J. Chem Soc. Nigeria, Vol. 43, No. 1, pp 140 - 146 [2018]

Characterization of Ashaka and Tango Bentonites surfaces after modification with Benzyl dimethyl dodecyl and dimethyl dioctadecyl ammonium chlorides.

Abdullahi S. L[1] and Audu A.A[2]

[1](Department of Science and Technology,Kano State Polytechmic, Kano Nigeria)

[2](Department of Pure and Applied Chemistry, Bayero University Kano, Nigeria)

Corresponding author: **slabdullahi39@gmail.com**

Received 22 September 2017; accepted 23 December 2017, published online 26 January 2018

Abstract

Bentonites from Ashaka and Tango of Gombe State, Nigeria were surface modified with two different surfactants viz; Benzyl dimethyl dodecyl and dimethyl dioctadecyl ammonium chlorides by cation exchange method. The surfaces of the modified products were characterized by means of Fourier-transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The FTIR spectra of the modified bentonites showed the C-H asymmetric ($\upsilon_{as}CH_2$), symmetric ($\upsilon_{s}CH_2$) stretching and bending (δ) vibrations (2926, 2920, 2918; 2851 and 1469cm^{-1}) in methylene groups of surfactant alkyl chains respectively. The basal spacing of the unmodified bentonite samples, determined by means of X-ray diffraction (XRD) was 15.23 Å and 12.99 Å and after modification with benzyl dimethyl dodecyl ammonium it increased to 20.07Å and 19.62Å while with dimethyl dioctadecyl ammonium it increased to 21.79Å and 26.75Å. Results of the SEM images revealed rougher surfaces with uniformly dispersed small particles of grain-like structures characteristic of the organomodified bentonites.

Keywords: Basal spacing, Cation exchange, Organobentonites, Quaternary ammonium surfactants, Surface modification

Introduction

Bentonite is smectite swelling clay derived from weathered volcanic ash which is largely composed of the clay mineral ***montmorillonite*** [1-3] The peculiar characteristics of bentonite clays; thixotropic, swelling and absorption/adsorption properties, have accounted for their demand in various fields of technical applications such as in civil engineering, food, chemical and pharmaceutical industries [1,4].

Bentonite being in the group of smectite consists of 2:1 layers, i.e. two tetrahedral silica sheets sandwiching a central octahedral alumina sheet (T-O-T). Due to an isomorphic substitution within the layers (e.g., Al^{3+} for Si^{4+} in the tetrahedral sheet and Fe^{2+}or Mg^{2+} for Al^{3+} in the octahedral sheet) the clay layers have negative crystal charge which is balanced by exchangeable cations such as Na^+, K^+, Ca^{2+} in the interlayer together with water molecules bonded by ion-dipole forces. The hydration of these inorganic cations causes the bentonite surface to be hydrophilic [4-7].

Surface modification is necessary for making natural bentonite clays suitable in wide spectrum of applications, such as adsorption, catalysis development of polymer nanocomposites etc [8-10].

The first approaches to montmorillonite-based organoclays are the ammonium based surfactants which usually contain long aliphatic chains (C_{12}–C_{18}) causing expansion of the distance between the layers [9] as applied in this study. The introduction of long-chain organic surfactants by ion exchange reactions of the inorganic cations located in the interlayer of the natural bentonite clays under hydrothermal conditions can modify substantially the surface properties of natural bentonite clays by decreasing the surface energy and expanding the interlayer spacing. These modified bentonites are called organo-bentonites [4]. It has been recognized that the ion exchange reaction has two consequences; first, the gap between the single sheets is widened, enabling organic cations chain to move in between them and secondly, the surface properties of each single sheet are changed from being hydrophilic to hydrophobic or organophilic [11,12].

This work was aimed at preparing and characterizing organo bentonite clays from Ashaka and Tango of Gombe State, Nigeria using two quaternary ammonium surfactants; benzyl dimethyl dodecyl ammonium chloride and dimethyl dioctadecyl ammonium bromide.

Materials and methods

The clay samples were obtained from the Ashaka and Tango deposits (Gombe State, Nigeria)

The chemical and mineralogical compositions of these samples as determined by XRF and XRD, showed that Ashaka sample is (Na-B) while Tango sample is (Ca-B) which are mainly montmorillonite with opal, quartz, calcite and feldspars. The cationic exchange capacities of the clays as determined by ammonium acetate method are as 0.72Meq/g and 0.63Meq/g respectively. The surfactants; benzyl dimethyl dodecyl ammonium chloride (BDMDAC) and dimethyl dioctadecyl ammonium bromide (DMDOAB) were used as purchased from SIGMA ADRICH (purity of 98%)

Synthesis of organo modified bentonite clays.

The sample [5g] was dispersed in 100mL of deionized water and subsequently heated to around 80 °C under continuous stirring. When the clay was completely dispersed, (1.22g, 1.07g and 2.27g, 1.99g) of surfactant equivalent to the CEC of the clays was slowly added, and stirring was maintained for 4h at 80^{o}C.

The resultant product was recovered by vacuum filtration and washed several times with deionized water until no halide anions were detected using the silver nitrate test. The product was then dried at 80 °C overnight and finally ground manually in an agate mortar and sieved into a plastic container [4, 7, 8, 12].

Characterization of unmodified and modified bentonites

FTIR technique was used to investigate the intercalation between the clays and surfactants used. The morphology and basal spacing of the unmodified and modified bentonites were investigated by XRD and SEM analyses, respectively.

Fourier transform infrared spectroscopy analysis (FTIR)

FTIR analysis was carried out using FTIR Cary 630 Agilent Technology USA equipment. All FT-IR spectra were recorded and analyzed in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} to know the nature of the functional group attachment.

X-ray diffraction analysis (XRD)

The Bragg angular zone was explored by X-ray diffraction (XRD) in GBC EMMA (Enhanced mini material) Analyzer, that generates a voltage of 40 kV and current 40 mA from monochromatic Cu Kα radiation source ($\lambda = 1.54$ Å). The diffraction angle 2θ was scanned from 2^o to 65^o at scanning rate of 2^o/min and step size of 0.05 ^{o}. In order to calculate the distance between the silicate layers, Bragg's law was used.

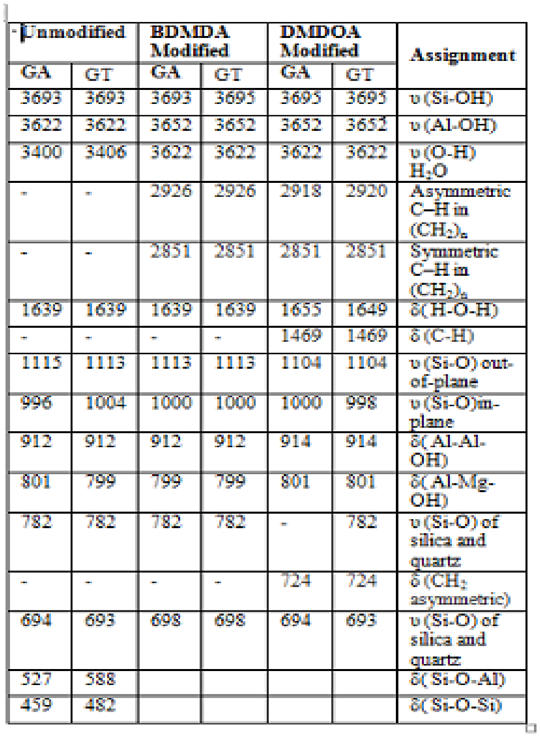
Scanning electron microscopy (SEM): Scanning electron microscope (SEM) (Phenom Proxy, PW 100-002, magnification-255x, Accelerating Voltage- 10KV) was used to evaluate the surface morphology of the bentonite samples.

Results and Discussion

Fourier transform infrared spectroscopy analysis (FTIR):

Table 1 presents the bands obtained from the spectra of the samples. Bands at 3693cm^{-1} and 3693cm^{-1}; 3622cm^{-1} of the unmodified bentonite samples (GA and GT respectively) in this study are assigned to OH stretching vibrations in the Si-OH and Al-OH groups of the tetrahedral and octahedral sheets of the clay samples. A slight shift at band 3693cm^{-1} to 3695cm^{-1} was observed in GT and GA of BDMDA and DMDODA modified bentonites. Vibrations due to C-H asymmetric and symmetric stretching of CH_2 groups for the GA and GT modified with BDMDA are 2926cm^{-1}and 2851cm^{-1}respectively. For the DMDODA modified GA and GT the asymmetric stretching were at 2918cm^{-1}and 2920cm^{-1} and both have their symmetric stretching at 2851 cm^{-1}. DMDODA modified samples show a band at 1469cm^{-1} which has been assigned to the CH_3 asymmetric bending vibrations.

Table 1: Infrared band positions and assignments of the studied bentonite sample

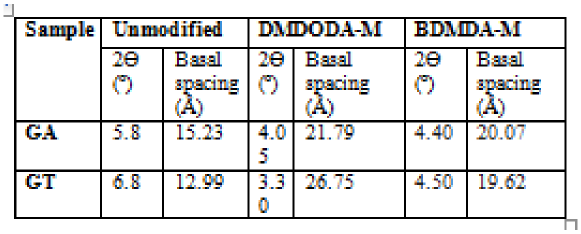


Unmodified		BDMDA Modified		DMDOA Modified		Assignment
GA	GT	GA	GT	GA	GT	
3693	3693	3693	3695	3695	3695	υ (Si-OH)
3622	3622	3652	3652	3652	3652	υ (Al-OH)
3400	3406	3622	3622	3622	3622	υ (O-H) H_2O
-	-	2926	2926	2918	2920	Asymmetric C–H in $(CH_2)_n$
-	-	2851	2851	2851	2851	Symmetric C–H in $(CH_2)_n$
1639	1639	1639	1639	1655	1649	δ(H-O-H)
-	-	-	-	1469	1469	δ (C-H)
1115	1113	1113	1113	1104	1104	υ (Si-O) out-of-plane
996	1004	1000	1000	1000	998	υ (Si-O)in-plane
912	912	912	912	914	914	δ(Al-Al-OH)
801	799	799	799	801	801	δ(Al-Mg-OH)
782	782	782	782	-	782	υ (Si-O) of silica and quartz
-	-	-	-	724	724	δ (CH_2 asymmetric)
694	693	698	698	694	693	υ (Si-O) of silica and quartz
527	588					δ(Si-O-Al)
459	482					δ(Si-O-Si)

υ – Stretching vibration; δ – bending vibration

The intensity of the bands associated with adsorbed water in the unmodified samples was reduced and as well shifted from 1639cm^{-1} to higher frequency of 1655 cm^{-1} and 1649 cm^{-1} for GA and GT- DMDODA modified respectively, while it remains unchanged (1639 cm^{-1}) in the BDMDA modified samples. This could probably be due to the long carbon chains attached to the central atom which increases the surface area that leads to better intercalation of the surfactant between the layers of the clay. It is also worth to mention the suggestion of Hongping *et al.* [9], that H_2O is less strongly hydrogen bonded at low-H_2O content and that the H_2O molecules clustered around exchangeable cations are polarized by close neighbourhood of the exchangeable cation. The intercalation of surfactant cations especially those with long alkyl chain length increases such polarization.

Table 2: Diffraction angles (degree 2Ө) and the basal spacing (d-Å) of unmodified and modified samples



Sample	Unmodified		DMDODA-M		BDMDA-M	
	2Ө (°)	Basal spacing (Å)	2Ө (°)	Basal spacing (Å)	2Ө (°)	Basal spacing (Å)
GA	5.8	15.23	4.05	21.79	4.40	20.07
GT	6.8	12.99	3.30	26.75	4.50	19.62

Slight shifts were also observed after modification in the bands associated with the stretching mode of Si–O (out-of-plane from 1115cm^{-1}GA to 1113cm^{-1}BDMDA-GA and 1104cm^{-1}DMDOA-GA then 1113cm^{-1}GT to 1104cm^{-1}DMDOA-GT BDMDA-GT is still 1113cm^{-1}). The Si-O (in-plane) band has shifted from 996 cm^{-1} GA to 1000 cm^{-1} for the BDMDA and DMDOD-GA respectively, then for the GT the shift was from 1004 cm^{-1} to 1000 cm^{-1} and 998 cm^{-1} for the BDMDA and DMDOA-GT respectively). The Al-Al-OH bending vibration of the GA and GT samples shifted from 912 cm^{-1} to 914 cm^{-1}for the DMDOA modified samples only, there was no change in the case of BDMDA-GA, GT samples.

X-ray diffraction analysis (XRD):

The XRD diffraction patterns of the unmodified bentonites (GA and GT) and modified bentonites (BDMDA-GA, GT and DMDODA-GA, GT) are shown below. The basal spacing values of the unmodified and modified bentonites are shown in **Table 2**.

From the diffraction patterns, the basal spacing of the unmodified GA and GT samples increased from 15.23Å (for GA) and 12.99Å (for GT) to 20.07Å and 19.62Å; 21.79Å and 26.75Å after the organic modification with BDMDA and DMDODA respectively. This increase resulted in the shift of the diffraction peak toward lower angles (from 5.8° and 6.8° to 4.40° and 4.50°; 4.05° and 3.30°) respectively. This implies that the interlayer distances were increased due to the intercalation of the surfactants between the silicate layers [10].

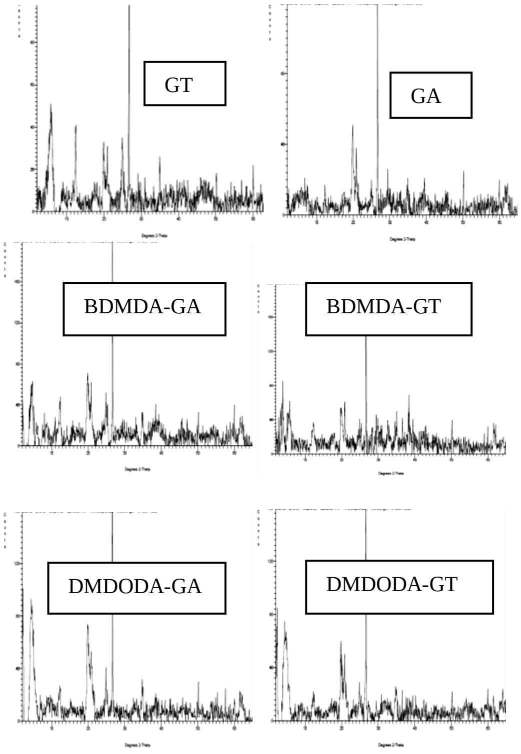
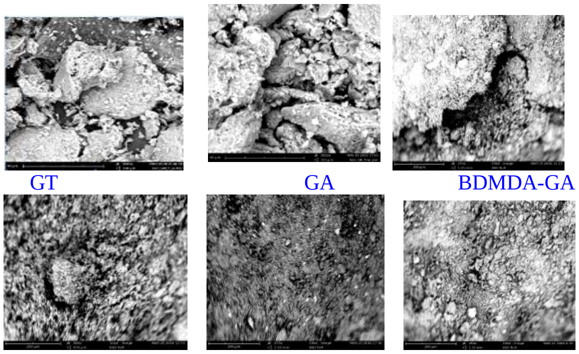


Fig 1: XRD patterns of unmodified bentonites (GA, GT) and modified organo-bentonites

The basal spacing values obtained in this study for the two surfactant modified samples were within the range of values obtained from previous studies elsewhere. Basal spacing of 26.11Å; 12.60Å; 37.10 Å; 36.00Å; 26.74Å; 38.40Å were reported for DMDODA modified montmorillonite [5,14-18] and for BDMDA – MMT, 23.9Å; 23.90 Å; 20.05 Å; 23.72Å; 17.9Å were reported [7,17,19-21]. It has been reported that the basal spacing of organoclays depends on the CEC of the clay mineral, the amount of organic cations, the chemical structure (alkyl chain length) of the surfactant, the arrangement and packing density of the organic cations within the clay interlayer [5,9,16,22-24]. The effect of the CEC and the alkyl chain has been seen from the results especially for the DMDODA modified samples. It is believed that the alkyl chains pack in a layered structure depending on the packing density and the chain length (monolayer 13-15Å, bilayer17-18 Å, pseudotrimolecular layer 19-21.7 Å and paraffin-type structure > 22). The alkyl chain may lie flat on and parallel to the silicate surface as a monolayer or bilayer. In the pseudotrimolecular layers, some chain ends are shifted above one another, so that the spacing is determined by the thickness of three alkyl chains. For the paraffin-type the chains radiate away from the silicate surface, assuming a tilted up-right position [5,9,16,22,23,25]. The basal spacing obtained for the GA-DMDODA and GT- DMDODA modified samples indicated the pseudotrimolecular (21.79Å) and paraffin-type (26. 75Å) arrangements respectively, while for the GA-BDMDA and GT- BDMDA modified samples, the pseudotrimolecular layer arrangements (20.07Å and 19.62Å) were formed respectively.

Scanning electron microscopy (SEM):

The surface morphologies of unmodified and modified bentonite samples are as shown in **Figure 2.** In the SEM images of unmodified, massive plates with some phase separations are observed as a heterogeneous surface morphology. It showed a soft surface where large lamellas tend to form big agglomerates with a layer disposition as shown in the images of GA and GT. After the modification with the organic surfactants significant changes were seen, whereby the surfaces turned rougher than in the unmodified samples with more fractionated lamellas and uniformly dispersed small particles with the form of flakes or grain-like structures. The aggregates of the unmodified bentonite appeared significantly larger than those for the organically modified, i.e to say modification reduces the clay particle size and aggregation as shown in the images of BDMDA-GA, GT and DMDOA-GT, GT.



GT GA BDMDA-GA

BDMDA-GT DMDODA-GA DMDODA-GT

Fig. 2: SEM images of unmodified (GA, GT) and organically modified bentonites

Conclusion

The surfaces of bentonites with different cation exchange capacities (CEC) were organically modified with surfactants of different hydrophobic groups and alkyl chain lengths. The results obtained from XRD analyses, FTIR spectroscopy and SEM study showed that the bentonite surfaces were significantly modified through the cation exchange of the surfactants. The basal spacing increased with increase in the alkyl chain length and the configurations of the surfactants. The arrangement of the surfactants within the clay structures were found to be pseudotrimolecular and paraffin type in nature. The appearance of peaks in the IR spectra of the modified clay due to the C-H asymmetric, symmetric stretching and bending vibrations in methylene groups of surfactant alkyl chains which were not present in the unmodified samples; the formation of rough surfaces with uniformly dispersed small particles of grain-like structures in the morphology of the organomodified samples confirmed the modification. These prepared surfaces have the potential for adsorption of various toxic compounds and other industrial applications.

Acknowledgements

The authors wish to thank Mr. Muhammad Musa from Bayero University Kano, Dr Wagini from Umaru Musa Yar adua University, Katsina and Mr Paul for their technical assistance in the provision the of FTIR, SEM micrographs and XRD spectra measurements respectively. The financial support to ASL by the Tertiary Educational Trust Fund of Nigeria (TETFUND) is highly appreciated.

References

[1] A. Asad, K. Shantanu, A.D. Mohammad, and H. Raquibul Suitability of Bentonite Clay: An Analytical Approach. *International Journal of Earth Science*, *2(3)*, 2013, *88-95*.

[2] L. Ahonen, P. Korkeakoski, M. Tiljander, H. Kivikoski, and L. Rainer (2008), Quality Assurance of the Bentonite Material. POSIVA OY Working Report 33.

[3] L. Carlson (2004); Bentonite Mineralogy. Part 1: Methods of Investigations – A Literature Review; Part 2: Mineralogical Research of Selected Bentonites. Posiva Oy, Working Report 02.

[4] N. Banik, S.A. Jahan, S. Mostofa, H. Kabir, N. Sharmin, M. Rahman and S. Ahmed, (2015), Synthesis and characterization of organoclay modified with cetylpyridinium Chloride. *Bangladesh J. Sci. Ind. Res.* **50(1)**, 65-70.

[5] Y. Xi, L.F. Ray and H. Hongping (2007), Modification of the surfaces of Wyoming montmorillonite by the cationic surfactants alkyl trimethyl, dialkyl dimethyl, and trialkyl methyl ammonium bromides. *Journal of Colloid and Interface Science 30; 150–158.*

[6] S. A. Jahan, S. Parveen, S. Ahmed and H. Kabir (2012), Development and characterization of organophilic clay from bentonite, *Material Science*, **8:** 67-72

[7] F. J. Rodrı´guez, L. A. Corte´s, A. Guarda, M. J. Galotto, and J. E. Bruna (2012), Characterization of cetylpyridinium bromide-modified montmorillonite incorporated cellulose

acetate nanocomposite films. *J Mater Sci. Published online.*

[8] C.S. Ezquerro, I.R. Gemma, C.M. Cristina and S.B. Javier (2015), Characterization of montmorillonites modified with organic divalent phosphonium cations, *Applied Clay Science* 111, 1-9

[9] W. Abdallah and U. Yilmazer (2011), Novel thermally stable organo-montmorillonites from phosphonium and imidazolium surfactants *Thermochimica Acta 525 (2011) 129–140*

[10] A. Tabak, B. Afsin, S.F. Aygun and E. Koksal (2007), Structural charachteristics of organomodified bentonites of different origins, *J. Therm. Anal. Cal*. 87; 375–381.

[11] H. A. Patel, S. S. Rajesh, C. B. Hari and V. J. Raksh (2007), Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. *Applied Clay Science 35; 194-200*

[12] P. Praus, T. Martina, Š. Soˇna and R. Michal (2006); Study of cetyltrimethylammonium and cetylpyridinium adsorption on montmorillonite. *Journal of Colloid and Interface Science 304; 29–36*

[13] H. Hongping, F.L. Ray and Z. Jianxi, (2004), *Spectrochim. Acta* A 60 2853–2859.

[14] M. Majdan, M. Oksana, A. Gładysz-Płaska, P. Stanisław and K. Ryszard, (2008) Spectral characteristics of the bentonite loaded with benzyldimethyloctadecylammonium chloride, hexadecyltrimethylammonium bromide and dimethyldioctadecylammonium bromide. *Journal of Molecular Structure* 874: 101–107

[15] L. Xu and L. Zhu (2009); Structures of OTMA- and DODMA-bentonite and their sorption characteristics towards organic compounds. *Journal of Colloid and Interface Science* 331: 8–14.

[16] H. He, M. Yuehong, Z. Jianxi, Y. Peng and Q. Yanhong (2010), Organoclays prepared from montmorillonites with different cation exchange capacity and surfactant configuration. *Applied Clay Science* 48; 67-72.

[17] Y. Cho,T. Kim, S. Han and C. Lee (2012), Adsorption removal of p-xylene by organo-clays. *Journal of Korean Society of Water and Wastewater* 26 (6); 747-756.

[18] W. Luo, A. Inoue, T. Hirajima and K. Sasaki, (2015), Sequential modification of montmorillonite with dimethyl dioctadecyl ammonium chloride and benzyl octadecyl dimethyl ammonium chloride for removal of perchlorate. *Microporous and Mesoporous Materials* doi: 10.1016/j.micromeso.2015.12.030.

[19] C. Bertagnolli and M.G. C da Silva, (2012), Characterization of Brazilian Bentonite Organoclays as Sorbents of Petroleum-derived Fuels. *Materials Research*. 15(2): 253-259.

[20] E.M. Araujo, M.D.L. Amanda, A.P. Rene, N.M. Vanessa, J.A.M. Tomas and L.L. Hélio (2011), Polyamide 6 Nanocomposites with Inorganic Particles Modified with Three Quaternary Ammonium Salts. *Materials 4;* 1956-1966.

[21] T. Kwolek, M. Hodorowicz, K. Standnick and J. Czapkiewicz (2003), Adsorption isotherms of homologous alkyldimethyl-benzylammonium bromides on sodium montmorillonite. *J. Colloid Interface Sci*. 264, 14–19.

[22] J.U. Calderon, L. Bruce and R. K. Musa (2008), Thermally stable phosphonium-montmorillonite Organoclays. *Applied Clay Science* 40, 90–98

[23] L. B. Paiva, R.M. Ana, R.V.D. Francisco (2008); Organoclays: Properties, preparation and applications. *Applied Clay Science* 42, 8–24

[24] S. Changchaivong, and S. Khaodhiar (2009), Adsorption of Naphthalene and Phenanthrene on Dodecylpyridinium-

modified Bentonite. *Applied Clay Science* 43; 317–321.

[25] D.R. Paul, Q.H. Zeng, A.B. Yu, G.Q. Lu (2005), The interlayer swelling and molecular packing in Organoclays. *Journal of Colloid and Interface Science* 292; 462–468