

Surfactant-induced changes in physicochemical characters of bentonite clay

ABSTRACT

Aims: In the present study a cationic surfactant i.e. cetyl tri methyl ammonium bromide (CTAB) was used in order to explore adsorption potential of natural bentonite for organic pollutant and anionic molecules.

Place and Duration of Study: The study was conducted during 2016-17 in the Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Banaras Hindu University.

Methodology: Pure bentonite and CTAB modified bentonite were characterized by means of Fourier transformation infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Atomic force microscopy (AFM), Brunauer–Emmett–Teller (BET) surface area and cation exchange capacity.

Results: An effective intercalation of quaternary ammonium ion 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. The roughness of bentonite clay has been decreased from 16.05 nm to 10.07 nm while surface area decreased from 33.03 m² g⁻¹ to 10.41 m² g⁻¹ after CTAB modification and was confirmed by SEM and AFM. Congo red (CR) an organic dye extensively used and disposed in soil and waste water was potentially adsorbed to a taller end from 12.2 mg g⁻¹ to 49.53 mg g⁻¹ by surfactant modified bentonite clay.

Conclusion: Cationic surfactant can put forward certain changes in physicochemical properties of bentonite clay. The CTAB modified bentonite clay can be used as a potential adsorbent for the anionic/organic pollutant.

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

1. INTRODUCTION

Clay minerals have innumerable applications and diversity of uses. Bentonite clay belongs to smectite group of 2:1 phyllosilicates minerals wherein two silica tetrahedral layers fused to an edge-shared octahedral sheet of alumina. The layer thickness is about 1 nm and the lateral dimension may vary from 30 nm to several microns leading to an aspect ratio of more than 1000. As a result, smectite clays have a higher cation exchange capacity of 80–150 meq. /100 g soil [1]. The van der Waals gap between the stacking of the layers is called the interlayer spacing 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. The permanent negative charge of bentonite clay 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 [2]. The significance of bentonite clay has been increased due to its ability to form organically modified clays, which are gaining a large attention in the field of polymer nanocomposites, cosmetics, waste water treatment and drug-delivery vehicle. In the present study, bentonite was treated by CTAB resulting in modification of interlayer spacing dominated by NH₄ ion behave as a new adsorbent, with improved the sorption capacity for acidic contaminants. Pure bentonite and CTAB treated bentonite were characterized by means of the spectral signature generated by FTIR, X-ray diffraction (XRD) analysis, SEM, TEM, AFM, BET surface area and cation exchange capacity.

2. EXPERIMENTAL DETAILS

Nano hydrophilic bentonite clay, N-Cetyl N, N, N- tri methyl ammonium bromide, Congo red and Sodium chloride were purchased from Sigma Aldrich., (USA) and quartz distilled water was used for

the preparation of modified bentonite. Organic solvents for synthesis, characterization and other essential chemicals were of analytical grade and procured from BDH, India.

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 10,000 rpm/10 min. This process was repeated three times and the saturation was achieved. In order to eliminate the excess of chloride ions, the solid was washed with quartz distilled water several times and a silver nitrate test was conducted to confirm the absence of Chloride ions. This was dried at 50 °C and the material obtained was 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. Ten gram of Na- bentonite was mixed with 100 ml of 2 % CTAB solution. The mixture was subjected to mechanical stirring for 3 h in the water bath at 80 °C for intercalation of quaternary ammonium ions. The suspended clay obtained after 3 h was separated by Whatman filter paper (grade 1, 125 mm), washed with hot distilled water for several times until the removal of bromide ions from the sample and further confirmed by using 0.1 mol/L AgNO₃ as indicator. The sample was dried at 60 °C for 24 h and finely crushed.

2.3 FTIR analysis

Infrared spectroscopy (IR) of the powdered samples of pure bentonite clay and modified clay was carried out by Perkin spectra 2 spectrophotometer. Clay samples 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 the same position) and bending (or deformation in which the position of atom changes relative to the original bond axis). All the spectra were recorded and analyzed to know the type and nature of the functional group attachment in pure clay and modified bentonite.

2.4 XRD

XRD patterns of the clay were recorded by X-ray diffractometer (XRD, Bruker D8 Advance Eco), USA using CuK α radiation ($k = 1.54 \text{ \AA}$) within 3 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 m A, scanning from 3° to 50° using APD (automated powder diffraction) software with the following setting of the instrument i.e. Radiation type-Cu-K α , scan step size-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 the randomly 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 clay.

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 a copper grid and subjected to image analysis.

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 a square cover slip. The particles were dried by heating to 200°C for a few minutes and subjected to image analysis.

2.8 BET surface area and EGME surface area of clay

The BET surface area (BET) of bentonite and CTAB treated bentonite were determined by MICROMERITICS-ASAP 2020 surface area and porosity analyzer instrument, by taking 0.5 g of sample. All the samples were degassed at 200°C prior to SBET measurement by using nitrogen gas adsorption at a relative pressure (P/Po) of 0.1-0.3 atmosphere.

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 P_2O_5 ; 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 $CaCl_2$ and 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 was 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 area 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 the 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 following the procedure given by Jackson [4]. 200 mg of clay was taken in the 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. The last steps have been repeated 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 versene titration method [4].

2.9 Adsorption of Congo red by modified bentonite clay

To study the effect of CTAB modification on bentonite clay adsorption an experiment was carried out. 1 g of adsorbent and 100 mL Congo red solution (initial conc. 100 mg/L, pH 6.9) was used. The method was operated under continuous shaking at 25°C till equilibrium adsorption was accomplished [18]. The quantities of CR removed by pure bentonite clay and modified bentonite clay was 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 both pure bentonite clay and CTAB modified clay were presented 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 cm^{-1} and 3455 cm^{-1} . The Al-Al-OH stretching frequency was observed at 3625 cm^{-1} while the bending frequency was at 914 cm^{-1} . The modified clay showed new characteristic vibrations at 2926 cm^{-1} and 2854 cm^{-1} , corresponding to asymmetric and symmetric CH_2 stretching modes, and at 1478 cm^{-1} corresponding to CH_2 scissoring.

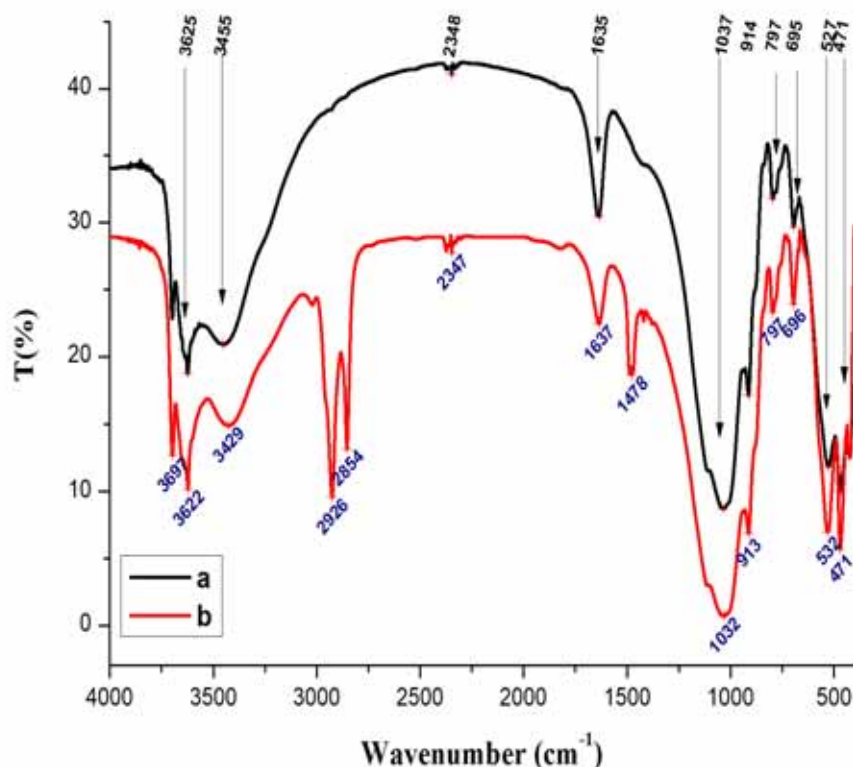


Fig.1. FTIR peaks for (a) bentonite clay and (b) CTAB modified bentonite clay.

The peaks between 3500 cm^{-1} and 3700 cm^{-1} and near 3400 cm^{-1} were indicative of bentonite-rich smectite clay. The band frequency near 3620 cm^{-1} , 1627 cm^{-1} were 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 ($-\text{CH}_3$) and band at 2926 cm^{-1} was assigned for the halo-alkyl group ($\text{CH}_3\text{-X}$) in the organo modified bentonite (TC). Similar results were obtained by [5],[6],[7] [10]. The peak between 3600 cm^{-1} to 3800 cm^{-1} represented bentonite rich smectite and peak at 3220 cm^{-1} represented N-H stretch [8]. Significant peaks at 2940 and 2850 cm^{-1} for modified nano clays, were ascribed to asymmetric and symmetric vibration of the methylene group (CH_2) of an aliphatic carbon chain. Peaks at 915 cm^{-1} and 836 cm^{-1} represented AlAlOH and AlMgOH bending vibrations, respectively [9]. In general, the intensity of these bands was enhanced as the chain length increases, indicating the decrease of hydrophilic character with increasing chain length [21].

3.2 XRD

One of the most important method for studying the interlayer spacing is X-ray diffraction (XRD) pattern, and the mineral peak displacement at 2θ is a suitable criterion to evaluate the interlayer spacing. A decrease in the 2θ angle indicated an increase in interlayer spacing. XRD pattern of bentonite and CTAB modified bentonite clay has been reflected in Figure 2.

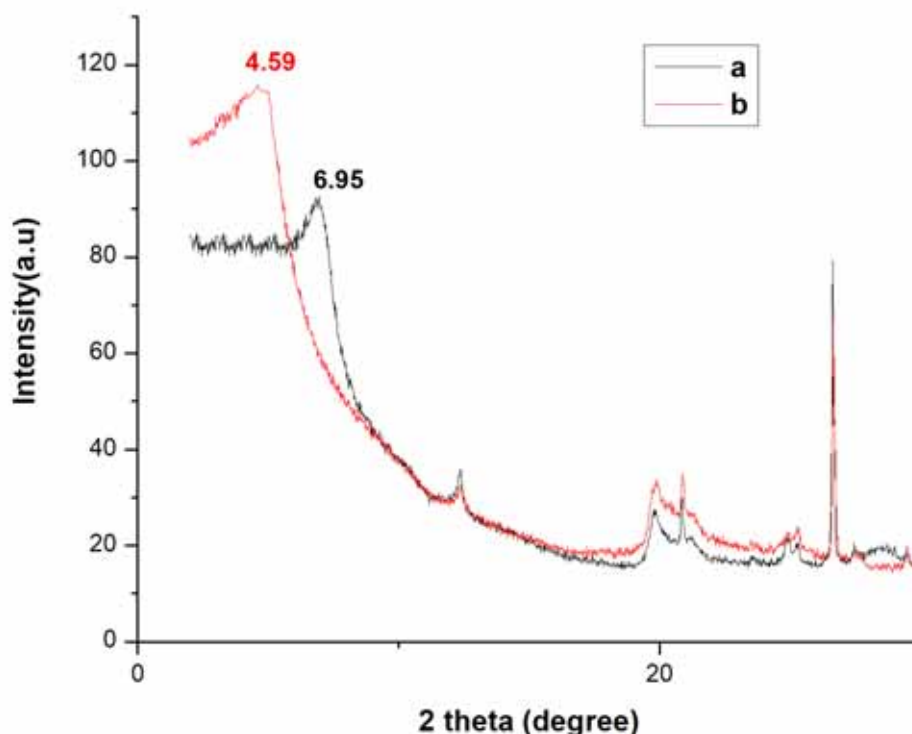


Fig. 2. XRD pattern of (a) bentonite clay and (b) CTAB modified bentonite clay

The characteristic peak of bentonite shown in figure 2, was at 6.95 2 theta which assigned to the interlayer distance of the bentonite with a basal spacing of 12.70 Å. The XRD study of CTAB-treated clay showed an increase in the *d*-spacing value of CTAB bentonite to 19.24 Å at 4.59 2 theta. This indicated that cationic surfactant was intercalated into the interlayer spacing of bentonite. The orientation of alkyl ammonium ions between silicate layers was variable. Alkyl ammonium ions formed a monolayer (13.7 Å), a double layer (17.7 Å), a pseudo tri molecular layer (21.7 Å) or a parafinic complex (>22 Å) [11], [12]. The bentonite obtained by treatment with CTAB equivalent to 100% the CEC of initial bentonite showed higher *d* spacing of 19.24 Å. 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 were not easily displaced by smaller cations like H⁺, Na⁺. The result corroborates with earlier findings of [13], [14] [21] [23].

3.3 SEM AND TEM

SEM images of clay were taken at 10,000 X magnification. The pure bentonite showed rough surface morphology while bentonite after modification with CTAB showed the smooth surface with large size particles. The surface morphology of pure bentonite and CTAB treated bentonite were shown in figure 3 and 4 (a and b), respectively. In the SEM images of pure bentonite, some phase separations were observed as a heterogeneous surface morphology. It could be seen that the bentonite have massive plates. However, the clay treated with organic surfactant showed significant changes in the morphology compared with the morphology of the bentonite. Similar results were observed by [9]. Due to the increase of basal spacing in organoclays packing density has been increased and the clay layers were observed clearly. [2] observed the agglomerates of bentonite contained few numbers of particles compared with those of CTAB modified bentonite. Several of the particles in bentonite and CTAB treated bentonite showed laminar crystalline habit characteristic of phyllosilicates. Interaction of surfactant molecules in the interlayers may also stand behind the domination of comparatively large laminar crystallites and large agglomerates [9]. It may be interpreted that that compact structure occurred in CTAB modified bentonite was because of the lateral interactions of the hydrophobic tails

of CTAB on the clay surfaces leading to a rather smooth surface with large size particles[10],[15]. [21] found that raw clay has apparent phase separations as well as cracks, i.e., heterogeneous surface morphology. The adsorption of CTAB has led to a more compact textural structure and a higher aggregation tendency between the clay plates as a result of hydrophobic interactions between the tails of the $C_{16}TABr$. It was also observed that a curved, fluffy conformation and irregular layer stacking for the surfactants with lower chain length and tight agglomeration [22].

TEM image clearly described the nano structure of bentonite clay and CTAB bentonite (Figure 5-a, b). Particles were of the size range between 30-50 nm. CTAB bentonite showed hexagonal morphology and pure bentonite had an irregular circular shaped morphology which was key feature of smectite group of phyllosilicates mineral. This finding corroborates with the earlier results of [16], [8].

3.4 AFM

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

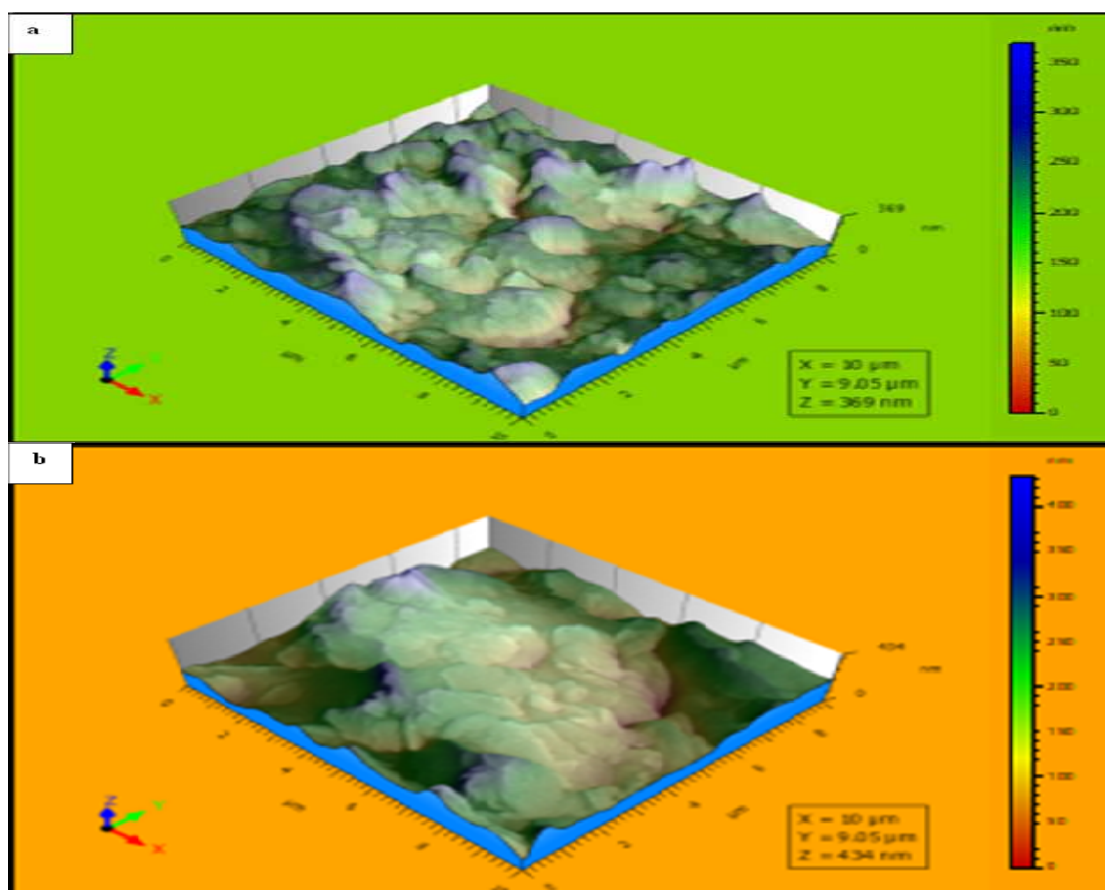


Fig.3. 3-dimensional image of bentonite and CTAB bentonite clay

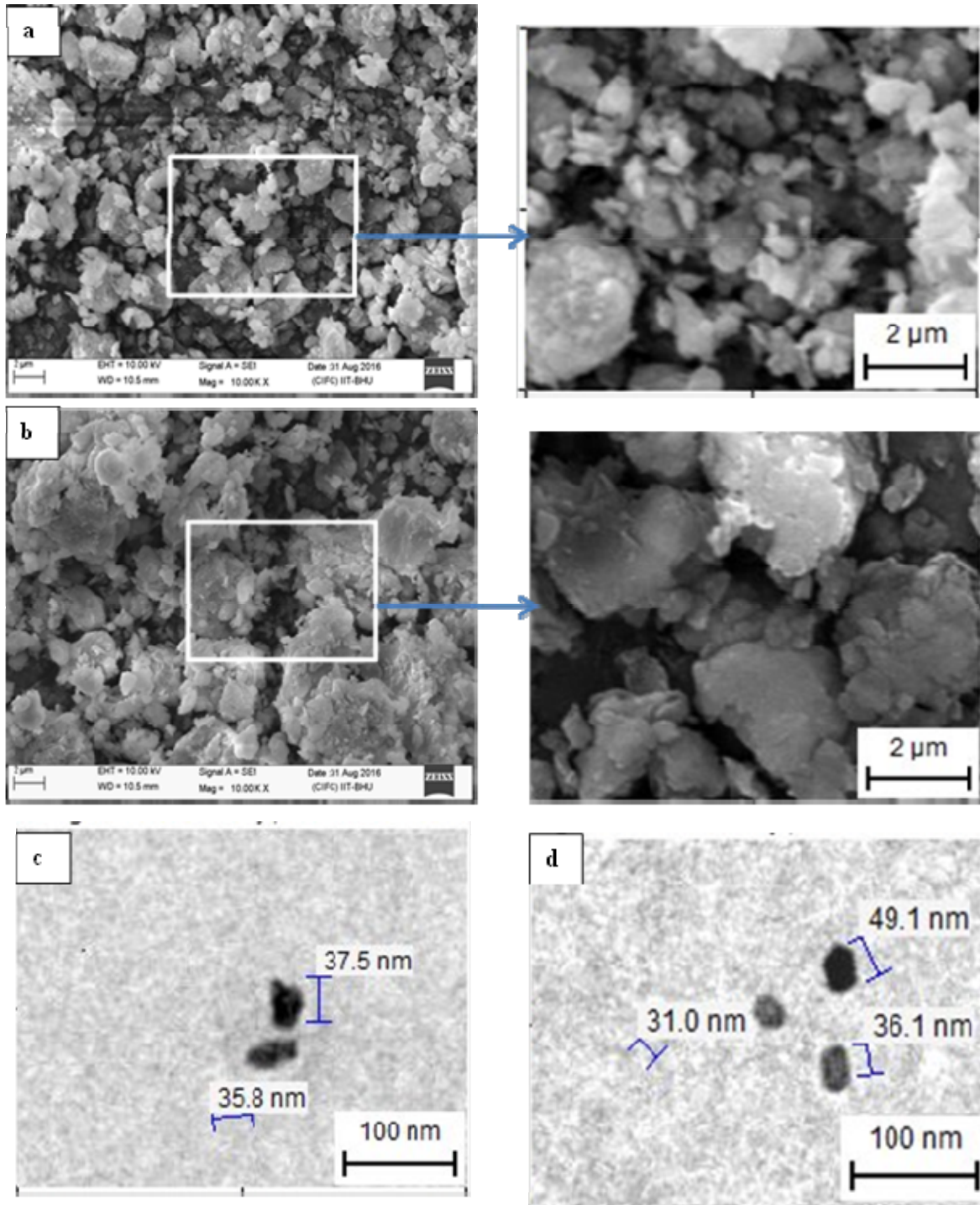


Fig. 4. SEM image of Bentonite clay (a), CTAB bentonite (b), TEM image of Bentonite clay (c), and CTAB bentonite clay (d)

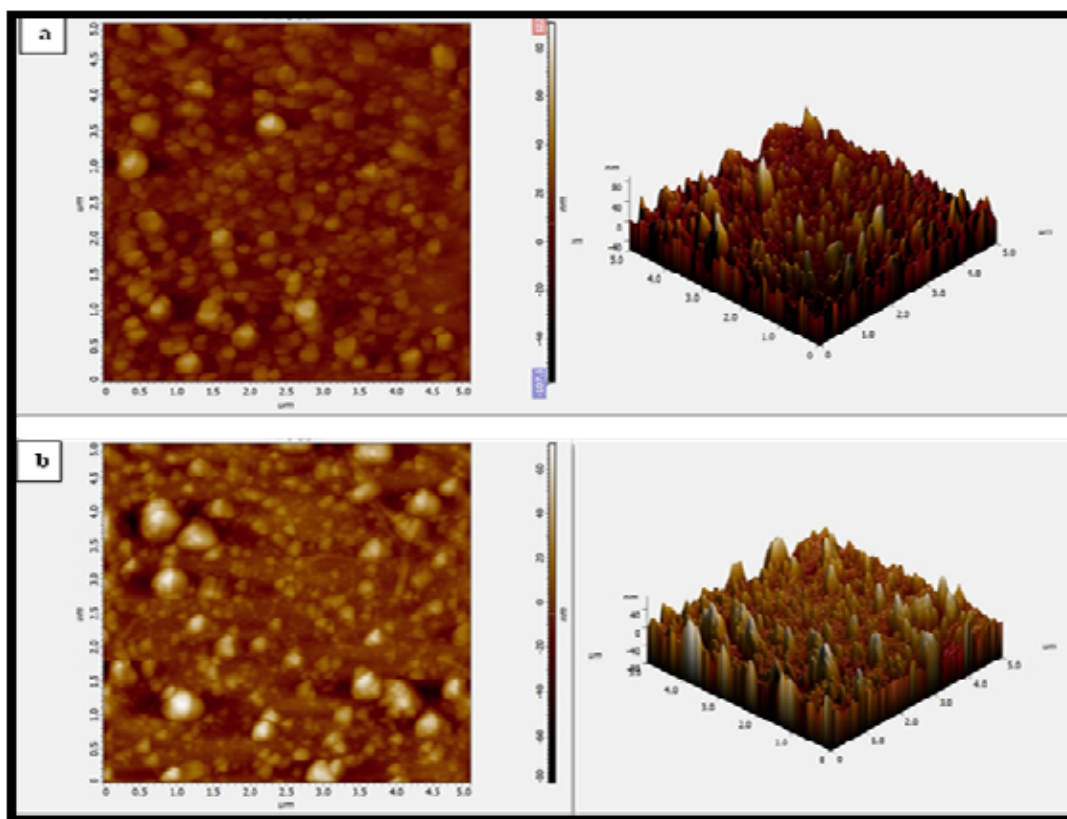


Fig. 5. AFM of bentonite clay (a), CTAB bentonite clay (b), and scanning area 5x5 μm .

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

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

The surface area, as well as micro and mesopore volume, was drastically reduced after cationic surfactant treatment. These decreases were attributed to the organo clay microstructure, since the quaternary salt intercalation caused an interlayer expansion, as seen in XRD analysis, so that salt ions blocked the passage of N₂ molecules, occupying active clay sites which might be available for N₂. Differences among pure and modified clay surface area were due to organic cations, which had been interlayered into the bentonite clay [14] & [17].

Adsorption of Congo red by modified clay

Modification of bentonite by CTAB had improved anionic dye adsorption properties of bentonite, results were described in table 3. It can be used as a 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 clay. Results obtained were in agreement with results of [9], [18]. The high adsorption capacity of CTAB-bentonite was due to the strong electrostatic interaction between the N⁺ (CH₃)₃ and dye anions [19], [20] & [24].

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(0.05)	1.64
±SE _m	0.41

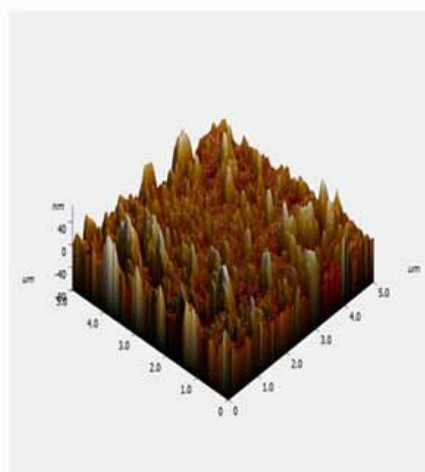
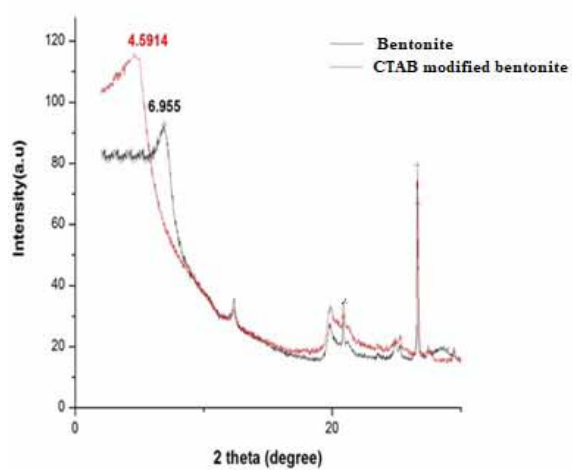
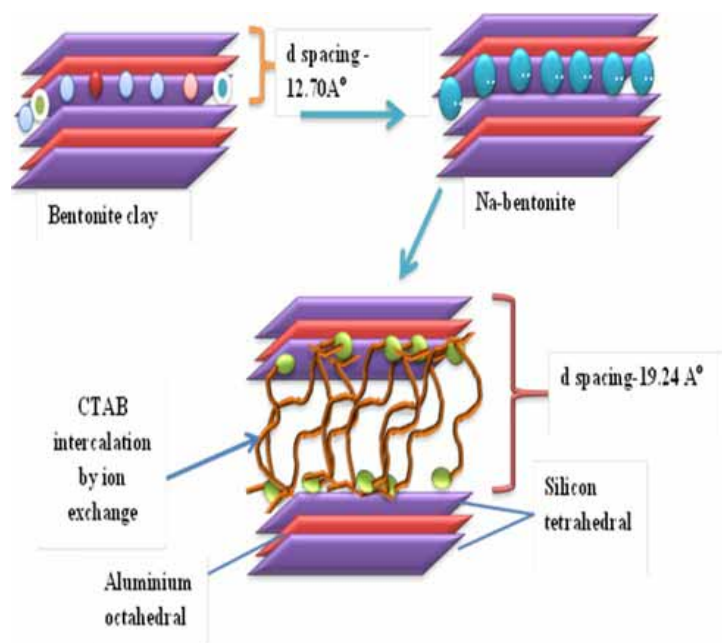
4. CONCLUSION

The cationic surfactant treated bentonite prepared by ion exchange process using N-Cetyl-N, N, N-tri methyl ammonium bromide (CTAB) and was examined for physical and chemical properties. The FTIR spectral signature reflected presence of functional groups like (-CH₃), halo- alkyl group (-CH₃X) in the modified clay. This was well supported by the XRD analysis which showed higher d-spacing, decreased surface area, higher pore size and abundance of mesopore in modified bentonite in comparison to pure bentonite. The ingenuity of our finding was that CTAB treatment or application of surfactant in smectite clay group may lead to certain characteristic change in physicochemical properties leading to decrease in adsorption potential of cationic pollutant *vis-a-vis* increase in adsorption potential for anionic molecules and organic pollutants.

REFERENCES

- Jahan SA, Praveen S, Ahmed S, Kabir H. Development and characterization of organophilic clay from bentonite. Material Science, 2012; 8: 67-72.
- Banik N, Jahan SA, Mostofa S, Kabir H, Sharmin N, Rahman M, Ahmed S. Synthesis and characterization of organoclay modified with cetylpyridinium chloride. Bangladesh J. Sci. Ind. Res., 2015; 50(1): 65-70.
- Carter DL, Heilman MD, Gonzalez CL. Ethylene glycol monoethyl ether for determining surface area of silicate minerals. Soil Science, 1965; 100:356-360.
- Jackson ML. Interlayering of expansible layer silicates in soils by chemical weathering. Clays and Clay Minerals, 1956; 11th Conf., Pergamon Press, London, 29-46.
- Lira junior CA, Silva SAD, da Costa Filho AP, Lucas EF, Santana SAA. Smectite Clay Modified with Quaternary Ammonium as Oil Remover. Journal of Brazilian Chemical Society, 2017; 28(2):208-2016.
- Xue W, He H, Zhu J and Yuan P. FTIR investigation of CTAB-Al-montmorillonite complexes. Spectrochimica Acta Part A. 2007; 67:1030-1036.
- Li Z, Jiang W-T and Hong H. An FTIR investigation of hexadecyltrimethylammonium intercalation into rectorite. Spectrochimica Acta Part A. 2008; 71:1525-1534.

8. Sonawane S, Chaudhari P, Ghodke S, Phadtare S, Meshram. Ultrasound assisted adsorption of basic dye onto organically modified bentonite (nanoclay). *J Sci. Ind. Res.*, 2009; 68: 162-167.
9. Akl MA, Youssef AM, Al-Awadhi MM. Adsorption of Acid Dyes onto Bentonite and Surfactant-modified Bentonite. *J Anal Bioanal Tech.* 2013; 4: 174.
10. Karaca S, Gurses A, Korucu ME. Investigation of the orientation of CTAB⁺ ions in the interlayer of CTAB pillared montmorillonite, *Journal of Chemistry.*, 2013; 20: 1-10.
11. Khenifi A, Zohra B, Kahina B, Houari H, Zoubir D. Removal of 2, 4-DCP from wastewater by CTAB/bentonite using one-step and two-step methods: A comparative study, *Chemical Engineering Journal.* 2009; 146: 345–354.
12. Sanqin W, Zepeng Z, Yunhua W, Libing L, and Jiansheng Z. Influence of montmorillonite exchange capacity on the basal spacing of cation–anion organo-montmorillonite. *Materials Research Bulletin*, 2014; 59: 59–64.
13. Koswojo R, Utomo RP, Ju YH, Ayucitra A, Soetaredjo JS, Ismadji S. Acid Green 25 removal from wastewater by organo-bentonite from Pacitan, *Applied Clay Science*, 2010; 48:81–86.
14. Ismail NHC, Bakhtiar NSA, Akil HM. Effects of cetyl trimethylammonium bromide (CTAB) on the structural characteristic of non-expandable muscovite. *Materials Chemistry and Physics*, 2017; 196: 324-332.
15. Alshameri A, Abood AR, Yan C, Muhammad AM. Characteristics, modification and environmental application of Yemen's natural bentonite. *Arab J Geosci.*, 2014; 7:841–853.
16. Motawie AM, Madany MM, EL- Dakrory AZ, Osman HM, Ismail EA, Badr MM, Komy D A, Abulyazied DE. Physico-chemical characteristics of nano-organo bentonite prepared using different organo-modifiers, *Egyptian Journal of Petroleum*, 2014; 23: 331–338.
17. Wang CC, Juang LC, Lee CK, Hsu TC, Lee JF, Chao HP. Effects of exchanged surfactant cations on the pore structure and adsorption characteristics of montmorillonite. *Journal of Colloid and Interface Science*, 2004; 280:27-35.
18. Zenasni MA, Meroufel B, Merlin A, George B. Adsorption of Congo red from Aqueous Solution Using CTAB-Kaolin from Bechar Algeria. *Journal of Surface Engineered Materials and Advanced Technology*, 2014; 4: 332- 341.
19. Yoshida H, Okamoto A, Kataoka T. Adsorption of Acid Dye on Cross-Linked Chitosan Fibers: Equilibria. *Chemical Engineering Science*, 1993; 48: 2267-2272.
20. Tangraj V, Marc-Janot J, Jaber M, Bechelany M, Balme S. Adsorption and photo physical properties of fluorescent dyes over montmorillonite and saponite modified by surfactant. *Chemosphere*, 2017; 84: 1335-1361.
21. Acisli O, Karaca S, Gurse A. Investigation of the alkyl chain lengths of surfactants on their adsorption by montmorillonite (Mt) from aqueous solutions. *Applied Clay Science*, 2017, 142: 90–99.
22. Luo W, Sasaki K, Hirajima T. Effect of surfactant molecular structure on perchlorate removal by various organo-montmorillonite. *Applied Clay Science*, 2015; 114:212–220.
23. Ken Sun K, Shi Y, Chen H, Wang X, Li Z. Extending surfactant-modified 2:1 clay minerals for the uptake and removal of diclofenac from water. *Journal of Hazardous Materials*, 2017; 323: 567–574.
24. Li Y, Hu X, Liu X, Zhang Y, Zhao Q, Ning P, Tian S. Adsorption behavior of phenol by reversible surfactant-modified montmorillonite: Mechanism, thermodynamics, and regeneration. *Chemical Engineering Journal*, 2018; 334: 1214–1221.



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