

# Application of Nanotechnology in Oil and Gas Industry: Synthesis and Characterization of Organo-modified Bentonite from Boane Deposit and its Application in Produced Water Treatment

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Ca-bentonite sample from Boane region, Maputo Province, Mozambique exhibiting a white colour was organo-modified and subsequently evaluated for uses as an adsorbent for the treatment of produced water from a natural gas production platform. The clay was subjected to organo-modification through ion-exchange reaction by cationic surfactants namely benzalkonium chloride and cetrimonium bromide. The organophilization process altered the natural hydrophilic character to hydrophobic. The effectiveness of the ion-exchange procedure was revealed by XRD patterns, wherein the main Ca-MMT  $d_{001}$  peak changed from 1.520 nm to 1.960 nm when the concentration of cetrimonium bromide used for organo-modification varied from 50 to 100 meq and from 1.520 to 1.830 nm when a fixed concentration of benzalkonium chloride was used. Wastewater treatment performance evaluation of synthesized products showed that the physico-chemical and bacteriological properties improved significantly, showing clearly that Boane bentonite has enormous potential to be applied as an adsorbent material for produced water treatment.

## 1. Introduction

The oil and gas (O&G) sector plays an important role in the world economy. In terms of the final energy consumption matrix, the sector largely exceeds the global energy demand in greater proportions when compared to the other energy sectors. This scenario will not change in the short and medium terms, even though in the present context of changing the energy paradigm focused on renewable energy sources. Nevertheless, like most industrial production activities, O&G production process generates produced water (PW) as the main residue. PW is the technical name given to the water that exists in subsurface formations and generated as a waste by-product of O&G industry. PW is the largest waste stream associated with O&G extraction (Miller et al., 2020). Given the complexity of its composition, normally consisting of microorganisms and organic and inorganic compounds (McLaughlin et al., 2020), PW has a great potential to pollute the environment and it is also responsible for inducing corrosion and scale problems in production and transport infrastructures (Amini et al., 2012). All these aspects and since water pollution has become a major problem in recent years (Muradova et al., 2016), makes the management of PW one of the most debated topics at a global level.

The alternatives usually adopted for the final destination are rejection, reinjection in the original well or reuse. In both cases, there is a need for specific treatment in order to comply with legal obligations, avoid negative impacts to the environment and to production facilities or in order to allow its reuse without causing damage to the processes in which this water will be used as an input. Among several techniques used in wastewater treatment, adsorption and membrane filtration system is the most preferred one (Alexander et al., 2019). Its low operating cost and effectiveness in removing a wide range of contaminants are pointed out as the main reasons behind this preference (Rathnayake, 2017). Clay minerals stand out among several adsorbents used

for this purpose. The high cation exchange capacity (CEC) and swelling ability, their technical viability which, associated with their abundance and low cost, make clay mineral-based adsorbents very desirable in many industrial and scientific applications. The use of clay-based adsorbents in adsorption and filtration system gives some advantageous related to economic and easiness. However, for some organic and toxic pollutant, the use of natural clay minerals is not efficient due to low adsorption capacity. By nature clays are hydrophilic because of the presence of inorganic cations located in the interlayer spaces. By this reason, clay will not adsorb organic and relatively hydrophobic compounds (Favre and Lagaly, 1991). The removal capability of natural clay minerals towards organic and inorganic contaminants can be improved by exchanging naturally occurring interlayer cations with other organic cations, getting what is called organoclays (Vaccari, 1999).

Organoclays are hybrids derived from an ion exchange reaction of the inorganic cations located in the interlayer spaces of natural or synthetic clays with long-chained quaternary ammonium salts under hydrothermal conditions (Favre and Lagaly, 1991). Surfactants such as alkylamine molecules are the most used organic compounds in organoclay synthesis. The main advantages of using organo-modified clays as an adsorbent in PW treatment processes is the fact that it can remove a wide range of contaminants, such as microorganisms, heavy metals, oil particles in suspension, chemicals added in the various stages of O&G production process and sometimes some radioactive materials.

Montmorillonite (MMT), the main constituent of Bentonite clay is the most commonly preferred organoclay in adsorption and filtration system. The high CEC, high surface area, swelling ability, high micro and meso-porosity are some features that make MMT very preferable. Although Mozambique has immense reserves of this clay mineral, practically all local industries, including those in the O&G sector, treat their wastewaters using imported products, a situation that has negative impact on the economy of companies operating in the sector. It is time to find local solutions for wastewater treatment which will contribute to the reduction in operational costs of the industries. This was the primary objective of the present work. The well-known and investigated bentonite deposit is located in the District of Boane, Maputo Province (Mozambique). Boane bentonite is composed mainly of MMT. High CEC and swelling power are just some interesting features exhibited by this bentonite. It is believed that these features can be improved through an organo-modification procedure. The present study aims to evaluate the suitability of this bentonite as an adsorbent material (in organo-modified form) for PW treatment process. The first part of the study focused on the synthesis, characterization and selection of samples with better response to the organo-modification process based on the basal spacings. The wastewater treatment performance of synthesized products was carried out using adsorption and membrane filtration system. In this stage of the study the focus was given to the effect of the wastewater treatment process on the selected physico-chemical and bacteriological parameters without looking at the mechanisms behind the adsorption and filtration phenomena.

## **2. Materials and Methods**

### **2.1 Materials**

Ca-bentonite sample from Boane region, Maputo Province, Mozambique, exhibiting a white colour was kindly supplied by the Industrial Minerals of Mozambique Lda. Previous studies on this clay revealed a CEC (determined by AAS) of 67.5 meq/100 and an intermediate swelling behaviour of 7.0 mL/g of clay. XRF measurements indicated the following chemical composition: 71.3 wt.% SiO<sub>2</sub>, 10.8 wt.% Al<sub>2</sub>O<sub>3</sub>, 3.08 wt.% Fe<sub>2</sub>O<sub>3</sub>, 0.39 wt.% CaO, 0.23 wt.% K<sub>2</sub>O, 1.05 wt.% Na<sub>2</sub>O, 2.57 wt.% MgO, 0.01 wt.% MnO, 0.19 wt.% TiO<sub>2</sub>, 0.02 wt.% P<sub>2</sub>O<sub>5</sub>, and 10.41 wt.% LOI. The raw bentonite was organo-modified using benzalkonium chloride (BC) and cetrimonium bromide (CB), both with a purity of 98 % and they obtained from Merck Chemicals (South Africa). All the chemicals were used as received. It should be noted that the two surfactants used here are very toxic for aquatic organisms (refer their safety data sheets). They were chosen because the wastewater to be treated, collected from one of the natural gas processing unit in the country, in addition to other pollutants also contains microorganisms. As is known, microorganisms are responsible for corrosion and therefore, it is intended that the formulated products have a double effect, that of water treatment but also of corrosion inhibitor. Given their toxicity, once the adsorption bed is saturated, appropriate waste material management measures should be adopted to avoid the environmental pollution. These include its reuse for energy production, regeneration via chemical extraction (using appropriate organic solvents) and regeneration via thermal desorption.

### **2.2 Methods**

The typical organo-modification process was as follows: 100 g of natural bentonite (<75 µm fraction) was first dispersed in about 500 mL of de-ionized water under mechanical agitation at room temperature for 4 h. The dispersion was allowed to repose for 30 min, and then a desired amount of CB or BC solution was slowly added under mechanical agitation. The concentrations of CB and BC varied from 50 to 100 meq. The

concentrations expressed as “meq” were pre-determined in accordance with the result of CEC of the clay and featured values of 30, 50, 80 and 100 meq. The reaction mixtures were stirred for 4 h at 60 °C. After this period, the container was closed and the suspension allowed to absolute repose for 24 h. The resulting materials were filtered under vacuum and washed with a large amount of de-ionized water to remove the excess salt and then dried in an air circulating oven at 60 °C for 24 h. The dried samples were then milled to a powder with an aggregate particle size <75 µm for further characterization. Using this procedure three formulations of organo-modified bentonites were prepared for each surfactant. The bentonite samples modified with CB were designated as CBx, while those treated with BC have been designated as BCx. The subscript x represents the concentration of the surfactant. For example, a sample named as BC50 means a clay sample modified with BC at a concentration of 50 meq.

The PW was collected in a sterilized 500 mL sample bottle from one of the natural gas production platform in Mozambique and taken to the laboratory in a cooler box containing ice cubes wrapped in cellophane bag to slowdown the temperature of the water samples and to inhibit bacteria growth in the PW as most bacteria grow best between 20 to 30 °C. Preservation of the sample was done in accordance with Norwegian O&G recommended guidelines for sampling and analysis of PW (2018). The wastewater treatment procedure was carried out using the membrane filtration process from water previously treated by adsorption with the two organomodified clays (CB100 and BC50) including the natural bentonite sample (NB). Typically, a desired amount of clay (in wt.%) was added to the PW, keeping the PW/bentonite mixture for 3 min at a constant speed and temperature. After this time, the mixture was allowed to rest for 30 min and finally filtered.

### 2.3 Sample characterization and analysis

The structure of the clay samples was analyzed by XRD using a PANalytical X'Pert Pro Multi-Purpose with Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å) in the  $2\theta$  range from 2 ° to 60 ° at a scan rate of 2.0 °/min. FT-IR spectra were recorded on a SHIMADZU spectrometer; model IR Prestige-21. The surface morphology of the natural and the two selected organo-modified clays was examined by SEM, using a JSM-6390 Scanning Electron Microscope. Thermal behavior of the neat and the two selected organo-modified clays were analyzed by TGA using a SHIMADZU Simultaneous DTA-TG Apparatus, model DTG-60. The wastewater treatment performance of synthesized products was carried out using practical analytical methods. This included analytical methods to determine some chemical species such as Chloride (Cl<sup>-</sup>) SMEWW 4500-Cl<sup>-</sup> D, Nitrites (NO<sub>2</sub><sup>-</sup>) NP EN 26777:1996, Nitrates (NO<sub>3</sub><sup>-</sup>) SMEWW 4500-NO<sub>3</sub><sup>-</sup> B, and Ammoniac (NH<sub>3</sub>) SMEWW 4500-NH<sub>3</sub> C. Other test conducted included: Conductivity NP EN 21888:1996, Total Hardness SMEWW 2340-C, pH L10-PT-MA-01, Total Suspended Solid (TSS) L10-PT-MA-16 and Turbidity L25-PT-MA-12. A bacteriological analysis was also carried out. This included Total Coliforms L25-PT-MA-01, Faecal Coliforms L25-PT-MA-01 and Escherichia Coli L25-PT-MA-01. All samples were analyzed in duplicates.

## 3. Results and discussion

### 3.1 X - Ray diffraction (XRD)

Figure 1 shows the XRD patterns of NB and the surfactant clay hybrids (CBx and BCx series) at surfactant concentrations of 50, 80 and 100 meq.

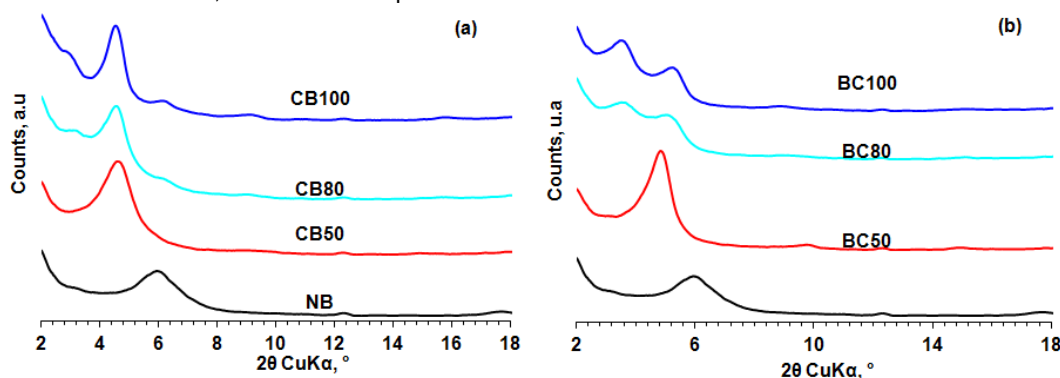


Figure 1: XRD patterns of NB and the organo-modified clays, with various CB (a) and BC (b) content

The main smectite phase reflection  $d_{001}$  was found at 1.520 nm, characteristic of Ca<sup>2+</sup> saturated smectites. From Figure 1a it can be seen that  $d_{001}$  of the organo-modified samples increased from 1.520 nm to 1.960 nm as the concentration of CB varied from 50 to 100 meq. The shift to the left side of MMT peak and the

consequent increase of  $d_{001}$  gives an indication that there is an effective intercalation of the surfactants in modified clays. From the configuration structure point of view, the  $d_{001}$  of 1.930 and 1.960 nm, for CB50, CB80 and CB100 are prescribed to the surfactant molecules that are positioned between lateral-bilayer and pseudotrimolecular layer structure. When modified with BC (Figure 1b), only BC50 showed a good response where  $d_{001}$  varied from 1.520 to 1.830 nm. The surfactant clay hybrids with 80 and 100 meq showed two peaks ( $d_{001}$ ~2.550 and ~1.700 nm). The appearance of two peaks suggests the formation of new crystalline phases, including layers with different charge densities. This corresponds to an intermediate disposition between a lateral-bilayer and paraffin-type arrangement. The concentration of 50 meq the sample modified with CB has slightly larger  $d_{001}$  than that of BC, suggesting that CB has more affinity with the clay than BC. Based on the  $d_{001}$  two organo-modified clays, those with a greater  $d_{001}$  (CB100 and BC50) were selected for wastewater treatment performance of evaluation and for further analysis.

### 3.2 Scanning electron microscopy (SEM)

The micrographs with magnification of 1000 times of NB and the two selected organo-modified samples (BC50 and CB100) are shown, in Figure 2a, 2b and 2c. From the micrographs it is clear that the three strains have very similar morphology. All samples presented some crystalline pseudo-hexagonal edges and semi rounded micro-sized particles on the surface of the clay mineral particles. However, some irregular shaped aggregates are also observed. From Figure 3a it can be seen that most of the particles were much smaller than 10  $\mu\text{m}$  in size. However, aggregates of the organo-modified samples appeared significantly larger than those for NB, reaching a particle size of about 50  $\mu\text{m}$ . This confirms the hydrophobic character of the clays. The hydrophobized clay particles gather together more easily than those of natural clay because the surfactants compensate for their negative charge and eliminate the repulsive electrostatic forces.

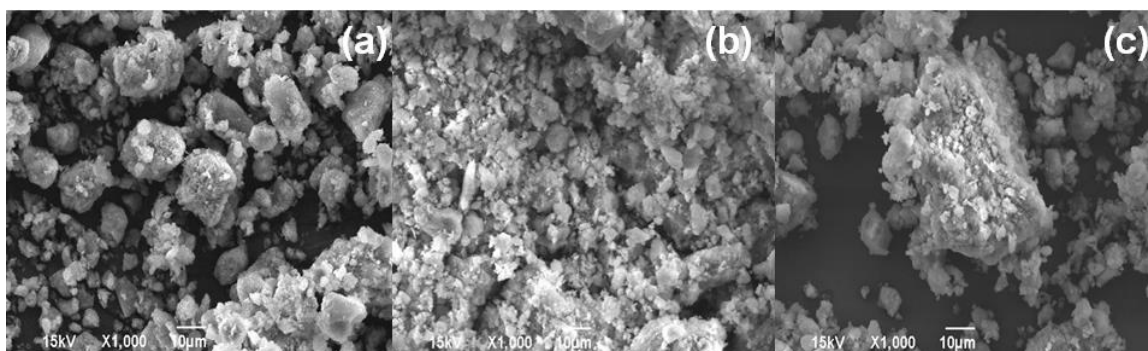


Figure 2: SEM micrographs of NB(a) and the two selected organo-modified bentonites BC50(b) and CB100(c).

### 3.3 Fourier Transform Infrared Spectroscopy (FT-IR)

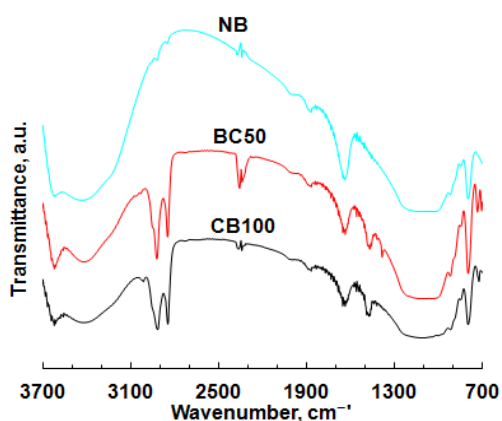


Figure 3: FT-IR spectra of NB and the two selected organo-modified bentonites (CB100 and BC50).

The spectrum absorption bands in the IV region of NB and the two selected organo-modified samples (BC50 and CB100) are shown in Figure 3. The spectrum of NB shows a band near 3,600  $\text{cm}^{-1}$  owing to the stretching vibrations of structural OH groups and a broad band near 3,400  $\text{cm}^{-1}$  due to the OH stretching vibrations of

H<sub>2</sub>O present in the smectite. The bands present in approximately 1,600 cm<sup>-1</sup> can be attributed to the adsorbed water present in the bentonite, corresponding to the HOH deformation. As can be seen, the untreated clay (NB) shows bands at characteristic wavelengths of the smectite group, which are also present in the modified clays, indicating the retention of the crystalline structure after the organophilization. The absorption bands in wavelength, independent of the surfactant used are the same, with the appearance of bands between 3,000 cm<sup>-1</sup> and 2,700 cm<sup>-1</sup> for both treated clays, related to the presence of the CH<sub>2</sub> groups. The band present at approximately 1,500 cm<sup>-1</sup> can be related to asymmetric angular deformation of (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> groups, from the surfactants. The presence of the bands due to the (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> and CH<sub>2</sub> in the IR spectrum of the organoclays shows the effectiveness intercalation of the surfactants in the interlayer spaces of the clay.

### 3.4 Thermogravimetric and Differential thermal analysis (TGA and DTA)

The TGA and DTA curves of NB and the two selected organo-modified samples (BC50 and CB100) are shown in Figure 4a and 4b. For NB initial mass loss between 20 °C and about 300 °C is observed, characteristic of smectite. Two endo-exothermic bands are also observed (see Figure 4b) in which the endothermic band at 60 °C is due to residual water and the exothermic band with a maximum at 185 °C which can be related to the initial decomposition of organic matter likely to be present in NB.

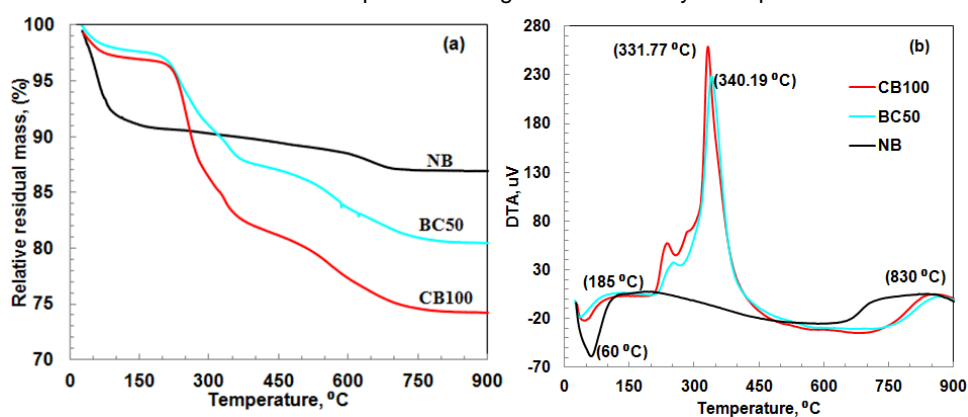


Figure 4: TGA and DTA curves in air environment of the NB, BC50 and CB100 samples

In the range of approximately 400 °C and 750 °C there was also a loss of mass with a very broad endothermic band (see Figure 4b) that can be associated with aluminosilicate dehydroxylation. Above 750 °C there is an exothermic band (see Figure 4b), with the maximum at 830 °C that can be related with the destruction of the crystal lattice (formation of new crystalline phases of the clay). Looking at the TGA and DTA curves of CB100 and BC50 can be seen that the two clays have very similar thermal behaviour. However, compared with the NB two more mass losses are observed on the two organo-modified clays, these losses are attributed to the decomposition of their salts. The first weight loss for the two clays is observed between 170 °C and about 430 °C with a maximum at 340.19 °C for BC50 and 331.77 °C for CB100 (see Figure 4b) corresponding to the initial decomposition of BC and CB. A second weight loss is observed between approximately 450 °C and 850 °C, associated with the final decomposition of the salts. The actual content of surfactant incorporated into the clay was determined based on the difference between the total weight loss occurred in the range 170 °C and 850 °C for the treated clay and the weight loss for the untreated clay in 400 °C and 750 °C. The surfactant content with the treatment was about 13 % for BC50 and about 19 % for CB100, values considered as good, and confirming the effectiveness of the procedure as observed by FT-IR and XRD.

### 3.5 Physico-chemical and bacteriological analysis

Table 1 shows the results of the various physico-chemical and bacteriological parameters obtained from laboratory analysis of the treated water. It is clear from the table that the use of clay in water treatment had a significant effect on the properties analyzed here, with an emphasis when the clay treated with CB was used. The use of clay in water treatment, for instance, resulted in the reduction of the conductivity by 71 %, 73%, and 88 %; total hardness by 76 %, 79 % and 86 %; total suspended solids by 79 %, 55 % and 84 %; total dissolved solids by 35 %, 30 % and 52 %; and turbidity by 86 %, 86 % and 92 %, when NB clay and the treated with CB and BC were used.

The bacteriological parameters such as Total Coliforms, Faecal Coliforms and Escherichia Coli also registered a significant reduction as a result of water treatment. However, the greatest reduction was registered for the

water sample treated with CB100. For example, Total Coliforms went from  $> 2.4 \times 10^6$  to  $< 3$  CFU/100 mL, while Faecal Coliforms and Escherichia Coli went from  $1.1 \times 10^6$  to  $< 3$  CFU/100 mL.

*Table 1: Selected physico-chemical and bacteriological parameters of the analysis*

Parameter	Feed PW	PW treated with NB	PW treated with CB100	PW treated with BC50	*NEDLN
Turbidity, NTU	50±0.50	7.01±0.03	3.84±0.04	6.89±0.13	>15
Total hardness, mg/L CaCO <sub>3</sub>	1,220±4.95	291±3.49	172±2.83	257±0.14	-
Ammoniac, mg/L NH <sub>4</sub>	32.1±0.12	30±0.01	20±1.56	30±0.71	-
Chlorines, mg/L Cl	3,315±4.24	1,345±4.24	300±2.12	876±1.41	600
Total dissolved solids (TDS), mg/L	970±4.04	632±3.54	467±2.83	675±0.71	5,000
Nitrates, mg/L	60±1.41	60±1.50	32±0.41	48±1.41	-
Total suspended solids (TSS), mg/L	140±2.83	29±0.28	23±0.28	63±1.41	>50
Electrical conductivity, µs/cm	5,867±0.71	1,678±3.54	678±2.12	1,567±2.83	No limit

\*NEDLN is Nigerian Effluent Discharged Limits for Neashore (Isehunwa and Onovae, 2011).

#### 4. Conclusions

XRD, SEM, FT-IR and TGA studies confirmed the effective intercalation of the surfactants in modified clays. This shows that the surface modification through ion-exchange reaction by cationic surfactants can be an effective method to improve the adsorption capacity of the Boane bentonite. After the organo-modification the main smectite phase reflection  $d_{001}$  increased from 1.520 to 1.960 nm and from 1.520 to 1.830 nm for clays modified with CB and BC as the concentration of CB varied from 50 to 100 meq and 50 meq for BC. Above 50 meq for BC showed destruction of the structure. Wastewater treatment performance evaluation of synthesized products showed that the physico-chemical and bacteriological properties improved significantly, showing clearly that Boane bentonite can be successfully employed in improving numerous properties of the PW.

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