

# Hexadecyl Pyridinium Cation Loading on Meionite Silicate and its Effect in the Sorption of Organic Contaminants

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**Abstract**—Meionite silicate modified with hexadecylpyridinium bromide (HDPB) at 25%, 50%, 75% and 100% of its original cation exchange capacity, C.E.E, was used in sorption of phenol and chlorophenol contaminants from solution. Sorption was determined over a range of solute concentrations. Increase in surfactant loading on the meionite clay up to 100% of its C.E.C, indicated enhanced sorptive property for aromatic organic compounds (phenol and Chlorophenol). The mechanism supporting the sorption of phenol and chlorophenol to the meionite inter layers were deduced from the shape of the isotherms. The shapes of the isotherms indicated a double sigmoid isotherm, suggesting multiple mechanisms as responsible for the enhanced sorptive characteristic of the hexadecyl pyridium cation modified meionite. A double sigmoid Isotherm is comprised of a type III isotherm and a sigmoid isotherm. Type III isotherm explains partitioning of organic solutes onto the organoclays while the sigmoid isotherm explains solvation.

**Keywords**— Meionite, surfactant, organoclay, sorption, phenol, chlorophenol

## INTRODUCTION

The environmental impact of organic contaminants is increasingly becoming a major cause of concern. Organic contaminants arising from household insecticides, pesticides, herbicides and the chemical industries do find their way into soil and underground water. The risk implications of this have been documented in other literatures [1] [2].

In Nigeria, the siting of fuel filling stations, the installation of underground oil storage tanks and oil tank farms have contributed to the contamination of soil and underground water.

Studies have shown that humid soil, to certain extent, can eliminate organic pollutants from solution [3]. Additional study had demonstrated that the total organic carbon content of the soil and sediments influences the soil's capacity to remove organic pollutants from solutions [4]. According to these investigations, organic pollutants in solutions could be eliminated by using materials with a high level of organic carbon.

In spite of their availability and affordability, clay minerals are not good sorbents because they typically have low levels of organic carbon. However, clay minerals known to have

permanent negative charges on their surfaces can be modified with quaternary ammonium surfactants of the form  $[(CH_3)_3NR]^+$  or  $[(CH_3)_2NRR']^+$  in order to raise their organic carbon content and therefore their sorption for organic pollutants. The use of surfactant modified clay (known as organoclay) to remove organic pollutants from solutions was earlier introduced by Boyd and his group [5]

Organoclays are therefore very important and find applications in the treatment of contaminated waters and as protective barriers in waste disposals and oil reservoirs.

In the modification process, the interlamellar spaces in the clay are filled with the alkyl groups of the surfactant. The alkyl groups of the surfactants are lipophilic. It is the aggregation of the alkyl chains on the clay surfaces and interlayer regions that results in the emergence of an organic phase that facilitates the sorption of organic contaminants from solution [6] [7] [8]

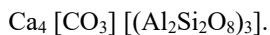
The sorption characteristics of the organoclays formed is attributed mainly to the size of the R- group [4]. Where it is a large alkyl group as in the case of the hexadecyls, the organoclays synthesized are more effective in sorption.

The sorptive properties of organoclays are attributed to several mechanisms. Researches have indicated that clays modified with the surfactant, hexadecyltrimethylammonium (HDTMA) effectively sorb organic contaminants either through a singular or a multiple mechanism(s). In the case of aliphatic compounds like trichloroethylene and carbon tetrachloride, sorption into the organic phase derived from the aggregation of HDTMA on the clay is noticed to be a singular sorption mechanism by HDTMA-clays, which is similar to solute sorption into soil organic matter [3] [9] [10].

In the present study, the effect of surfactant loading on the sorption characteristics of organoclay was examined. Clay modified with hexadecylpyridinium bromide (HDPB) at 25%, 50%, 70% and 100% of its original cation exchange capacity (C.E.C) was used to sorb organic contaminants from solution. Sorption was determined over a wide range of solute concentrations. The mechanisms responsible for the sorption property of the organoclay were also deduced.

The clay mineral used in this study was meionite. Meionite belongs to the silicate family of the tectosilicate, which is a framework silicate. Like all phyllosilicate clay minerals,

meionite has an isomorphous substitution of Aluminium in its silicate structure as shown;



This Isomorphous substitution gives an overall negative charge to the mineral which is often balanced by metal cations such as Ca<sup>2+</sup> in this case. The presence of these inorganic cations causes the mineral to be hydrophilic and therefore cannot be utilized for sorption of neutral organic compounds. However, upon replacing these metal cations with quaternary ammonium cations, their sorptive properties for organic compounds are enhanced greatly owing to the inclusion of a lipophilic bulk [7] [11]

The quaternary ammonium surfactant used in this study was hexadecyl pyridinium bromide with a large alkyl group. The chemical structure is given below:

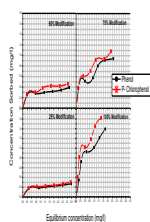


Figure (i) 1-Hexadecyl pyridinium bromide, monohydrate - C<sub>21</sub> H<sub>38</sub> BrN

### MATERIALS AND METHODS

#### Clay Extraction;

The clay particles were obtained through wet sedimentation of the ore obtained from Edo north geographical area of Nigeria and subsequent decantation of the <2µm particles through a 2µm mesh filter in accordance with Stokes' law. The C.E.C was measured to be 30.10Meq/100g. The major exchangeable cation was Ca<sup>2+</sup>, with Mg<sup>+2</sup> and Fe<sup>+2</sup> in small amounts.

#### Na-Clay;

Na-Clay was obtained by saturation of the pure clay with sodium chloride and subsequent washing with de-ionized water until pH was 7. Na-Clay obtained was stored in a sealed bottle.

#### Organoclay;

In the preparation of organoclay, the Na<sup>+</sup> on the Na-clay is replaced with the quaternary ammonium cation in order to raise the total organic carbon content of the clay and enhance its sorptive behaviour.

20g of Na- clay was first dispersed in about 300ml of de-ionized water to which a desired amount of the hexadecyl pyridinium bromide was slowly added. The concentration of the hexadecyl pyridinium cations were 0.25 CEC, 0.50 CEC, 0.75 CEC and 1.00 CEC of the clay respectively.

The reaction mixture was agitated overnight on a magnetic stirrer at room temperature. The organoclays suspensions were then washed with de-ionized water repeatedly until free of bromide ions as indicated by AgNO<sub>3</sub> in the classical silver mirror test for bromides. All products were dried at 90°C in the oven and ground in an agate mortar and then stored in sealed bottles for further use. The organoclays prepared at the

concentration of 0.25 CEC, 0.50 CEC, 0.75 CEC and 1.00 CEC were labeled DX, CX BX and AX respectively.

#### XRD Characterization

XRD was used to determine the mineralogical composition of the raw material component of the clay.

Aqueous suspension of the clay was made by dispersing grains of the clay in few drops of de-ionized water. Drops of the suspension were then placed on the glass slide which was immediately covered with a Teflon tape to prevent vapourization. X-ray diffraction patterns were recorded using a Philips APD3720 automated X-ray diffractometer.

#### Adsorption Of Phenol & Chlorophenol Using 25%, 50%, 75% And 100% Hexadecyl Pyridinium Cation Modified Meionite From Aqueous Solutions

The batch equilibrium method was employed in obtaining the adsorption isotherms of phenol & chlorophenol on HDPB – modified clay at various percentages [12].

0.2g of 25%, 50%, 75% and 100% HDPB modified clay were each weighed into corex glass centrifuge tubes. 25ml of phenol or chlorophenol solution at different concentrations were added to the tubes. The tubes were capped with Teflon – backed septa immediately. The tubes were shaken for 24 hours with a mechanical shaker at room temperature. Preliminary experiments showed that sorption reached equilibrium within 18hours. After equilibrium, the tube was centrifuged at 400 rpm for 30 minutes to obtain the supernatant.

Aliquot was taken from the supernatant and its absorbance was measured from the spectrophotometer. From the calibration curve obtained by a set of working standards of phenol or chlorophenol, the concentration of phenol or chlorophenol in the supernatant was determined.

Amounts of phenol or chlorophenol adsorbed were then calculated from the differences between the amount added and that remaining in the final equilibrium solutions.

### RESULTS AND DISCUSSIONS.

The C.E.C was determined to know the exchange capacity of cations in the clay as well as that of the modified clay as surfactant loading progresses. The C.E.C values are given in Table 1.

Table 1. C.E.C value for Clay/organoclays

| Clay Type         | C.E.C (Meq/100g) |
|-------------------|------------------|
| Raw Clay          | 30.10            |
| 25% Modification  | 13.28            |
| 50% Modification  | 9.42             |
| 75% Modification  | 5.30             |
| 100% Modification | 3.61             |

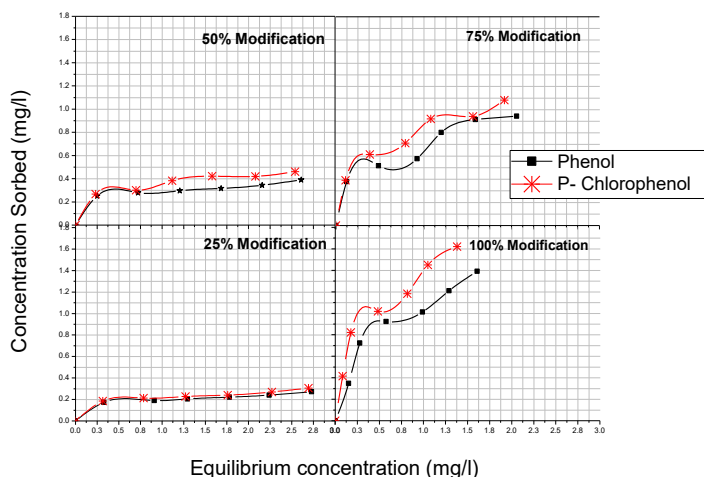


Figure 2: Sorption Isotherm of phenol and p- chlorophenol at 25%, 50%, 75% and 100% modification.

Sorption isotherms of phenol and p-chlorophenol from aqueous solution onto the organoclay at different modifications levels are shown in figure 2. The distribution and interaction of the surfactant cations in the interlayers of meionite has a pronounced effect on the adsorption of phenol and chlorophenol. The results indicated that partial replacement of  $\text{Na}^+$  (of the Na- clay) with hexadecyl pyridinium cations increases the adsorptive property of meionite to some extent. With increase in surfactant loading, more sodium ions were replaced by the surfactant cations and sorption was further increased.

From Table 1, it is seen that the C.E.C of the organoclay started diminishing as the percentage of surfactant loading increases. The low values of C.E.C indicate that  $\text{Na}^+$  are being exchanged by hexadecyl pyridinium cations that seem to have greater affinity for the inter layers of the meionites. A similar study by Sheng and Boyd in 1998 also showed this inverse proportional trend in the adsorption of trimethyl phenyl ammonium (TMPA) cations by a calcium saturated smectite and the subsequent discharge of  $\text{Ca}^{2+}$ .

It is also noticed that subsequent increase in the concentration of both phenol and Chlorophenol had progressive effect on their sorption.

This is evidenced in the gradual rise of the curves. This is more pronounced in the adsorption of chlorophenol

The mechanism supporting the sorption of phenol and chlorophenol onto the meionite inter layers can be deduced from the shape of the isotherms. The shapes of the isotherms indicated a double sigmoid isotherm, suggesting multiple mechanisms as responsible for the solute sorption. A double sigmoid Isotherm comprises of a type III isotherm and a sigmoid isotherm. Type III isotherms explain partitioning of organic solutes onto the organoclays while the sigmoid isotherm explains solvation [8] [10].

From figure 1, the earliest linearity of the isotherms indicated a type III isotherm which implied partitioning of phenol and chlorophenol onto the modified meionite. With further

increase in the total organic content, solvation of the ammonium centers by the aromatic compounds occurred, bringing about the wavelike nature of the isotherms pronounced in figure 2.

It had been previously shown that multiple mechanisms were involved in the sorption of aromatic compounds from solution by hexadecyl trimethyl Ammonium clays (HDTMA – Clays) [9]. Owing to their planar shape and delocalized  $\pi$  – orbital, aromatic molecules interact very well with HDTMA, causing a reorganization of the alkyl chains. Solute molecules solvate the cationic ammonium centers and alkyl chains of HDTMA, causing a transition from a parallel to a more vertical orientation relative to the silicate sheets. This led to the solutes molecules being simultaneously adsorbed on to the vacated mineral surfaces giving a sigmoid isotherm [8][9]. It gives explanation to the increase in sorption with increase in concentration of solutes. It is the combination of the sigmoid isotherm (arising from solvation) and the type III isotherm (arising from solute partitioning) that produces the double sigmoid shaped isotherms which was also observed in this present work.

## CONCLUSION

Increase in surfactant loading on meionite clay up to 100% of its C.E.C by hexadecyl pyridinium cations enhances its sorptive property for aromatic compounds (phenol and Chlorophenol).

Multiple mechanisms comprising of partitioning and solvation were also found to be involved in the enhanced sorption characteristic of the hexadecyl pyridium cation modified meionite on aromatic contaminants.

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