The Use of TEAB-Modified Sodium bentonite in the Sorption of Crude Oil Fractions

Chidi Obi*, Okwaraji Sylvester Tochukwu

Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Rivers State. Nigeria
zarasexcom@yahoo.com; Phone: +23408036682351

Abstract: The adsorption capacity of tetraethylammonium bromide (TEAB)-modified sodium bentonite and the unmodified sodium bentonite was tested for products that are likely to be involved in oily wastewaters and land-based oil spills using water, premium motor spirit (PMS), automotive gas oil (AGO) and dual purpose kerosine (DPK), respectively. The process parameter such as sorbent dosage and contact time were reported. Results showed that adsorption capacity of the organoclay was clearly higher than of the unmodified clay. Gasoline showed progressive increase in adsorption capacity from 0.1 g to 0.5 g. The organophilic bentonite results show an increase in the amount adsorbed for organic solvents but little or no increase in water and the degree of adsorption are of PMS > AGO > DPK > Water order. This study illustrates that the adsorption of hydrocarbon onto the organoclay is a fast process rendering the organoclay economically applicable material for removal of organic pollutants from waste water and the environment.

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1. Introduction

Environmental authorities all over the world have been involved in the development of processes and regulations to avoid and prevent the release of pollutants into water and environment. Series of pollutants are produced from oil and petrochemical industries, which are reported to have high polluting potentials. These pollutants are characterized as being stable towards light and heat and are also biologically undegradable (Brandao et al., 2010). The presence of these pollutants also decreases the contact area between water surface and atmospheric air, which prevent oxygen transfer (Namasivayam et al., 2001). Consequently researchers are involved in development of new materials, new procedures and techniques for removal of pollutants and hazardous materials from waste streams before releasing into the environment.

Pollutants in the environment have caused considerable harm to nature, aquatic life and man in a broader dimension. The poor means of crude oil exploration in the country has even lead to a series of organic pollutants which proves very resistant to most adsorbents.

The shift in economic base of coal to crude oil and petroleum products, more especially after the World War II, greatly increased the volume of these commodities being transported across the high seas. The above, coupled with their storage underground, involve high environmental risks (Short et al., 2002).

The major concern with crude oil spill has been its contamination of ground water, and the subsequent clean up. Petroleum hydrocarbons also cause huge changes in environment and physicochemical properties of water. Many procedures were studied and developed for removal of these types of pollutants. One of the most important employed processes used to remove these pollutants is the adsorption process, which has accepted great importance due to its low cost and available natural materials and biomass materials (Amin et al., 2008). A wide range of materials have been modified and studied as adsorbent material for oil and petroleum pollutants as biomass and natural materials (Carrott et al., 2003). These materials are highly hydrophobic with high porosity, have adsorption characteristics towards oils, and have high tendency to adsorb organic contaminants. Natural materials could be used for oils decontamination either as it is or modified.

Clay material is one of the adsorbents recently applied for the treatment of hydrocarbon contaminated water effluents. Clay minerals are natural materials, abundant with low cost and have large surface areas, as it has high mass transfer rates (Qu et al., 2009). The adsorption of hydrocarbon onto clay materials is hindered through the competition of water molecules in relation to non-polar compounds to the surface of the adsorbent material. The adsorption of organic compounds onto clay mineral surface can be improved by exchanging the inorganic cations present on the clay surface (Frost et al., 2007).

The physicochemical modifications of clay minerals have been studied for the preparation of improved adsorbents. Different procedures have been studied for clay modification e.g., adsorption of surfactant and intercalation of organic polymers (Bergaya et al., 2006). The modification of clay material creates a porous material, which is more effective in adsorption of organic compounds (He et al., 2006). The properties of the modified clay minerals render it as promising materials in adsorption technologies and other applications. Several types of organoclay have been prepared under different reaction conditions (Inam, 2005; Xu and Zhu, 2009; Masomeh et al., 2010).

The present work deals with studying the adsorption behavior of hydrocarbons using organically modified bentonite produced by cation exchange of interlayer cations with quaternary ammonium salt, tetraethylammonium bromide (TEAB). The adsorption process was optimized in terms of time of contact, surfactant concentration and adsorbent dose.

2. Materials and Method

The bentonite used in this experiment was obtained from Enugu in Nigeria. The clay particle was brownish in colour and was finer than 75 microns. Tetraethylammonium bromide used has a molar mass 210.16 g/mol.

The calcium bentonite is converted to sodium bentonite using four different sodium compounds which include sodium carbonate (Na_2CO_3), sodium chloride (NaCl), sodium hydroxide (NaOH), and sodium phosphate (Na_3PO_4), respectively. Calcium bentonite (30 g) was added into 300 ml of distilled water in a 1000 ml flat bottom flask. The mixture was allowed to settle overnight, after which 5 g each of the sodium compounds was added to the mixture, and placed on a magnetic stirrer at a temperature range of 70-80^{o}C. The solution was allowed to heat and stir for about 2 hrs, and the resultant solution was allowed to settle overnight. The solution was transferred to a 400 ml beaker for decanting, and was washed with distilled water. The clay settled at the bottom of the vessel was collected and dried in an oven at 80^{o}C. The resultant products were the sodium bentonite samples. The elemental compositions of the samples were analyzed using Atomic Absorption Spectrophotometer (AAS). The sodium compound that gave the best result was modified to organophillic bentonite using tetraethylammonium bromide.

The dried sodium bentonite (obtained from Na_2HPO_4) was introduced into a 1000 ml flat bottom flask, and dissolved with 200 ml of distilled water, after which the solution was allowed to settle for 24 hrs. The mixture was placed in a magnetic stirrer for a period of 30 mins to destroy agglomerates. A 0.160 M (10 g) of tetraethylammonium bromide (TEAB) was added to the sodium bentonite, and the mixture was stirred and heated continuously at a constant temperature of about 60-85^{o}C to maintain the salt in a soluble state for about 2 hrs. The resultant bentonite was filtered and washed with distilled water after which it was oven-dried at 80^{o}C for a period of 2-3 days. It was then crushed to the desirable size.

A 100 ml of distilled water was measured into a 250 ml beaker, and different weights (0.1-0.5 g) of modified bentonite was measured and put into a mesh bucket. A rope was used to lower the mesh bucket into the beaker for a period of 30 mins. The weight of the mesh bucket was obtained before and after and subtracted to determine the weight of water adsorbed. The same process was repeated using PMS, AGO, and DPK, and also carried out independently on the various bentonite samples (calcium bentonite, and sodium modified bentonite). Sorption capacity was measured following a method based on the "Standard Methods of Testing Sorbent Performance of Adsorbents" (ASTM F716-82 and ASTM F 726-99). Experimental analysis was carried out to test for the adsorption capacity of unmodified calcium bentonite, sodium bentonite and modified sodium bentonite using water, PMS, AGO, DPK. The organic solvents were obtained from NNPC. The adsorption capacities were calculated using the expression below adopted by Masomeh et al., (2010):

$$\text{Sorption capacity (g oil/g sorbent)} = \frac{S_s}{S_o} \text{ or } \left[\frac{(S_{st} - S_o)}{S_o}\right]$$

Where S_o is the initial dry weight of sorbent, S_{st} is the weight of sorbent at end of oil test and S_s is (S_{st}-S_o) net oil adsorbed.

3. Results

The results of elemental analysis and adsorption test are presented below:

Table 1. Elemental compositions of the various bentonite samples

Sample Type	Al (mg/L)	Ca (mg/L)	Fe (mg/L)	Mg (mg/L)	Na (mg/L)	Si (mg/L)
Ca-bentonite	6.74	19.18	0.20	1.32	0.58	48.60
Na_2CO_3-bentonite	4.89	3.27	31.96	0.85	5.58	26.75
NaCl-bentonite	5.70	1.52	35.49	0.61	3.65	50.88
NaOH-bentonite	6.35	4.93	1.76	0.17	3.42	7.70
Na_2HPO_4-bentonite	4.09	0.73	34.31	0.97	7.03	6.42

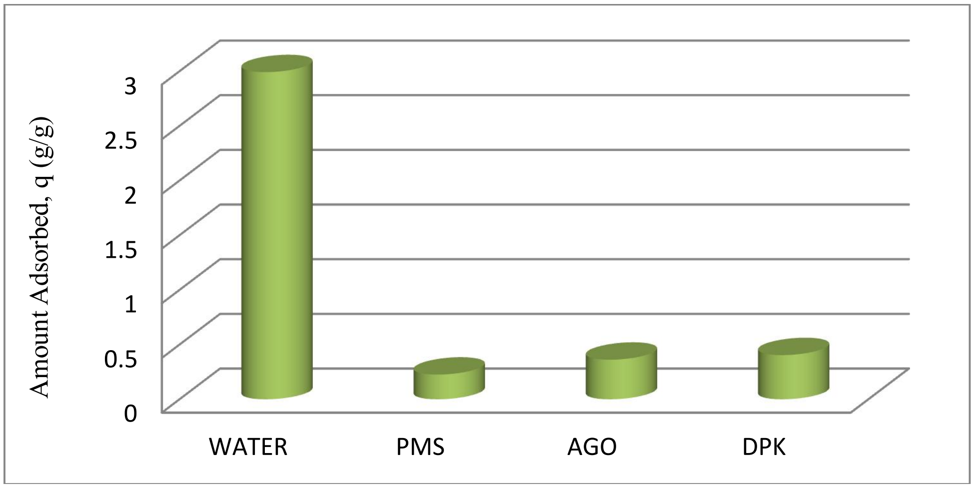

Figure 1. Adsorption capacity of water and organic solvents on unmodified calcium bentonite

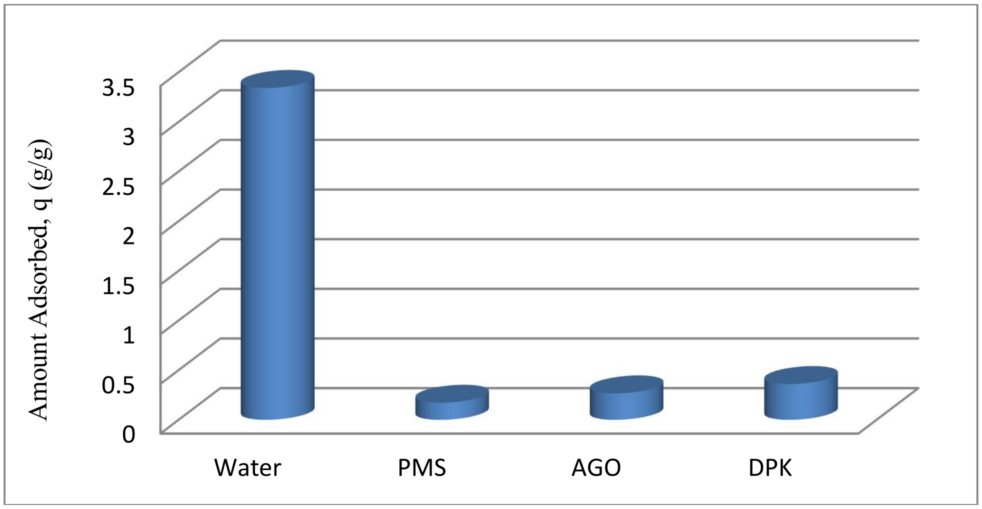

Figure 2. Adsorption capacity of water and organic solvents on sodium bentonite

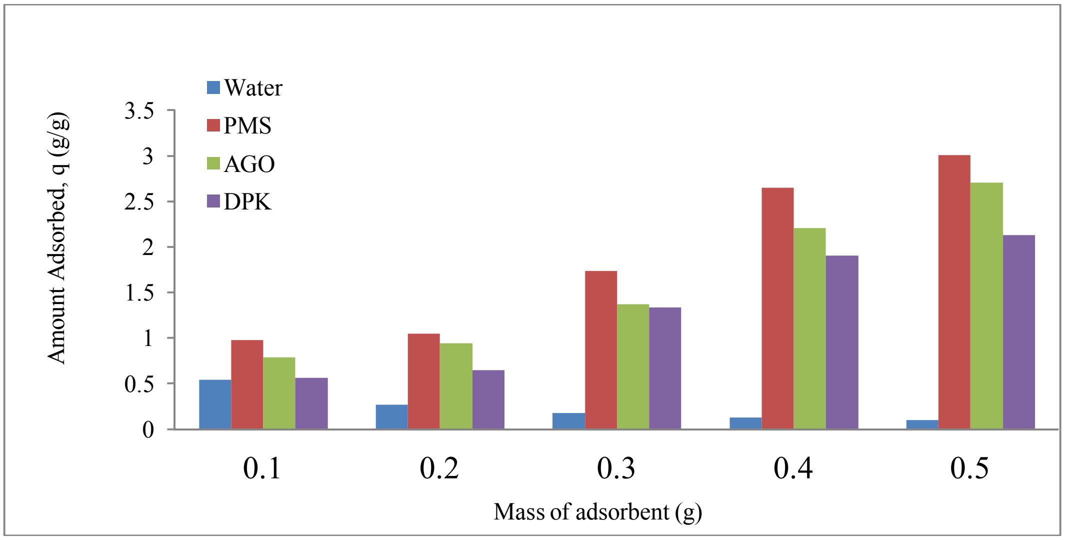

Figure 3. Adsorption capacity on TEAB-Modified bentonite

4. Discussions

The result of the elemental composition of the beneficiated bentonite samples show that sodium phosphate (Na_3PO_4) and sodium carbonate (Na_2CO_3) had better sodium exchanged on the bentonite, but the sodium carbonate was preferred because of its great level of separation (water/clay interaction when allowed to settle) and proper washing as presented in Table 1 and was subsequently used for the production of the organophilic bentonite.

The adsorption capacities of water, gasoline, DPK, AGO on unmodified calcium bentonite clay are presented in Figure 1. The results revealed that there was considerable adsorption of water on the unmodified bentonite clay, with very little adsorption observed in the case of the organic solvents. This could be as a result of the hydrophilic/organophobic nature of the unmodified bentonite clay which allows water adsorb at the surface thereby increasing its weight, but allows very little organic solvent adsorbing at the surface (Rodriques et al., 2010).

The adsorption capacity of sodium (Na_2CO_3) bentonite is presented in Figure 2. From the result above, it was observed that the water adsorption capacity of the bentonite increased in the sodium bentonite when compared to that of the calcium bentonite. However, there was slight difference in the adsorption capacities of the calcium and sodium bentonites respectively for organic solvents.

The result of the adsorption capacity of the organophilic bentonite obtained varies as the mass increases and is shown in Figure 3. The results showed comparison in adsorption capacity of various test solvents (Water, PMS, AGO, DPK) on TEAB-Modified Bentonite using ASTM F726-99. Gasoline showed progressive increase in adsorption capacity from 0.1 g to 0.5 g. The results showed an increase in the amount adsorbed for organic solvents, but little or no increase in water. Degree of adsorption ranged from; PMS > AGO > DPK > Water. The key factor responsible for the differences in sorption capacities of modified TEAB-Bentonite clay was the composition of the solvent. Gasoline is among the lightest liquid fractions of petroleum and consists mainly of aliphatic and aromatic hydrocarbons in the carbon number range C4-C12. Intermediate distillates cover a broader range of hydrocarbons, typically C6-C25. This includes comprise kerosene and diesel (C10-C16), and are blends of up to 500 different compounds. These intermediates tend to be denser, more viscous, less volatile, less water soluble and less mobile than gasoline. They also contain low percentages of light aromatics from the BTEX group, which may not be noticeable due to degradation or transport (Frost et al., 2000). However, the results went below the literature values obtained for organoclays used to remove petroleum hydrocarbons (Frost et al., 2007). This could be as a result of the short alkyl chain length of the organic modifier (TEAB) used. It is known that the hydrocarbon sorption by organoclays depends on the materials and surfactants used in the modification process. Although the clay starting material plays a role, the clays and the use of different surfactants are the primary determinants which enhance hydrocarbon uptake. The influence of the clay CEC on basal spacing and surfactant packing densities has been reported in the literature (Pereira and Hanna, 2005). The result of diesel adsorption capacity with the modified organophilic clay, reported in the present work, is in agreement with similar findings of Masomeh et al, (2010).

Conclusion

In this study, the adsorption of petroleum fractions and water on bentonite clay treated with tetraethylammonium bromide was investigated and its adsorption efficiency compared with the unmodified clay. There was little adsorption of organic solvents on the unmodified bentonite clays, which indicates its poor use as an adsorbent in the removal of petroleum spills and oils from the environment. Organoclay adsorbent based on exchanging surfactant within the clay surface could be prepared for potential adsorption of hydrocarbons with good efficiency and sorption capacity. The adsorption capacity of the prepared organoclay is highly dependent on the hydrocarbon type, surfactant concentration on the clay surface and chain length (type), amount of adsorbent and time.

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