

Chemical and Physical Characterization of Moroccan Bentonite Taken from Nador (North of Morocco)

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Abstract Clay samples of bentonite taken at Nador region of North-Eastern Morocco have undergone a series of mineralogical, chemical and physico-chemical analyzes including mineralogical composition (X-ray diffractions and infrared spectroscopy), chemical analysis, cation exchange capacity, specific surfaces and thermal analysis. The crude bentonite contained calcium-rich smectite (>80%). It also contained other mineralogical content of less than 20 by weight, consisting mainly of quartz. The fine fraction ($\leq 2 \mu\text{m}$) was purified and exchanged with sodium cations. The chemical composition of the fine fractions and the low crystalline phases bound to Fe-, Al- and Si-phases isolated by selective extractions were used in the calculation of chemical formula of smectite clay. The mineralogical and chemical compositions of the samples are typical of bentonites, mainly consisting of montmorillonite. The results revealed that this clay have quality necessary in various applications such as cosmetics, medicinal, paints, nanomaterials etc.

Keywords Moroccan Bentonite, Clay, Mineralogical composition, Chemical composition, Cation exchange capacity, Specific surface area

1. Introduction

Geological characteristics of the world bentonite mineral resources are mainly concentrated in magmatic activity (volcanic activity) related areas, the volcano-sedimentary deposit types, the weathered residual and hydrothermal are related to volcanic activity. According to the material, the global bentonite of North African origin is mainly distributed in North East Morocco in the region of Nador city (Figure 1). Industrial Minerals Company is engaged in the production of white bentonite in Nador region, with an annual output of 150,000 tons which represents an estimated value of 1.5% of world coumption. The Nador bentonite deposits are exploited and not industrially used in Morocco but in Europe. The main destination countries for the Nador bentonite were Spain and Greece. These latter's increase their potential reserve of bentonite for commercial use and export, due to the Moroccan bentonite importation.

Commercial importance of bentonites depends on the contents of their clay and nonclay minerals. Dominant clay minerals in bentonites are smectites irrespective of their origin such as montmorillonite, beidellite, saponite and hectorite [1]. Bentonite and their major clay mineral smectites have been among the most important industrial raw material. Some of the applications are civil engineering and

environmental ones, animal litter, paint, paper, plastics, decolorization, foundry bondants, drilling fluids, desiccants, sealants, cosmetics, adhesives, and catalysts [2].

The purification and physicochemical modifications of pure smectites have a great importance to prepare some high technology materials such as pillared clays, organo-clays, and polymer/smectite nanocomposites.

For many years, the clay materials have been used for adsorption of heavy metals [3, 4], dye molecules [5], herbicides [6], anions such as nitrates [7], like phosphates and sulphates, or gas adsorption [8], like SO_2 . In industry, these materials are also used as a catalysator in organic syntheses or as excipient in pharmacy. The application of clay materials is greatly governed by their surface properties like adsorption capacities, surface charges, large surface area, charge density, the type of exchangeable cations, hydroxyl groups on the edges, silanol groups of the crystalline defects or broken surfaces and Lewis and Brønsted acidity [9]. Phyllosilicate surfaces contain two basic types, *i.e.*, siloxane surface and hydroxyl surface.

The quality of a bentonite that refers to the performance of the material in its different applications depends largely on the quality and quantity of the smectite, which the most common mineral is montmorillonite. Therefore, the isolation of some smectite group minerals from bentonites is of great importance. A specific purification method for each bentonite needs to be developed depending upon the properties of its clay and nonclay minerals. The particle sizes of the smectite particles are smaller than 2 micrometer in aqueous suspensions. This property is of great importance in

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the purification of bentonites since it permits the separation of smectites from the bentonites.

The grade of a bentonite which refers to the smectite content of the bentonite, can be assessed by measurement of the cation exchange capacity (CEC) and/or its total specific surface area usually determined with ethylene glycol.

The present paper is the outcome of such an effort conducted to develop the potential use of mineral resources of North East Moroccan clay deposits. The studied Bentonite clay was taken from the deposits of Azzouzete in the district of Nador (Morocco) at 20 Km south of Nador city (35°01' 56,49° N and 2°52' 11,37°O with 106 m of Altitude) **Figure 1 et 2.**

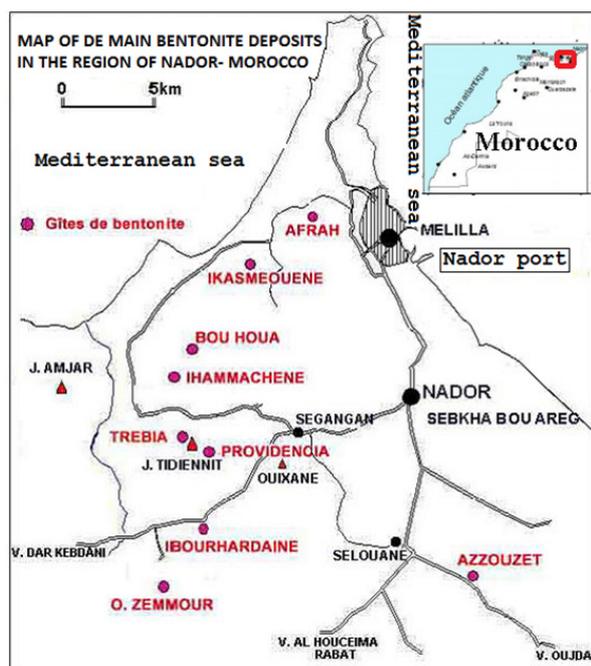


Figure 1. Location of Nador city: site of the clay samples



Figure 2. Location of the clay sample sites: Nador deposit of Azzouzete (Source: Google Earth 35°01' 56,49° N and 2°52' 11,37° O with 106 m of Altitude)

Deposits of Azzouzete were visible sedimentary layers on the surface that can reach a thickness exceeding 6 meters. The age of these rocks ranges between 2 and 10 million years which means that the formation began as early as the Miocene magmatism.

This deposit is currently in exhaustion and other deposits with the similar bentonites in the vicinity are in operation or in reserve. A study by Mohammed Essafi in 1986 [10], recalls the different deposits of bentonites from North East of Morocco and identifies their geological and mineralogical characteristics.

This paper reports the results of a study dealing with the chemical and mineralogical characterization, specific surface area measurements, the cation exchange capacity of clay determination and the physical technics characterization (XRD, IR, ATD & ATG).

This study is performed in order to supply some of the necessary background data on the Moroccan bentonites as well as evaluate their potential industrial use and academic research.

2. Technics and Methods

The studied Azzouzete's bentonite comes from deposit located in the north of Morocco (Nador area). For our study, we collected a mass of clay from 50 Kg to a depth of 6 meters. The bentonite clays of this deposit are essentially white color. The investigated characteristics of chemical analysis and charge surface determination were compared to those of a commercial Wyoming bentonite supplied by the Clay Minerals Society a source clay Wyoming SPV.

2.1. Preparation of Sodium Homo Ionic Bentonite

We carry out the elimination of all the crystalline phases (quartz, feldspar, calcite...) by a pretreatment of the sample rough by sodic homo-ionization. A series of washing has made it possible to eliminate the impurities and to obtain a well defined granular fraction of a size $\leq 2 \mu\text{m}$. In practice, this process consists of dispersing a mass of 1 Kg in 5 liters of distilled water in a solid / liquid report of 20% under agitation for an hour until complete homogenization of the suspension. The obtained mixture was then treated by HCl (0,5 M) to eliminate the carbonate. After washing, hydrogen peroxide (10%) was added to oxidize an eventual organic present matter.

Subsequently, we conduct the cation exchange by adding NaCl solution of 1M to have a sodic bentonite (sodic smectite).

Agitation-centrifugation wash cycle is repeated 5 times. The dark grey background in the centrifuge tubes is eliminated: it contains the fraction enriched in impurity (quartz, cristalobalite...). The remaining chloride is removed by dialysis.

2.2. Characterization Methods

2.2.1. XRD, IR and Thermal Analysis

Raw clay and purified samples are subjected to mineralogical, physical analysis and identified by X-Ray diffraction (XRD), infrared spectroscopy (IR) and thermal analysis (ATD and ATG).

The XRD analysis was conducted using automatic diffractometer Siemens D500, working on copper $K\alpha_1$ (1.54 Å) monochromatic radiation.

The angular scan was performed in discrete steps of 0.05° (2θ) with a counting time of 5 seconds per step. The material is dried and finely ground and the powder sieved through 0.63 mm sieve was placed directly on a sample holder (plastic).

Thermal analysis was conducted by a thermal Analyzer type (STRATON) with a speed of heating of $5^\circ \text{C}/\text{min}$ to 1000°C , under a controlled atmosphere of helium.

IR spectra have been made using a spectrometer Shimadzu Fourier Transform on a range of 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} and samples were conditioned in dispersion in a KBr Pellet (1/200 in weight).

2.2.2. Nitrogen Adsorption/Desorption

Adsorption-desorption experiments using N_2 were carried out at 77°K on a Sorptomatic 1900 Carlo Erba porosimeter. Before each measurement, the samples were outgassed at 140°C , and vacuumed for more than 12 hrs. The N_2 isotherms were used to determine the specific surface areas (SA) using the BET equation. The t-plot method was used to calculate the micropore volume and micropore area.

2.2.3. Ethylene Glycol and Methylene Blue Adsorption

The cation exchange capacities (C.E.C) were determined by the Copper Ethylene Diamine method Cu-EDA [11] and

the total surface was determined by methylene blue adsorption [12]. The total surface area was determined by ethylene glycol gaz adsorption [13].

2.3. Chemical Analysis

The elementary analysis was conducted by Varian 220 ICP/AES spectrometer. The choice of analytical rays has been done in such a manner to avoid spectral interfaces in the emission of inductive plasma. To perform chemical analysis. The studied clay samples studied were attacked by mixture of (2/3 HCl + 1/3 HNO_3). All elements pass in solution except silica evaporates by use of HF.

3. Results and Discussion

3.1. Chemical and Mineralogical Characterization

3.1.1. XRD on Powder

The sample of initial raw bentonite and Sodium exchanged bentonite (Na-bentonite) were examined by XRD analysis on powder-oriented samples and results are presented in Figure 3.

The diffraction of X-rays (XRD) on the raw bentonite powder shows that the bentonite is of the same family of smectite with reflection (001) located at 14Å . This shows that the natural bentonite is calcium form. The presence of the line (06,33) $d = 1.49 \text{ Å}$ shows that it is formed by montmorillonite and is confirmed by the reflexion of $d(003) = 4.43$ and $d(004) = 3.07 \text{ Å}$. It also notes the presence of crystalline phases in forms of impurities of Quartz (Q) $d = 3.34 \text{ Å}$. The presence of calcite at $d = 3.03\text{Å}$ (C) or $d = 2.28 \text{ Å}$ cannot be confirmed on this diagram. The mineral composition of montmorillonite (m) in the bentonite raw material is more than 80%.

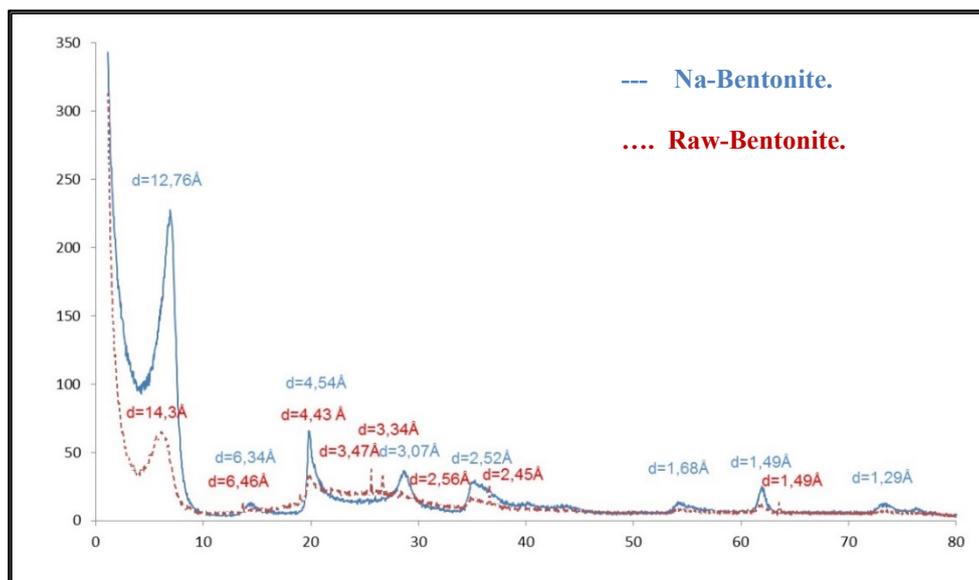


Figure 3. Diffractograms of the fine fraction powder of Brute and purified Na-Bentonite

Comparative XRD diagram of raw bentonite and of purified sodium exchanged bentonite actually confirms a good purification of bentonite by comparison of the lines with the (001) peak.

A shift in the position of the (001) line from 14.3 to 12.7 Å, which shows that the exchange between calcium and sodium was produced. The diagram shows the disappearance of a peak characteristic of the crystalline phases as impurities, particularly that of quartz at $d=3.34$ Å, and an intensification of certain lines corresponding to those of montmorillonite at $d = 12.7$ and $d = 3.07$ Å. The peak at $d = 1.49$ Å characterizes the reflexion of (060) which is symmetric showing good crystalline behavior of this montmorillonite.

Most of the mineral impurities were removed by sedimentation, purification and sieving.

3.1.2. XRD-oriented Slide

The first blade contains therefore purified bentonite oriented, the second one, the bentonite purified with undergoes heat treatment and the last contains the purified exchanged sodium bentonite.

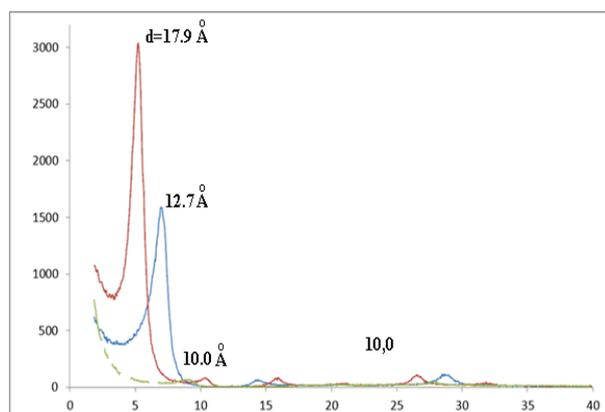


Figure 4. Diffractograms of oriented aggregates: nontreated; solvated by ethylene glycol; heat-treated at 550 °C for 3 h

The diffractograms analysis shows that the saturation to ethylene glycol induces a shift towards small angles of reflection located at 17,9 Å. This behavior is an indication of the presence of a mineral swelling, which confirms the presence of smectite. The diffractogram of the sample heated to 550°C indicates a displacement of the reflection from 17.9 Å to 10 Å. The decrease in the interlayer space is due to the loss of interlayer water.

3.1.3. FT-IR Spectroscopy Measurements

The infrared spectroscopy of the clay samples of raw bentonite and purified sodium bentonite are presented in figure 5 and are almost identical.

The spectra show two absorption bands located between 3200 and 3800 cm^{-1} and between 1600 and 1700 cm^{-1} . Most of the bands such as 3621, 3435, 1635, 1027, 914, 840, 845, 523, 462, 454, 432, 421 cm^{-1} show the presence of montmorillonite [14] and [15] a strong band at 3621 cm^{-1} , 3435 cm^{-1} indicates the possibility of the hydroxyl linkage.

However, a broad band at 3435 cm^{-1} and a band at 1635 cm^{-1} suggest the possibility of water of hydration in the bentonite at di-octahedral surface.

The inter layer hydrogen bonding in clay is assigned by a characteristic band at 3621 cm^{-1} . This band characterizes montmorillonite and corresponds to the groups stretching vibrations OH coordinated octahedral layer to Al + Mg (3621 cm^{-1}) [14, 15].

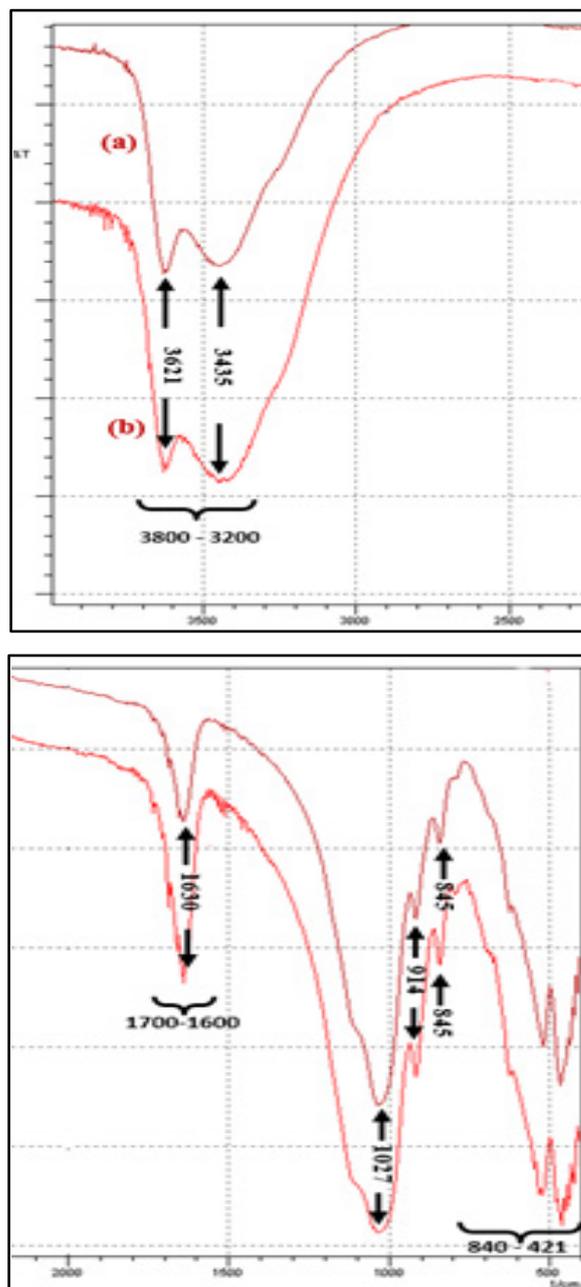


Figure 5. Infrared spectra: (a) Raw- Bentonite; (b) Na- Bentonite

The band, which runs between 1600 and 1700 cm^{-1} , is attributed to the vibrations of valence of the OH group of water constitution.

The band towards 1635-1639 cm^{-1} is attributed to the vibrations of deformation of the H_2O molecules adsorbed between the layers. The bands at 1027 cm^{-1} and 417 cm^{-1} are

associated with the stretching vibrations of Si-O and Al-O tetrahedral vibration, Al, Fe and Mg octahedral and Si-O-Si octahedral vibrations. The intense band between 900 and 1200 cm^{-1} centred at 1028 cm^{-1} corresponds to the bending vibrations of Si-O-Si. Bands located at 425 cm^{-1} and 525 cm^{-1} are respectively assigned to vibration deformation of Si-O-Al bonds, Si-O-Mg and Si-O-Fe [9]. The corresponding values are given in **Table 1**.

Table 1. Band assignments of crude and sodium bentonite

Raw Bentonite band (cm^{-1})	Na-Bentonite Band (cm^{-1})	Assignments
3621	3626	OH stretching of water
3435	3462	OH stretching of structural hydroxyl groups
1635	1639	H-O-H deformation of water.
1027	1029	Si-O-Si, Si-O stretching of silica and quartz
914	916	Al-Al-OH deformation
840	842	Si-O-Mg stretching
845	794	Si-O str., Si-O-Al stretching.
	786	(Al, Mg)-O-H.
	675	Si-O- (Mg, Al) stretching.
523	517	Al-O-Si stretching,
462	467	Fe-,
454	457	Fe ₂ O ₃
432	-	
421	417	Si-O deformation

3.1.4. Thermal Analysis: ATD and ATG

In general, the analyzed bentonites of Raw and exchanged sodium bentonite showed similar behavior characteristic of 2/1 dioctahedral clays as shown in figure 6. This showed that the studied bentonite has similar structure to montmorillonite [16].

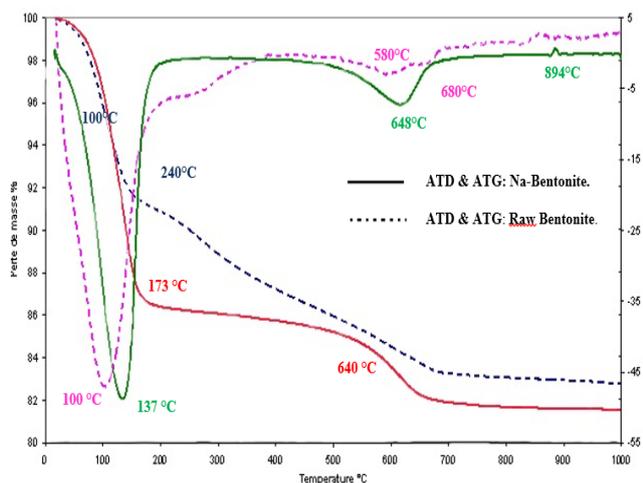


Figure 6. Thermal analysis: (a) Raw Bentonite; (b) Na-Bentonite

The examination of the thermal analysis of purified sodium bentonite curve showed in the low temperature range, the existence of an intense and large endothermic peak at

137°C. This initial endothermic peak over a wide temperature range between 100°C and 250°C is due to the loss of adsorbed water on the external surface. It was held between the basal planes of the lattice structure. The loss of the mass that accompanies these thermal accidents is very important. It is approximately 13.5% of the initial mass. Another endothermic phenomenon of low-intensity occurs at a temperature of 640°C. It corresponds to the loss of hydroxide ions from clay material and causes irreversible modification of the crystal structure. The high octahedral substitution of iron and magnesium in montmorillonite clay causes a shift of the endothermic peak from nearly 640°C to about 700°C compared to Aluminium octa-hedral substitution [17, 18]. The loss of the mass associated with this phenomenon is about 3.6% by weight.

The ATD curve also presents an exothermic peak at 894°C due to the modification of bentonite structure and formation of crystalline phases.

Raw bentonite on DTA curve presents two endothermic phenomena at 100°C and 240°C. This duplication is due to the presence of two types of water molecules, adsorbed water or interlamellar water respectively.

Two others endothermic phenomena of low intensity, manifested in the 580°C and 680°C range temperature. They correspond respectively to structural water of bentonite and associated minerals.

The ATD curve also presents a very broad exothermic accident in 820°C and 930°C temperature range corresponding to the mineral transformation phases.

3.1.5. Chemical Analyses

Elemental analysis of the studied clay samples studied showed that they are composed essentially of Si, Al, Fe, Mg, O, Na and Ca. The elements present in clays have been presented as relative percentages of the elements expressed as oxides and expressed as relative oxide percent by weight in the entire sample in **Table 2**.

Table 2. Everage elemental composition of selected clays

Clay sample	Raw bentonite	Na-Bentonite	Wyoming SPV
SiO ₂	60.17	54.30	56.69
Al ₂ O ₃	15.13	16.01	19.93
Fe ₂ O ₃	3.44	2.00	3.07
MgO	5.69	5.28	1.82
Na ₂ O	-	2.54	2.09
CaO	4.13	0.36	0.28
MnO	0.11	<0.01	0.01
TiO ₂	0.02	<0.01	0.17
P ₂ O ₅	0.03	<0.01	0.34
LOI	11.30	19.45	15.60

*LOI is lost on ignition signifying an estimate of matter lost when the clay was heated.

Azzouzet crude clay contains approximately 60% silicon dioxide, mainly derived from smectite clay and is also composed of quartz minerals and possibly other minerals such as feldspar. It also contains a relatively large percentage of calcium oxide $\approx 4\%$, which may be derived from minerals such as calcite.

The following chest will gather the percentage in weight related to the elements present in clay.

These formulae were determined from the method given by Van Olphen (1977) [19]. For Nador Bentonite and Wyoming, oxides TiO_2 and P_2O_5 were considered impurities, and were not taken into account in the calculations to obtain the chemical formula in **Table 3**.

Table 3. Formulae of selected clays

Na-Bentonite (Nador)
$[Si_{7.97} Al_{0.03}^{3+}]^{IV} [Al_{2.737} Fe_{0.221} Mg_{1.157}]^{VI} O_{20} (OH)_4 (Na_{0.722} Ca_{0.056})$
Wyoming SPV
$[Si_{7.94} Al_{0.06}^{3+}]^{IV} [Al_{3.23} Fe_{0.322} Mg_{0.381}]^{VI} O_{20} (OH)_4 (Na_{0.568} Ca_{0.042})$

*The Roman numerals IV and VI on the cells designate the octahedral and tetrahedral sites respectively.

To deduce the lattice parameters, the vector modulus, the following relationships eq.1 and eq.2, are used according to Grim (1968) [1];

$$b = 9,91 + 0,06r + 0,034s + 0,048t \text{ (\AA)} \quad (1)$$

$$a = \frac{b}{\sqrt{3}} \text{ (\AA)} \quad (2)$$

With r: the number of Al^{3+} in tetrahedral coordination.

s: the number of Mg^{2+} in octahedral coordination.

t: the number of Fe^{3+} or Fe^{2+} in octahedral coordination.

The lattice parameters (a, b, c), the area A_m , the volume V_m and the charge density of the selected clays are reported in **Table 4**.

Table 4. Main lattice parameters of the Wyoming and Nador montmorillonite (Na-bentonite)

	a (\AA)	b (\AA)	c (\AA)	A_m (\AA ²)	V_m (\AA ³)	Charge density δ^-
Wyoming SPV	5.16	8.9	9.3	46.1	429	0.656
Na-bentonite	5.17	8.96	9.3	46.3	431	0.84

Montmorillonite is negatively charged and has a total charge density of 0.840 due for 90% to a substitution of the octahedral layer (Al by Mg) and 10% due to a substitution of the tetrahedral layer (Si by Al). The negative charges of the montmorillonite sheets are compensated mainly by sodium ions (93%) and calcium ions (7%).

The cation exchange capacity of the Na-bentonite and of the Wyoming are calculated from chemical formula and

measured by adsorption of methylene blue method or by copper ethylene diamine (EDTA) complex method using reference mass of clay heated at 950°C (**Table 5**).

Table 5. Ability to exchange cation by the method of methylene blue MB, copper-ethylene diamine tetra-acetic complex Cu-EDTA and from chemical analysis

	CEC by methylene blue method meq/100g	CEC by Cu-EDTA complex method meq/100g	CEC from chemical analysis
Bentonite-Na	109	119	118
Wyoming SPV	100	98	93

The results of CEC following these methods for clay samples are generally in rather good agreement and compare to the values accepted for smectite clays between 80 and 120 meq/100g.

It can be concluded from elemental analysis, that montmorillonite from Nador bentonite is similar to that obtained from Wyoming bentonite SPV.

3.1.6. Determination of Bentonite Surfaces

The measurement of specific surface brings to clays of both mineralogical and textural information. In general, it uses two approaches to determine the specific surface of clays:

1- The adsorption of single molecules, such as nitrogen low temperature to determine the outer surface using data of adsorption isotherm and applying the theory of BET [20].

2- The measurement of the total surface area by adsorption of polar liquid (Liquor), its advantage is the capacity to swell the mineral impurities and replace them, which is not the case for nitrogen adsorption method [21]. In this case, Eltantawy Arnold [13] proposed a protocol that measures surfaces for which the molecular size is independent of the nature of the cation and equal to 2.22 m²/mg ethylene glycol (EG).

a. Nitrogen adsorption and desorption isotherms

The adsorption-desorption isotherm of nitrogen on Raw and Nador Na-bentonite are shown in **Figure 7**.

Similar nitrogen adsorption-desorption isotherms are obtained for raw bentonite and sodium bentonite for fine powder fractions less than 0,056 mm.

It is observed that the shape of the isotherms exhibits a hysteresis, which reveals the presence of mesopores. The full points on the graph (figure 7) materialize the isotherm of desorption and the empty points isotherm of adsorption.

The specific surface area is of 70 m²/g and 107 m²/g for raw material and Na-bentonite respectively. The B.J.H method has been used to determine the cumulative volume of the sample's mesopores. The pore volume at $p/p^0 = 0.99$ is of 0.105 cm³/g for raw material and 0,112 cm³/g for Na-bentonite. The t – plot method has been used to determine the specific area and the volume developed by micropores of the samples. These values are respectively of

29.86 m²/g and 0.01148 cm³/g for raw material, respectively of 40.7 m²/g and 0.02034 cm³/g for Na-bentonite.

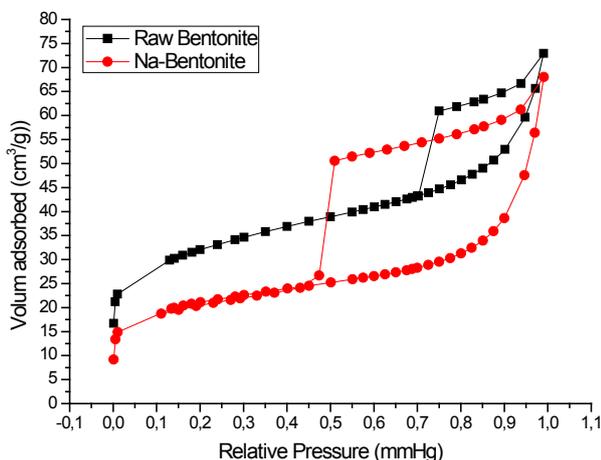


Figure 7. Adsorption-desorption isotherms of nitrogen on Raw and Na-bentonite

b. Total specific surface area (A_s)

The values of the external surface and the total surface area as well as the value of the internal surface measured by ethylene glycol adsorption area are given in Table 6.

Table 6. Surface area measured by ethylene glycol

	S _{ex} (m ² /g)	S _{in} (m ² /g)	S _{tot} (m ² /g)	S _{tot} (m ² /g) from chemical structure
Wyoming	133	654	787 ± 10	770
Na-Bentonite	153	622	775 ± 10	785
Raw-Bentonite	66	395	462 ± 10	-

S_{ex}: external surface area; S_{in}: internal surface area, S_{tot} (m²/g): Total Surface area determined by gravimetric method after gaz adsorption of ethylene glycol EG.

The low surface measured by the EG for raw clay is related to the persistence of mineral impurities.

Nador bentonite has approximately the same surface characteristics measured with ethylene glycol as that of Wyoming montmorillonite and is about 780 m²/g in average.

The experimental measures of specific surface area include basal and lateral slip surfaces. Caillère and al. (1982) [22] examined the relationship form-surface of the clay sheets. They estimated the relative importance of lateral surfaces and the basal surfaces. For minerals such as the smectite, lateral surfaces are negligible.

By comparing surface measurements obtained by BET nitrogen adsorption and EG adsorption, we note that specific surface determined by the BET method is relatively lower than the EG adsorption. This is due to the fact, that the nitrogen molecules are non-polar and cannot penetrate the interlayer space, which constitutes a relatively large internal surface of the smectite. This determined surface is external, whereas the adsorption of polar molecules (EG), can be used for the measurement of the total surface area [23]. The comparison of the results between the two measures of total

external surface can give an estimation of the inner surface [24]. The measured value of the outer surface for the raw clay is 66 m²/g (70 m²/g by BET). In the case of the purified clay, this value is 153 m²/g, greater than that measured by nitrogen adsorption (107 m²/g). Differences in results are explained by the fact that some pores remain inaccessible to molecules of nitrogen and the EG is a polar molecule that adsorb by intercalation between clay sheets.

4. Conclusions

X-ray diffraction, infrared spectroscopy and thermal analysis show that the gross Nador bentonite is a di-octahedral bentonite (montmorillonite type) in calcium form that contains very few impurities as quartz and calcite. The physicochemical characterization of purified and sodium exchanged Nador bentonite compared to the reference Wyoming bentonite SPV shows that it is a di-octahedral clay of montmorillonite type and also presents a very similar chemical composition and physical-chemical characteristics by reference Wyoming montmorillonite SPV.

By means of Chemical Analysis, it can be said that the smectites that constitute Nador bentonites are montmorillonites rich in magnesium at the octahedral site.

The high montmorillonite content (>80%) of Nador bentonite and its chemical and physical properties determine its great commercial value and potential use in a wide variety of technical applications.

ACKNOWLEDGMENTS

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