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IMPACT OF ACID ACTIVATED BENTONITES ON FOSTER SWELLING CAPACITY AND SORPTION DYNAMICS OF HYDROCARBONS, PHENOL AND WATER

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ABSTRACT

The successful protonation of the dissociable H^+ *from different organic acids (with varying alkyl chains) to supplant sodium ions in the inter layers of bentonites resulting in increased surface area has been carried out. The resultant materials were characterized using foster swelling and adsorption capacity techniques. Results show that the foster capacities of acid activated bentonites were greater than the un-activated bentonite (UAB) upon interaction with petroleum hydrocarbons. The bentonite activated with the organic acid having the most alkyl chain, hexanoic acid activated bentonite (HAAB) showed high affinity for all petroleum hydrocarbons. This demonstrates the hydrophilicity of UAB and upon activation, the hydrophobic properties of HAAB. The adsorption capacity result records that bentonites and HAAB adsorbed more petroleum hydrocarbon solvents than other lower alkyl chain acid activated bentonites and UAB. This study shows that HAAB is an excellent adsorbent for the removal of hydrocarbons from industrial wastes.*

Keywords: Acid Activated Bentonite, Foster Swelling, Adsorption Capacity, Organic Acids, Phenol

INTRODUCTION

The growth of the petroleum refining, manufacturing and petrochemicals industry in modern times has invariably generated a rise in the levels of pollution in our environment, particularly through the means of waste discharge into land and water environments from the different production stages within these industries (Cavalcanti *et al.,* 2012; Senturk *et al.,*2009). Hydrocarbon solvents, dyes, heavy metals, phenol and its by-products are few of the pollutants released into the environment without proper treatment (Abdelkreem, 2013; Kojima *et al.*, 1995). They constitute both environmental and health hazards to humans (Slein & Sansone, 1980) and aquatic lives in riverine areas (Abdelkreem, 2013; Eman, 2013).

Due to their high profile toxicity at minute concentrations, phenolic compounds are classified as critical pollutants in waste discharges from chemical industries (Banat, *et al.*, 2000; Dutta, *et al*, 1998). Biological treatment (Aksu & Yener 2001), reverse osmosis (Goncharuk, *et al.*, 2002), solvent extraction (Kujawski *et al.*, 2004), and ion exchange (Kojima *et al.*, 1995) are few of the frequent techniques beneficial to the elimination of phenol-based compounds. Adsorption process provides an attractive alternative treatment to other removal techniques because it is more economical and readily available (Senturk *et al.*, 2009).

Bentonite (BTE) is a typical adsorbent in adsorption and purification of oils. Un-activated bentonites (UAB) are used widely as mud constituents in water and oil drilling, and also as binding agents in foundry sand and iron ore pelletization (Tyagi *et al.*, 2006). Bentonites treated with acids have attractive properties which make them ideal agents for service as catalysts and catalyst supports for important industrial reactions (Didi, *et al.*, 2009; Vaccari, 1999). By using organic acids, BTE can go through suitable chemical alteration so as to increase its adsorption efficiency and range of application (Foletto, *et al.*, 2011). Furthermore, BTE activated with acids have found usefulness in industrial applications (Usman *et al.*, 2012).

Commercial BTE is majorly imported by the petroleum and refining industries as mud for drilling purposes. Therefore it is important to investigate BTE deposits as potential substitutes for various applications. Apart from optimizing local clay adsorbent properties for combating environmental pollution, this potentially cost effective activation process can point to the full fiscal profiteering of local clay by reducing imports and thus, contributing a big part to the growth of Nigeria's economy. The objective of this study is to activate BTE while monitoring the changes on some physicochemical characteristics of BTE with respect to motivation and its adsorption kinetics and performance of the activated BTE on phenol and petroleum hydrocarbons.

EXPERIMENTAL

MATERIALS AND METHOD

The Nigerian clay mineral, sodium BTE used for this study was obtained from Mansid Nigeria Limited in Anambra State, Nigeria. The BTE was used for activation without any further purification. All chemicals used are of analytical grade and obtained from QUALIKEMS Fine Chem Pvt. Ltd. Surat, India unless otherwise stated.

Activation of Bentonite

Activation of bentonite was achieved by adopting the technique described by Foletto *et al*. (2011) and Hussin *et al*. (2011). One molar (1M) solution of organic acid is suitable for activation (Khan *et al*., 2015; Usman *et al*., 2012). Bentonite (10g ± 0.0025) was weighed using an electrical weight balance (AS220/C/2) and soaked in 200 mL of distilled water obtained from (HF-super-NW series water purification system model: NW30VF) for twenty four hours prior to treatment with acid. 200 mL Acetic acid (1M) was added to the blend, the reaction temperature set at 100°C under reflux with magnetic stirring (Model No.US152) for three hours. The samples obtained were cooled and filtered followed by exhaustive washing using distilled water. The activated samples were dried in an electric oven (Model No.2001243565025) for three hours to ensure maximum removal of moisture. The activated samples were kept in a desiccator and put away in hermetically sealed plastic bottles for further use. The experimental procedure was repeated using propanoic, butyric and hexanoic acids obtained from (Merck KgaA, Darmstadt, Germany). The activated bentonites were labeled AAAB (acetic acid activated bentonite), PAAB (propanoic acid activated bentonite), BAAB (butyric acid activated bentonite) and HAAB (hexanoic acid activated bentonite) while the unactivated bentonite was labeled UAB.

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Physical Characterization

Foster Swelling Test

This technique was selected to carry out studies on the compatibility of the activated BTEs with various organic liquids. This test was consistent following a technique based on the "Standard Test Method for Swell Index of Clay Mineral Component of Geo-synthetic Clay Liners" (ASTM D 589095). The solvents for the investigation of the swelling phenomena were: Premium Motor Spirit (PMS), Dual Purpose Kerosene (DPK), Automotive Gas Oil (AGO) and Lubricant (obtained from Total Nig. Ltd), distilled water and phenol (obtained from JHD, Guangdong GuanghuaSci-Tech Co., Ltd, China). The analysis comprised of adding 0.5g of the activated sample to 50 ml of the solvent each in a graduated test tube. After 24 hours of inactivity, the assessment of clay column volume (swelling of the clay without shaking) was recorded. Afterwards, the test tube was agitated and after a further 24-hour settling period; a new inspection of the sample column volume (swelling of the clay agitation) was recorded. The following parameters have been established for the findings of the test (Burgentzlé, *et al.*, 2004): non-swelling (minor or equal to 2ml/g of clay), intermediate swelling (between 6 and 8 ml/g of clay and high swelling (more than 8ml/g of clay).

The swelling factor of both raw and activated bentonite was assessed using equation 1.0.

$$SF = (\frac{VS - VD}{VD}) \qquad (1.0)$$

Where SF = Swelling Factor, VS = Volume of swollen bentonite and VD = volume of dried bentonite (Burgentzlé *et al.*, 2004).

Adsorption Capacity

The PMS, DPK, AGO, lubricant, crude oil and phenol sorption capacities were determined using the technique established on the "Standard Method of Testing Sorbent Performance of Adsorbents" (ASTM F716-82 and ASTM F726-99). In this procedure, 0.5g of the sample (un-activated and activated bentonites) was weighed and the exact value recorded. The test cell filled with an initial tier of test liquid while the adsorbent was placed in a glass mesh bucket of known weight, which was submerged into the test cell. The adsorbent was allowed to float openly in the test cell. After half an hour, the glass mesh bucket with the adsorbent was removed manually in a vertical direction and allowed to drain for 15 seconds before weighing the entire system. All tests were done in triplicates and used for calculations. Based on data collected, the capacity of oil retained was calculated as a weight ratio of retained oil to dry adsorbent. By applying equation 1 the volume of solvent adsorbed is derived. The data's collected were reported in grams of solvent retained per gram of clay.

$$(AC = (\frac{WB - WB_0}{WB_0}) \qquad 1$$

Where AC = Adsorption Capacity, WB = the weight of bentonite after adsorption, and WB_0 = the weight of bentonite before adsorption (Bandura, *et al.*, 2017).

RESULTS AND DISCUSSION

Foster Swelling Test

The swelling capacities in water, PMS, AGO, lube oil; DPK and phenol of un-activated and acid activated BTE were evaluated using the system outlined by Valenzuela-Diaz (1994). This system categorized the degree of swelling designated by the subsequent values and symbols with respect to a volume of 0.5g dry BTE. No swelling for values equal or less than 2.0 ml/g (S0), low swelling for values of 2.5 to 4.0 ml/g (S↓), medium swelling for values of 4.5 to 7.5 ml/g (SM) and high swelling for values above 7.5 ml/g designated by (S↑). The swelling factor (SF) was further employed to verify how many times the clay swelled in the solvent as against the dry volumes of the clay. According to Burgentzlé *et al.* (2004) the swelling factor is as expressed by equation 1.0. The foster swelling results are displayed in figures 1.0 – 6.0. The results of the swelling capacity in water of the un-activated and acid activated BTE are shown in figure 1.0. In the first part of the test, the highest swelling was observed for un-activated BTE with 2 mL/g and SF value of 3 times its dry volume which corresponds to similar observations from literatures (Ajemba and onukwuli 2013; Cavalcanti *et al.,* 2012; Ejikeme *et al.,* 2013). According to Santos (1989) the swelling of UAB in water is dependent upon the space in internal and external surfaces. The presence of exchangeable cations in the clay helps to align water molecules through hydrogen bonding (Moore and Reynolds, 1989) between the spaces in the internal and external surface illustrated by Santos (1989). The degree of swelling observed for acid activated BTE in water are categorized as non swelling BTE (Valenzuela-Diaz, 1994). The highest value was recorded for AAAB with 1.1ml/g and SF value of 1.2 while the lowest value was recorded for HAAB with 1.4ml/g after the first part of the test and a swelling factor of 0.6. The absence of swelling of these activated BTE in the water is due to the organophilic character impacted on the BTE during activation therefore limiting interactions with polar solvents. These observations further prove the successful activation of the BTE with different acids. UAB upon interaction with AGO, PMS, DPK, lube oil and phenol showed no sign of swelling when categorized under the Valenzuela-Diaz (1994) scale. The inability of molecules of the different petroleum solvents to reach the internal pores of the clay according to (Valenzuela-Diaz, 1994) is the reason for the observed behaviour and another prove of the affinity of un-activated BTE to water. A trend is noted in the increased swelling of activated BTE in petroleum solvents as the alkyl chain of acid used for activation increases. HAAB was recorded to have the highest swelling strength in both steps of the test. This behavior points toward the acquired organophilic character from activation of the BTE this makes it possible for interaction with the organic solvents to circulate through the layers in the BTE. HAAB was recorded to have swelled up to 6 times its dry volume 0.5g in phenol. This observation can be associated to the degree of decrease in polarity of the BTE by the alkyl chain of the acid used for activation. HAAB with the longest alkyl chain recorded the highest swells in all organic solvents. An observation of the increased swelling of activated BTE was recorded in all organic solvents in the second steps after agitation. Jones (1983) gave reasons for these observed increase; the distortion of the cluster of settled clay after 24h leads to the breaking of Van der waals interaction. This further leads to increased surface layer wetting and slow settling of BTE. In addition, interactions also change from face-to-face in the direction of edge-to-edge between particles.

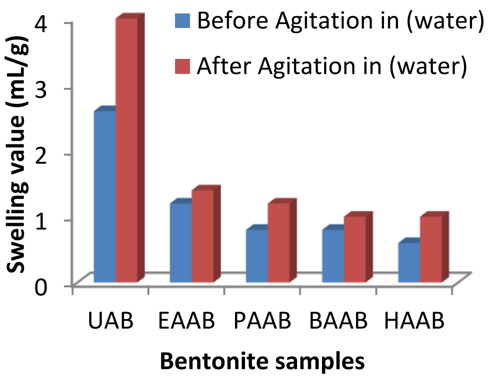

Figure 1.0 Swelling capacities in water of un-activated and activated BTE

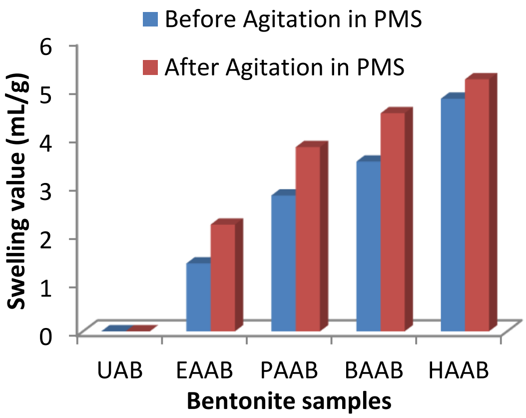

Figure 2.0 Swelling capacities in PMS of un-activated and activated BTE

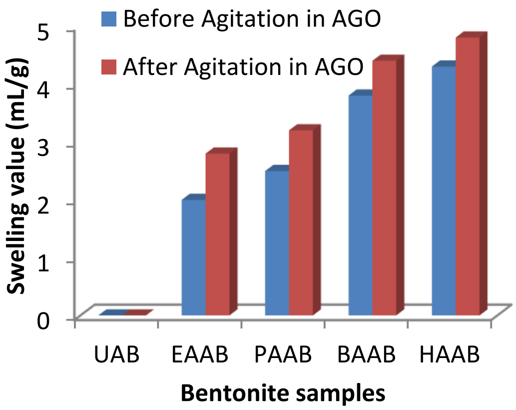

Figure 3.0 Swelling capacities in AGO of un-activated and activated BTE

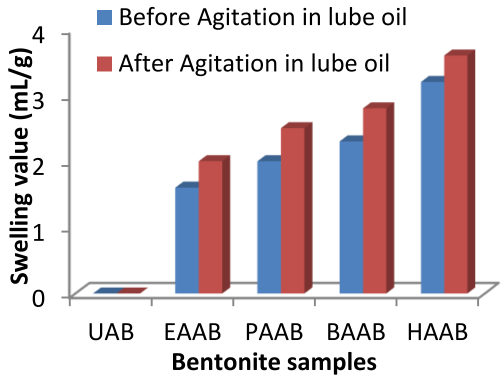

Figure 4.0 Swelling capacities in lube oil of un-activated and activated BTE

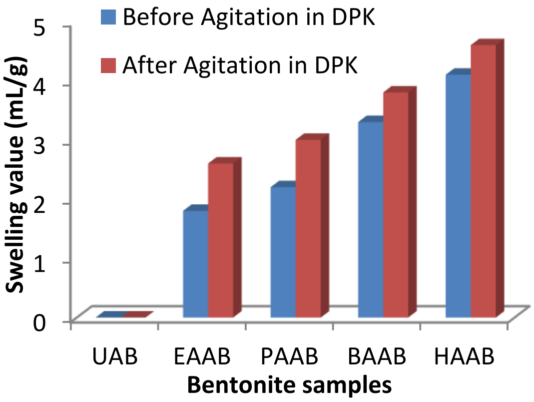

Figure 5.0 Swelling capacities in DPK of un-activated and activated BTE

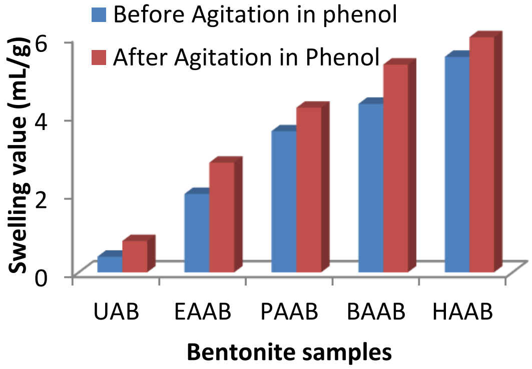

Figure 6.0 Swelling capacities in phenol of un-activated and activated BTE

Adsorption Capacity Test

The adsorption capacity test of un-activated and activated BTE has been conducted to analyze the variations in the adsorption of different solvents. Figure 7.0 gives detailed analysis of all adsorbents and their adsorption capacities in all solvents. The analysis revealed that the un-activated BTE adsorbed water almost triple its dry weight owing to its hydrophilic nature. The un-activated BTE obtained the highest adsorption capacity when immersed in water than all acid activated BTEs. Adsorption capacity values decreased as the acid activated BTEs were immersed in water. Bentonite activated with hexanoic acid had the least value. This trend is due to the hydrophobic property of the alkyl chain incorporated into the internal layers of the BTE during activation and is not easily solvated by water molecules.

Upon interaction with organic solvents, un-activated BTE showed little affinity for petroleum products due to its hydrophilic nature which is dominant over the hydrophobicity of the solvents. The sequence for UAB adsorption capacity in different solvents is given as water > phenol > AGO > PMS > Lube oil > DPK with sorption values ranging from ($2.7489 gg^{-1}$ to $0.0029\ gg^{-1}$). Adsorption of phenol on activated BTE showed a rise with increase alkyl chain of organic acid used for activation with HAAB having the highest adsorption capacity value of $2.4280\ gg^{-1}$. Activation according to Zohra *et al*. (2008) creates new pores thus providing more adsorption sites leading to further adsorption of organic solvents. HAAB obtained higher degree of adsorption capacity than AAAB, PAAB and BAAB thus confirming the infusing of its longer alkyl chain into the BTE surface, hence its improved adsorbent behavior in petroleum products. A similar change in adsorbent behavior was recorded by Khan *et al*. (2015) using acetic, phosphoric, citric and oxalic acids for the activation of fuller's earth. Apemiye *et al*. (2017) pointed out that the change observed in the adsorptive properties of modified Enugu BTE is related to the hydrophobicity of the cationic surfactant used for activation.

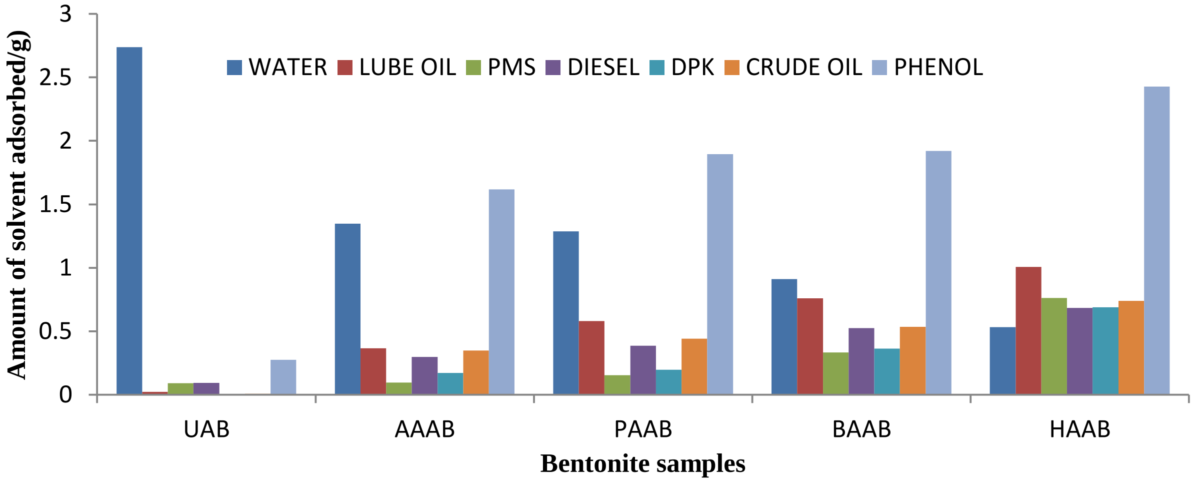

Figure 7.0 Adsorption capacities of UAB, AAAB, PAAB, BAAB and HAAB in different solvents

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CONCLUSION

In this study, the acid activated bentonite showed high sorption efficiency for hydrocarbons before and after agitation, while UAB had no compatibility. The results also indicated that the hydrogen ions incorporated in the bentonite during activation impacts on its adsorbent properties. The application of acid activated Ebenebe bentonite has been successfully tested and proven to be a promising adsorbent for the removal of organic compounds from waste water.

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