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Development and characterization of organophilic clay from bentonite

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ABSTRACT

Commercially available smectite clay (bentonite) was modified by ion exchange reaction using N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) to prepare organophilic clay. The reaction was carried out in acidic medium (conc. HCl) under controlled stirring at a temperature of 80°C for a specific period of time. Physico-chemical and thermal properties of the clay before and after modification were determined and compared using X-ray diffraction (XRD), Fourier transform infra red (FTIR) and thermogravimetric analyzer (TGA). The chemical composition of bentonite was determined by X-ray fluorescence (XRF) and the cation exchange capacity (CEC) of the clay was determined by methylene blue method. The CEC value is found 29 meq/100g of the sample and the XRD analysis showed the enhancement of basal spacing from 12.2 Å to 12.9 Å after the modification of the clay. The results revealed that desired modification of bentonite has been achieved.

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KEYWORDS

Organophilic clay;
Smectite;
CEC;
Basal spacing;
CTAB.

INTRODUCTION

Clay minerals find almost innumerable applications and the diversity of its use is still increasing. In addition to applications well-known for a long time, new uses are found and new types of materials are created. The suitability of clay for a specific application is based on its mineralogical and chemical composition. Due to unique structure of montmorillonite, the mineral platelet thickness is only one nanometer, although its dimensions in length and width can be measured in hundreds of nanometers, with a majority of platelets in 200–400 nm range after purification^[1]. Smectite are constituted

by layer and belong to the Phyllosilicate family. Each layer is composed from an octahedral sheet surrounded by two tetrahedral sheets (T.O.T.). They form a group of clay minerals with a very large compositional range. Substitutions are extensive both in the tetrahedral and octahedral sheets. Bentonite in its pure natural form is hydrophilic, because of the presence of inorganic cations on the basal planar of montmorillonite. Clay minerals and clays are more and more involved in material science studies and are parent materials of organic-inorganic composites. An additional driving force originates from the need to remove toxic compounds from the environment and to reduce the dispersion of pollut-

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ants in soil, water and air. Bentonite is smectite group clay formed from the alteration of siliceous, glass-rich volcanic rocks such as tuffs and ash deposits. The major mineral in bentonite is montmorillonite, having hydrated sodium, calcium, magnesium and aluminium silicate. Bentonite is used in a wide range of applications such as drilling mud, foundry and binding, iron-ore pelletizing and civil engineering uses such as water proofing and sealant^[2]. The significance of bentonite has increased due to its ability to form organically modified clays or nanoclays, which are gaining a large market place in the field of polymer nanocomposites, paints, greases, inks, cosmetics, waste water treatment and drug-delivery vehicle in the last decade^[3]. Montmorillonite gives to bentonite its typical properties-high sorption capacity, characterized by a high value of cation exchange, internal swelling after contact with water, high plasticity and binding ability. Bentonite also contains other clay minerals (uaolinite, illite, beidellite), Fe compounds, quartz, feldspars, volcanic glass etc., which represent impurities and if possible they are removed during the mineral processing^[4].

There are different types of modification with organic molecules e.g. ion exchange, impregnation, intercalation and grafting. Organoclays have been categorized as the good adsorbents for toxic metals e.g. Cr, Pb, Cd, Hg and Zn^[5]. To reach adequate modification of a clay sample, it is necessary to know their cation exchange capacity (CEC) and the amount of organic surfactant that can enter between the layers, thus ensuring a complete modification of the clays. Many methods exist to measure the CEC and methylene blue can be used in a rapid qualitative procedure. The methylene blue stain test makes it possible to quantify the ionic adsorption capacity of a soil by measuring the quantity of methylene blue necessary to cover the total (external and internal) surface of the clay sample^[6]. This testing technique works on the basis of the chemical reactions triggered by an excess in negative electric charges in the clay particles and (or) the ionic exchange phenomena taking place between the easily exchangeable cations of the clay and the methylene blue cations released by methylene blue during its decomposition in water^[6]. Clay modification using ion exchange process is the common method to make the clay more organophilic.

In this study, bentonite was modified with N-Cetyl-N,N,N-trimethylammonium bromide (CTAB). The obtained organo bentonite was characterized by XRD, FTIR, TGA and methylene blue index value (MIB).

EXPERIMENTAL

Materials

Bentonite clay was collected from the local market. N-Cetyl-N, N, N- trimethylammonium bromide, hydrogen peroxide, concentrated HCl, sulphuric acid (H_2SO_4), methylene blue and distilled water were used for the preparation of organobentonite. All the chemicals above were used as received without any further purification. Organic solvents for the synthesis and characterization were analytical grade and were obtained from Merck Germany.

Methods

Organoclay preparation and characterization

Locally collected bentonite clay sample was dried, ground and stored in a bottle. A requisite amount (20g) of air-dried clay were heated at 110°C for 24 hours to determine the moisture content^[7]. From the dried sample 1g clay was calcined at 1000°C for 1h to determine the loss on ignition (LOI) from the final mass. Chemical analysis of the clay was done by the sophisticated X-ray fluorescence spectrophotometer (XRF, PANalytical XRF, Model No. PW2404). The cation exchange capacity (CEC) of the clay was estimated by methylene blue titration method^[8]. The test was performed on 2g of bentonite sample (weighed dry sample after oven drying at 110°C for 12h). The sample is placed in a 600 mL of distilled water and kept in suspension with a stirrer. The test must be performed in an acid environment (pH between 2.5 and 3.8) through the progressive addition of 0.1N sulphuric acid until the pH was stabilized at the desired value. Methylene blue solution of concentration 0.01N was added to the suspension with a burette. A small quantity of the suspension was collected with a rod after stirring the suspension and a small drop was made to fall onto a standard filter paper. This produces a dark blue stain surrounded by a colourless wet area. Methylene blue solution was added more and more drops were deposited on the filter paper until a

light blue halo was seen to form inside the wet area and around the blue stain. American Society for Testing and Materials (ASTM) standards define the blue index (MIB, in mequiv/100g) as follows^[8]:

$$\text{MIB} = \text{EV}100/\text{W} \quad (1)$$

Where E is the milliequivalents of methylene blue per millilitre, V is the volume in mL of the solution used in the titration process and W is the weight (in g) of the dry sample.

Thus the blue index can be determined from the following formula^[8]:

$$\text{MIB} = 0.5V \quad (2)$$

Again, the index supplied by the Association française de Normalization (AFNOR) testing method is referred to as the blue value of the soil (V_B in g/100g) and is given by^[6]:

$$V_B = V \times 0.01 \times 100/\text{W} \quad (3)$$

Where V is the volume (in mL) of the methylene blue solution used, 0.01 is the concentration (g/mL) of methylene blue solution used and W is the dry weight (in g) of the specimen.

If the blue index (MIB) determined by the equation (1) is correlated with the blue value (V_B) by means of equation (3), keeping in mind that in this case the concentration of the blue solution is 3.1986×10^{-3} g/mL (instead of 10×10^{-3} g/mL):

$$V_B = V \times 3.1986 \times 10^{-3} \times 100/\text{W} \quad (4)$$

Where 3.1986×10^{-3} is the concentration of the solution in g/mL.

Most of the studies have reported modification of clays using aliphatic quarternary ammonium ions^[9] and N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) was used in this study. 20g of bentonite clay sample was measured into the 1000mL of hot water into a 2 L capacity beaker and allowed to disperse under mixer rotating 250 rpm for 90 minutes at a temperature of 80°C. A solution containing 10g CTAB with 4.2mL concentrated hydrochloric acid (HCl) in 500mL hot distilled water subsequently added into the mixture and allowed to mix for another 90 minutes at the same speed of rotation. After this, the solid was filtered through hot distilled water using vacuum filtration apparatus. The modified clay was dried in an oven for 24 hr at 80°C, then ground into a fine powder using mortar and pestle. The obtained organo modified clay was labeled as TC in this study. All procedures were carried out thoroughly

in order to ensure appropriateness of the successful ion-exchange reaction.

In order to obtain unmodified clay, 20g bentonite was dispersed in 1000 mL of hot distilled water at 80°C and was thoroughly mixed for 90 minutes at 250 rpm. The obtained solid was then filtered with vacuum filtration apparatus and dried at 80°C for 24 hr. The resultant solid was the untreated clay used in this study and was labeled as UTC.

The Fourier transform infrared (FTIR) 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. The *d* spacing and hK bands were measured by using PANalytical (X'Pert PRO XRD PW 3040). The modified and unmodified clay materials were investigated by thermo gravimetric analysis using TG/DTA 6300 (Model- EXSTAR 6000, SII, Seiko Instrument Inc.) to obtain the estimated organic contents and the decomposition temperature. The clay sample was loaded in platinum pan and the sample was heated from room temperature to the maximum of 1000°C at the rate of 10°C/min. The TGA trace was used to determine the % weight loss at 1000°C which is a sufficient temperature to degrade the organic contents present in TC and the differential thermo gravimetric (DTG) analysis was performed using TGA results.

RESULTS AND DISCUSSION

Physical and chemical analysis

The moisture content of oven-dried clay was 1.19% by mass. The chemical composition of the sample clay is shown in TABLE 1.

The loss on ignition (LOI) is due to the dehydration and dehydroxylation of clay minerals. Calculated blue index and blue value of the clay along with specific gravity value of the sample and modified clay are shown in TABLE 2.

The cation exchange capacity (CEC) value is not locally constant, but varies from layer to layer, and must be considered as an average value over the whole crystal. CEC values of bentonite with methylene blue index

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TABLE 1 : Chemical composition of bentonite

| Compound formula (in oxide) | Concentration % |
|--------------------------------|-----------------|
| SiO ₂ | 59.78 |
| Al ₂ O ₃ | 17.01 |
| Na ₂ O | 0.42 |
| MgO | 2.19 |
| K ₂ O | 2.17 |
| CaO | 1.97 |
| TiO ₂ | 0.70 |
| Fe ₂ O ₃ | 1.65 |
| SO ₃ | 0.88 |
| Others | 0.17 |
| LOI | 13.06 |

TABLE 2 : Properties of clay

| Properties | UTC | TC |
|------------------------------|---------|-----------|
| Colour | Reddish | Off-white |
| CEC (meq/100g clay) | | |
| Blue Index (MIB) | 29.0 | - |
| Blue Value (V _B) | 9.28 | - |
| Specific gravity | 2.02 | 1.67 |

(MIB) and blue value (V_B) are slightly lower than that of smectite reported in the literature. The reduction of specific gravity value for organo modified clay (TC) over that of untreated clay (UTC) can be explained by the fact that organic ions were attached which makes the clay to be more organophilic and less hydrophilic. Hence it caused the reduction in the density of the clay sample, so the specific gravity value is also reduced.

FTIR analysis

FTIR spectra of bentonite (UTC) and organobentonite (TC) are shown in Figure 1(a) and (b) respectively.

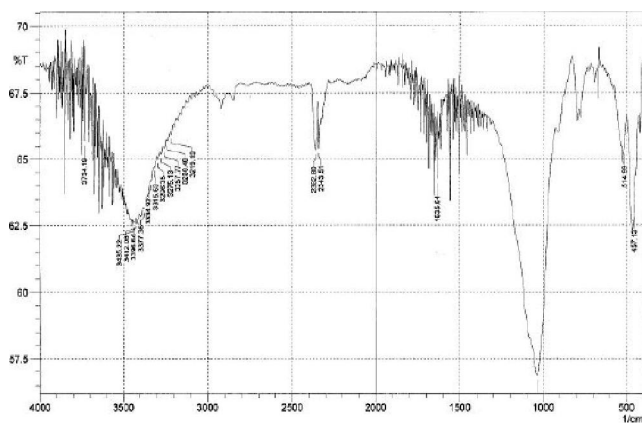


Figure 1(a) : FTIR spectrum of UTC

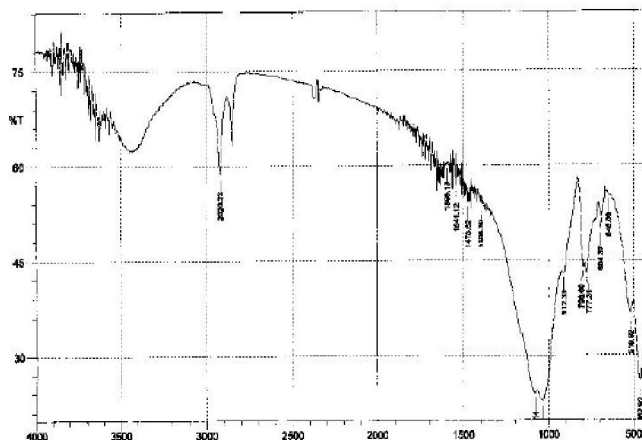


Figure 1(b) : FTIR spectrum of TC

The peaks between 3500 and 3700 cm⁻¹ and near 3400 cm⁻¹ are indicative of montmorillonite-rich smectite clay^[10]. The band frequency near to 3620 cm⁻¹, 1627 cm⁻¹ due to -OH (free), -OH (bending) vibration respectively^[11]. The Al-Al-OH stretching frequency was observed at 3620 cm⁻¹ while the bending frequency was at 914 cm⁻¹. These can be considered as characteristic of dioctahedral smectite^[11]. The band frequency of 1473 cm⁻¹ and 2850 cm⁻¹ represents the general alkyl group (-CH₃) and band at 2918 cm⁻¹ was assigned for halo-alkyl group (CH₃-X) in the organo modified bentonite (TC)^[12]. FTIR study clearly indicates the formation of organic-inorganic hybrid which is supported by the XRD and thermal analysis as well.

XRD analysis

One of the most important methods for studying the interlayer spacing is X-ray diffraction (XRD), and the montmorillonite mineral peak displacement at 2θ is

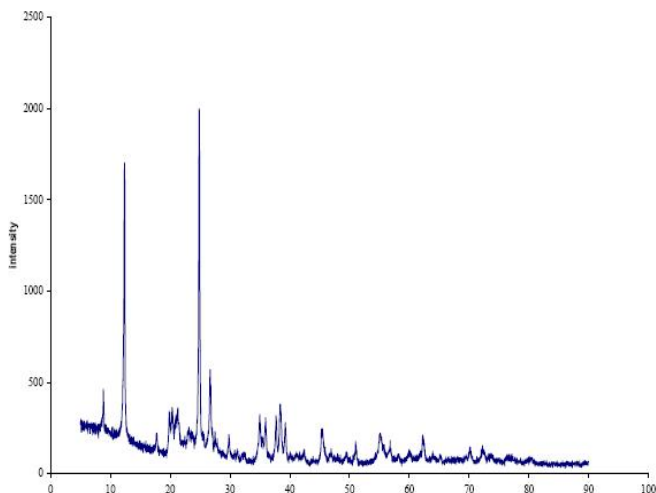


Figure 2(a) : XRD spectrum of UTC

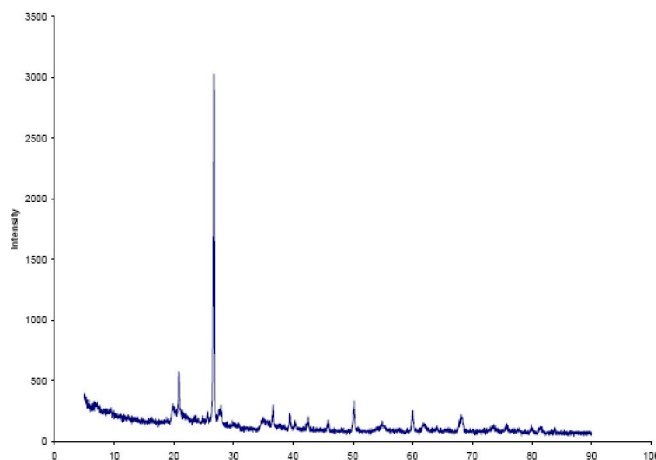


Figure 2(b) : XRD spectrum of TC

a suitable criterion to evaluate the interlayer spacing specifically a decrease in the 2θ angle indicates an increase in interlayer spacing^[13]. It is also reflected in the XRD pattern of UTC and TC shown in Figure 2(a) and (b) respectively.

The characteristic peaks of montmorillonite shown in Figure 2(a) are at 7.2° , 19.8° and 26.8° 2θ and Na-MMT shows a d_{001} diffraction peak at $2\theta=7.2^\circ$ which assigns to the interlayer distance of the natural montmorillonite with a basal spacing of 12.2 Å from the literature^[14]. The XRD study of CTAB-treated clay (TC) is shown in Figure 2(b) and the increase in d -spacing value of TC to 12.9 Å at 6.9° 2θ indicates that organic modifier is intercalated into the interlayer spacing of bentonite. This feature is also supported by the thermogravimetric analysis of the samples. Furthermore XRD pattern indicates the presence of impurities such as kaolinite and quartz in the bentonite sample. The most intense peak at 24.88° 2θ along with the peaks at 21° - 26° 2θ reflects the presence of quartz^[14]. The presence of kaolinite can be attributed from the peak at 12.4° 2θ with basal spacing of 7.14 Å and the intensity of the peak is changed after the modification of the clay. The measured lower CEC value for bentonite can be explained by these two impurities present in bentonite.

Thermal analysis

Thermogravimetric analysis of UTC and TC was carried out within 30-1000°C temperature range at the rate 20°C/min. Figure 3(a) and (b) show the differential thermogravimetric (DTG) and TGA curves of both the untreated clay (UTC) and CTAB-treated clay (TC).

UTC shows comparatively higher weight loss at

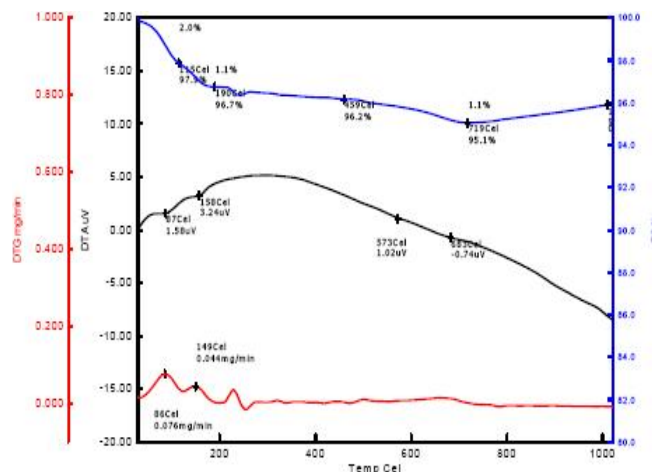


Figure 3(a) : TG/DTG of UTC

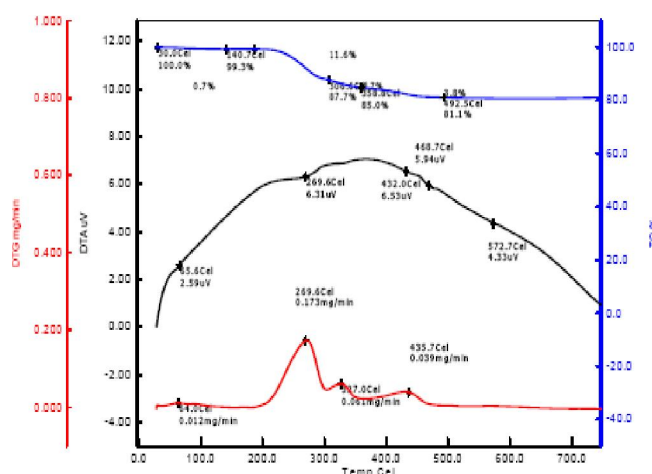


Figure 3(b) : TG/DTG of TC

<200°C than organoclay (TC), which is due to loss of adsorbed water. It is indicated that there is a small weight loss for UTC between 200 and 500°C, while three steps weight loss appeared for organo modified clay (TC) in the same temperature range.

There are two distinct types of water present in bentonite. Type I was the adsorbed water which has a great mobility being easy to be removed. Type II constituted the hydration shell around the exchangeable cations and its presence depended on the number of hydrated cations residing in the interlayer space. Between 200° and 550°C, bentonite did not undergo any thermally induced changes. Therefore the peaks in this region for organo-bentonite are attributed to the decomposition of the organic reagent.

CONCLUSION

The organo modified clay prepared by ion exchange

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process using N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) as modifying agent was examined for physical, chemical and thermal properties. The specific gravity of the modified clay reduced after modification of bentonite. This is due to the organic compound attachment to the clay surface. The FTIR result shows the presence of functional groups like (-CH₃), haloalkyl group (-CH₃X) in the modified clay. This is well supported by the XRD analysis which shows the increasing of d-spacing value of organo-bentonite in comparison to that value of bentonite (UTC). The TGA curve for TC shows three steps degradation that is an evidence of the intercalation of organo modifier in the clay. Although bentonite is mixed with some impurities like quartz and kaolinite, it is possible to modify it with organic modifier. The prepared organo modified clay can be used as a good adsorbent of different toxic pollutants from textile and industrial wastewaters.

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