Journal of Experimental Research

December 2017, Vol 5 No 2
www.er-journal.com
Email: editor-in-chief@er-journal.com

Received: May, 2017
Accepted for Publication: August , 2017

DETERMINATION OF MONTMORILLONITE CONTENT IN NIGERIAN BENTONITIC CLAYS USING FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

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Abstract

This research focused on characterising the raw, beneficiated and treated Nigerian bentonitic clays using Fourier Transform Infrared Spectroscopy (FTIR) with the aim of determining their mineralogical compositions for application in oil and gas drilling fluid formulation. The frequencies of absorption for all the samples in which the AIAIOH stretching band typically occurs at approximately between 3620-3630 cm^{-1} and for bending band is situated at approximate values of 920-930 cm^{-1} which indicates that all the studied bentonite samples are Al-rich montmorillonite of smectite group. The samples also showed small CO^{3-} stretching band at approximately 1430 cm^{-1} indicating the presence of carbonate impurities.

Key words: Bentonite, FTIR, Frequencies, Montmorillonite, Smectite and Stretching band

INTRODUCTION

Bentonite is a rock formed of highly colloidal and plastic clays composed mainly of montmorillonite, a clay mineral of the smectite group and is produced by *insitu* devitrification of volcanic ash (Parker, 1988). The transformation of ash to bentonite apparently takes place only in water (certainly seawater, probably alkaline lakes, and possibly other fresh water) during or after deposition (Grim, 1968; Patterson & Murray, 1983).

Montmorillonite clay minerals occur as minute particles, which, under electron microscopy, appear as aggregates of irregular or hexagonal flakes or, less commonly, of thin laths (Grim, 1968). Differences in substitution affect and in some cases control morphology. The predominant isomorphous substitutions are Mg and Fe for AI in the octahedral sheet, but AI^{3+} may be substituted for Si in the tetrahedral sheet (Carlos and George, 2004).

Bentonite clays exist in the North-east quadrant of Nigeria (Borno, Yobe, Taraba and Adamawa) where a probable reserve of more than 700 million tones has been indicated. Similarly, over 90 million tones have been reportedly found in Afuze, Ekpoma-Igunebon road, Ovibiokhuan and Okpebho areas of Edo State. Some occurrences have also been reported in Abia, Ebonyi and Anambra States. (RMRDC, 2010). Bentonite occurrence has also been reported in Benue State, (Abdullahi, 1996) in Azara; Nasarawa State and Akiri Hill in Plateau state (Onaogu, 1996).

FTIR (Fourier Transform Infrared) is the preferred method of infrared spectroscopy. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. *Information provided by FTIR includes:* identification of unknown materials, determination of the quality or consistency of a sample and the amount of components in a mixture (TNC, 2001).

Smectite gives rise on inner-surface OH stretching bands at 3660 & 3630 cm^{-1} (for beidellite), 3632 cm^{-1} (for montmorillonite) or 3564 cm^{-1} (for nontronite) (Farmer & Russell 1967). Usually the band for smectites is broad and several unresolved spectral components contribute to it. The exact position of the band depends on the chemical composition of the smectite, AlAlOH stretching band is typically at 3620-3630 cm^{-1}, AlMgOH stretching band at 3687 cm^{-1} and AlFe^{3+}OH stretching band at ~3597 cm^{-1} (Farmer 1974). Usually the two latter bands are not resolved from AlAlOH band in Al rich smectites (Farmer 1974). In kaolin minerals, inner-surface OH stretching bands are seen at 3697 cm^{-1}, 3669 cm-1, 3652 cm^{-1} and 3620 cm^{-1} (Farmer1974).

Structural OH bending vibrations for clay minerals are found at 950-600 cm^{-1}(Farmer, 1974). AlAlOH bending band can be assigned to smectite and/or kaolin minerals at 919-913 cm^{-1}. AlFe^{3+}OH bending band for smectite locates at 890-870 cm^{-1}. The position of this band is decreasing with increasing Fe content. At 860-840 cm^{-1} are AlMgOH bending bands for smectite. Fe^{3+}Fe^{3+}OH bands at 850 and 818-815 cm^{1} are indicating the presence of nontronite. The exact position and molar absorptivity of all above mentioned OH bending bands depends on water content and type of exchangeable cation (Xu et al. 2000). The band at approximately 920 cm^{-1} is least affected by type of exchangeable cation, but most affected by water content.

This research work focused on the characterisation of the raw and beneficiated bentonitic clays using Fourier Transform Infrared Spectroscopy (FTIR) with the aim of determining the mineralogical compositions of the Nigerian bentonitic clays obtained from various locations of north eastern Nigeria, for application in oil and gas drilling fluid formulation.

MATERIALS AND METHODS

The raw Bentonitic clay samples were collected from five different locations of the marine environment of upper Benue Trough, north eastern Nigeria (Bilal et al., 2015 & Bilal et al., 2016)

The samples were brought to the Department of Material Science laboratory, Centre for Energy Research and Training (CERT) for free silica (Quartz) removal and activation with Sodium carbonate as explained by Bilal et al., (2015) and Bilal et al., (2016).

FTIR Spectrophotometer Analysis

FTIR Spectrophotometer analysis was done using the FTIR-8400S Fourier transform infrared spectrophotometer at NARICT, Zaria. Investigations were performed by the transmission technique. Bands were recorded as the transmittance function, within the wave number range 4000–450 cm^{-1} at a resolution of 10 cm^{-1}. The montmorillonite content was determined on the basis of the medium spectrum.

RESULT AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR) was used for the identification of clay minerals (especially montmorillonite of smectite group), poorly crystalline mineral phases and also for identification of possible adsorbed elements or functional groups.

The clay minerals identified in FTIR results of all studied bentonite samples depicted in Figure 2 to 6 proved to be montmorillonite of the smectite group when compared with FTIR result of the standard API (American Petroleum Institute) bentonite in Figure 1. The studied samples showed that the AlAlOH stretching band occurred at 3622 cm^{-1}, 3619 and 3635 cm^{-1} for raw, Na activated and treated Garin Hamza bentonite (Figure 2 (a), (b) and (c)) respectively, while for Pindiga samples the AlAlOH stretching band occurred at 3639 cm^{-1} for raw sample, 3629 cm^{-1} for Na activated sample and 3627 for treated sample (Figure 3 (a), (b) and (c)) respectively. The Tongo sample AlAlOH stretching band occurred at 3627 cm^{-1}, 3623 cm^{-1} and 3612 cm^{-1} for raw, Na activated and treated samples (Figure 4 (a), (b) and (c)) respectively. The Bulabulin Maiduwa AlAlOH stretching band occurred at 3622 cm^{-1}, 3621 cm^{-1} and 3622 cm^{-1} for raw Na- Activated and treated samples (Figure 5 (a), (b) and (c)) respectively. lastly, the AlAlOH stretching band for Sabongarin Ngalda sample occurred at 3621 cm^{-1}, 3847 cm^{-1} and 3622 cm^{-1} for raw, Na activated and treated samples (Figure 6 (a), (b) and (c)). The frequencies of absorption for all the samples indicate that the smectites are Al-rich. This confirmed the discovery of Farmer (1974) that the AIAIOH stretching band typically occurs at 3620-3630 cm^{-1} while the AIMgOH stretching band occurs at 3687 cm^{-1} and the A1Fe^{3+}0H band at 3597 cm^{-1} (Farmer, 1974). The broadness of the band is due to the contribution of Mg and Fe in the octahedral sheets and might also indicate that the smectite structure is poorly ordered (Farmer, 1974).

The OH-vibrations are better determined or resolved in the bending frequencies as compared to the stretching frequencies. The AlAlOH band is situated at 920-930 cm^{-1}, the A1Fe^{3+}0H band at 880-890 cm^{-1} and the AlMgOH band at 840 cm^{-1} (Farmer, 1974). The intensities of these bands in the spectra indicate the proportions of Al, Fe and Mg in the octahedral sheets of montmorillonite. The FTIR characterised samples indicate that they are generally Al-rich montmorillonite and none of the samples is either Fe or Mg rich because no absorption band appeared with respect to Fe and Mg content in all the results.

All the analysed samples showed small CO^{3-} stretching band at approximately 1430 cm^{-1} signifying the presence of carbonate impurities, this is also in accordance with the findings of Russell (1987).

The Si-O stretching bands were observed at 1105 and 1110 in Pidiga sample, it was also observed at 1113 and 1151 in Tongo and Sabongarin Ngalda samples with the exception of Garin Hamza and Bulabulin Maiduwa. The Si-O stretching band of quartz at approximately 778 - 780 cm^{-1}, the Si-O stretching band of quartz at 780 cm^{-1} (very weak in most spectra), the Al-O + SiO vibrations were absent in all the samples, the Al-O-Si bending vibration at approximately 522 - 536 cm^{-1} appeared in Garin Hamza, Tongo and Sabon garin Ngalda samples. The Si-O-Si bending vibration at 468 cm^{-1}. The absence of the 798 cm^{-1} band (quartz and silica) and the presence of the 780 cm^{-1} band (quartz) in many spectra could indicate the presence of well ordered ('amorphous') SiO$_2$ in the sample.

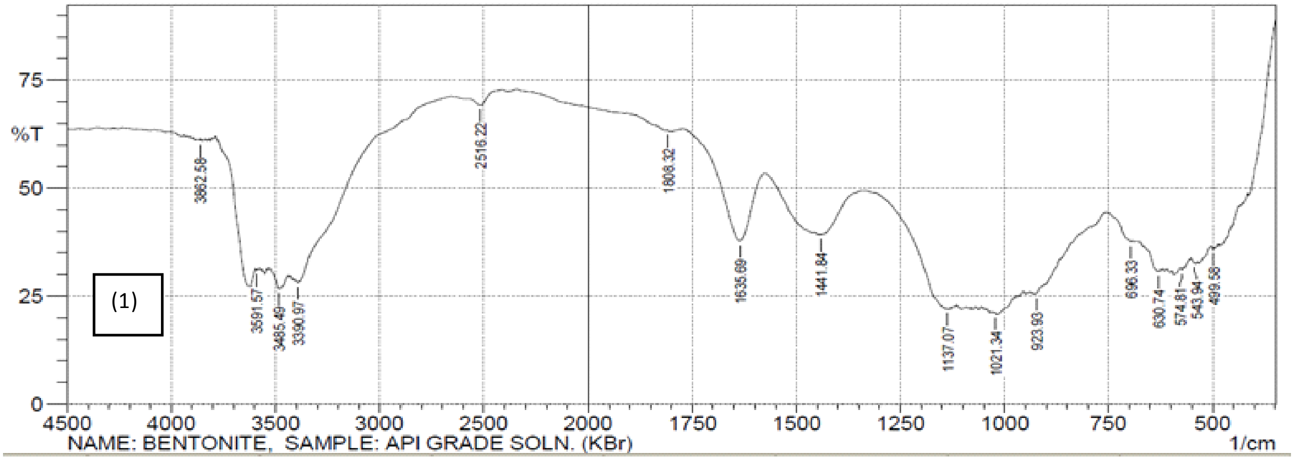

Figure 1: FTIR Spectrum of Standard (API) Grade Bentonite.

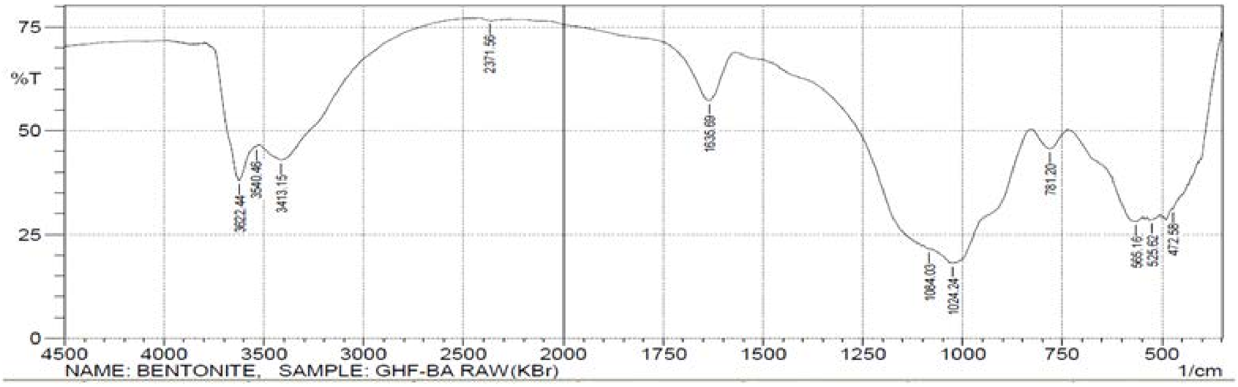

Figure 2(a): FTIR Spectrum of Raw Garin Hamza Bentonite.

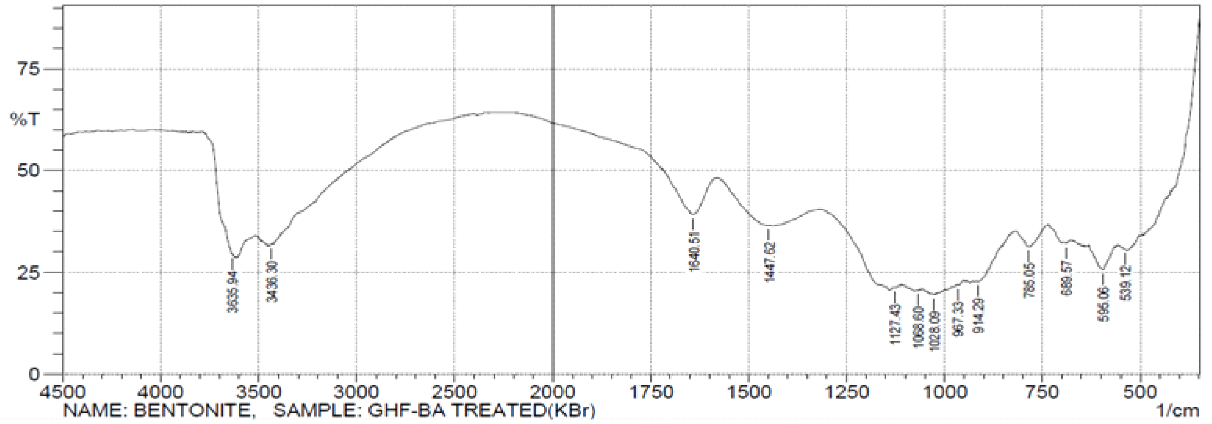

Figure 2(b): FTIR Spectrum of Na Activated Garin Hamza Bentonite.

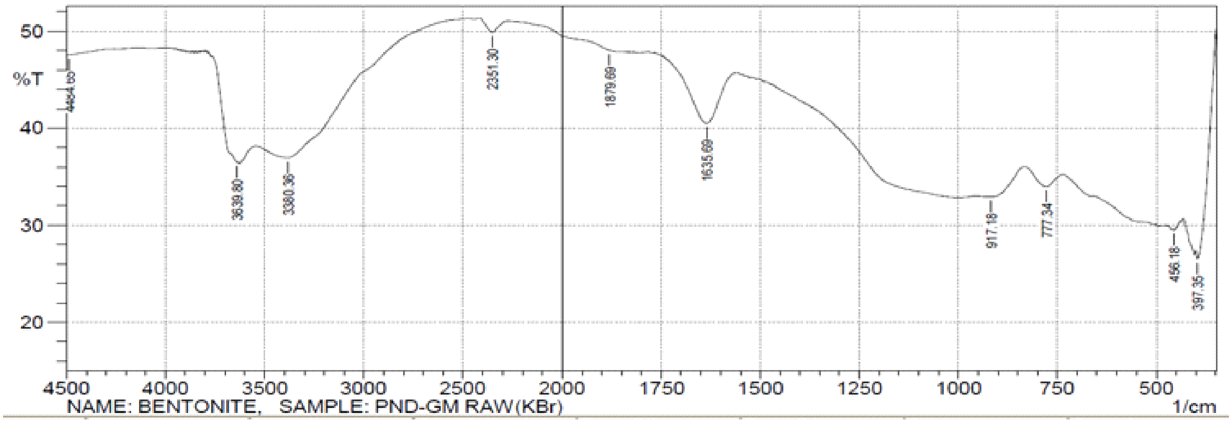

Figure 2(c): FTIR Spectrum of Treated Garin Hamza Bentonite.

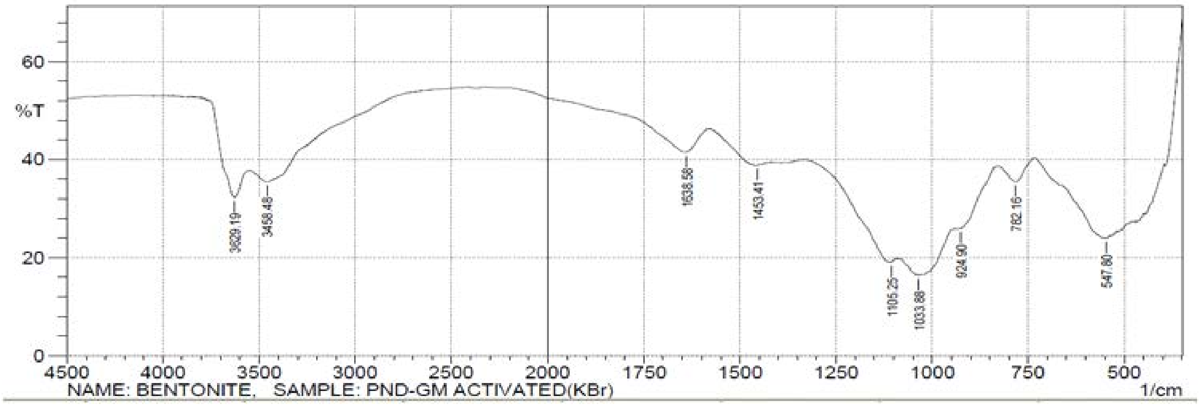

Figure 3(a): FTIR Spectrum of Raw Pindiga Bentonite.

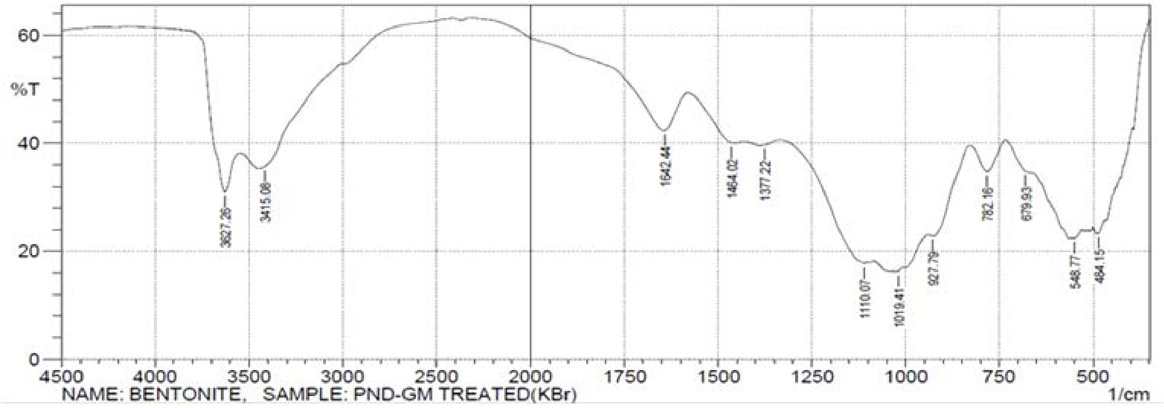

Figure 3 (b): FTIR Spectrum of Na Activated Pindiga Bentonite.

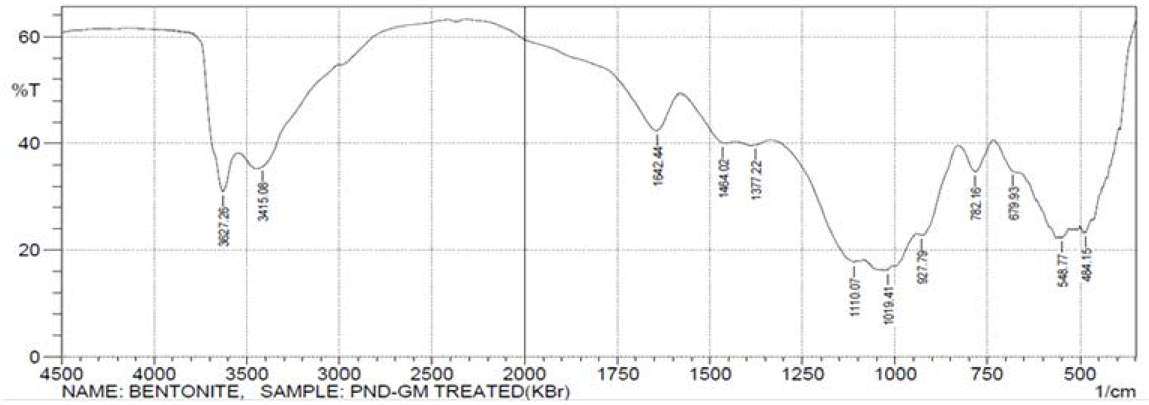

Figure 3 (c): FTIR Spectrum of Treated Pindiga Bentonite.

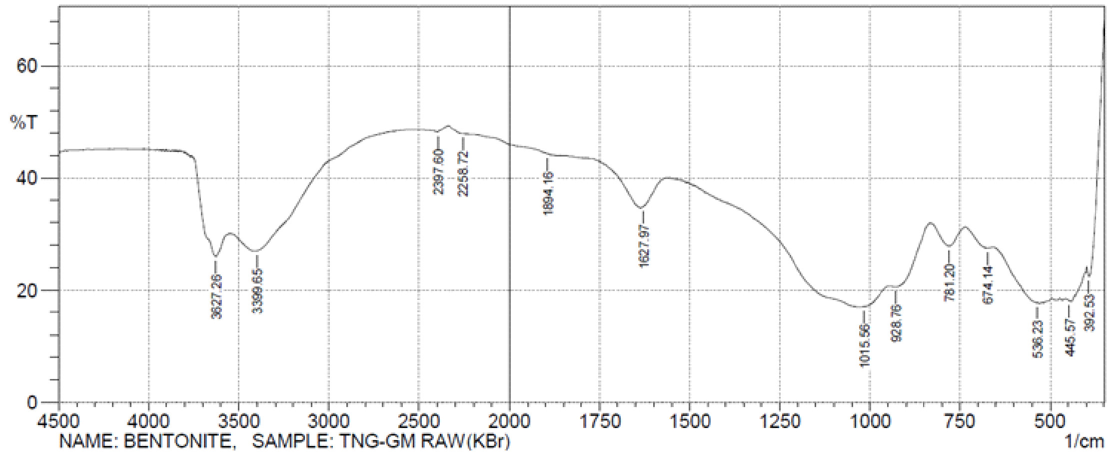

Figure 4(a): FTIR Spectrum of Raw Tongo Bentonite.

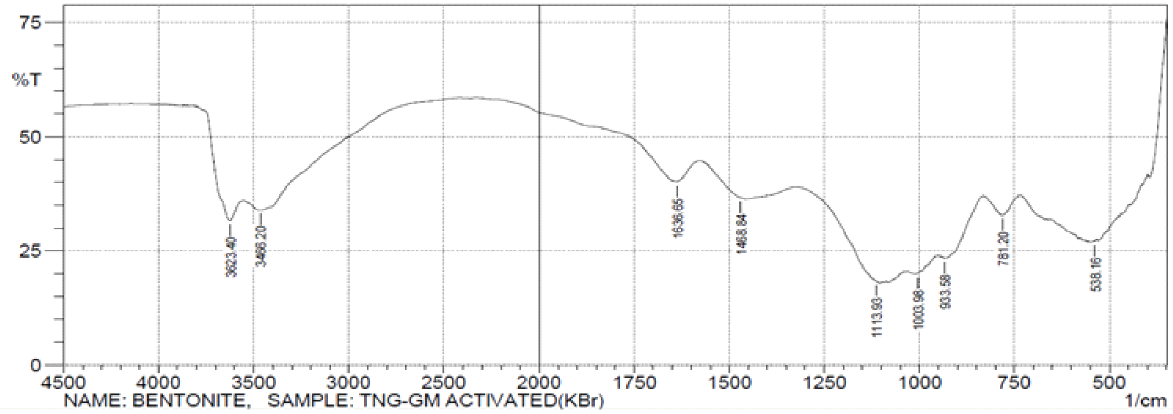

Figure 4 (b): FTIR Spectrum of Na Activated Tongo Bentonite.

Figure 4 (c) : FTIR Spectrum of Treated Tongo Bentonite.

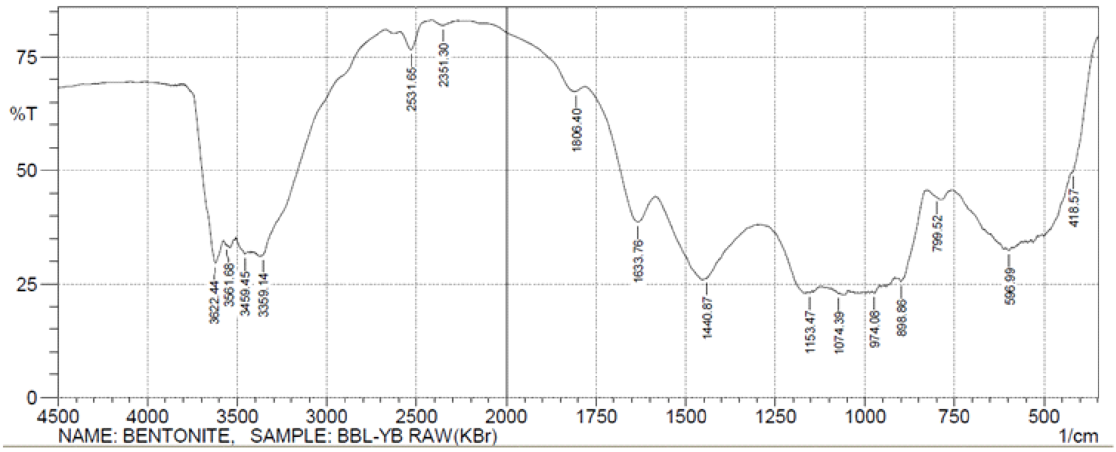

Figure 5 (a): FTIR Spectrum of Raw Bulabulin Maiduwa Bentonite

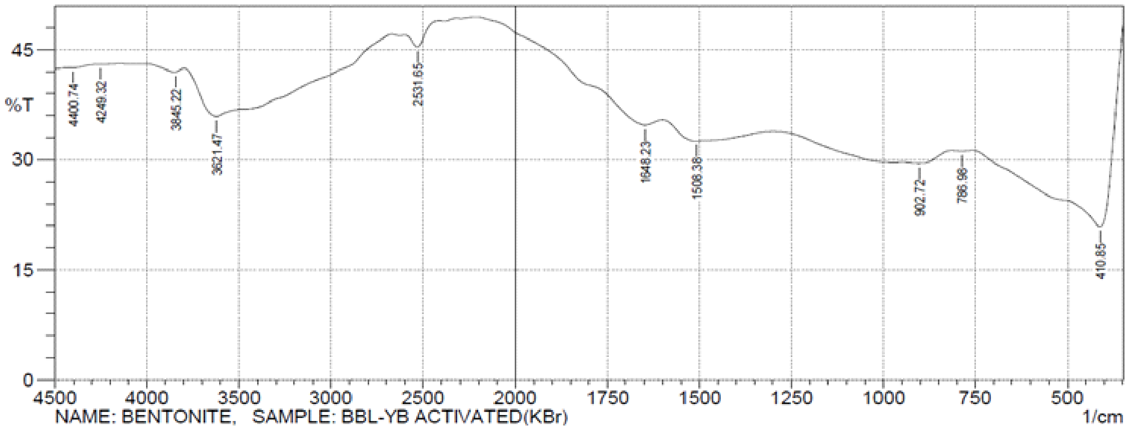

Figure 5 (b): FTIR Spectrum of Na Activated Bulabulin Maiduwa Bentonite

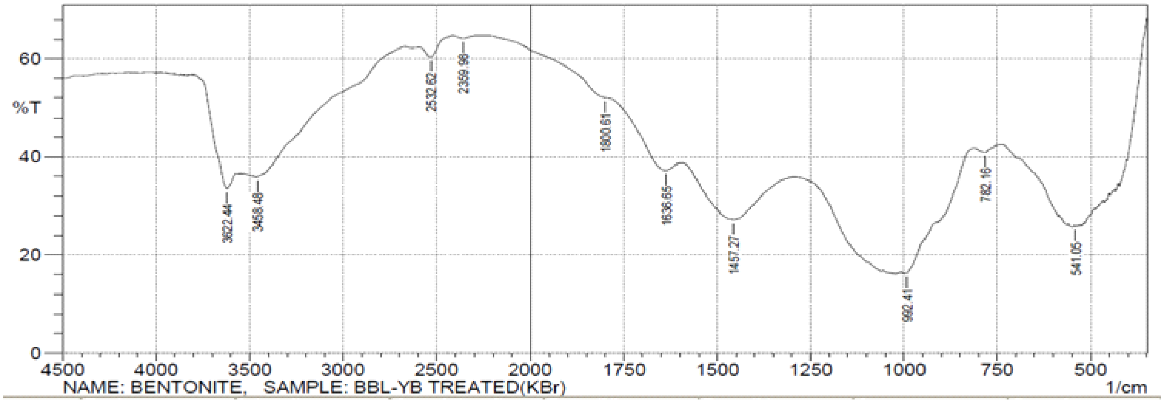

Figure 5 (c): FTIR Spectrum of Treated Bulabulin Maiduwa Bentonite.

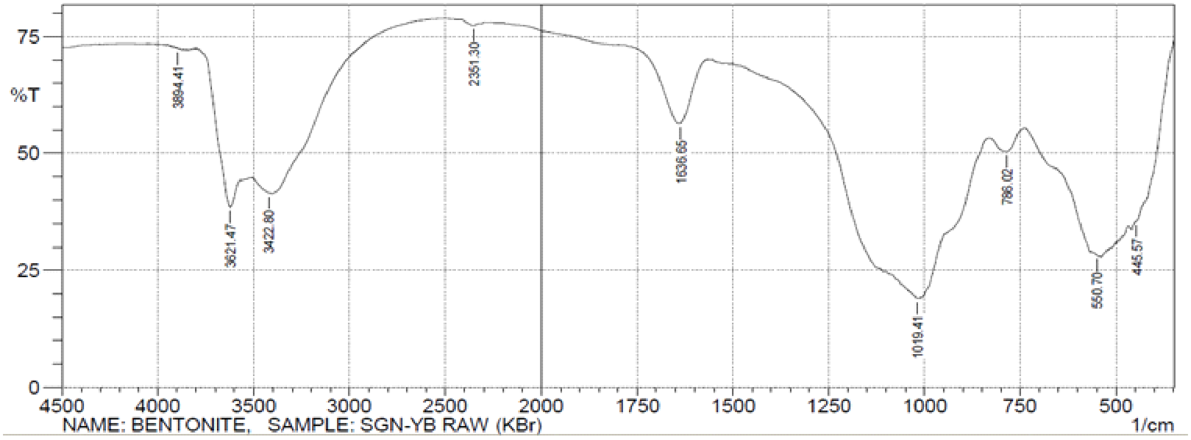

Figure 6(a): FTIR Spectrum of Raw Sabon garin Ngalda Bentonite.

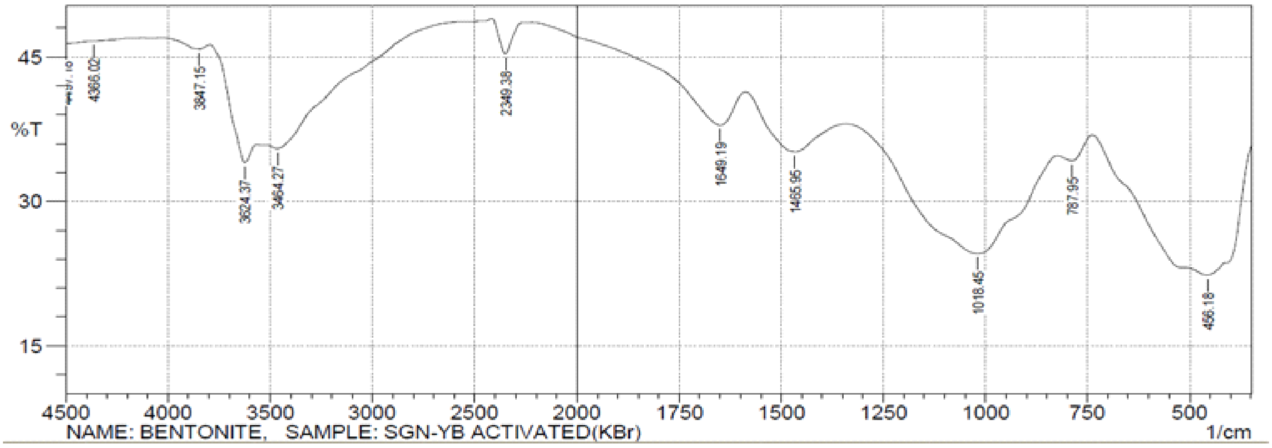

Figure 6(b): FTIR Spectrum of Na Activated Sabon garin Ngalda Bentonite.

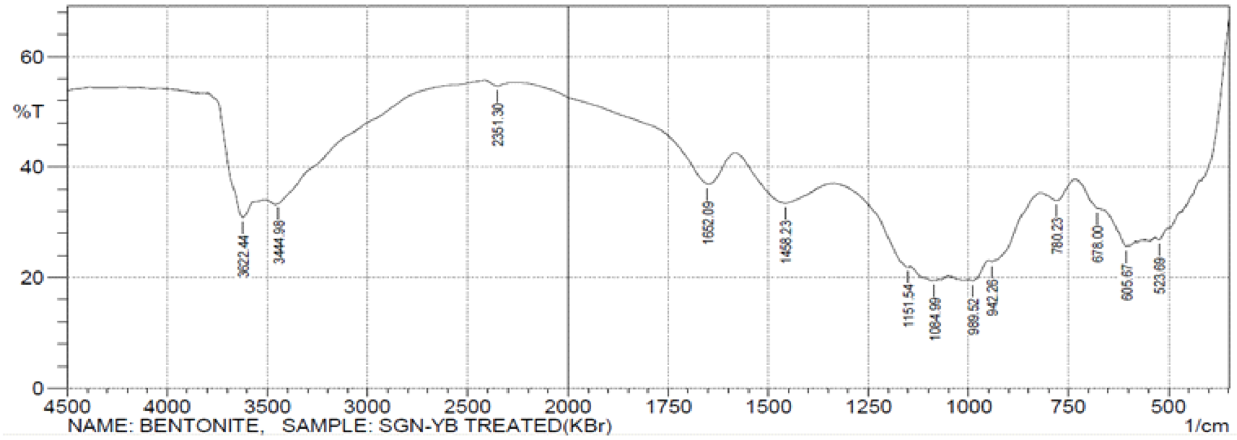

Figure 6 (c): FTIR Spectrum of Treated Sabon garin Ngalda Bentonite.

It was observed that FTIR supports the mineralogical observations in the samples. It is also fast, cost-effective, and doesn't require much sample material. FTIR-analysis is useful in detecting small amounts of accessory minerals and impurities present in the samples.

CONCLUSION

The clay minerals identified in FTIR results of all studied bentonite samples proved to be montmorillonite of smectite group. The frequencies of absorption for all the samples indicate that the smectites are Al-rich, in which the AIAIOH stretching band typically occurs at approximately between 3620-3630 cm^{-1} and for bending band is situated at approximate values of 920-930 cm^{-1}. Presence of small CO^{3-} stretching band at approximately 1430 cm^{-1} in all the samples signifies the existence of carbonate impurities.

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