

The Performance of Surfactant Modified Bentonite in Removing Mobil Oil

Sabrina Mostofa, Nipa Banik, Shirin Akter Jahan, Samina Ahmed, Nahid Sharmin

Abstract: Adsorption of petroleum hydrocarbon (mobil oil) by bentonite modified with cetyltrimethylammonium bromide (CTAB), and sodium dodecyl sulfate (SDS) has been investigated in this study. Observed result revealed that modification of bentonite by surfactants hugely improved the adsorption of petroleum hydrocarbon as compared to the unmodified bentonite. Adsorption efficiency of organoclay increases from 15% to 50 % with various time interval.

Index Terms: Adsorption, Bentonite, FT-IR, Organoclay, Petroleum Hydrocarbon, Surfactant, XRD.

INTRODUCTION

Clays are profitably effective to immobilize toxic environmental contaminants due to their inexpensive availability, environmental stability and high adsorptive and ion exchange properties. Additionally, clay materials can potentially be modified using a variety of chemical/physical treatment to achieve the desired surface properties for best immobilization performance of specific compounds. Normally clays are highly hydrophilic. When inorganic cations are replaced by surfactants like quaternary ammonium cations in the form of $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$ the hydrophilicity of clays can be transformed into hydrophobicity [1],[2]. During the intercalation of the surfactants, the interlayer of the clay minerals is expanded as shown by the XRD patterns. The d -spacings of the organoclays depend on the length of the alkyl chains and the packing density of the surfactants within the galleries of clay minerals [3]. Applications for organoclays are cleanup of storm water, boiler steam condensates, landfill leachates, ground water, boiler feed water, produced water from oil production wells, wood-treating water, degreasing operations, truck and heavy equipment wash, refinery and rendering operations wastewater, and other manufacturing process water [4]. Clays have been mostly modified for waste

water treatment. The new pesticide formulation using clay minerals can be used for potential applications such as removal of toxic compounds from environment and to reduce dispersion of pollutants in soil and water.

Objective of the present study is to determine the adsorption capacity of organically modified bentonite using XRD, FT-IR, and subjected to removal of hydrocarbon.

EXPERIMENTAL

MATERIALS

Bentonite clay with cation exchange capacity (CEC) of 110meq/100 gm (obtained from Kunimine Mining Industries Co., Tokyo, Japan) was taken as the starting material. Surfactant used in this study were cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) with a purity of 99% were purchased from Merck (Germany). Mobil oil (purchased from local market) was the hydrocarbon used in this study.

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PREPARATION OF ORGANOCLAY

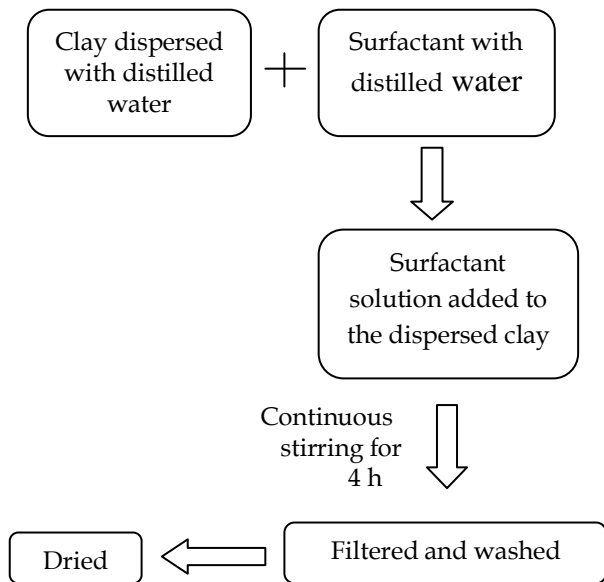


Fig 1. Schematic diagram of preparation of organoclay

5 g of clay was first dispersed in 400 mL of distilled water under continuous stirring. The surfactant solution was prepared in 200 mL of water in a separate container. The amount of surfactant added was calculated with the CEC value (110meq/100g clay) of bentonite. The calculated amount was added to 200 mL of water in the separate container and was dissolved by continuous stirring. After this, homogeneous surfactant solution was added to the dispersed purified bentonite solution. After continuous stirring for 4 h, the resulting product was separated by filtration and washed with distilled water for 3 times. Then the product was washed with ethanol for drying. Synthesized organoclay was dried in an oven for 48 h and ground into a powder.

CHARACTERIZATION

d-spacing of raw clay and organoclay were analyzed by using PANalytical (X'Pert PRO XRD PW 3040). The Fourier transform infrared (FT-IR) spectra were obtained by IR Prestige 21, Shimadzu using KBr disks and the samples were scanned in wave number range of 4000 cm⁻¹ – 400 cm⁻¹ with an average of 30 scans and resolution was 4 cm⁻¹. All spectra were recorded and analyzed to know the nature of the functional group attachment.

ADSORPTION TEST

A method based on ASTM F726-99 [5] and ASTM F716-82 [6] (Standard Test Method for Sorbent Performance of Adsorbents) was used for hydrocarbon sorption capacity measurements. The focus of this method concerns the evaluation of sorbents performance for removing non-emulsified oils and other floating, immiscible liquids from the surface of water bodies and also gives idealization laboratory data which can be used to compare the oil adsorbing capacity of one adsorbent with another and relative cost effectiveness.

0.5 mL of the hydrocarbon (mobil oil) was poured into a pre-weighed sample bottle. 0.5 g of the sorbent and a 2 mL of distilled water also added to that sample bottle. Then the sample bottle was placed in an ultrasonicator. After various time interval of immersion the sample bottle with the sorbent was removed from the ultrasonicator. Extra oil and water was then decanted from the sample bottle. Finally the sorbent was washed and dried. Final weight of the sample bottle was recorded. All tests were carried out in triplicate with the mean of the three runs used for calculations. If the value of any run (g/g) deviated by more than 15% from the mean of the three runs, then the sample was rejected and the test repeated with three new specimens. The hydrocarbon pick-up ratio on a weight basis was calculated as follows:

Adsorption efficiency:

$$A = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \quad (1)$$

Where:

W_1 is the weight of adsorbed material

W_2 is the weight of unadsorbed material
and

A is the adsorption efficiency for the fluid and adsorbent being tested.

RESULT AND DISCUSSION

X-RAY DIFFRACTION ANALYSIS

The XRD data were widely used to clarify the arrangement of sorbed surfactant in the clay interlayer [7]. Fine powder of organoclay was scanned on diffractometer for the measurement of *d*-spacing. The recorded values of pure bentonite clay and organoclay are reported on the Table-1. The *d*-spacing of pure bentonite, CTAB-O (CTAB-Organoclay) and SDS-O (SDS-Organoclay) are shown in Table-1. X-ray diffractogram of pure bentonite and

organoclay exhibits an increase in *d*-spacing compared to the original unmodified clay, indicating the formation of intercalated structures. The high intensity reflection for organoclay confirms a high degree of order for a lamellar stacking of layers of these organically modified clays.

increases the *d*-spacing increases to a large extent as seen from the Table-1 and corresponding XRD pattern.

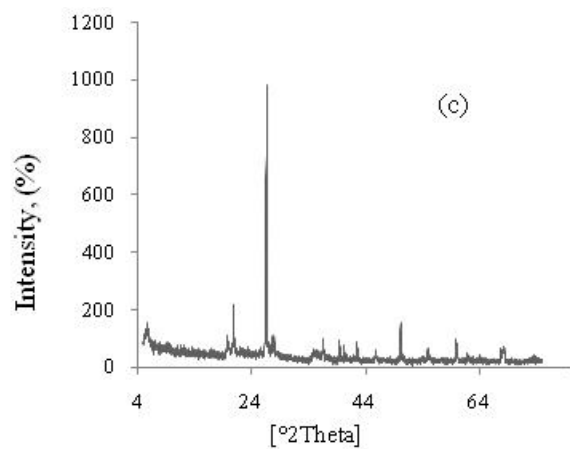
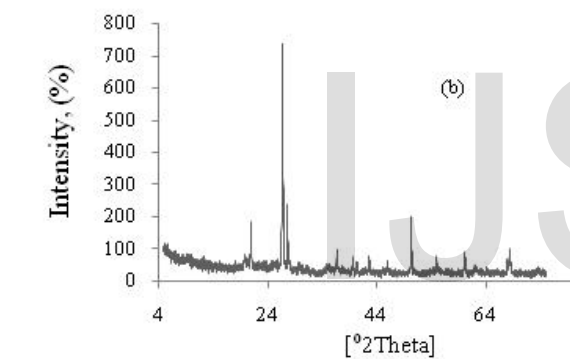
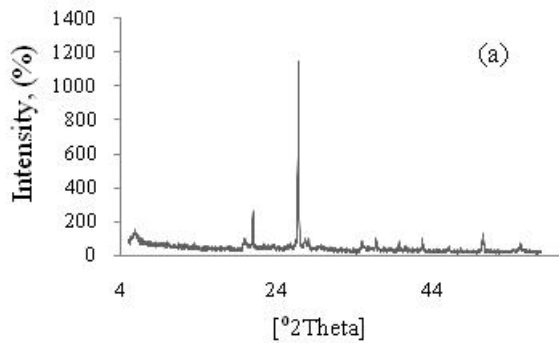


Fig 2. XRD patterns of (a) pure bentonite, (b) CTAB-O, (c) SDS-O

The increase in the value of *d*-spacing depends upon two factors. One is the presence of large hydrophobic groups on surfactants and second is the decrease in the surface energy of pure bentonite. As the size of the hydrophobic group

TABLE 1

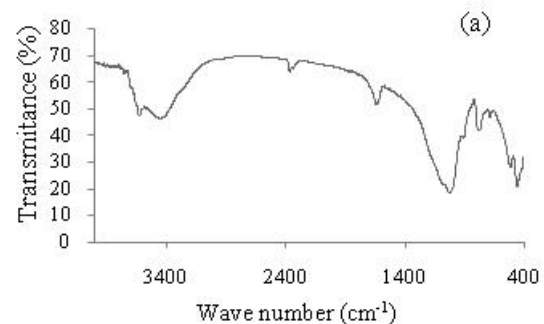
D-SPACING RECORDED FOR PURE BENTONITE AND ORGANOCLAY

Sr. No	sample	<i>d</i> -spacing
1.	Pure bentonite	14.99
2.	CTAB-O	16.88
3.	SDS-O	15.42

Table-1 clearly shows the increase in the *d*-spacing from the untreated clay to organoclay. The increase in the *d*-spacing for the modified clay is attributed to the interlayer of bentonite [8].

FTIR ANALYSIS

Fig 3. shows infrared spectra of pure bentonite and organoclay sample in the range of 400-4000 cm^{-1} for comparison. Hence, infrared spectrum of pure bentonite sample (Fig 3a.) shows characteristic clay mineral peaks at 3622, 3450, 1637, 1456, 1033, 794, 779 cm^{-1} . Infrared spectra of clay sample shows no intense peaks corresponding to organic matter [11]. Infrared spectrum of the CTAB-O sample (Fig 3b.) shows the characteristic peaks of untreated clay sample, albeit of low intensity that indicate the organophilic nature of the treated clay. It also shows intense peaks of CTAB-O at 2922, 2850 and 1470 cm^{-1} . The 1470, 2850 and 2922 cm^{-1} peaks are assign to the $-\text{CH}_2$ scissor vibration band, the symmetrical $-\text{CH}_3$ stretching absorption band and the $-\text{CH}$ stretching band, respectively. Similarly (Fig 3c.) shows characteristic peaks of SDS-O at 2920, 2852 and 1465 cm^{-1} . The 1465, 2852 and 2920 cm^{-1} peaks are assign to the $-\text{CH}_2$ scissor vibration band, the symmetrical $-\text{CH}_3$ stretching absorption band and the $-\text{CH}$ stretching band, respectively. These bands confirm the intercalation alkylammonium in the interlayer of galleries of the clay mineral [10],[11].



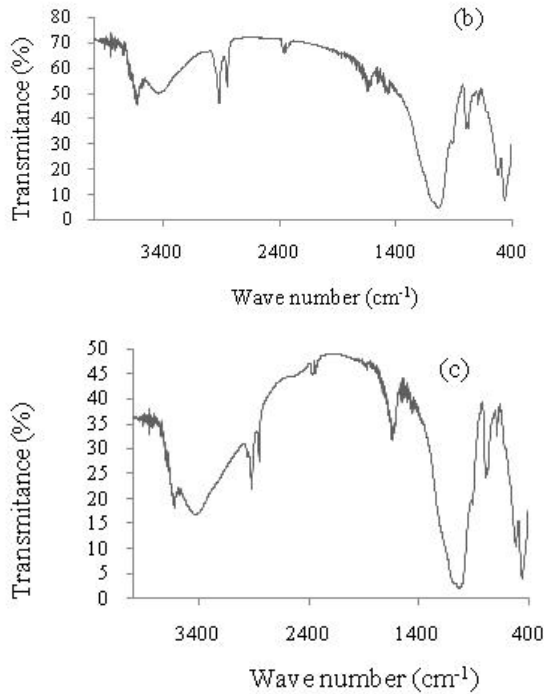


Fig 3. FT-IR Spectra of (a) pure bentonite, (b) CTAB-O, (c) SDS-O

ADSORPTION TEST ANALYSIS

Fig 4. shows the adsorption results of organic compounds on bentonite and organoclay. The data shows that organoclay adsorb more mobil oil than untreated clay. It shows that the adsorption capacity of the organoclay is higher than that of the clay. The data indicate that the organoclay adsorb hydrocarbon more than 5 times of its weight. These results exceeded the literature values obtained for organoclays used to remove petroleum hydrocarbon [9],[10].

The amount of hydrocarbon adsorbed on the modified clay was studied at different contact time periods ranging from 10 min to 1 h. The results show that the adsorption of organoclay is higher than that of uncreated clay. The results clarify that, increasing the contact time up to 1 h give slight increase in the amount adsorbed of hydrocarbon onto the modified clay. The adsorption efficiency of organoclay increases from 15% to 50 % with 10 min to 1 h respectively.

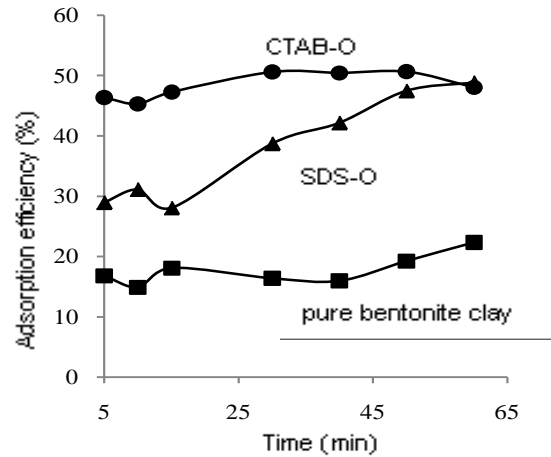


Fig 4. Variation of hydrocarbon adsorption with time

CONCLUSIONS

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 hydrocarbon with high efficiency and high sorption capacity. The prepared organoclay adsorbents show high adsorption efficiency for hydrocarbon relative to its weight. The adsorption efficiency of the prepared organoclay depend on time.

The adsorption of the 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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