# ORGANICALLY MODIFIED CLAY FOR ADSORPTION OF PETROLEUM HYDROCARBON

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Organically modified clay mineral was prepared by exchanging hexadecyltrimethylammonium bromide (HDTMA) onto kaolinite clay mineral. The prepared organoclay was characterized using FTIR, XRD and TGA for assigning the surface groups, layer spacing and thermal stability. The adsorption efficiency of the produced organoclay towards hydrocarbons that likely to be present in oily wastewaters and oil spills (gasoline and kerosene) was studied. Different process parameters as contact time, adsorbent dose and HDTMA concentration were studied. The obtained results clarified that the adsorption capacity of the prepared organoclay was potentially enhanced than that of unmodified clay. The batch adsorption capacity was found to be more than 5 g g$^{-1}$ and 7 g g$^{-1}$ with respect to kerosene and gasoline, respectively after 24 h of contact.

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## Introduction

Environmental authorities all over the world have been involved in development of processes and roles to avoid and prevent the release of pollutants into water and environment. A 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.[1] The presence of these pollutants also decreases the contact area between water surface and atmospheric air, which prevent oxygen transfer. Consequently researchers are involved in development of new materials, new procedures and techniques for removal of pollutants and hazardous materials form waste streams before releasing in the environment. 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 process used to remove these pollutants is the adsorption process, which has accepted great importance due its low cost and available natural materials and biomass materials.[2,3] A wide range of materials have been modified and studied as adsorbent material for oil and petrochemical pollutants as biomass and natural materials.[4-12] 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 constitutes were studied as an adsorbent material is one of the techniques recently applied for the treatment of hydrocarbon contaminated water effluents. Clay minerals are natural materials, abundant with low cost and have large surface area, as it has high mass transfer rates.[13] The clay

materials have hydrophilic nature, so they are ineffective adsorbent for aromatic compounds present in contaminated sites as petrochemical sites. 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 presents on the clay surface and within the interlayer space by surfactant cations, such as: hexadecyletrimethylammonium (HDTMA), tetra-methylammonium (TMA), tetraethylammonium (TEA), tetrabutylammonium (TBA), and tribenzylmethyl-ammonium (TBMA).

The physico-chemical 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 adsorption and intercalation of organic polymers. The modification of clay materials creates a porous material, which is more effective in adsorption of organic compounds.[14] The properties of the modified clay minerals render it as promising materials in adsorption technologies and other applications. The suggested mechanism for reaction of clay with organic surfactants is based on the displacement of interlayer water molecules in smectites and vermiculites with the organic surfactant molecule. The organic molecules can form complexes with the interlayer cations also. Different chemical interactions like hydrogen bonding, ion-dipole interaction, co-ordination bonds, acid-base reactions, charge transfer and van der Waals forces, control the adsorption of neutral organic molecules onto the clay. Another reaction type is grafting reactions, in which covalent bonds are formed between reactive surface groups and organic species. It has been established that the 2:1 clay minerals could undergo grafting reactions, due to the presence of silanol and aluminol groups on surface which react with organic molecules.

The preparation of organoclays is generally based on cation exchange reactions,[15-17] involving the exchange of quaternary alkylammonium cations with interlayer cations of the clay mineral in aqueous solution. Several types of organoclay have been prepared under different reaction conditions.[18-24]

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

## Experimental

### Materials

Kaolinite clay, provided by (Sigma-Aldrich), was used for preparation of organoclay. The kaolinite sample was sieved to the sieve No 200 (0.074 mm). HDTMA, purchased from Aldrich Chemical Company Inc. was used as surfactant.

### Preparation of organokaolinite

The organokaolinite was prepared a cation exchange reaction, adapted from a reported procedure.[25] The procedure involves firstly the dispersion of the clay in distilled water with agitation (4 % w/w) for 30 min, then it was allowed to settle for 24 h. HDTMA was added to the suspension, then the mixture was stirred for further 20 min and left to settle for 24-h. The organoclay was filtered out, dried at (60 ± 5) ᵒC till constant weight and sieved at 230 (0.063 mm) sieve. The process was repeated using different initial concentrations of HDTMA. The concentrations of HDTMA were reported as a ratio of kaolinite cation exchange capacity (CEC) at a given conditions. HDTMA solutions of different concentrations were prepared, and then 2 g of kaolinite clay was added as the previously mentioned procedure. The concentration of unreacted HDTMA was determined through complexation with methyl orange in acidic conditions, followed by chloroform extraction, water–chloroform phase separation and then spectrophotometric determinationt at 401 nm.[26]

### Characterization

The XRD patterns of the samples were recorded on a XPert Philips X-ray diffractometer. All patterns were obtained using Cu/Kα1 radiation with a graphite monochromator at 0.02° min⁻¹ scanning rate at King Khalid University. Analyses were performed upon the original and modified clay. Thermogravimetric analysis (TGA) experiments were conducted using Shimadzu TGA-50H thermal analyzers at King Khalid University. All experiments were performed using a single loose top loading platinum sample pan under nitrogen at a flow rate of 30 mL min⁻¹ and a 10 °C min⁻¹ heating rate for the temperature range 25–800 °C. Fourier transform infrared (FT-IR) spectra of kaolinite, HDTMA and modified kaolinite using were recorded by KBr method on a NICOLET 6700 FTIR thermo scientific.

### Sorption Experiment

The sorption capacity of petroleum hydrocarbons (gasoline and kerosene) was studied using a standard method,[27,28] which used for determining the efficiency of the sorbent for removing oily liquids form surface water. The hydrocarbon (400 mL) was taken to a beaker and then 0.5 g of the organoclay clay was put into a 200 mesh stainless steel basket. The organoclay basket was placed into the beaker of hydrocarbon consequently the modified clay particles were completely immersed in the hydrocarbon. After the appropriate contact time the organoclay sorbent was withdrawn in a vertical way and left to drop out of liquid for about 30 min into a pre-weighed vessel. The adsorbent loaded with hydrocarbon was directly transferred to a pre-weighed vessel and weighed. The experiment was performed three times and the mean value was considered. The amount of hydrocarbon adsorbed onto the organoclay was calculated as follows:

$$\varphi = \frac{W_s - W_c}{W_c}$$

where

$\varphi$ - amount adsorbed (g hydrocarbon g⁻¹ sorbent)

$W_c$ is the initial weight of dry clay,

$W_s$ is the weight of the loaded adsorbent at end of experiment.

The effect of different parameters on the adsorbed amount of hydrocarbon onto organoclay was studied.

## Results and Discussion

### Characterization of adsorbent organoclay

#### X-ray diffraction analysis

The presence and the arrangement of the organic compound within the clay interlayer are assigned using XRD analysis for the clay before and after treatment.[29] The results in Figure 1 show the XRD diffraction patterns of kaolinite clay before and after treatment. The produced layer spacing expansion due to the intercalation of organic surfactant (HDTMA), into the clay interlayer, was confirmed by the shift of peak position (change in the 2 theta values consequently change in the layer spacing. The slight decrease in 2 theta value of peak position corresponds to an increase in the basal spacing of the organo-clay, could be assigned to the intercalation of the organic surfactant into the interlayer spacing of kaolinite depending on the ion exchange capacity CEC.[30,31]

#### FTIR studies

The FTIR spectra of kaolinite clay before and after treatment were represented in Figure 2. The results in this figure show infrared spectra of kaolinite, HDTMA and kaolinite-HDTMA within the range of 400-4000 cm⁻¹ for comparison.
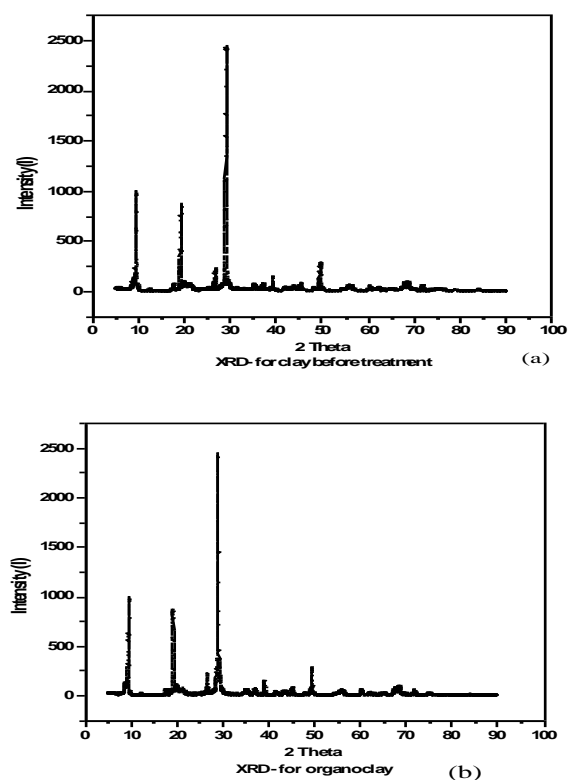
**Figure 1.** XRD of kaolinite clay mineral (a), and organokaolinite (b).

The peak observed at 1000-1100 cm$^{-1}$ was assigned for the stretching vibration of Si-O-Si and Si-O-Al, while the peak at 3400-3650 cm$^{-1}$ corresponds to the stretching absorption of Si-OH.[32]
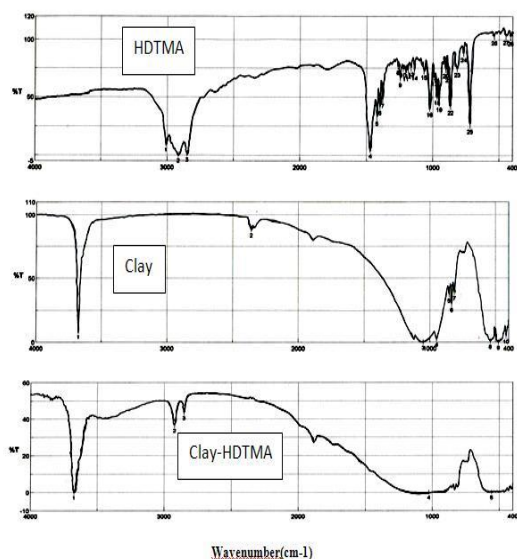


**Figure 2.** FT-IR spectra of kaolinite, HDTMA and orgo-kaolinite.

The results in the FTIR spectrum of the untreated clay clarify the presence of the characteristic peaks of the clay with no presence of characteristic peaks of organic surfactant.

While in the FTIR spectrum of the modified clay, the characteristic peaks of clay were clearly observed, and the peaks characteristic for the organic surfactant. This finding indicates the presence of the surfactant with clay. The peaks at 2950, 2850 and 1450 cm$^{-1}$ could be assigned for the stretching vibration of CH$_2$ and CH$_3$. This observation confirms the intercalation of the organic surfactant into the interlayer spacing of clay.[19]

**Thermal analysis**

TGA was performed upon the modified kaolinite. The weight loss against temperature was represented in Figure 3, while the degradation of samples was studied by TGA. Sample of 7 - 10 mg was heated from 25 to 800 °C at a rate of 10 °C min$^{-1}$. The weight loss percentage (%) was used to determine the degradation temperature of the organic content in the modified clay. It is well known that the ammonium surfactants have low thermal stability, while it suffers degradation and leading to variety of undesirable effects in the final compound. The TGA of the organoclay shows four degradation steps are observed. Firstly from the ambient to 70 °C a weight loss is assigned for water desorption, secondly from 150 to 300 °C, the observed weight loss is due to releases of hydration water of interlayer cations. The third mass loss observed at 450 °C is assigned for the degradation of surfactant. The fourth step of mass loss was observed at 500-700 °C, which could be attributed to the dehydroxylation of the clay hydroxyl groups. These findings reflect the thermal stability of organokaolinite.
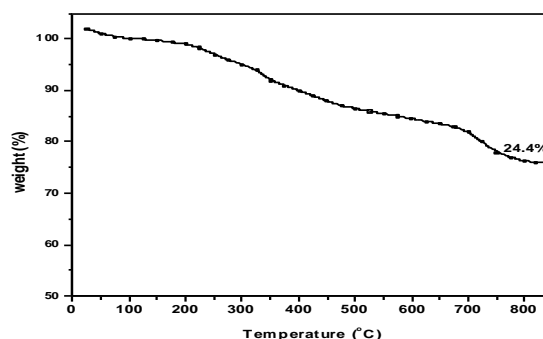


**Figure 3.** Thermogravimetric analysis of organokaolinite.

**Adsorption results**

**Effect of contact time**

The amount of hydrocarbon adsorbed onto the modified clay was studied at different contact time periods ranging from 5min to 48 h. The results (Figure 4) show that the adsorption process of kerosene and gasoline hydrocarbons on organkaolinite reached equilibrium fastly in the first hour with adsorbed amount reached 5 and 6 g g$^{-1}$ of kerosene and gasoline, respectively. The results clarify that, increasing the contact time up to 48 h give slight increase in the amount adsorbed of hydrocarbon onto the modified clay and reached 5.5 and 6.5 g g$^{-1}$ of kerosene and gasoline, respectively after 48 h.
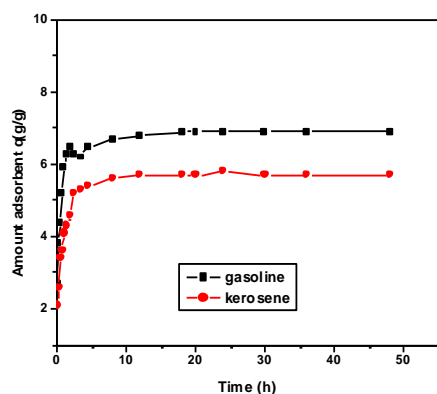
**Figure 4.** Effect of contact time on the adsorbed amount of hydrocarbon onto organokaolinite.

**Effect of adsorbent amount**

The adsorption of kerosene and gasoline onto the modified clay was studied using different amounts of organoclay while keeping all other parameters constant. The results given in Figure 5 show that the adsorbed amount of hydrocarbon increases sharply with increasing amounts of adsorbent up to 0.5 g, however, further increase in adsorbent amount from 0.5-2 g leads only to slight increase in the amount adsorbed of hydrocarbon per gram of organoclay adsorbent.
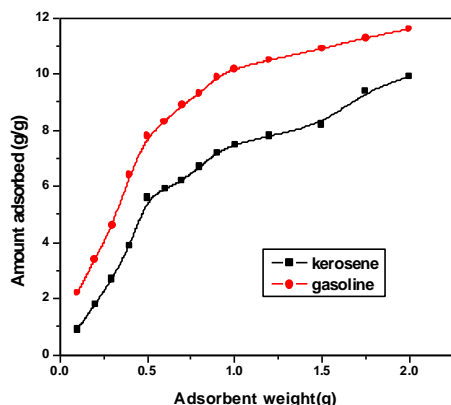


**Figure 5.** Effect of weight of adsorbent on the adsorbed amount of hydrocarbon onto organokaolinite.

The initial sharp increase in adsorption could be explained as the increase the available adsorption sites on the surface relative to the hydrocarbon concentration on increasing the amount organoclay. The less effect of increase in the amount of organoclay, in the higher range, could be due to particles aggregation with increasing adsorbent dose. Possible interactions between particles of adsorbent could be also responsible for these phenomena, as the adsorption occurs within the interlayer surfaces of the organoclay which involve intra and inter-particle diffusion mechanisms.[33,34] Increasing the adsorbent dose increases, the possibility of floc formation with greater size, consequently the intra particle diffusion resistance increases leading to the ineffective increase or slight decrease in adsorbed amount of hydrocarbon per gram of adsorbent.[35]

**Effect of surfactant concentration on the adsorption of hydrocarbon**

The adsorption of hydrocarbon was studied onto modified clay with different concentrations of surfactant. The results in Figure 6 show that the amount of hydrocarbon adsorbed increase with increasing the amount of surfactant adsorbed onto the modified clay. The results also reflect that the maximum hydrocarbon removal was achieved at concentration of surfactant corresponding to 100% of the CEC of kaolinite clay. This finding proves firstly the presence of strong chain interactions and multilayer formation as well. Also the change in the exchanged concentration of the surfactant has a pronouced effect on the adsorbed amount of hydrocarbon onto the modified clay. An increase in the concentration of surfactant more than that of the CEC of the clay have very slight effect upon the adsorbed amount of hydrocarbon upon the organoclay. This finding could be due to the formation of second layer of adsorbed surfactant, which is weakly bonded to the surface compared to the first layer bonded through strong chain interactions, keeping the surfactant within the first layer.[36]
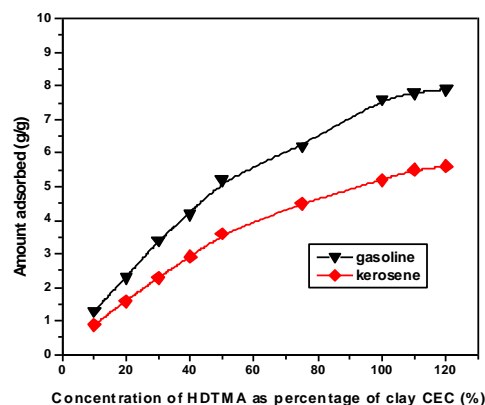


**Figure 6.** Effect of surfactant concentration as a percentage of the clay CEC on the adsorbed amount of hydrocarbon onto organokaolinite.

**Conclusion**

Based on the obtained results it could be concluded that:

Organoclay adsorbent based on exchanging surfactant within the clay surface could be prepared for potential adsorption of hydrocarbons with high efficiency and high sorption capacity. The prepared organoclay adsorbent shows high adsorption efficiency for hydrocarbon relative to its weight.

The adsorption efficiency of the prepared organoclay is highly dependent on hydrocarbon type, surfactant concentration on the clay surface, amount of adsorbent and time.

The adsorption of hydrocarbon onto the organoclay is a fast process rendering the organoclay economically applicable material for removal of organic pollutants from waste waters.

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