

Effect on physico-chemical characterization of bentonite clay by CTAB modification

ABSTRACT

Aims: In present study modification of natural bentonite by CTAB, a cationic surfactant i.e. cetyl tri methyl ammonium bromide was performed in order to improve adsorption potential of natural bentonite for organic pollutant and anionic molecules.

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Methodology: Bentonite and CTAB modified bentonite were characterized by means of FTIR, XRD, SEM, TEM, AFM, BET surface area and cation exchange capacity.

Results: An effective intercalation CTAB between the clay layers was confirmed by FTIR study. Basal Spacing of bentonite was increased from 12.70 Å to 19.24 Å after CTAB modification. Roughness of clay has been decreased after CTAB modification confirmed by SEM and AFM. Surface area of bentonite decreased from 33.03 m² g⁻¹ to 10.41 m² g⁻¹ after CTAB modification. CTAB modification of bentonite increased congo red adsorption from 12.2 mg g⁻¹ to 49.53 mg g⁻¹.

Conclusion: CTAB modification changed the physicochemical properties of bentonite clay. The CTAB modified bentonite clay can be used as potential adsorbent for the anionic and organic pollutant.

Keywords: [CTAB, Bentonite clay, AFM, XRD, TEM }

1. INTRODUCTION

Clay minerals have 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. Smectite groups belong to the family of 2:1 phyllosilicates. Their crystal structure consists of stacked layered made of two silica tetrahedrons fused to an edge-shared octahedral sheet of alumina to give a silicate–gibbsite–silicate stacking sequence. The layer thickness is about 1 nm and the lateral dimension may vary from 300 Å to several microns depending upon the type of Smectite used leading to an aspect ratio >1000. As a result, smectite clays have a higher cation exchange capacity of 80–150 mequiv. /100 g [1]. There is a van der Waals gap between the stacking of the layers called the interlayer or gallery. Negative charges generated by the isomorphous substitution of the layers are counter balanced by alkali or alkaline earth cations placed inside the galleries. Bentonite comprises of one octahedral alumina sheet lying between two tetrahedral layers of silica. The permanent negative charge of bentonite is attributed to the isomorphous replacement of Al³⁺ for Si⁴⁺ in the tetrahedral layer and Mg²⁺ for Al³⁺ in the octahedral layer. This negative charge is balanced by the presence of replaceable cations (Ca²⁺, Na⁺, etc.) in the lattice structure, which enhance adsorbing cationic pollutants [2]. The significance of bentonite has increased due to its ability to form organically modified clays, which are gaining a large market place in the field of polymer nanocomposites, cosmetics, waste water treatment and drug-delivery vehicle. In the present study, bentonite was modified by CTAB resulting in a new adsorbent, to improve the sorption capacity for acidic contaminants and better intercalation of polymer between clay layers for preparation of nano clay composites. Bentonite and (CTAB- bentonite) were characterized by means of FTIR, X-ray diffraction (XRD) analysis, SEM, TEM, AFM, BET surface area and cation exchange capacity.

2. EXPERIMENTAL DETAILS

[Nano hydrophilic bentonite clay was purchased from Sigma Aldrich. (USA), N-Cetyl N, N, N- tri methyl ammonium bromide, sodium chloride from Hi media, 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

2.1 Preparation of sodium-exchanged bentonite or Na-bentonite

The solid phase was saturated with sodium ions by stirring in a 1 M sodium chloride solution for 12 h, the bentonite was separated from the suspension by centrifugation at 1,000 rpm/10 min. This process was repeated three times and the saturation was achieved. In order to eliminate excess chloride ions, the solid was washed with distilled water several times and a silver nitrate test was conducted to confirm the absence of Cl ions. This was dried at 50 °C and the material obtained is called sodium-exchanged bentonite or Na-bentonite.

2.2 Organoclay preparation

Modified bentonite (MB) was synthesized by exchanging cetyl trimethyl ammonium cations for inorganic ions on the bentonite: 10 g of bentonite was mixed with 100 ml of 2 % CTAB solutions. The mixtures were subjected to mechanical stirring for 3 h in water bath at 80 °C. In this condition, the MB was obtained completely. The precipitate was separated by filter paper, washed with hot distilled water for several times until the removal of bromide ions from the sample as 0.1 mol/L AgNO₃ was used indicators. The sample was dried at 60 °C for 24 h and finely crushed.

2.3 FTIR analysis

Infrared spectroscopy of the powdered samples of clay was carried out by Perkin spectra 2 spectrophotometer. Clay samples and polymer composites were scanned in the region of 4000-400cm⁻¹ using KBr pellets. The energy (E) of absorption in IR region is associated with the vibration of molecules, including stretching (in which the distance between two bonding atoms changes but the atoms remain in same position) and bending (or deformation in which the position of atom changes relative to original bond axis). All the spectra were recorded and analyzed to know the type and nature of the functional group attachment in clay and superabsorbent.

2.4 XRD

XRD patterns of the clay were recorded by X-ray diffractometer (XRD, Bruker D8 Advance Eco), USA using CuKα radiation ($k = 1.54 \text{ \AA}$) within 5 to 80, 2 theta range. XRD is a non-destructive method for characterization of crystalline compounds. XRD was obtained with X-ray tube having Cu-anode (Philips) running at 40 kV and 20 mA, scanning from 3° to 50° using APD (automated powder diffraction) software with the following setting of the instrument: Radiation type-Cu-Kα, scan stepsize-0.1, time per step (Sec):4.00 and type of scan: continuous. Sample holder, made up of aluminum, was cleaned with acetone solution and samples were filled in the space defined for specimen. The specimen holder was inserted in the X-ray diffractometer for the analysis of random oriented sample.

2.5 SEM

Scanning electron micrographs (SEM) produced the morphological image of clay by an electron beam and was recorded on Zeiss EVO 18 (SEM) instrument. The accelerating voltage used was 15 kV and the applied magnification of the image was 10000 X. It provides information about the morphology of superabsorbent.

2.6 TEM

Microstructural analysis was carried out using transmission electron microscopy (TEM) using TECNAI 20 G2, operating at 200 KV in imaging modes. The samples for TEM were prepared by ultrasonically dispersing the clay powder in deionized water and putting a drop of dispersed clay solution on copper grid.

2.7 Atomic force microscopy

The surface morphology, roughness were further examined by atomic force microscopy (NT-MDT SOLVER AFM/STM). AFM images were analyzed using Nova Image Analysis 2.0 software. For the AFM studies, bentonite particles were immobilized on glass cover slip from a dilute suspension in water. Three drops of ammonia solution were added to disperse the bentonite. A small amount of suspension (1 or 2 droplets) was placed on square cover slip. The particles were dried by heating to 200 °C for a few minutes.

2.8 BET surface area and EGME surface area of clay

The BET surface area (BET) of bentonite and CTAB bentonite were determined by MICROMERITICS-ASAP 2020 surface area and porosity analyzer instrument; about 0.3-0.5 grams of sample is weighed and all the samples are degassed at 200°C prior to SBET measurement by using nitrogen gas adsorption at a relative pressure (P/P_0) = 0.1-0.3.

For EGME surface area analysis approximately 200 mg of clay were weighed into a tarred aluminum can, including a lid, and the sample was spread evenly over the bottom of the can. The can, with lid beneath, was placed in a vacuum desiccator over about 250 g of P₂O₅; the desiccator was evacuated

by applying a vacuum pump for one hour and dried to constant weight. Samples were wetted with approximately 2 mL of reagent- grade ethylene glycol monoethyl ether (EGME) to form clay-adsorbate slurry and placed over the CaCl_2 -EGME solvate. The entire culture chamber was placed in a vacuum desiccator containing CaCl_2 . Period of 30 minutes or more was allowed for the sample - solvate slurry to equilibrate then evacuated the desiccator with a vacuum pump for about 45 minutes. The can, lid, and sample were weighed and returned to the culture chamber and the culture chamber to the desiccator. The desiccator was evacuated by applying a vacuum pump for 45 minutes. The samples were weighed at 2 to 4 h intervals, evacuating between weighing, until constant weight was attained. Calculation of specific surface was done by the equation [3]

$$A = W_a / (W_s \times 0.000286)$$

Where A = specific surface in m^2/g , W_a = weight of ethylene glycol monoethyl ether (EGME) retained by the sample in g, W_s = weight of P_2O_5 -dried sample in g, and 0.000286 is the weight of EGME required to form a monomolecular layer on a square meter of surface.

2.8 Cation exchange capacity of clay

CEC of clays were determined by following procedure given by Jackson [4]. 200 mg of clay was taken in centrifuge tube; 10 ml of 0.25M CaCl_2 solution was added to it and centrifuged for 10 minutes at 5000 rpm. The supernatant was decanted and the above process was repeated for another four times. Then the sample was washed two times with distilled water (10 mL) followed by washing two times with 10 mL 50 % acetone and two times washing with 80 % acetone to remove chloride from the sample. The washing process was repeated until the sample was chloride free which was checked by treating the supernatant liquid with AgNO_3 . The chloride free sample was added with 10 mL of 0.25M MgCl_2 and centrifuged for 10 minutes at 5000 rpm. The supernatant was collected in 100 ml volumetric flask. Repeat the last step two more times and supernatant were collected. The volume was made up to 100 mL by distilled water and Ca concentration in the 100 mL supernatant was determined by AAS.

2.9 Adsorption of Congo red by modified bentonite clay

To study effect of CTAB modification on bentonite a sorption experiment was carried out. 1 g adsorbent and 100 mL Congo red solution (initial conc. 100 mg/L, pH 6.9) was used. The method was operated under shaking at 25°C till adsorption balance was accomplished. The quantities of CR removed by sorbents can be calculated by the equation:

$$Q = \{(C_o - C_e)V\}/m$$

Where Q is the maximum adsorption capacity in mg/g, C_o is the initial concentration and C_e is the concentration at equilibrium of Congo red dye solution in mg/L, V is the volume of the Congo red solution in mL and m is the mass of clay in grams.

3. RESULTS AND DISCUSSION

3.1 FTIR

The FTIR spectra for clays are shown in figure 1. The characteristic vibration peaks of nano bentonite were at 471 cm^{-1} corresponding to the clay structure and Si-O-Si bending. The peaks at 1037 cm^{-1} (Si-O stretching) and 527 cm^{-1} (Si-O-Al bending) were also presented. Sorbed water contributed to H-O-H bending region at 1635 cm^{-1} and to O-H asymmetric and symmetric stretching region at 3625 and 3455. The Al-Al-OH stretching frequency was observed at 3625 cm^{-1} while the bending frequency was at 914 cm^{-1} . The organoclays presented new characteristic vibrations at 2926 and 2854 cm^{-1} , corresponding to asymmetric and symmetric CH_2 stretching modes, and at 1478 cm^{-1} , corresponding to CH_2 scissoring.

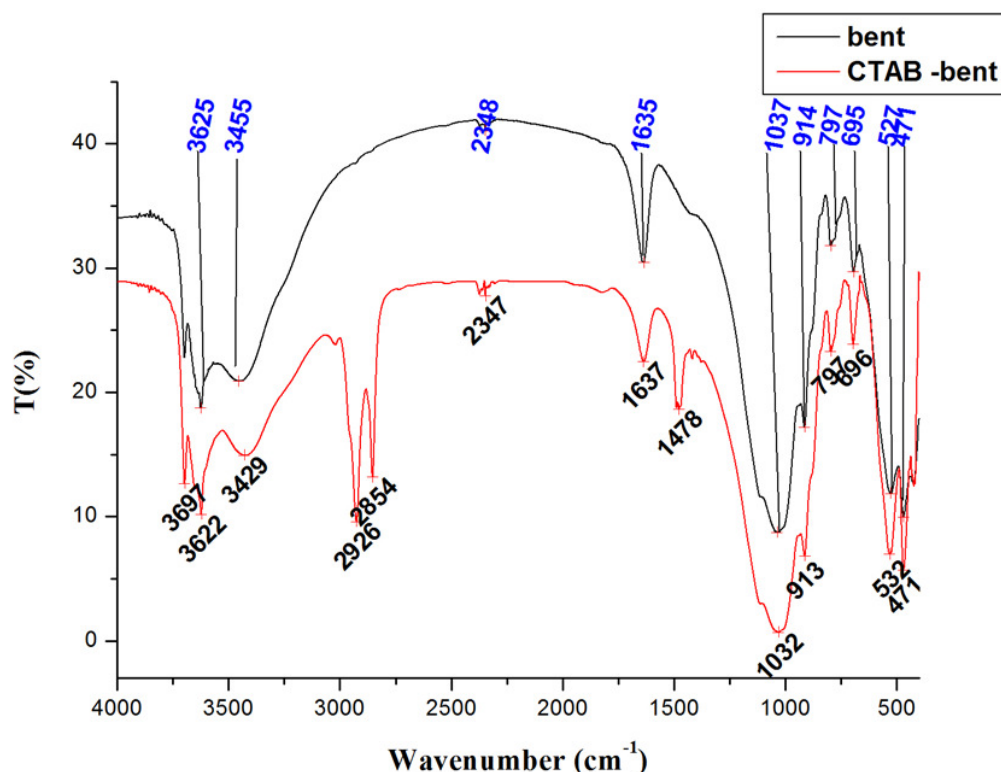


Fig.1. FTIR peaks for bentonite and CTAB bentonite

The peaks between 3500 and 3700 cm^{-1} and near 3400 cm^{-1} are indicative of montmorillonite-rich smectite clay. The band frequency near to 3620 cm^{-1} , 1627 cm^{-1} due to OH (free), -OH (bending) vibration respectively. 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 di octahedral smectite[1]. The band frequency of 1478 cm^{-1} and 2854 cm^{-1} represents the general alkyl group (-CH₃) and band at 2926 cm^{-1} was assigned for halo- alkyl group (CH₃-X) in the organo modified bentonite (TC). Similar result were obtained by [5],[6],[7]. Peak between 3600 to 3800 cm^{-1} representing montmorillonite rich smectite. Peak at 3220 cm^{-1} indicates N-H stretch[8]. Significant peaks at 2940 and 2850 cm^{-1} for modified Nano clays, are ascribed to asymmetric and symmetric vibration of methylene group (CH₂) of aliphatic carbon chain. Peaks at 915 and 836 cm^{-1} represent AlAlOH and AlMgOH bending vibrations, respectively. [9] modified bentonite by CTAB for absorption of acid dye found two bands at 2850 and 2925 cm^{-1} , assigned to the asymmetric and symmetric stretching vibrations of the CH₃ and CH₂ of the aliphatic chain of the CTAB[10].

3.2 XRD

One of the most important methods for studying the interlayer spacing is X-ray diffraction (XRD), and the mineral peak displacement at 2 theta is a suitable criterion to evaluate the interlayer spacing specifically a decrease in the 2 theta angle indicates an increase in interlayer spacing. It is also reflected in the XRD pattern of bentonite and CTAB bentonite clay as shown in Figure 2.

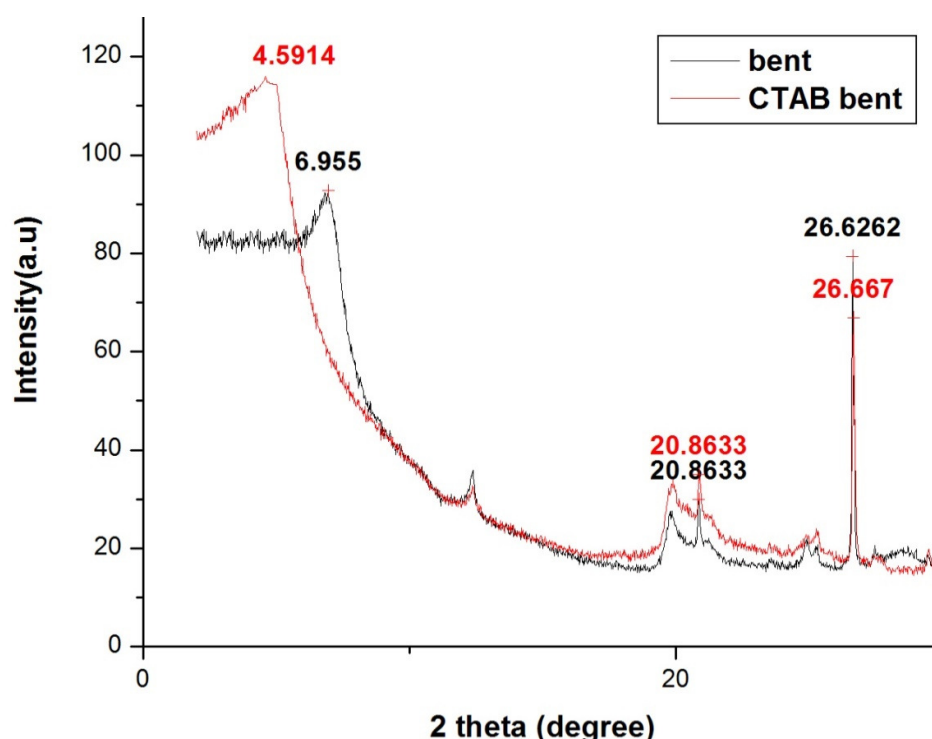


Fig. 2. XRD pattern of bentonite and CTAB modified bentonite

The characteristic peak of bentonite shown in Figure 2 was at 6.95° which assigns to the interlayer distance of the bentonite with a basal spacing of $12.70 \text{ \AA}$. The XRD study of CTAB-treated clay shown in Figure 2 and the increase in d -spacing value of CTAB bentonite to $19.24 \text{ \AA}$ at 4.59° indicates that organic modifier is intercalated into the interlayer spacing of bentonite. The orientation of alkyl ammonium ions between silicate layers is variable. Alkyl ammonium ions form a monolayer ($13.7 \text{ \AA}$), a double layer ($17.7 \text{ \AA}$), a pseudo tri molecular layer ($21.7 \text{ \AA}$) or a parafinic complex ($>22 \text{ \AA}$) [11], [12]. The bentonite obtained by treatment with CTAB equivalent to 100% the CEC of initial bentonite showed high spacing of $19.24 \text{ \AA}$. This basal spacing corresponds to a bilayer of organic cations between the silicate layers. In aqueous systems, quaternary ammonium cations can be retained by both the outer and interlayer surfaces of clay via an ion exchange process and are not easily displaced by smaller cations as H^+ , Na^+ . Similar result were obtained by [13], [14].

3.3 SEM AND TEM

SEM of clay were taken at 10000 X magnification, bentonite showed rough surface morphology, bentonite after modification with CTAB showed smooth surface with large size particles. The surface morphology of pure bentonite and CTAB bentonite are shown in figure 3 and 4 (a and b), respectively. In the SEM images of pure bentonite some phase separations are observed as a heterogeneous surface morphology. It can be seen that the bentonite have massive plates. However, the clay treated with organic surfactant shows significant changes in the morphology. Compared with the morphology of the bentonite, there are many small and aggregated, compact particles and the plates become relatively flat layers; similar results were observed by [9]. Due to increase of basal spacing in organoclays packing density increases and the clay layers are observed clearly. Banik *et al.*, 2015 [2] observed the agglomerates of bentonite contain few numbers of particles compared with those of CTAB-modified bentonite. Several of the particles in bentonite and CTAB bentonite show laminar crystalline habit characteristic of phyllosilicates. However, these certain particles dominate more in CTAB bentonite. Interaction of surfactant molecules in the interlayers may also stand behind the domination of comparatively large laminar crystallites and large agglomerates [9]. It can be said that compact structure occurs with the lateral interactions of the hydrophobic tails of CTAB on the tactoid surfaces [10], [15].

TEM image clearly describes the nano structure of clay bentonite and CTAB bentonite (Figure 5 a, b). particles were of size range between 30-50 nm. CTAB bentonite showed hexagonal morphology, bentonite have irregular circular shaped morphology which is key feature of smectite group of phyllosilicates mineral. Similar type of results were obtained by [16], [8].

200

201 **3.4 AFM**

202 Atomic force microscopy was employed to investigate and visualize the change in the surface
203 topography resulting from interaction of CTAB with bentonite clay (Figure 5 a, b). AFM images of
204 bentonite before and after CTAB modification showed significant morphological changes. The
205 roughness of the clay surface was characterized by the root mean square roughness (R_{ms} , S_q) and
206 average roughness (S_a) values. The R_{ms} roughness (S_q) and average roughness (S_a) as measured
207 by AFM are 16.05 nm, 12.04 nm, respectively, for bentonite clay, and values were decreased to 10.07
208 and 7.92 nm after CTAB modification. Results were in agreement with SEM results i.e. clay surface
209 become more fluffy and smooth after CTAB modification and its roughness decreases. Particles
210 dimension of both bentonite and CTAB modified bentonite were in nanometer range below 100 nm.
211 An average of 30 clay particles has been taken into consideration for analysis. AFM showed particle
212 size slightly less than that obtained from TEM results (Table 1).

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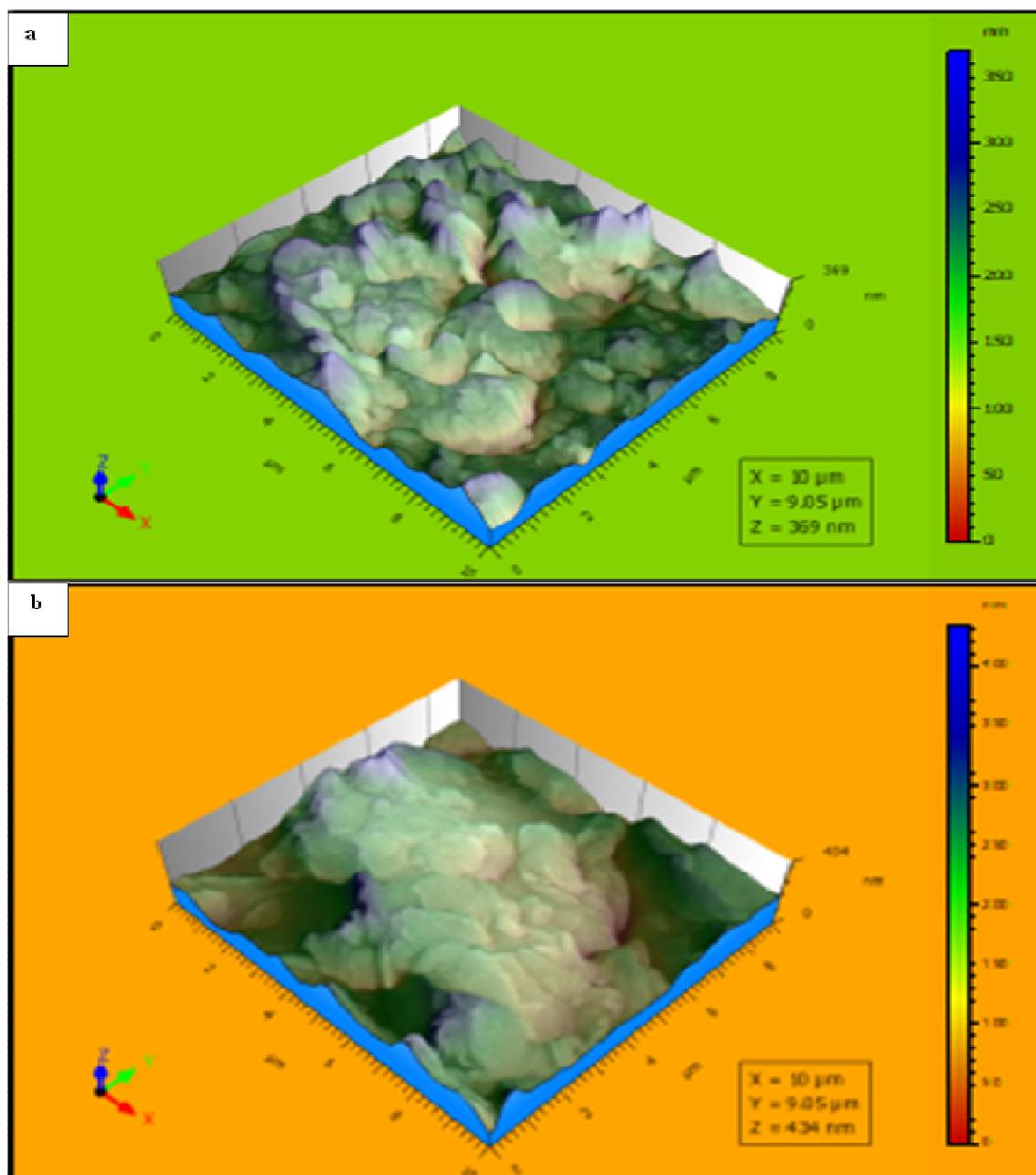


Fig.3. 3 dimensional image of bentonite and CTAB bentonite clay

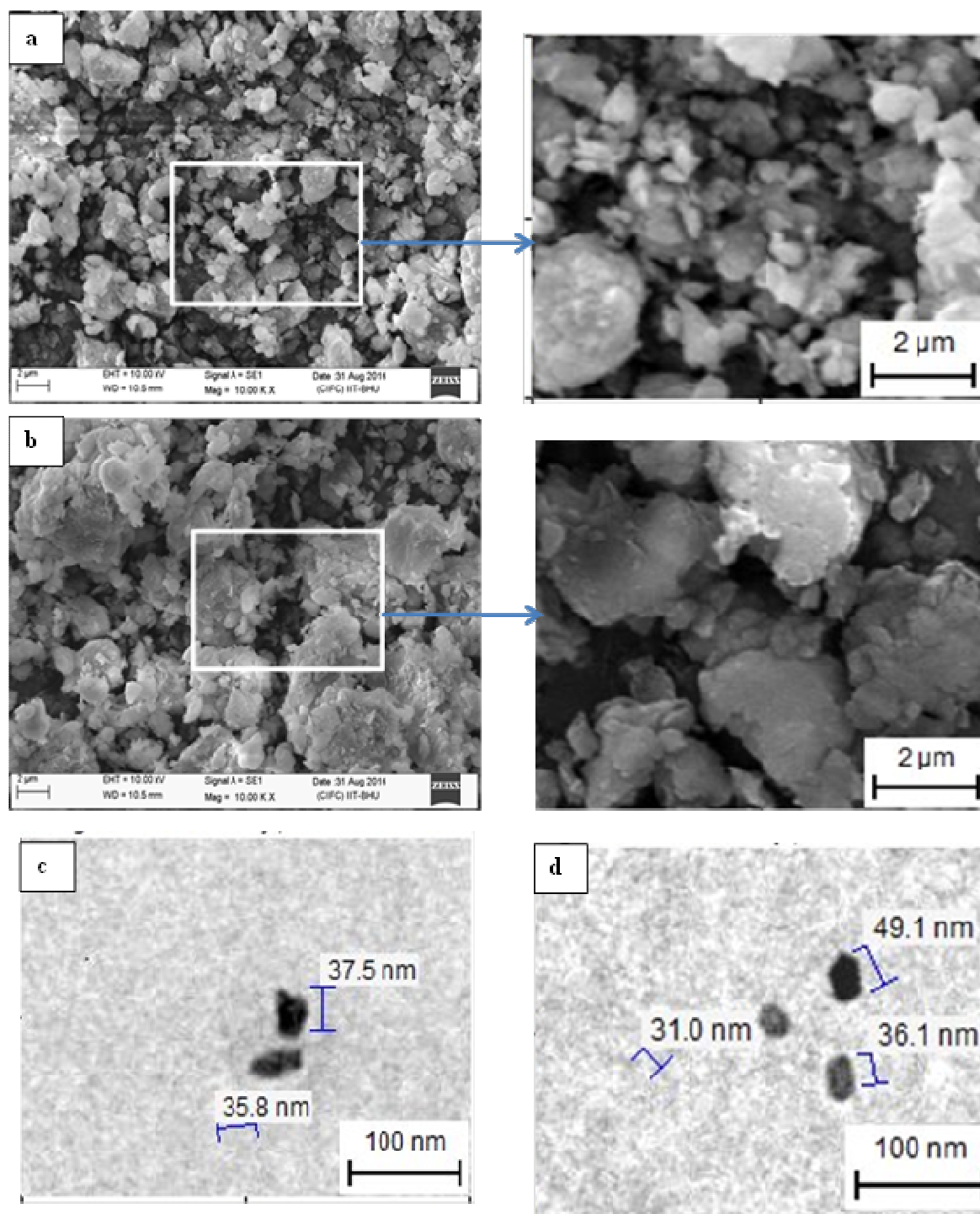


Fig. 4. SEM image of Bentonite clay (a), CTAB bentonite (b), TEM image of Bentonite clay (c), and CTAB bentonite clay (d)

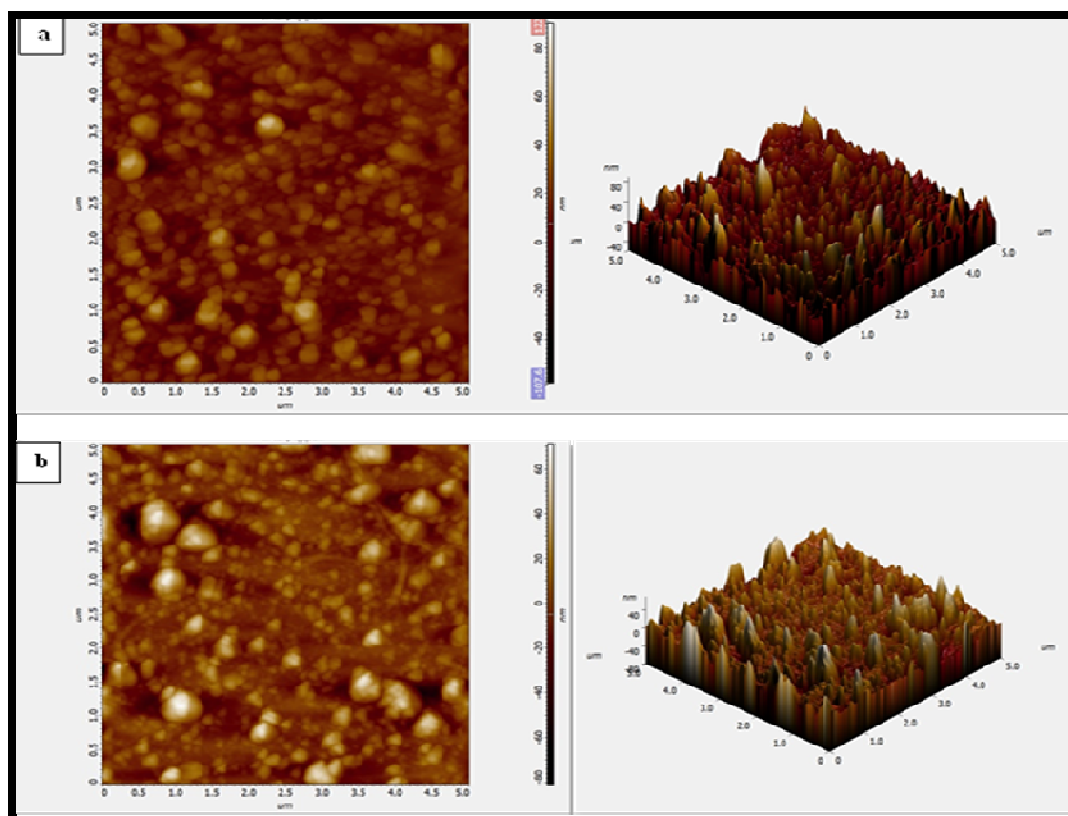


Fig. 5. AFM of bentonite clay (a), CTAB bentonite clay (b), and scanning area 5x5 μm .

Table 1: AFM study of clay

Clay	Average roughness Ra (nm)	Root mean square roughness Rms (nm)	Area of particle (nm^2)	Length (nm)	Mean width (nm)	Average size (nm)	Diameter (Nm)
Bentonite	12.04	16.05	442	17.3	23.9	19.7	22.2
CTAB-Bentonite	7.92	10.07	324	14.6	20.8	16.9	19

Table 2: BET surface area, EGME surface area and CEC

Clay	Pore size (nm)	Pore volume (cm^3/g)	BET surface area(m^2/g)	EGMG surface area (m^2/g)	CEC ($\text{meq}/100\text{g}$)
Bentonite	11.52	0.10	33.02	568	97.6
CTAB-bentonite	16.11	0.04	10.40	264	ND

Pore size of bentonite was found to be 11.51 nm and CTAB modified bentonite was found to be 16.11 nm, Pore volume of bentonite was found to be 0.10 (cm³/g) and CTAB bentonite was found to be 0.04 (cm³/g). BET surface area and EGME surface area for bentonite and CTAB bentonite was found to be 33.03 m²/g and 568 m²/g and 10.40, 264 m²/g. The BET surface area of the organically modified clays had decreased, attributed to formation of closely packed aggregates due to antiparticle hydrophobic interactions. In the case CTAB bentonite, the total pore volume decreased which might be due to the close packing of particles.

The organoclay surface areas, as well as micro- and mesopore volumes were drastically reduced after organophilization. These decreases were attributed to the organo clay microstructure, since the quaternary salt intercalation caused an interlayer expansion, as seen on X-ray diffraction analysis, so that salt ions blocked the passage of N₂ molecules, occupying active clay sites which might be available for N₂. Differences among modified clay areas are due to organic cations, which had been layered, and to their interlayer orientation [17].

Adsorption of Congo red by modified clay

Modification of bentonite by CTAB improved anionic dye adsorption properties of bentonite. It can be used as potential adsorbent for application in the treatment of industrial wastewater and water polluted with dyes. After modification with CTAB, bentonite clay removed 40.5 % more Congo red from solution than natural bentonite. Result obtained were in agreement with results of [9],[18]. The high adsorption capacity of CTAB-bentonite is due to the strong electrostatic interaction between the N⁺ (CH₃)₃ and dye anions[19].

Table 3: Adsorption of Congo red by modified clay

Clay	Adsorbed amount (mg g ⁻¹)
Bentonite	12.2±0.44
CTAB- Bentonite	49.53±0.37
CD	1.64
SEM	0.41

4. CONCLUSION

The organo modified clay prepared by ion exchange process using N-Cetyl-N,N,N-tri methyl ammonium bromide (CTAB) as modifying agent was examined for physical, chemical and thermal properties. This is due to the organic compound attachment to the clay surface. The FTIR results the presence of functional groups like (-CH₃), halo- alkyl 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 bentonite. After modification with CTAB surface area of bentonite clay has decreased but pore size increased suggesting abundance of mesopore. The prepared organo modified clay can be used as a good adsorbent of different organic, anionic pollutants from wastewater.

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