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The Performance of an Organo - Modified Natural Bentonite in the Adsorption of Petroleum Fractions

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Abstract

Nigerian bentonite was modified with cetyltrimetylammoniumbromide (CTAB), a quaternary ammonium compound which possesses surfactant properties. Modification was achieved via impregnation techniques and also varying the concentration of the modifier from 0.02 - 0.15mol/L. Adsorption test was carried out using Water, Petrol (PMS), Kerosene (DPK) and Automotive Gas Oil (AGO) on both modified and unmodified bentonite. The result showed that unmodified bentonite adsorbed more water than hydrocarbons while modified bentonite adsorbed more hydrocarbons than water. The result also shows that the amount of each hydrocarbon adsorbed increases with an increase in the concentration of CTAB with a subsequent decrease in the amount of water adsorbed. This clearly indicates that the modified bentonite was now organophilic. Therefore, this research shows that the bentonite modified with CTAB can be used in oil spill remediation and also to mop up hydrocarbons from the environment.

Keywords: CTAB; Bentonite; Adsorption; Organophilization; Environment

List of abbreviations: CTAB: Cetyltrimetyl Ammonium Bromide

Introduction

Crude oil is an unrefined product from petroleum that consists of deposits of organic matter and hydrocarbons. Usual petroleum products such as diesel, kerosene and petrochemicals are obtained from crude oil refining. Crude oil is non-renewable and also known as, fossil fuel, which means that it, cannot be naturally replaced at consumption rate. Nigeria has crude oil as one of the most vital natural resource [1].

Refined products from crude oil are useful in heat generation, fueling vehicles, driving machinery and airplanes. Petrochemicals derived from crude are also used in the manufacture of chemical products such medicines, detergents and paints. However, environmental pollution through hydrocarbon contamination is a very serious problem and very critical because of the toxicity to man and the environment. Crude oil spills from operational activities is a contributory factor to environmental contamination [2]. The release of hydrocarbons accidentally to the environment is known global challenge [3]. Body organs such as the kidney, liver and lungs can be affected through the toxicity from hydrocarbon ingestion. In addition, high concentration of water contaminated by hydrocarbons is reported to be mutagenic and carcinogenic [4]. The natural equilibrium interruptions between the natural environment and living species are caused by some hydrocarbon pollutants resident in water bodies [5]. To avoid these disruptions, there is an urgent need for wastewater treatment before releasing into water bodies and oil spill remediation.

Absorbent clay, also called bentonite has montmorillonite as its main constituent. Montmorillonite possess various properties such as swelling, catalytic, surface acidity, surface area and particle size [6]. Bentonite is formed through the weathering of volcanic ash in an aqueous condition. Bentonite is an impure chemical form of aluminiumphyllosilicate. The two types of bentonite clay are Calcium and Sodium bentonite, Calcium bentonite is termed "Non-swelling" while sodium bentonite is termed "Swelling". People with sensitive palates can be aided by glazing their food with bentonite [7]. Clay minerals like bentonite play a crucial role in the oil industry [8]. Bentonite can act as an adsorbent and binder [9]. Bentonite is used in adsorbing metallic pollutants to prevent them from groundwater contamination; also used as a drilling mud and in the production of ceramic structures, adhesives and cosmetics.

Organophilization of clay mineral is defined as the conversion of the natural clay from hydrophilic to hydrophobic using a surfactant for a specific application [10,11]. Surfactants undergo substitution into the clay to achieve organophilization. Surfactants are represented by $[(CH_3)_3NR]^+$, where R- long chain hydrocarbon.

This work is focused on the detailed study of organically modified clay, obtained by impregnation method from natural bentonite. The adsorption properties using Gasoline, Diesel, Kerosene and Water were examined. This research, aims at obtaining modified clay which can be used as precursors to nano-composites or as sorbents in pollution prevention and environmental remediation, for example, in the treatment of spills, wastewater and hazardous waste landfills.

Materials and Methods

Reagents

The reagents used to carry out this experiment were:

i. Bentonite (obtained from Anambra State)
ii. CTAB 97% Purity (LSS Scientific limited)
iii. Gasoline (NNPC Mega Station)
iv. Diesel (NNPC Mega Station)
v. Kerosene (NNPC Mega Station)
vi. Distilled Water (Central Instrument Lab, Uniport)

Organiphilization Procedure

I. The modifier used was CTAB. The bentonite used in this experiment was obtained from Anambra State.
II. The weight of bentonite used in the experiment was kept constant at 25 g while the concentration of the modifier was varied.
III. The concentration of CTAB used was also varied between 0.02 to 0.15 mol/l (0.02, 0.05, 0.07, 0.10 and 0.15 mol/l).
IV. 25 g of bentonite was weighed into a 250 ml beaker.
V. 0.729 g of CTAB was measured and dissolved in 100 ml (0.1l) of distilled water.
VI. This solution of QAC (CTAB) was slowly added to the bentonite after which it was placed on a magnetic stirrer hot plate at a temperature of 80 ^{o}C with stirring until point of incipient wetness where a paste was obtained.
VII. The beaker was then put into the oven and dried at 105 ^{o}C.
VIII. The modified clay was ground to fine powder, then labeled.
IX. This procedure was repeated for unmodified bentonite and different concentrations of modifier (0.05, 0.07, 0.10 and 0.15 mol/l).

Adsorption Test

Solvents (PMS, AGO, DPK and Water) were adsorbed separately on both modified and unmodified bentonite.

- 0.5 g of the organoclay was weighed into an empty mesh bucket .The weight of the empty mesh bucket and organoclay was recorded. The Mesh bucket containing the sample was immersed into 150 ml of different Solvents (PMS, AGO, DPK and WATER) respectively for 30mins using a Stop watch.
- After 30 mins, the bucket was removed from the solvent and allowed to drain for 10 secs. The weight of the mesh bucket was taken before and after and subtracted to determine the weight of Solvent adsorbed. 0.5 g of each of the different concentrations of modified bentonite was repeated with same procedure.
- The same process was repeated using PMS, AGO and DPK. The adsorption of these organic solvents was studied according to [12].
- The weight of Solvent Adsorbed was determined by:

(Weight of solvent + Clay + Mesh Bucket) – (Weight of Clay + Mesh Bucket) [13].

Results and Discussions

Natural clay mineral and same modified with dodecyltrimethylammonium bromide (DTAB) were used to carry out adsorption properties on petroleum fractions and petrochemical wastes such as toluene, ethylbenzene and xylene. Records show a higher percentage removal for the organic compounds and a high adsorption capacity than the natural clay mineral. The adsorption capacity were reported to be directly proportional to the time of contact between the concentration of DTAB and adsorbents [14].

Figures 1,2 and 3 show the adsorption capacities on different concentrations of the Modified and Unmodified Clay. The adsorption capacity of the clay was determined using [12]. The Modified Clay adsorbed more of diesel than other solvents (Figure 2). However, after the process of organophilization, the modified clay showed the lowest adsorption with Water. When bentonite clay swells in any aqueous medium like water, it is as a result of the internal and external of the clay to be hydrated. Modified calcium bentonite showed swelling in petroleum fractions as expected. The presence of swelling is due to the organophilic nature of the modified clay that permits interaction with the petroleum fractions [15].

From the results, the modified clay adsorbed petroleum fractions (DPK, PMS and AGO) more efficiently than the unmodified clay. The "Standard Methods of Testing Sorbent Performance of Adsorbents" [12,16], was used in the Adsorption study of organic compounds. The order of adsorption capacity in the Modified clay was:

AGO > PMS> DPK> Water (Figure 2)

From the above order, it can be suggested that Modified clay have better adsorption capacity in organic solvents when compared with unmodified clay. The order of Adsorption Capacity in the unmodified clay was:

Water> PMS> AGO> DPK (Figure 1)

Figure 1 suggests that unmodified clay adsorbs water more efficiently than organic solvents.

Nevertheless, the concentration of the CTAB were varied, the effect of concentration on adsorption was monitored, and the results were reported in Figures 1, 2 and 3 and Tables 1, 2, 3, 4 and 5. However, It was observed that with an increase in the Concentration of the CTAB (modifier), there was an increase in the Adsorption of PMS, AGO and DPK and a decrease in the Adsorption of water.

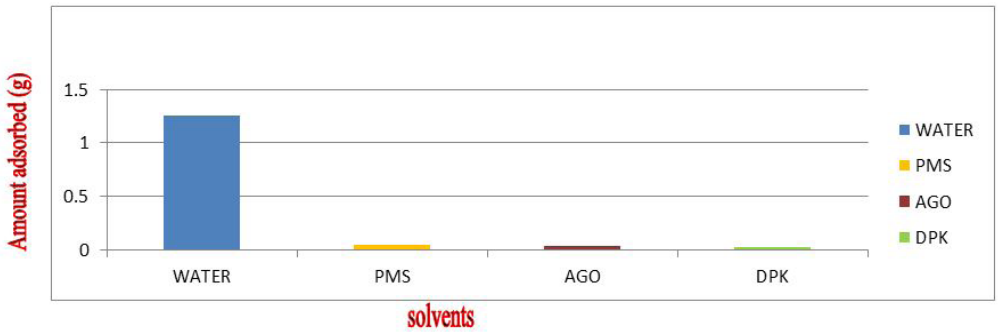

Figure 1: Adsorption of Water, PMS, AGO and DPK on unmodified bentonite

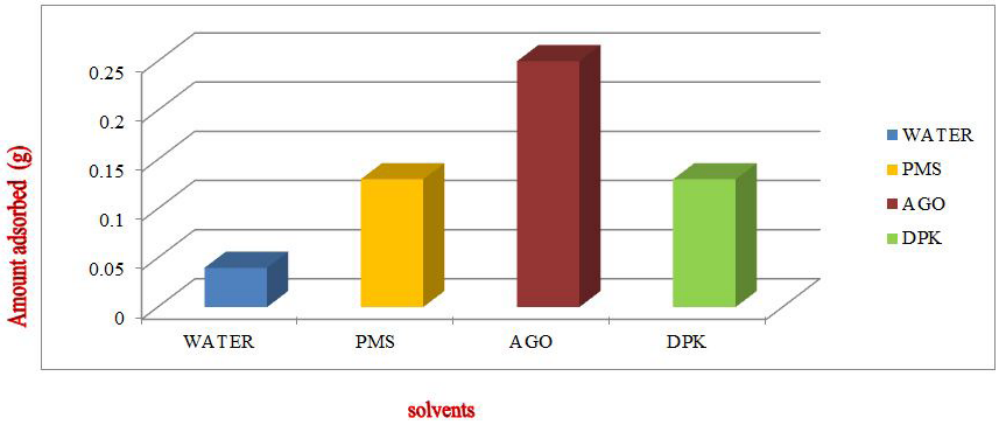

Figure 2: Adsorption of Water, PMS, AGO and DPK on modified bentonite using 0.1M CTAB

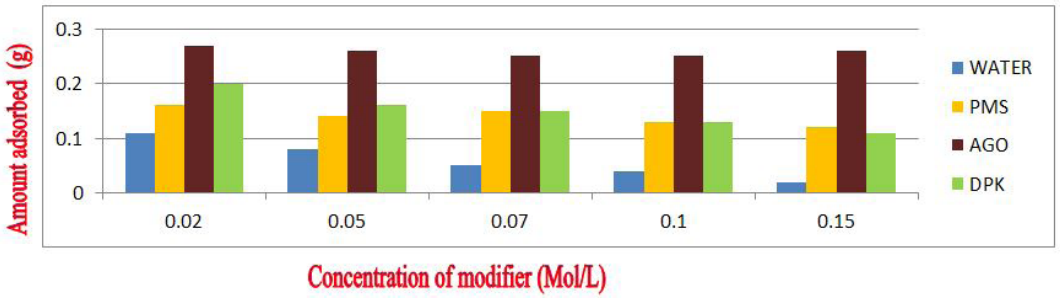

Figure 3: Adsorption of Water, PMS, AGO and DPK on bentonite modified with different concentration of CTAB

S/N	Conc. (Mol/L)	Weight of Mesh Bucket(G)	Weight of Sample (G)	Weight of Mesh Bucket+ Sample (G)	Weight of Mesh Bucket+ Sample+ Solvent (G)	Amount of Solvent Adsorbed (G)
1	0.02	5.88	0.50	6.38	6.54	0.16
2	0.05	5.88	0.50	6.38	6.53	0.14
3	0.07	5.88	0.50	6.38	6.53	0.15
4	0.10	5.88	0.50	6.38	6.51	0.13
5	0.15	5.88	0.50	6.38	6.50	0.12

Table 1: Diesel concentration in the modified clay

S/N	Conc (Mol/L)	Weight of Mesh Bucket (G)	Weight of Sample(G)	Weight of Mesh Bucket+ Sample (G)	Weight of Mesh Bucket+Sample + Solvent(G)	Amount of Solvent Adsorbed (G)
1	0.02	6.39	0.50	6.89	7.16	0.27
2	0.05	6.39	0.50	6.89	7.15	0.26
3	0.07	6.39	0.50	6.89	7.14	0.25
4	0.10	6.39	0.50	6.89	7.14	0.25
5	0.15	6.39	0.50	6.89	7.15	0.26

Table 2: Gasoline concentration in the modified clay

S/N	Conc. (Mol/L)	Weight of Mesh Bucket (G)	Weight of Sample (G)	Weight of Mesh Bucket +Sample (G)	Weight of Mesh Bucket+ Sample+ Solvent (G)	Amount of Solvent Adsorbed (G)
1	0.02	5.66	0.50	6.16	6.36	0.20
2	0.05	5.66	0.50	6.16	6.32	0.16
3	0.07	5.66	0.50	6.16	6.31	0.15
4	0.10	5.66	0.50	6.16	6.29	0.13
5	0.15	5.66	0.50	6.16	6.48	0.11

Table 3: Kerosene concentration in the modified clay

S/N	Conc. (Mol /L)	Weight of Mesh Bucket(G	Weight of Sample(G)	Weight of Sample+Bucket (G)	Weight of Sample+Bucket+Solvent (G)	Amount of Solvent Adsorbed (G)
1	0.02	6.39	0.50	6.89	7.00	0.11
2	0.05	6.39	0.50	6.89	6.97	0.08
3	0.07	6.39	0.50	6.89	6.94	0.05
4	0.10	6.39	0.50	6.89	6.93	0.04
5	0.15	6.39	0.50	6.89	6.91	0.02

Table 4: Water concentrations in the modified clay

Solvents	Weight Before (G)	Weight After (G)	Amount Adsorbed (G)
Ago	6.89	6.93	0.04
Pms	6.38	6.43	0.05
Dpk	6.16	6.19	0.03
Water	6.89	8.15	1.26

Table 5: Amount of solvents adsorbed by unmodified bentonite (control)

Conclusion

The Adsorption properties of Bentonite modified with CTAB was investigated in this study. Modification of the Clay was achieved using impregnation techniques. At the end of this study, the modified bentonite was shown to adsorb PMS, DPK and AGO. The modified bentonite showed greater Affinity for Organic Solvents compared to the Unmodified.

The Unmodified showed high affinity for Water compared to the Modified Clay.

This Study demonstrates that natural clay treated with CTAB has more efficient Adsorption Capacity in organic solvents than unmodified Clay.

This research therefore demonstrates this organoclay can be used as sorbents in pollution prevention, oil spill and environmental remediation such treatment of landfill leachate.

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