



Foster Swelling Capacity and Sorption Dynamics of Unmodified Sodium and HDTMA-Modified Bentonite for Hydrocarbons and Water

Michelle A. Apemiye, Chidi Obi*

Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Rivers State, Nigeria

Abstract This study demonstrated the impregnation of hexadecyltrimethylammonium bromide (HDTMA) to exchange sodium ions in the inter-layers of bentonite clay to form organoclay. The resultant materials were characterized using foster swelling and adsorption capacity techniques. The result showed that the foster swelling capacity of HDTMA-modified bentonite (HMB) was greater than unmodified sodium bentonite (USB) on interaction with petroleum hydrocarbons in the trend of m-xylene > PMS (premium motor spirit) > AGO (automotive gas oil) > DPK (dual purpose kerosene) (before and after agitation) while USB gave the following order: m-xylene < PMS < AGO < DPK < H₂O. This proves the hydrophilicity of the USB and the hydrophobicity of the HMB. The adsorption capacity result reveals that HMB obviously adsorbed more organic solvents than UMB. This study shows that HMB is an excellent adsorbent with high adsorptivity, retention tendency and swelling capacity than the USB for the removal of hydrocarbons from industrial wastes.

Keywords Water, clay beneficiation, HDTMA-bentonite, foster swelling, sorption capacity, petrochemical waste treatment

Introduction

The growing demand of crude oil or petroleum products in developing countries such as Nigeria has improved the economy. Though, it has also led to environmental hazard which is a greater challenge in petroleum industry in the world today. This crucial matter has made researchers to find better techniques for eradicating or eliminating pollutants arising from industrial wastes, oil and fuel spills, contaminated water and waste reservoirs [1]. These pollutants like volatile organic compounds (VOCs) are exceedingly harmful which has pose threat to the lives of humans and aquatic organisms [2]. Carcinogenesis, chromosomal and bone marrow damages are the treats that arise on human health and animals when exposed to benzene, toluene, ethyl benzene and xylene (BTEX) in industrial effluents [3]. Reports have shown that toxic effluents from refineries have caused drastic effects on the growths and reproduction of aquatic animals [4].

Nowadays, adsorbents are introduced as means to reduce the high level of VOCs. Clay minerals are adsorbents that serve as a protective barrier to curb the wastes in soil and water and their accessibility and availability makes them an economical feasible adsorbent [5]. Montmorillonite is known to be the major component of bentonite. The framework is obtained by isomorphous substitution which is composed of two Si tetrahedral sheets and Al octahedral sheet in between them as shown in Figure 1.

Bentonite clays are natural clay that is made up of montmorillonite, notable for its unique properties which are applied environmentally [6]. These properties are particle size, surface area, cation exchange capacity, swelling capacity, surface acidity and catalytic activity [7-8].

The exchangeable ions aid to balance the negative surface charge. Furthermore, organic surfactant is substituted into the clay minerals leading to a process called organophilization. Organophilization is the treatment of clay minerals with surfactant $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$ (where, R is a long chain alkyl hydrocarbon)



transforming it from hydrophilic to hydrophobic for special application [9-10]. There are many ways of preparation of organophilic bentonite which include aqueous dispersion involving solid-liquid medium, solid-solid mixture in the absence of any solvent, etc [11-13].

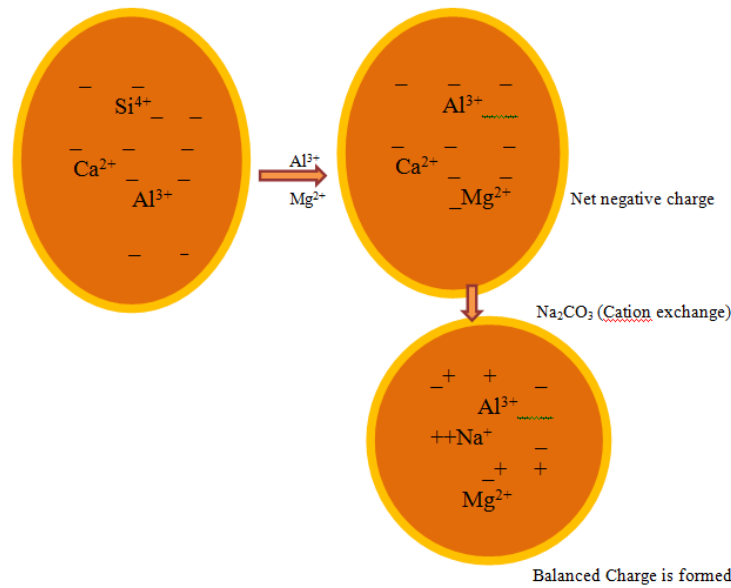
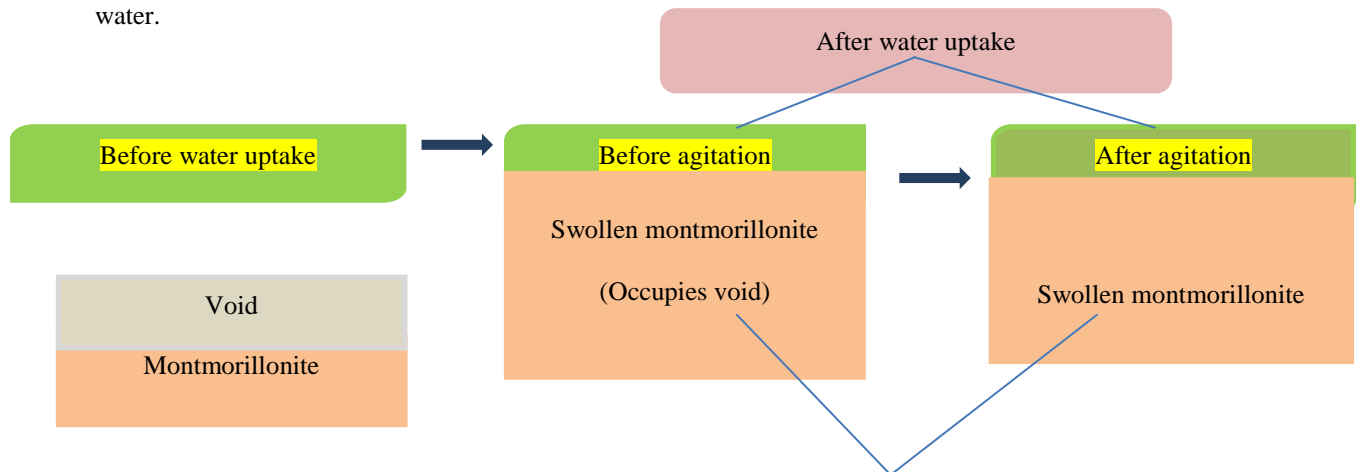


Figure 1: Isomorphous substitution of montmorillonite

The swelling mechanism in clay minerals occur due to two major forces; the attractive and repulsive forces. These forces are responsible for the alteration of montmorillonite [14]. The swelling character of bentonite is beneficial in most industries to form viscous liquid suspension. There are basically two categories of swelling which are: crystalline swelling and osmotic swelling [15]. The exchange of cations and split up of montmorillonite particles influence these mechanisms [16-17].

The importance of swelling behaviour is the fact that it relies on the space between particles when the number of stacked unit layers decreases.

The aim of this paper is to examine the behaviour of the swelling and sorption capacity of unmodified sodium (USB) and hexadecyltrimethylammonium-modified bentonite (HMB) in the presence of hydrocarbons and water.



Absorption of water into the inter-layers of montmorillonite

Figure 2: Swelling mechanism of bentonite clay

Experimental

Sample Collection

The bentonite used for this study was obtained from Enugu local bentonite deposit from the eastern part of Nigeria. The samples were sieved to less than 1mm. The sodium carbonate salt (Na_2CO_3) was purchased from

Jochem, used for ion exchange and quaternary ammonium salt (hexadecyltrimethylammonium bromide) at 97% purity was purchased from Merck KGAA Company, Darmstadt, Germany.

Beneficiation and Modification of Bentonite

Ion exchange method was adopted in solid-liquid reaction for pre-treatment of bentonite (40 g) using 8.48 g of Na_2CO_3 (sodium carbonate salt) to convert it from Ca-Bentonite to Na-bentonite. The monovalent ion substitute the divalent into the lamellae of the bentonite at 60-80°C under stirring for about 2-3 hrs. The pre-treated unmodified bentonite was washed thoroughly with distilled water until free of Br^- as tested by AgNO_3 . It was decanted, dried at 105°C, ground, sieved and labeled USB. Furthermore, the above process was repeated adopting impregnation method thereby replacing the sodium cation with 0.1 M HDTMA [18].

Foster Swelling Test

The hydrocarbons for this study include m-xylene, gasoline, diesel oil, kerosene, lubricating oil and water. Unmodified sodium bentonite (USB) (0.5 g) was measured into the burette and 50 ml of solvents were added respectively. After 24 hrs of settling period, the bentonite column volume (bentonite swelling before agitation) was noted and then agitated. After another 24 hrs, a new reading was detected and recorded [19]. Burgentzle et al [20], proposed an expression to determine the swelling capacity as shown in equation 1.

$$S.F = \frac{(V_s - V_D)}{V_D} \dots\dots\dots 1$$

Where S.F = Swelling Factor, V_s = Volume of swollen bentonite clay and V_D = Volume of dry bentonite. Pereira et al [9] fixed parameters for the interpretation as:

- a) Non-swelling (less than or equal to 2mlg^{-1} of clay)
- b) Minute swelling ($3\text{-}5\text{mlg}^{-1}$ of clay)
- c) Medium swelling ($6\text{-}8\text{mlg}^{-1}$ of clay)
- d) Great swelling (greater than 8mlg^{-1} of clay)

Adsorption Capacity Test

The distilled water and organic solvents used for this technique was carried out based on ASTM F716-82 [21] and ASTM F726-99 [22]. The distilled water was tested for adsorption separately on both modified and unmodified bentonite. A glass mesh bucket was held by a thick thread which was weighed empty. Bentonite clay sample (0.5 g) was measured and put into the mesh bucket and weighed. Solvent (50 ml) was measured into 50 ml beaker. The adsorbent in the mesh bucket was sunk in the liquid test cell (beaker) of water for 30 mins. It was removed and left to drain for 15 s (a tarred weighing support was placed beneath to get any drip). The entire system was weighed, and then weight of solvent absorbed was taken from the difference between weight of adsorbent after adsorption and adsorbent weight when dried. The test was repeated for 0.5 g of both unmodified and modified bentonite. This was repeated using m-xylene, PMS, AGO, DPK and lubricating oil, respectively.

Results and Discussion

Foster Swelling Capacity

The experimental result of the foster swelling tests is presented in Figure 3. The HMB indicated swelling in contact with organic solvents because of diffusion of the molecules of the solvent between bentonite layers.

It was noted that an increase in volume occurred after agitation because the shear destroyed the agglomerates of clay thereby breaking the van der Waals interactions. However, the layer's surface wetting was improved. The interactions between particles changes from face to face and edge to edge.

The result depicted in Figure 3 showed that water in contact with the sodium bentonite swelled more than twice its dry weight after agitation. This may be possible as a result of the mineral galleries of the bentonite occurring due to the hydrophilic nature (hydrogen bonds) of unmodified bentonite [23] and also the time interval of 24 hrs left for it to absorb water. Therefore, expansion occurs as water molecules penetrate beyond the external surface to the interstice of the bentonite layers. While in contact with petroleum solvents, no swelling occurred because of its non-affinity for organic solvent. HMB was observed to show no swelling in water. Hence, organophilic fraction was predominant. USB in contact with xylene, gasoline, diesel, kerosene and lubricating oil, respectively showed no sign of swelling due to its organophilic attributes of non-interaction with organic solvents. It was deduced that HDTMA-bentonite presented a greater swelling ability before agitation and after agitation when analyzed with m-xylene. On interaction with PMS and AGO revealed a range of high swelling



to low swelling (before and after agitation). HMB mixed with kerosene showed low swelling to no swelling (before and after agitation) [9].

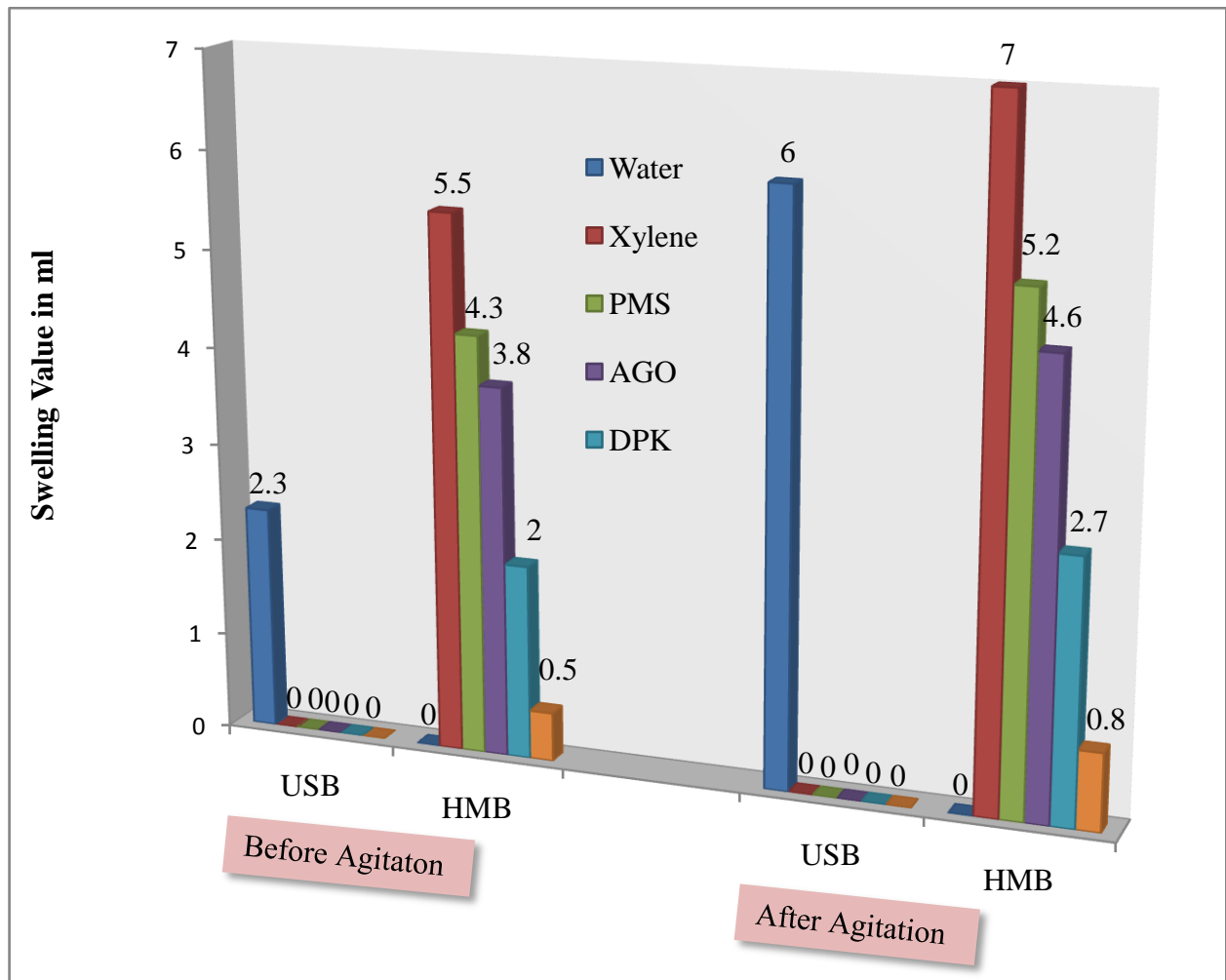


Figure 3: Foster swelling tests performance before and after agitation for USB and HMB in different hydrocarbon solvents

It was observed that low swelling occurred with lubricating oil and water. This character can be explained because no change in the burette volume occurred. Hence, HMB depicted higher affinity for organic solvents thereby swelling more, while USB do not show any significant swelling. This is an indication that the concentration of quaternary ammonium salt content in bentonite yields a high swelling capacity [24]. This result is in line with the organoclay used to remove petroleum hydrocarbons [25]. This observation of the swelling behaviour of bentonite depends on the chemical composition in line with the degree of isomorphous replacements in their framework, the amount and nature of the associated exchangeable cations. The result also revealed that increase in concentration of HDTMA⁺ yields better swelling performance [26, 27]. Therefore, this property makes the organophilic clay efficient and effective in separation processes in the refining industry.

Adsorption Test

The adsorption capacity result revealed that the amount of water and petroleum fractions adsorbed by the unmodified sodium (USB) and hexadecyltrimethylammonium-modified bentonite (HMB) samples varied. It showed that the unmodified sodium bentonite absorbed water almost three times its dry weight due to its hydrophilicity/organophobicity nature (hydrogen bond). Water proved to favour unmodified bentonite and possessed the highest adsorption capacity than all the organic solvents tested as presented in Figure 4.



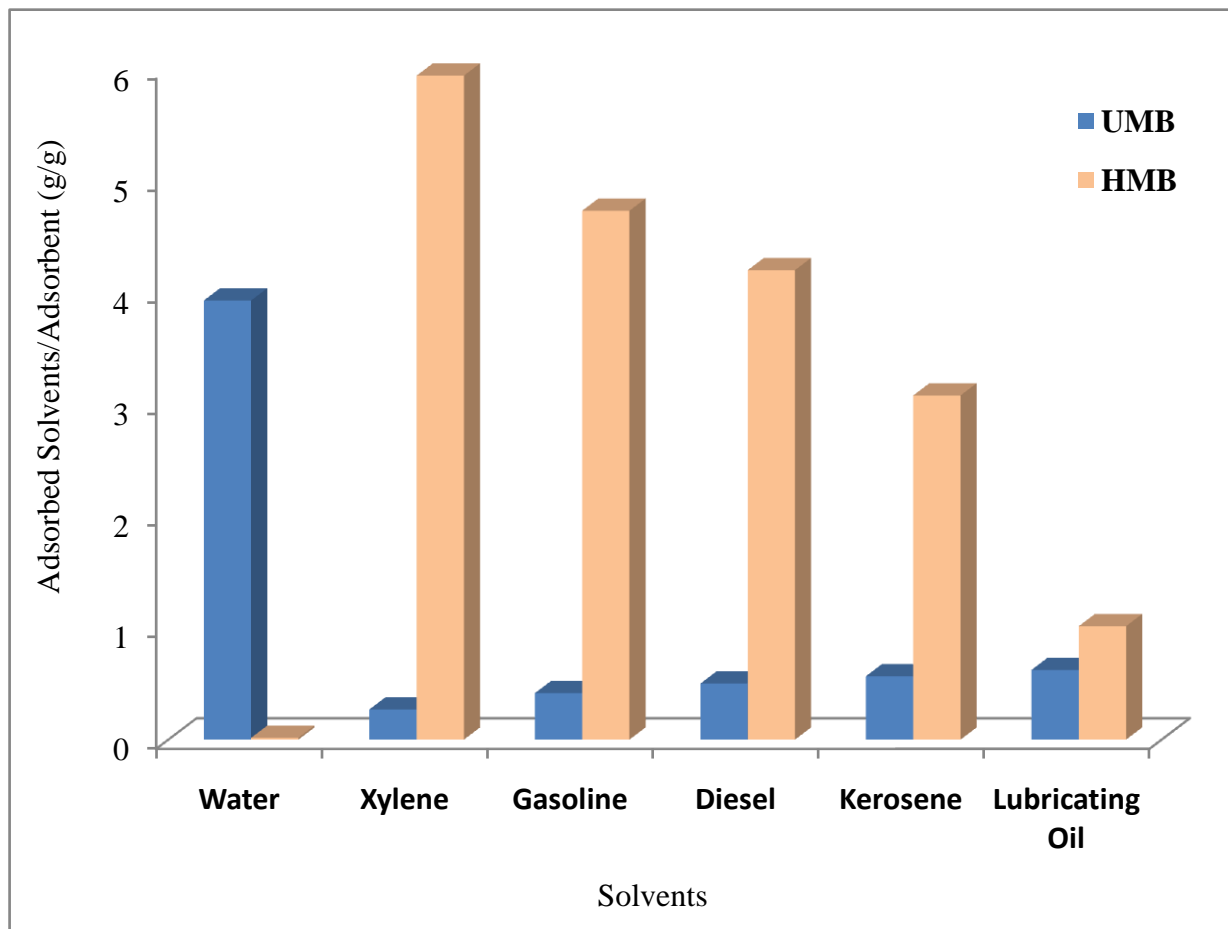


Figure 4: Adsorption capacity of USB and HMB in different solvents

Hence, on interaction with petroleum solvents, the USB adsorbed very minute organic solvents; this can be possibly explained from the frame work of unmodified sodium bentonite due to its hydrophobicity behaviour. The order of USB adsorption capacity was water > lubricating oil > kerosene > diesel > gasoline > xylene. The sorption values were between (0.624 to 3.932 gg^{-1}). HMB possess an adsorption values of the following order: water (0.016 gg^{-1}) < lubricating oil (1.016 gg^{-1}) < kerosene (3.082 gg^{-1}) < diesel (4.204 gg^{-1}) < gasoline (4.736 gg^{-1}) < xylene (5.946 gg^{-1}).

Adsorption of m-xylene on HDTMA-modified bentonite showed an increase in adsorption capacity on interaction with petroleum fractions as revealed in the result. It was depicted generally that organophilic bentonite had greater potential for sorption when analysed with organic solvents compared to water. Therefore, HDTMA-modified bentonite exhibited higher adsorption capacity than the unmodified sodium bentonite due to the surface properties from hydrophilicity to hydrophobicity [28]. This equally revealed the intercalation of HDTMA⁺ on the surface of sodium bentonite [29]. The result corresponds to “Standard Methods of Testing Sorbent Performance of Adsorbents” [21-22].

Conclusion

In this study, the prepared organophilic bentonite showed high sorption capacity for hydrocarbons before and after agitation while UMB had no affinity. The result also indicated that the HDTMA⁺ incorporated in the bentonite clay influences a better adsorbent behavior. The application of Enugu surfactant modified bentonite has been successfully tested and proven to be a good adsorbent for the elimination of organic compounds from waste water.



Acknowledgements

The authors gratefully acknowledge Nigerian National Petroleum Company, Merck KGAA Company, who supplied hexadecyltrimethylammonium bromide and Jochem Nigeria, limited.

References

- [1]. Inam, D. (2005). Organoclay preparation for anionic contaminant removal from water. PhD thesis submitted to the graduate school of natural and applied sciences of Middle East Technical University.
- [2]. Sharmasarkar, S, Jaynes, W. F. and Vance, G. F. (2000). BTEX sorption by montmorillonite organo-clays: TMPA, ADAM, HDTMA. *Water Air and Soil Pollution*. 119(1-4): 257-273.
- [3]. Tiburtius, E. R. L, Peralta-Zamora, P. and Leal, E. S. (2004). Contamination of waters by BTXs and processes used in the remediation of contaminated sites. *Química Nova*. 27: 441-446.
- [4]. Wake, H. (2004). Oil refineries. A review of their ecological impacts on the aquatic environment. *Estuarine, Coastal and Shelf Science*. 62: 131-140.
- [5]. Rodrigues, M. G. F, Silva, M. L. and Da-Silva, M. G. C (2004). Characterization of smectite clays for application in the removal of lead from synthetic effluents. *Cerâmica*. 50 190-195.
- [6]. Lee, S. Y, Kim, S. J, Chung, S. Y. and Jeong, C. H. (2003). Sorption of hydrophobic organic compounds onto organoclays. *Journal of chemosphere*. 781-785.
- [7]. Astudillo, J. P. (2001). The deep geological storage. General Principles, National Radioactive Waste Company, Enresa.
- [8]. Wang, J. (2006). Deep geological disposal of high-level radioactive wastes in china. *Chinese Journal of Rock Mechanics and Engineering Geology*. 25: 4
- [9]. Pereira, K. O, Hanna, R. A, Vianna, M. M, Pinto, C. A, Rodrigues, M. G. and Valenzuela-Diaz, F. R. (2005). Brazilian organoclays as nanostructures sorbents of petroleum-derived hydrocarbons. *Material Research*. 8: 77-80.
- [10]. Safaei, M, Aghahozorg, H. R, Shariat, H. and Panahi, S. (2008). Modification of domestic clays for preparation of polymer nanocomposites. *Nashrieh Shimiva Mohandesi Shimi Iran (NSMSI)*, 27.
- [11]. Zhu, J, He, H, Zhu, L, Wen, X. and Deng, F. (2005). Characterization of organic phases in the interlayer of monmorillonite using FTIR and ¹³C NMR. *Journal of colloid and Interface Science*. 286: 239-244.
- [12]. Raiz, U. and Ashraf, S.M. (2011). Effect of solid state intercalation conditions in controlling the self-assembled nanostructured polycarbazole-montmorillonitenanocomposites synthesized by mechano-chemical and microwave-assisted techniques. *Applied Clay Science*. 52: 179-183.
- [13]. Lee, J. F, Mortland, M. M, Chiou, C. T, Kile, D. E. and Boyd, S. A. (1990). Adsorption of benzene, toluene, and xylene by two tetramethylammonium-smectites having different charge densities. *Clays and Clay Minerals*. 38(2): 113-120.
- [14]. Komine, H. and Ogata, N. (1996). Prediction for swelling characteristics of compacted bentonite. *Canada Geotechnology Journal*. 33: 11-22.
- [15]. Madsen, F. T. and Müller-Vonmoos, M. (1989). The swelling behavior of clay. *Applied Clay Science*. 4: 143-156.
- [16]. Liu, L. and Neretnieks, I. (2010). Interaction between colloidal particles SKB Technical Report TR-10-26. Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.
- [17]. Yang, T, Knutsson, S. and Liu, X. (2016). Swelling Properties and Permeability of Expandable Clays of potential use for Nuclear Waste Disposal. *Journal of Earth Sciences and Geotechnical Engineering*. 6(2): 49-61.
- [18]. Yilmaz, N. and Yapar, S. (2004). Adsorption properties of tetradecyltrimethyl ammonium bentonites. *Applied Clay Science*. 27: 223-228.
- [19]. Vanezuela-Diaz, F. R. V. (1999). Preparation and synthesis of organophilic bentonite clay, proceeding of 43th Brazilian congress of ceramics, Florianopolis, Brazil.



- [20]. Burgentzle, D, Duchet, J, Gerald, J. F, Jupin, A. and Filloni, B. (2004). Solvent based nanocomposite coatings. Dispersion of organophilic montmorillonite in organic solvents. *Journal Colloidal Interface Science*. 278: 26-34.
- [21]. ASTM-American Society for Testing and Materials (1982). Standard Methods of Testing Sorbent Performance of Adsorbents. ASTM Designation F716-82.
- [22]. ASTM-American Society for Testing and Materials (1999). Standard Methods of Testing Sorbent Performance of Adsorbents. ASTM Designation F726-99.
- [23]. Kim, J. H, Shin, W. S, Kim, Y. H, Choi, S.J. and Jeon, Y. W. (2003). Song, D.I. Sequential sorption and desorption of chlorinated phenols in organoclays. *Water Science Technology*. 47: 59-64.
- [24]. Mota, M. F, Silva, J. A, Queiroz, M. B, Laborde, H. M. and Rodrigues, M. G. F. (2011). Organophilic clay for oil/water separation process by finite bath tests. *Brazilian Journal of Petroleum and Gas*. 5(2): 097-107.
- [25]. Frost, R, Carmody, O, Xi, Y. and Kokot, S. (2007). Adsorption of hydrocarbons on organoclays: Implication for oil spill remediation. *Journal of Colloid and Interface Science*. 305: 17-24.
- [26]. Gamal, M. E, Mohamed, A. M. O. and Zekri, A. Y. (2005). Effect of asphaltene, carbonate and clay mineral contents on water cut determination in water-oil emulsions. *Journal of Petroleum Science and Engineering*. 46: 209-224.
- [27]. IBP (2009). Institution of Brazillian Petroleum, Gas and Biocombustive, Portuguese.
- [28]. Rawajfih, Z. and Nsour, N. (2006). Characterization of phenol chlorinated phenol sorption onto surfactant modified bentonite. *Journal Colloid Interface Science*. 298: 39-49.
- [29]. Oliveira, G. C, Mota, M. F, Silva, M. M, Rodrigues, M. G. F. and Laborde, H. M. (2012). Performances of natural sodium clay treated with ammonium salt in the separation of emulsion oil in water. *Brazilian Journal of Petroleum and Gas*. 6(4): 171-183.

