

# Structural textural study and physicochemical properties of a Tunisian locally clay mineral

A. Ben Othman, F. Ayari, S. Khelifi, R. Abidi

**Abstract**— Bentonite clay minerals belonging to the smectite group have a wide range of chemical and industrial uses. The structure and chemical composition, exchangeable ion type and small crystal size of smectite are responsible for several properties, including a large chemically active surface area, a high cation exchange capacity and inter-lamellar surface having unusual hydration characteristics it has hydrophilic property in nature. A sample collected from Ain-Berda (North Tunisia), was studied by some physico-chemical methods. Results of X-ray diffraction, chemical analysis, Infrared Spectroscopy, TEM, SEM, X-Fluorescence, Granulometry, Thermogravimetric (TGA) and differential thermal analysis (DTA), cation exchange capacities, specific and total surface, confirm the general smectite character of the collected sample.

**Index Terms**— Bentonite clay, Caracterisation, Spectroscopics analysis, Chemical analysis.

## I. INTRODUCTION

Clay materials are abundant in most continents of the world and are familiar due to their low cost, high sorption properties, ion exchange and good adsorbent [1-2-3]. Since it's a low cost material and frequently presented in nature; Clay minerals have been widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high specific surface area, and consequential strong adsorption capacity [1-4]. Accordingly many researchers pinpoint their interest to exploit this material in many domains and industries such as medicine, pottery, and battement, ceramic. As adsorbent, for wastewaters purification by many industries such as: textiles industries, tannery, papers productions etc...

Consequently studies have been conducted to evaluate the potential of clay minerals like montmorillonite, kaolinite and illite in several domains. The abundance of bentonite and its low cost make it a strong candidate used in several domains. Bentonite is a clay material (2:1 type) consisting essentially of the montmorillonite group. The inner layer is composed of one octahedral alumina sheet placed between two tetrahedral silica sheets. Bentonite surface is negatively charged due to the isomorphous substitutions within the layers of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sheet and  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral sheet. The charge imbalance is offset by exchangeable cations (e.g alkali-metal  $\text{Na}^+$  and alkaline-earth-metal  $\text{Ca}^{2+}$ , etc...) in the interlayer.

For these motivations, this investigation was therefore undertaken to evaluate physic-chemical properties and

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mineralogy composition of a clay mineral collected from "Ain Berda" from Bizerte (North-East of Tunisia). This clay mineral was studied at the first time; results suggest that it enclose potential adsorption properties due to its high cation exchange capacity, specific surface area, and pores size. It is found to be porous material.

## II. MATERIALS AND METHODS

### A. Characterization of collected clay

The processing of the clay sample collected from the Ain-Berda preparation included air drying, crushing by mortar and pestle and passing through a 60-mesh sieve. The clay fine fraction (particle size  $< 2 \mu\text{m}$ ) was purified by the classic method [1-5], by several cycle exchanged with NaCl solution ( $1 \text{ mol L}^{-1}$ ) under stirring during 24 h for five times to form the sodium-saturated clay sample. At that time, the Na-saturated clay was washed with distilled water until chloride free as confirmed by the  $\text{AgNO}_3$  test [1-2]. The obtained sample denoted (AB-p) was dried at  $80^\circ\text{C}$  and grounding.

Characterization of the clay included surface area measurement, mineralogical analysis. The chemical analyses were obtained by using X-ray diffraction studies (Philips goniometer, PW1730/10, using the  $K\alpha$  radiation of copper). The infrared spectra obtained by using KBr pellets were recorded with a Perkin Elmer 783 dispersive spectrometer from  $4000$  to  $400 \text{ cm}^{-1}$ . The cation exchange capacities (CEC) were estimated by the MANTIN method [6-7]. Specific surface area of pur and crud sample were estimated by adsorption of

methylene blue dye on bentonite in solutions, this method is used to determine either their cation-exchange capacities (CEC) or their total specific surface area (Ss) via Uv-spectrometer [1-2]. thermal analysis were also studied.

As a complimentary technic for clay characterization, the sample morphology was recognized by Transmission electron microscopy (TEM). BET surface area ( $S_{\text{BET}}$ ) and pore volumes of clay sample were measured using the physical adsorption of nitrogen by Quantachrome Autosorb-1 instrument.

## III. RESULTATS AND DISCUSSION

### A. X-ray diffraction

As shown in Figure I. Quartz (reflection at  $3.34\text{\AA}$  and  $4.27\text{\AA}$ ) and calcite (reflection at  $3.03\text{\AA}$ ) are the major impurities. The positions of 001 reflections of the smectite appear at  $14.25\text{\AA}$  for the sample, suggesting that the fraction might be in the Ca-exchange form [1-8-9]. The purified sample with Na-exchange shows the position of the 001 reflection at  $d_{001}=12.30\text{\AA}$ , characteristic of a sodium smectite or an interstratified sample of these minerals with illite.

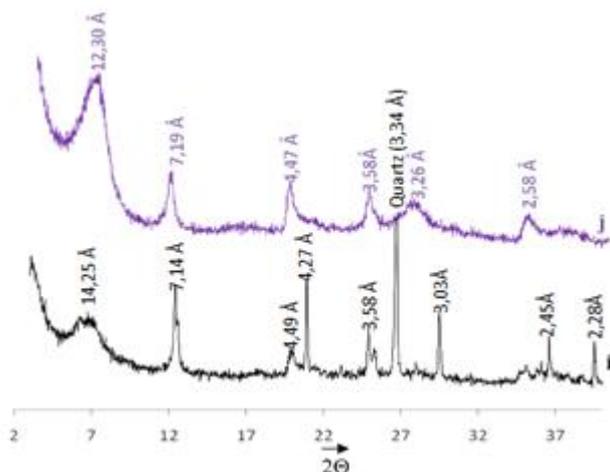


Fig.I. X-ray diffractograms of raw (i) and purified (j) clay.

**B. Infrared spectra**

Infrared spectra (Fig.II) are evident in the frequency range of 4000–400 cm<sup>-1</sup>.

The most significant adsorption bands were discerned and identified by means of previous work in literatures.

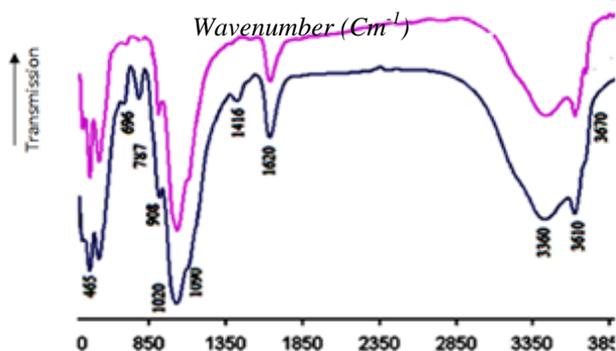


Fig.II: Infrared spectra of crude and purified sample

The infrared spectra of the crude (AB-r) and purified (AB-p) samples show the main bands show (Table I):

samples	AB-r	AB-p
Elements	Wavenumber (cm <sup>-1</sup> )	
quartz	787	-
carbonates	1416	-
Al-Al-OH	3610	3622
	908	915
Si-O	1020 - 1090	1032 - 1105
Si-O-Fe	465	472
Si-O-Al	529	538
σ(OH)	1620	1625
ν(OH)	3360-3378	3437-3627

Table I: Most important absorption bands in AB-r and AB-p samples determined by IR spectroscopy

Band that lies between 1600 -1700cm<sup>-1</sup> relate to the OH<sup>-</sup> deformation of water (H-O-H bending), suggests the presence

of adsorbed water. The band that appears between 3200 -3800 cm<sup>-1</sup> is typical for bentonite with large amounts of Al in the octahedral sheet, attributed to H–O–H stretching vibration of adsorbed water.

The Si-O group is characterized by an intense band between 900 -1200cm<sup>-1</sup>, centered around 1020cm<sup>-1</sup> corresponding to stretching vibrations of Si-O [2-8-9]. Bands observed at 787cm<sup>-1</sup> was due to stretching vibrations of Si-O-Al group [1-8-9].

**C. X Ray Fluorescence**

Samples (AB-r and AB-p) were analyzed by X-Ray Fluorescence to determine their chemical composition. Result of chemical analysis for clay composition is shown in Table II.

M <sub>x</sub> O <sub>y</sub> (wt %)	Samples	
	AB-r	AB-p
SiO <sub>2</sub>	59,431	54,149
Al <sub>2</sub> O <sub>3</sub>	13,828	17,668
Fe <sub>2</sub> O <sub>3</sub>	6,688	5,878
CaO	2,696	0,106
MgO	0,819	0,951
K <sub>2</sub> O	0,828	1,248
Na <sub>2</sub> O	0,656	1,382
PF	15	16

Table II: Chemical composition of AB-r and AB-p(wt %)

Examined chemical analysis let conclude the following suggests [1-8-9]:

- The (SiO<sub>2</sub>/ (Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> + MgO)) close to 2, suggested a 2:1 phyllosilicate smectite group.
- Ratio of CaO increases after purification from 12.82 to 0.106%: carbonate which is considered as impurity was roughly removed.
- Sample appear rich with iron (≤ 6%)
- K<sub>2</sub>O ratio increases after purification what inspires the occurrence of small portion of illite with smectite fraction

**D. Structural formulas of exchanged samples**

Chemical formula was estimated using Charle Mauguin method (1928) [1]



The number of atoms in the octahedral layer was approximates equal to 4 rather than 6 , which confirms the dioctahedral character already deduced by the calculation of SiO<sub>2</sub>/ (Al<sub>2</sub>O<sub>3</sub> + MgO + Fe<sub>2</sub>O<sub>3</sub>) report.

**E. Transmission electron microscope (TEM)**

MET has been used in order to determine the morphology and size of the clay particles. Scan picture of AB-p shows organized sheet structure (Figure III). sheets seem to be united having a micrometric size. Thickness of the sheet is equal to 12.30Å which is in good agreement with the value identified by XRD.

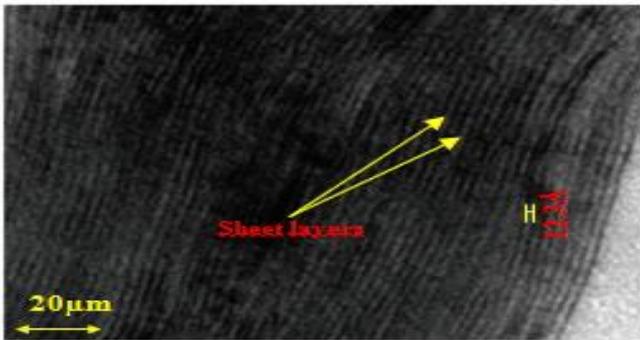


Fig.III: Observations transmission electron microscope (TEM) of the clay.

Semi-quantitative analysis that gives the microanalysis X-ray energy dispersion EDS (EDAX probe), allow to estimate atomic percent of the major elements that contain purified sample (Figure IV, Table III). These results reflect those of chemical analysis.

Results show the existence of sodium (interlayer cation) reflecting the sodium exchange take place.

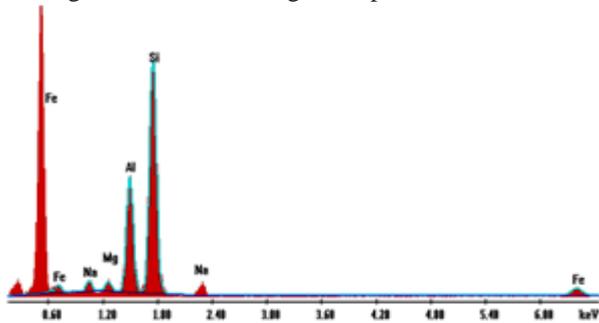


Fig.IV : EDS spectrum of AB-p

composition	Si	Al	Mg	Fe	Na
Wt%	54.61	18.23	1.02	5.52	<b>1.62</b>

Table III: Atomic percent of major elements enclosed in AB-p

#### F. Adsorption-Desorption Nitrogen isotherm at 77K

Adsorption-desorption isotherms of nitrogen at 77K by the AB-r and AB-p are shown in Figure V. isotherms were of type (IV) characterizing mesoporous materials. The hysteresis loop is of H4 type characterizing slot pores. Textural study of AB-r and AB-p shows that the specific surface area ( $S_{BET}$ ) increased after purification (Table IV). This increase may be due to the removal of impurities associated with the clay fraction.

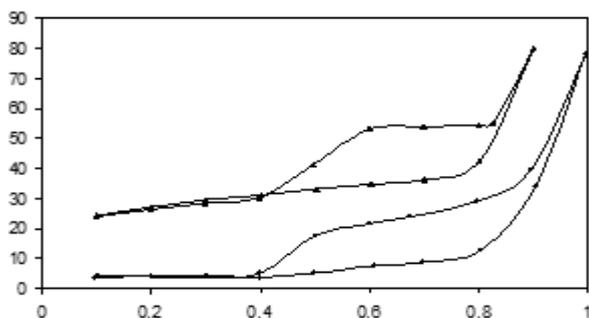


Fig.V: adsorption-desorption isotherm of nitrogen at 77K AB-r and AB-p

Table IV:  $S_{BET}$  of AB-r and AB-p

Sample	$S_{BET}$ ( $m^2/g$ )	$S_{externe}$ ( $m^2/g$ )	$V_p$ ( $cm^3/g$ )	$V_{\mu p}$ ( $cm^3/g$ )
AB-b	32,67	26,98	0,085	0
AB-P	78,6	34,12	0,138	0,014

\* $V_p$  : total pore volume. \*  $V_{\mu p}$  : Volume microporous .

#### C. Particle analysis

Granulometric analysis of AB-p sample powder was performed by laser granulometry in aqueous suspension. The method consists of a collected volume of an aqueous suspension of the sample which will be dispersed in the apparatus column. Experience was measurement was repeated three times with a time interval of 10s and a time of 60s measurement.

The particle size distribution curve of (Figure VI) shows a distribution with a single population. This Gaussian shape has a maximum around  $10\mu.m$ . This clearly shows the fineness of AB-p grain sample.

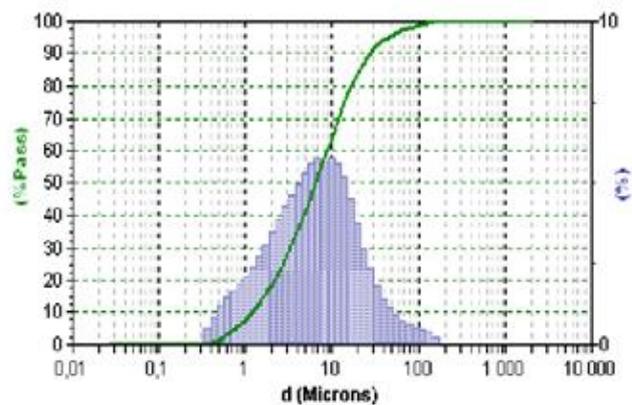


Fig.VI. Particle size distribution of the AB-p clay

#### D. CEC measurement and Specific surface area

Fixing cations is due to the existence of a negative structural charge of the clay.

The results obtained by the Mantin method as described in previous work [6] for CEC determination are given in Table V. Specific surface area show that the CEC increases after purification and it corresponds to that of a smectite group. In fact the values obtained belong to the CEC interval of a smectite (CEC between 80 and 150 meq / 100g).

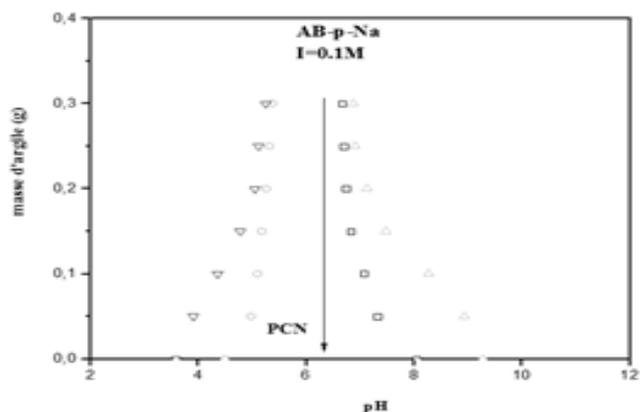
Table V: CEC and  $S_s$  of AB-r et AB-p

Sample	$S_s$ ( $m^2g^{-1}$ )	CEC(meq/100g hydrated clay) Mantin Méthod
Raw clay	336.27	50.86
Pure clay	531.2	76.16

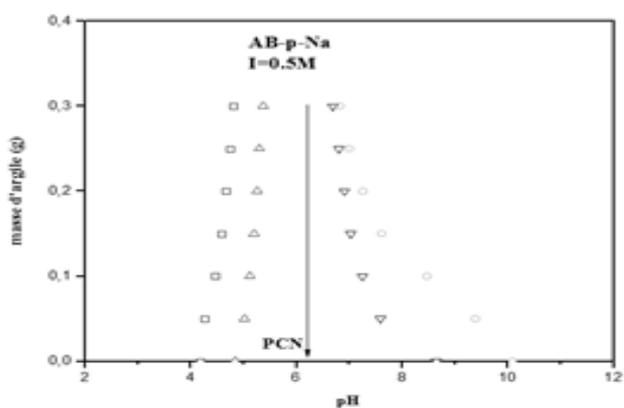
#### I. Point of zero charge $pH_{PZC}$ and effect of ionic strength

Mass Titration is used to determine pH of zero charge  $pH_{PCN}$  of the purified clay fraction. Used method is that adopted by Noh & Schwarz (1989) [10]. Added mass of AB-p-Na clay was carried out for three ionic strength  $I=0.5M$ ,  $I=0.1M$  and

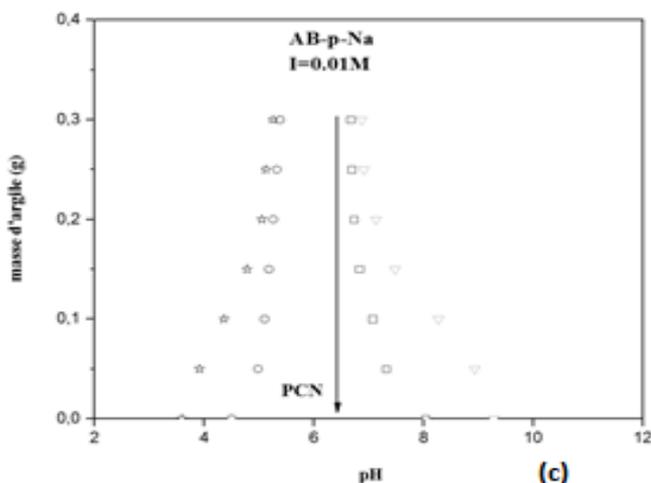
I=0.01 (Figure VII). Values of zero charge points are shown in Table VI



(a)



(b)



(c)

Fig.VII: pH measurements according to added mass of the AB-p-Na clay for three ionic strengths (a) I = 0.01; (b) I = 0.1M and (c) I=0.5M

Table VI: PZC values of AB-p-Na clay determined by mass titration for different ionic strengths

	I=0.5 M	I=0.1M	I=0.01M
AB-p-Na	6.34	6.58	6.42

J. Specific charge density  $\sigma$

The specific charge density is the ratio of cation exchange capacity CEC vs surface area Ss of the clay particle:  $\sigma \text{ (mmol.m}^{-2}\text{)} = \text{CEC/Ss}$ . Results show that  $\sigma \text{ (AB-r)} = 0.151 \text{ mmol/m}^2$  and  $\sigma \text{ (AB-p)} = 0.143 \text{ mmol/m}^2$ . Data of the specific charge density ( $\sigma$ ) of the raw and purified sample have a lower value ( $\sigma < 1 \text{ mmol.m}^{-2}$ ) suggest that this clay is swelling. This result reminded that of Lefebvre and al. (1987) [11].

K. Thermal analysis

Differential thermal analysis and thermogravimetric analysis (DTATGA) DTA and TGA were merely used as complementary methods with respect to the other techniques. The interpretation [1-8-9] of the DTA-TGA curves of the raw and purified samples leads to the following results (Figure VIII:a,b):

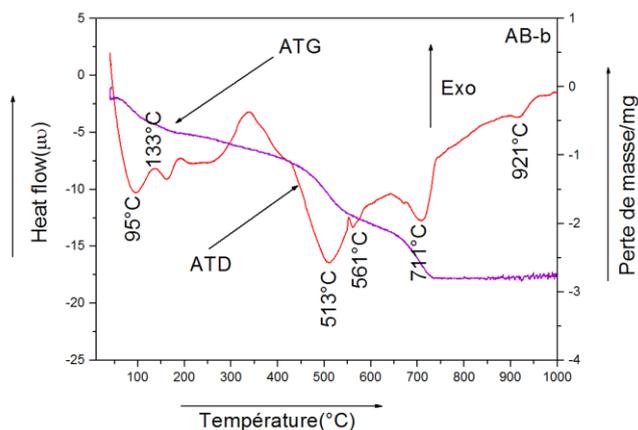


Fig.VIII, a : ATD-ATG of AB-r

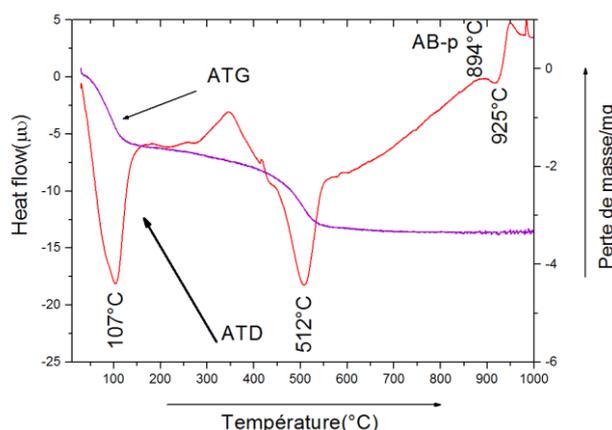


Fig.VIII, b: ATD-ATG of AB-p

Thermogram ATD of the raw sample AB-r (Figure VIII, a) shows two peaks between 95 and 133°C; these transformation are due to the removal of adsorbed and interlayer water from the clay mineral. A high intensity endothermic peak at 513°C which corresponds to the loss of hydroxyl groups from the clay mineral structure (clay dehydroxylation). This probably indicates the presence of a beidellitique character or presence of illite-smectite inter-stratification. The peak at 561°C relates to the transformation of the  $\alpha$  quartz  $\beta$  quartz. The thermogram of the sample purified AB-p (Figure VIII, b) shows an

endothermic peak at 107°C with loss of interlayer water and a peak at 512°C relative to the dehydroxylation of the purified clay.

The curves of thermogravimetric (TGA) analyzes to track the loss of mass of the sample. These curves represent three mass losses for the raw clay and two losses for purified clay. The first mass loss is between 100 and 130°C, corresponding to the loss of moisture and water interlayer. The second mass loss to 513°C and 512°C, corresponding to the loss of water content. The third mass loss occurs at 561°C and corresponds to the decarbonisation of clay. This loss appears only on the thermograms of raw clay AB-r. loss percentages waters constitution and hydration are illustrated in the following Table VII:

Table VII : (%) Loss of water

Sample	(%) water hydration loss	(%) water constitution loss
AB-r	2,24	4,097
AB-p	6,522	5,261

#### IV. CONCLUSION

Results obtained reveal that collected clay from Ain Berda from Bizerte (North-East of Tunisia) is a phyllosilicate of 2:1 type.

Sample has swelling nature and belongs to smectite family group. This smectite is calcium smectite in nature since  $d_{001}$  of crud sample appeared at 14.5Å before purification.

XRD and chemical composition suggest that the fine fraction of smectite is of dioctahedrique type with it is associated a minor fraction of kaolinite and illite. This clay mineral is porous material with important CEC and Ss which allow it to be used as a good adsorbant. Percentage of estimated smectic fraction is 78%. The chemical formula has been established:  $Ca_{0,015}K_{0,222}Na_{0,386}(Si_{7,692}Al_{0,038})(Al_{3,018}Fe_{0,648}Mg_{0,208})O_{22}$ .

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