contained the Montmorillonite and the particle size analysis confirmed the presence of nano particles in this extract.

Keywords— Montmorillonite, clay, extraction, nano-composite, nanoparticles

I. INTRODUCTION

Montmorillonite clay have attracted great deal of attention in recent time due to their involvement in nano composite fabrication. Due to their swelling property Montmorillonite was widely used in the oil drilling industry as a lubricant. Other than that it also used in paint, paper, pharmaceutical, and agriculture industrieswith variety of applications (Hartwell, 1965). The chemical formula of Montmorillonite is $(Na,Ca)_{0.3}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ and it belongs to the smectite clay group. Recent research conducted on the synthesis of polymer-clay nano-composites have greatly increased the attention given to Montmorillonite since these composites have shown superior mechanical and thermal properties (Tiwari *et al.*, 2008; Chieng *et al.*, 2010) which are not possible to achieve in conventional materials. With these new discoveries industries are switching to fabricate these composites from conventional polymers. At the moment all the Montmorillonite needed in industrial processes are being imported to the country.

In Sri Lanka Montmorillonite can be found in many clay deposits. Previous characterizations of local clay deposits have found out that Montmorillonite is abundantly found in the dry region clay deposits (Herath, 1973). These clay deposits are being mined currently to be used in traditional ceramic ware fabrication such as bricks, roofing tiles, and pottery items. Because of this reason the true potential of these deposits are not being utilized. If Montmorillonite can be extracted from these deposits they can be used in local industries and will help in value addition of these clay deposits.

According to the characterizations that have been carried out it has found that dry region clay deposits are a mixture of Montmorillonite and Kaolinite. Structure wise both Montmorillonite and Kaolinite has a small difference. But Montmorillonite is a 2:1 (an octahedral sheet is sandwiched between 2 tetrahedral sheets) while Kaolinite is 1:1 clay. Furthermore on addition of water Montmorillonite tend to swell a great deal due to water molecules penetrating inside interlayer spaces which does not take place in Kaolinite. Due to this reason the density of the two minerals vary in aqueous medium (Wada & Wada, 1977). This factor becomes useful in separating the two minerals since other parameters of the two clays are almost the same. The composites fabricated using Montmorillonite need to have the particle size of the clay minerals in nano scale. Therefore this research was focused on extracting nano sized Montmorillonite particles from clay deposits located in the dry region that can be used in the synthesis of polymer-clay nano-composite. The clay deposits selected for this research are located in the Nachchaduwa area in the Anuradhapura district. These clay deposits are already being mined for tradition clay fabrications mentioned above.Since Montmorillonite is already being used in the industry it is viable to extract these minerals by local clay deposits. This reduce the dependency of the local industry on the imported minerals and will increase the value addition to the local minerals. This research is mainly focused on extracting nano particles of Montmorillonite clay from local clay deposits, which can be used in the existing industrial processes without much pre-processing.

II. METHODOLOGY

Initial clay samples were collected from five sites located in Nachchaduwa area. Exact locations are listed below.

Clay 1- Kalathirappane clay deposit (Latitude: 8 18 N and Longitude: 80 32 E)

Clay 2- Dematawewa clay deposit (Latitude: 8 16 N and Longitude: 80 35 E)

Clay 3- Galkulama clay deposit (Latitude: 8 18 N and Longitude: 80 57 E)

Clay 4- Illanthagahawewa clay deposit (Longitude: 8 19 N and Longitude: 80 34 E)

Clay 5- Pallankulama clay deposit (Longitude: 8 47 N and Longitude: 80 48 E)

Collection of samples was done at a depth of 0.9 m from the surface. Collected samples were then wet sieved from 53 μm to remove any organic and coarse particles present in clay. Then each of specimens was dried in the oven at 110 ˚C, ground using mortar and pestle to make them powder and dry sieved from 53 μm sieve. Initial particle size analysis was carried out for each specimen using the hydrometer technique. In order to remove organic materials from the specimens these were heated up to 300 ˚C for a period of 1 h. Resultant powder then subjected to Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Differential Thermal Analysis & Thermogravimetric Analysis (DTA & TGA) to verify the presence of Montmorillonite.

FTIR tests were carried out by using the Bruker alpha-T instrument with the KBr pellet method for frequency range of 4000-500 cm^{-1}. Peak values of resultant spectra were compared with literature data.Specimens were subjected to XRD to ensure the presence of Montmorillonite and to verify the results of FTIR. Specimens were first spread on a flat surface in a desiccator and ethylene glycol was added to the bottom of the desiccator. It was then put in to the oven and heated for 60 ˚C and kept at that temperature for 1 h. Then it was kept as it is for 24 h before being subjected to XRD analysis. XRD was carried out using Siemens D5000 X-Ray diffractometer. After the analysis peak values were compared with literature values.

DTA and TGA test were done using Differential Thermal Analyser, Rigaku Thermoflex TG 8110 by heating the specimens from room temperature to 990 ˚C. Resultant graphs then compared with literature values.Chemical analyses for selected samples were carried out at Geological Survey and Mining Bureau. Known weight of the sample was fused (1000 ˚C - 1100 ˚C) for 1 h. Silica content was determined by treating the residue with hydrochloric (HCl) and hydrofluoric (HF) acid. To determine Al_2O_3 content; filtrate from SiO_2 separation was treated with Ammonium Hydroxide. The precipitate obtained was treated with Bromine water and ignited on a platinum crucible at 1100 ˚C for thirty minutes and weight of the residue gives Al_2O_3 content. Na_2O, K_2O CaO, MgO, Fe_2O_3 and TiO_2 content were determined using atomic absorption spectrophotometer. Isolation of clay fraction of the specimens was carried out by using a combinational method of sedimentation and centrifuging. The final supernatant was collected and dried at 80 °C until the complete water evaporation. The same process was repeated at least three times on the successive settled clay specimens (Thuc *et al*, 2010) until the mass ratio of the solid fraction collected in the final supernatant obtained after the latter centrifugation step was found negligible. Such isolated clay were then subjected to XRD and particle size analysis to identify the minerals present in them. Those which showed clear sign of presence of Montmorillonite then selected for the isolation process. The extraction of Montmorillonite after the sedimentation was carried out using a centrifuging method with the addition of NaCl. Resultant was then dried and subject to XRD and particle size analysis. This entire procedure is summarized and given in Figure 1 below.

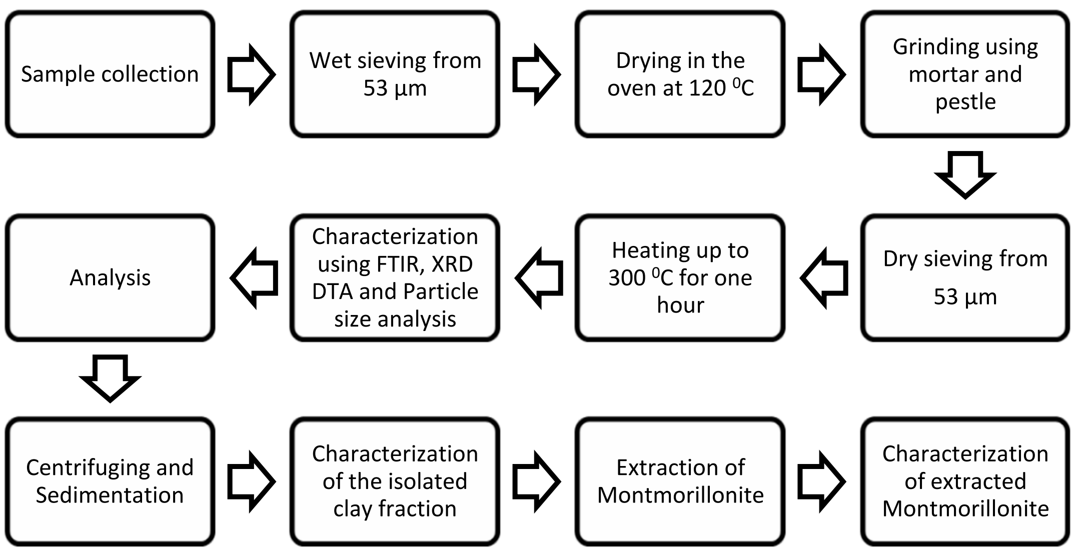

Figure 1: Methodology Flowchart

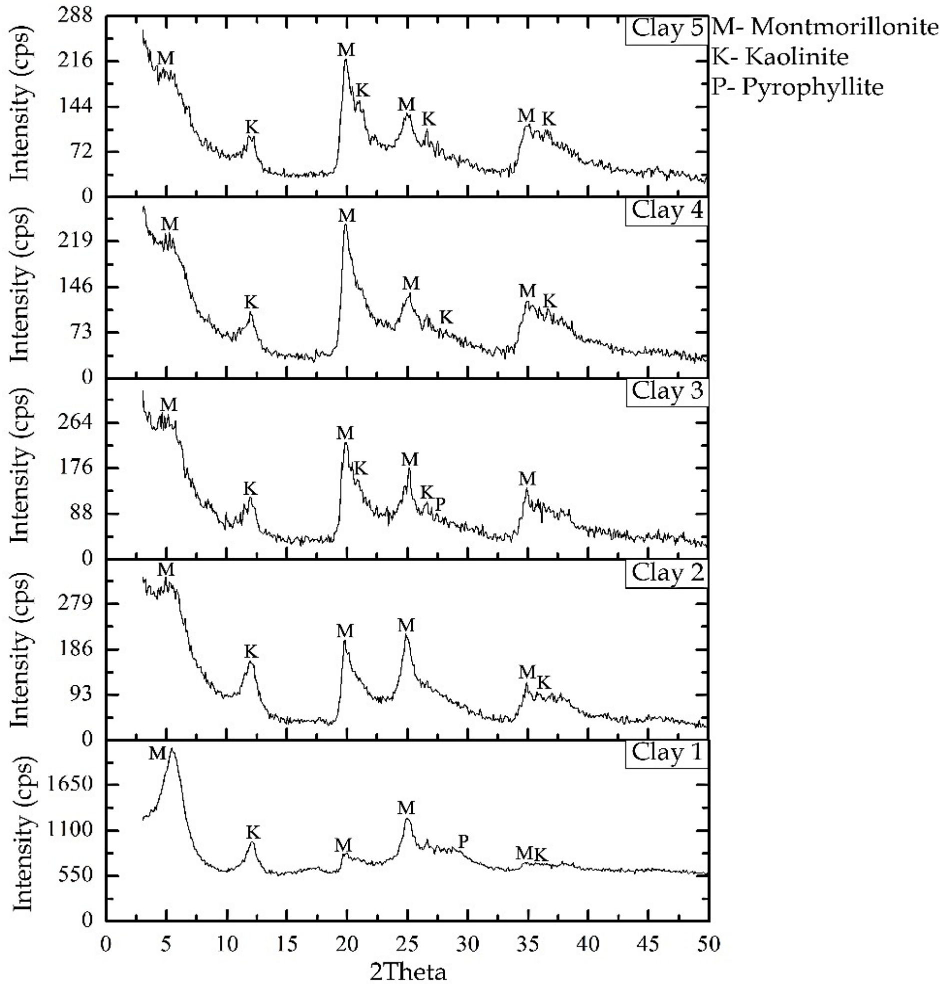

Figure 2: XRD results of clay subjected to isolation

III. RESULTS AND DISCUSSION

Initial characterizations done using XRD, DTA & TGA, FTIR, and chemical analysis revealed that these specimen contain both Montmorillonite and Kaolinite with major impurity being quartz. This finding correlates with the findings obtained from previous research (Wanasinghe & Adikary, 2012; Herath, 1973). Since all the specimens showed the presence of Montmorillonite all of these specimens were then subjected to clay fraction isolation process.

This was carried out using a combination of sedimentation and centrifuging as mentioned above. Main purpose of this technique was to remove any possible impurities and coarse particles which may be above the nano range. The resultants after the centrifuging was collected and analysed using XRD and particle size analysis. The XRD patterns, which are shown in Figure 2, clearly show that the clay fractions of the specimen have been isolated while major impurities, including Quartz, have been removed.

The particle size analysis given in Figure 3 showed that majority of the particles are in the nano meter range. However it is known that Montmorillonite is very difficult to deflocculate. Usage of traditional defloculant chemical has no or very small effect to this type of clay (Rolfe *et al*, 1987). In order to overcome this problem the clay specimens were subject to ultrasonication for a period of 12 H. This greatly increased the particle size distribution of the specimens which is shown in Figure 3.

However due to the limitations of the instruments the minimum particle size that was detectable was limited to 300 nm. But the size distribution graph shows that there are more particles that falls below this size.

After this analysis it was confirmed that these specimens contained only the clay constituent and therefore subjected to the extraction process. The extraction of Montmorillonite is problematic since the two type of clays mixed in these, namely Kaolinite and Montmorillonite, has very much similar physical characteristics. However it has shown from previous research that their densities become different in aqueous solution due to water molecules moving inside the interlayer spaces of Montmorillonite, which cannot be achieved in the Kaolinite structure (Wada & Wada, 1977).

However the same research has shown that in the absence of water Montmorillonite has a lower density than Kaolinite. Since all the process of this research was carried out in deionized water medium it can be assumed that water molecules have been inserted between the Montmorillonite layers which would increase the density of the clay. Therefore if the interlayer water molecules can be removed from these then the density of Montmorillonite will lower and hence can be effectively be separated by an accelerated gravity process. This would also eliminate higher density agglomerated particles and also the higher density impurities other than Kaolinite (Shi et al, 1989; Bray et al, 1998; Powellet al, 1997).

Out of the five specimen used for the separation the first specimen showed better results when comparing with the other. Its XRD analysis is shown in Figure 4 which indicates the constituent materials that were present in this clay from the beginning.

Some of the specimens showed trace amount of Kaolinite in their XRD analysis which is shown in Figure 5. Except for Clay 2 and Clay 4 specimens all the other specimens shows only the main Kaolinite peak in their XRD analysis.

After the final centrifuging the collection of the two layers were done manually at which some of the two phases may get mixed. However in all the specimens the maximum intensity peak was recorded for Montmorillonite.

IV. CONCLUSION

The initial analysis of the specimens revealed that dry zone clays are rich in Montmorillonite and Kaolinite and can be used for wider variety of applications. The main impurity of the clay is quartz which along with some other impurities can be removed through sendimenting the clay and collecting the supernatant liquid. The flocculation characteristic of Montmorillonite is huge problem when determining the particle size of the clay, which is minimized by the application of ultrasonic which breaks the flocculation to greater degree than conventional deflocculants.

Separation of Montmorillonite from Kaolinite is difficult due to their near identical physical characteristics. However the extraction process was carried out by centrifuging with NaCl and analysis of the extracted clay revealed that Montmorillonite have been separated from Kaolinite but care should be taken when collecting the separated layers as mixing of the two can occur at this step.

The final results from this research show that the Montmorillonite particles have been separated from the clay mixture and the majority of the particles are in the nano meter range. Further research work is needed to be carried out to find how these particles can be used in industrial applications.

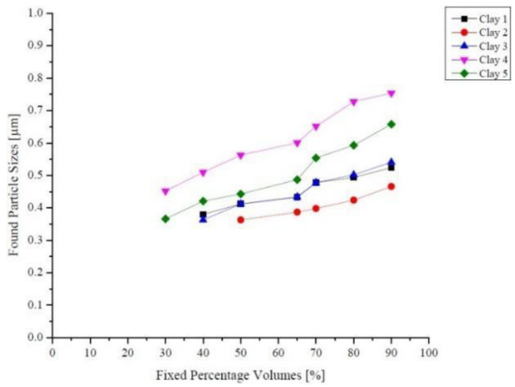

Figure 3: Particle size distribution of isolated clay

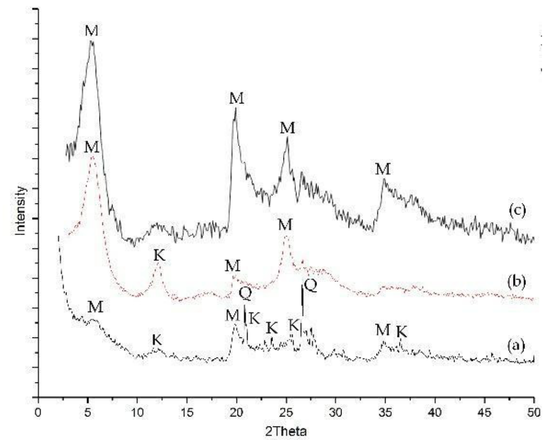

Figure 4: XRD analysis of Clay 1 (a)- initial, (b)- after subjecting to clay isolation, (c)- after separation M- Montmorillonite, K- Kaolinite, Q- Quartz

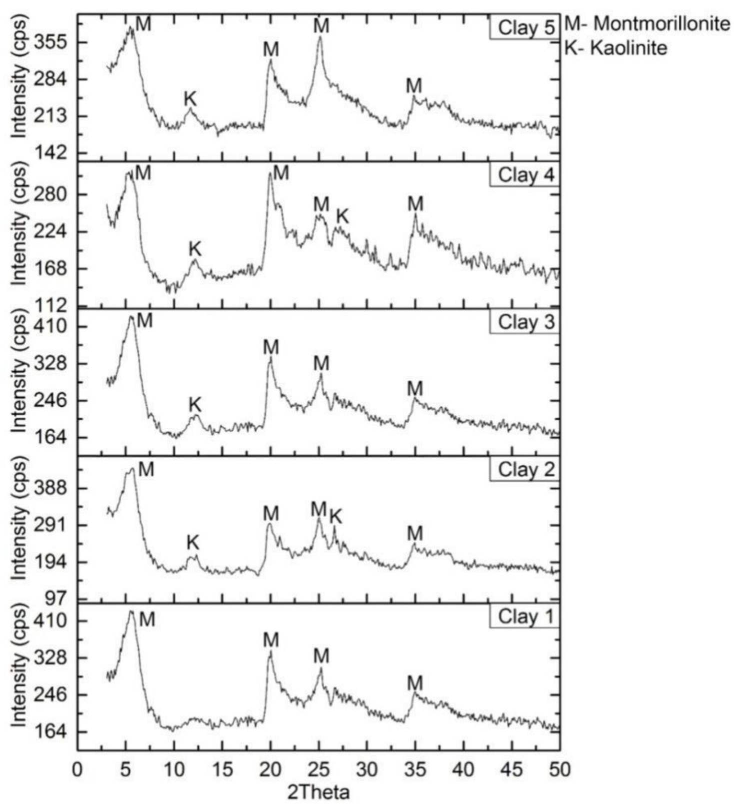

Figure 5: XRD analysis of extracted clay specimens

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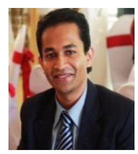

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