Comparison of two purification methods of Algerian bentonite: chemical, mineralogical and physicochemical properties

Nabil Babahoum, Malek Ould Hamou, Amira Merchichi, and Farid Aghilas Mansour

Abstract− The aim of this work is to evaluate the efficiency of two methods of purification on Algerian bentonite clay. The first method was performed by centrifugation treatment, using sodium hexametaphosphate $(NaPO_3)_6$ as a dispersing agent. The second method involves a chemical purification with NaCl, followed by sedimentation technique. The study concerns mineralogical, chemical, structural aspects and a series of physical testing. The results have shown that the raw bentonite (RBN) contain (~ 59%) of montmorillonite, illite (~ 5) and (~26%) of quartz, and feldspar (orthoclase + albite), with 5% of calcite. In the purified state by NaCl (RBN-2), the mineralogical and physicochemical properties including cation exchange capacity and specific surface area are higher than the purified samples by physical beneficiation (by centrifugation - RBN-1). Moreover, the treatment with NaCl increased the montmorillonite content of the bentonite from 56 % to 100%. The quartz impurities were totally removed in RBN-2, whereas impurities (quartz + feldspar) were still observed by the X-ray diffraction (XRD). Finally, the results obtained from the morphological, mineralogical and chemical characterization confirm that the bentonite RBN -2 was more effective , and it has promise as an engineering material compared to the RBN and RBN-1, indicating its possible application in various industrial applications.

***Keywords*− Bentonite, Centrifugation, Mineralogical, Beneficiation, Material.**

NOMENCLATURE

RBN	Raw Bentonite Clay.
RBN-1	Purified Bentonite By Centrifugation.
RBN-2	Purified Bentonite By NaCl.

I. INTRODUCTION

As a geological term, bentonite is a rock formed from altered volcanic ashes and largely composed of montmorillonite type smectites [1]. Depending on their genesis, bentonite clay, in addition to smectite, contain a variety of accessory minerals. These minerals may include mainly quartz, feldspar, calcite, illite and mica [2]. Due to their unique physical and chemical properties, bentonites are used in great varieties of industries. The major uses of bentonites in industry are as foundry , sand bonds, drilling mud, pet litter and iron ore pelletizing , cosmetics, foods, pharmaceuticals, thickeners and extenders for paints, additives in ceramics, coating and filling of paper, organ clays and acid activated bleaching earths [3,4] . The commercial importance of bentonites depends on the quality and quantity of smectites and other minerals [5] as well as other technological proprieties like ; the cation exchange capacity and specific surface area . Enrichment of bentonite clays is very important step in the production of bentonite – based products for any industry [5] . Many different methods of enrichment are proposed in the literature to purify bentonite materials . The magnetic separation , centrifugation and sizing methods can be applied to extract the montmorillonite (fraction < 2 µm) and remove quartz and kaolinite impurities . On the other hand, the chemical purification was proposed in order to eliminate the iron oxides and the carbonates onto the clays [6,7-8]. .

In this study, a bentonite clay, taken from the Hammam Boughrara one of the largest bentonite deposits in Algeria and Africa , was subjected in order to describe and compare the properties of the bentonitic clay after purification with tow deferent process : (1) by centrifugation technic and (2) by NaCl treatment . The purification process are carried out at the research laboratory of mining engineering department (National Polytechnic School , Algiers) .

II. MATERIALS AND METHODS

The raw bentonite was collected from a mine located in Hammam Boughrara, Maghnia district in Tlemcen province (Algeria). The samples were mixed and quartered to obtain a representative sample of the completely bentonitic deposit. Then the samples were sieved, dried at 60 °C in a laboratory for a period of 24 h

A. Method -1: Physical purification by centrifugation

This processing was described by Thuc et.al [8] , Five grams of natural bentonite sample were agitated for 60 min in 1 L of deionized water with about 0.25 g of sodium hexametaphosphate $(NaPO_3)_6$ as a dispersing agent. After centrifugation for 5 min at 2500 r/min, the fine fraction in

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dispersion was collected and dried at 70ºC. Then, the dried bentonite was re-ground to obtain fine powder for experimental purpose. Fig.1 shows a simplified flow sheet for the beneficiation by centrifugation. The centrifugation time was estimated from the following relation based on Stokes' law:

t = [η log10 (R/ S)] / [3.81 N2 r2 ΔS]

with:

t centrifugation time (second)
R distance from the deposit surface to the axe of rotor (12 cm)
S distance from the suspension surface to the axe of rotor (4 cm)
N rotation speed = (2500 r/min)
r maximum radius in cm of the desired particles (cm) = ($2{\bullet}10^{-5}$ cm)
ΔS specific gravity difference between the particles and the liquid suspension (0.00528 g cm^{-3})
η viscosity of the fluid (0.00748 poise at 25 °C)

B. Method -2: Chemical purification of bentonite by Na^{+} ion exchange

The raw bentonite was chemically purified according to classical purification method of Bergaya et al. 2013 [9,10] . About 25 g of raw bentonite was first dispersed in 400 mL of 1 M NaCl solution, stirred magnetically overnight and centrifuged at 3000 r/min for 2 h . Then , the supernatant liquid was added to the same volume of 1 M NaCl. This same process (agitation + centrifugation) was repeated several times to give sodium saturated bentonite (Na^{+} bentonite). Finally chloride free slurry was obtained by washing with deionized water (as confirmed with the silver nitrate test). The particles smaller than 2 µm (montmorillonite particles) were collected by sedimentation [11] (Fig.2)

C. Mineralogical analysis

Bentonite samples (natural and after treatment; RBN and RBN-1. RBN-2) were mineralogicaly characterized at the research center CRPEC (Centre de Recherche Scientifique et Technique en Analyses Physico – Chimiques - Bou Ismaïl) , with an X'Pert Pro PANalytical diffractometer (CuKα radiation), 40 kV accelerating voltage, and 20 mA intensity. The scan was recorded in the angular range of 2°–30° (2θ) with a step size 0.017° (2θ) and a scanning speed of 2° per minute [10].

D. Chemical analysis

Chemical compositions (major element contents) of all samples were obtained with a Philips X-ray fluorescence spectrometer, model PW2400 [10].

E. SEM observations

Morphological characteristics of bentonite samples were checked with scanning electron microscopy (SEM), using QUANTA 250 SEM equipment. The SEM images were acquired with an applied acceleration voltage of 300 kV [10]. The scanning electron microscopy (SEM) and chemical analysis are carried out at the research center CRPEC (Centre de Recherche Scientifique et Technique en Analyses Physico – Chimiques - Bou Ismaïl) .

D. Cation exchange capacity (CEC) and specific surface area (SSA)

SSA and CEC measurements were determined using the methylene blue method (spot test) [10, 12-13].

The CEC was computed by Eq. (1) [14]:

CEC = (100 • Vcc • Nmb) / ms (1)

Where, ms is the mass of the specimen (g), Vcc is the volume of the methylene blue titrant (mL) and Nmb is the normality of the methylene blue substance (meq / mL).

Specific surface area (SSA) values were calculated from the following Eq. (2) [13]:

$$SSA = \frac{1}{319.8}\ \frac{1}{200}\ (0.5N)\ A_V\ A_{MB}\ \frac{1}{10} \qquad (2)$$

where N is the number of MB increments added to the soil suspension solution, Av is Avogadro's number, and A_{MB} is the area covered by one MB molecule.

E. Particle size analysis

In this part, The raw and purified samples were studied by means of a laser granulometer Mastersizer (2000 Ver 4.00) to determine the range of particle sizes in our bentonite samples and to identify the efficiency of tow purification methods in separating the small particles from all materials.

III. RESULTS AND DISCUSSIONS

A. Mineralogical analysis of natural and purified bentonites (RBN, RBN-1 and RBN-2)

The mineralogical study aimed to determine the mineralogical composition of the clays studied before and after purification, and also to follow the influence of each purification method on the quality of bentonite clays . Comparative X-ray diffraction (XRD) diagrams for the RBN, RBN-1 and RBN-2 samples are presented in Figs. 3, 4 and 5 respectively.
The mineralogical analysis clearly reveal important significant differences. XRD results shown in Table1 indicate that the raw bentonite (RBN) within the Hammam Boughrara area is mainly composed of montmorillonite (~ 59%) and illite (~ 5%). The major non clay minerals are quartz (11%), feldspar (15%), calcite (5%) and (orthoclase + albite) (Fig. 3).
Compared with the raw material, the examination of the diffractograms recorded on the clay sample after the treatment by method 0-1(RBN-1) , the results demonstrated that an decrease in certain characteristic lines of the crystalline phases in the form of impurities, particularly those of quartz with a total disappearance of the intensity corresponding of feldspar (orthoclase + albite) and illite (Fig. 4).
On the other hand, XRD analysis of the purified sample RBN-2 showed that it was composed mostly of montmorillonite (≥ 99%). Quartz, feldspar and other impurities were totally absent (Fig. 5). The obtained mineralogical results confirms that the purification procedure as carried out, by method -2 is more efficient.

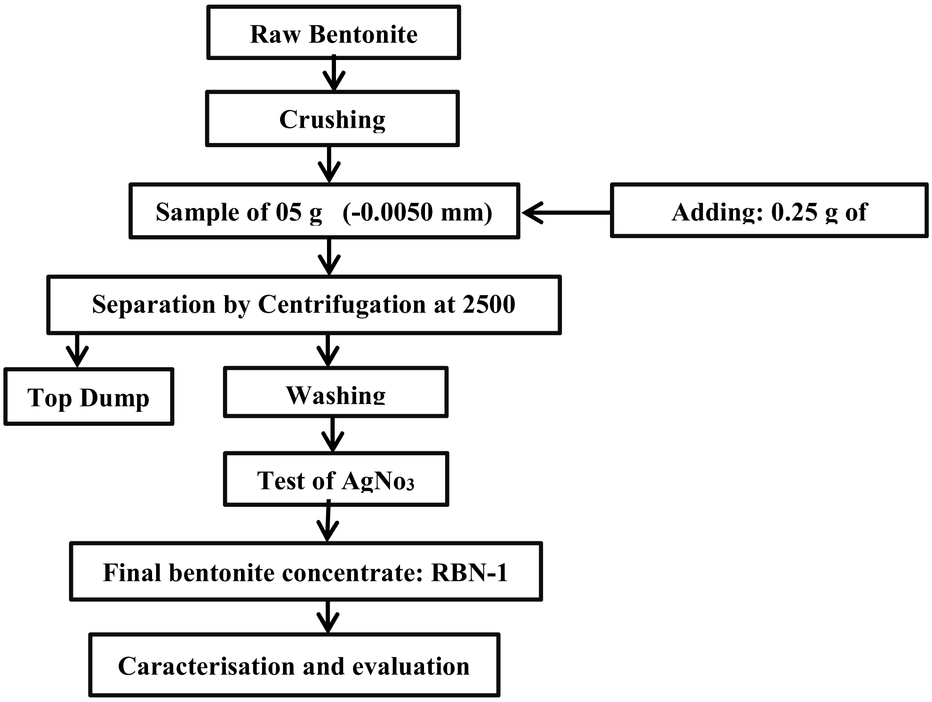

Fig. 1: Flow sheet of beneficiation by centrifugal scheme (method 1)

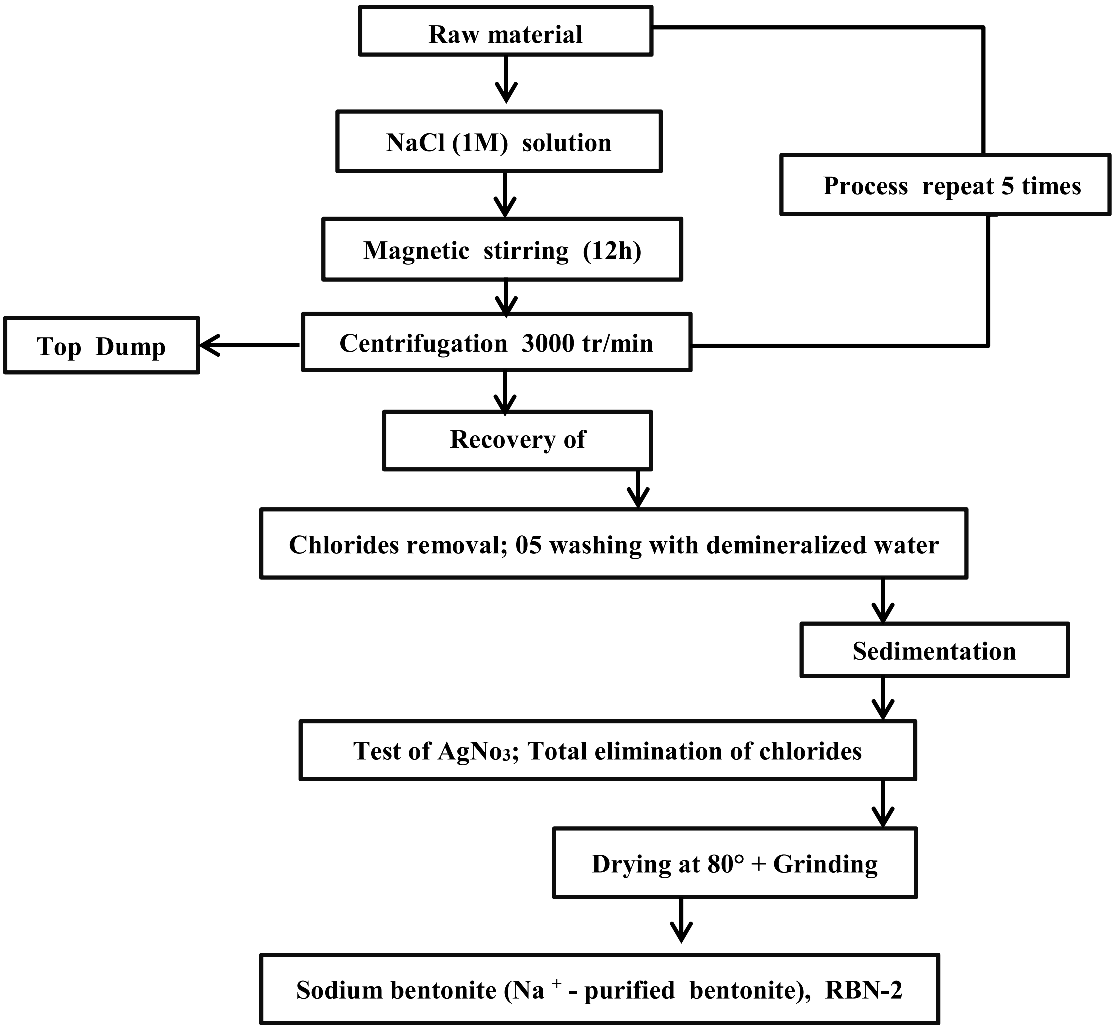

Fig. 2: Flowsheet of chemical purification by Nacl (method -2)

Table 1
MINERAL CONTENT OF RAW AND PURIfiED SAMPLES (RBN , RBN-1 AND RBN-2) DETERMINED BY XRD

Sample	Montmorillonite (%)	Illite (%)	Feldpar (%)	Calcite (%)	Quartz (%)
RBN	59	5	20	5	11
RBN-1	85	0	0	5	10
RBN-2	100	0	0	0	0

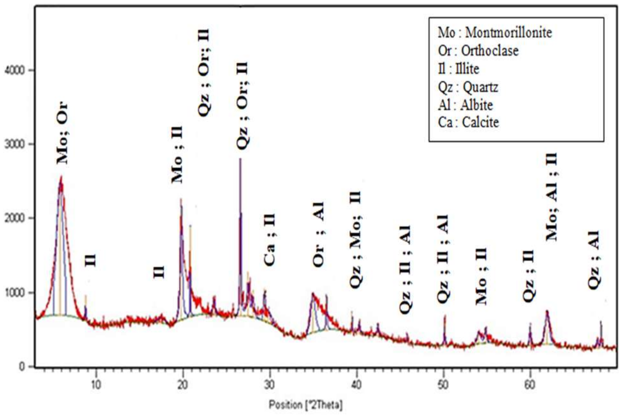

Fig. 3: X-ray diffraction patterns of RBN

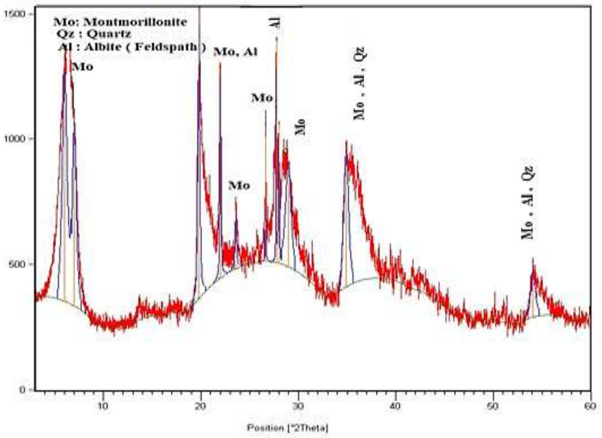

Fig. 4: X-ray diffraction patterns of RBN -1

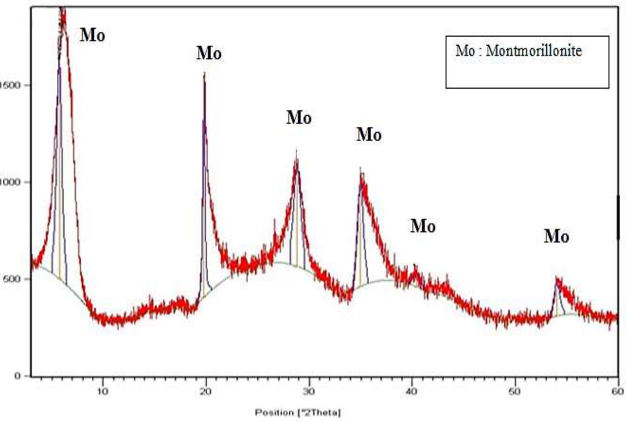

Fig. 5: X-ray diffraction patterns of RBN -2

B. Chemical analysis

The results of chemical compositions of bentonite samples (RBN, RBN-1 and RBN-2) are reported in Table 2. The major element oxides found in all samples were SiO_2, Al_2O_3 and Fe_2O_3, and small quantities of other compounds such as CaO, MgO, Na_2O, TiO_2 and SO_3. Increased silica (SiO_2 %) and alumina (Al_2O_3 %) contents in RBN-1 and RBN-2 were probably associated with the low percentages of quartz and feldspar minerals which is in agreement with the XRD data [15].
The contents of CaO and MgO were low for RBN-1 and RBN-2, which is related to the absence of carbonates. The purification process by two methods increased the content of TiO_2 and SO_3.
High amounts of Na_2O were observed in the RBN-2 sample, and this difference was due to the transformation of Ca^{2+} bentonite into Na^+ bentonite [16].

C. SEM observations

The studies by SEM were conducted to study the change in morphological characteristics of natural and purified samples. The images obtained by scanning electron microscopy of all samples bentonite, with different magnifications, are shown in the figures 6 A, B, D, E, F . The original bentonite (RBN) was composed of large pseudo spherical aggregates of smectite, generally sized from 5 to 100 µm (Fig. 6A, B) and Most of the particles were unconnected from each other.
In the case of purified bentonite method 1(RBN-1) , an excess of bentonite clay is observed in irregular angular shape and the presence of a greater proportion of spherical particles, and association of small circular particles generally sized from 10 m to 100 m (Fig. 6C,D). It also reveals that the surface morphology was almost compact as the same of natural sample.
After purification with NaCl (RBN-2), the surface morphology was changed significantly. When looking at higher magnification, we can observe a significant presence of macros pores arranged in the form of sheets for the sodium bentonite (Fig. 6E, F) and which we did not observe on the raw material. This is probably due to the various processing steps that the clay raw material has undergone (sodification by NaCl + sedimentation and total elimination of impurities) at the side surfaces of the particles.

Table 2
CHEMICAL COMPOSITIONS OF THE RAW AND PURIFIED BENTONITE EXPRESSED AS WEIGHT PERCENT OF MAJOR ELEMENT OXIDES BASED ON X-RAY ﬂUORESCENCE ANALYSES

Sample	SiO_2 (٪)	Al_2O_3 (٪)	Fe_2O_3 (٪)	MgO (٪)	CaO (٪)	Na_2O(٪)	K_2O(٪)	TiO_2(٪)	SO_3(٪)	LOI(٪)
RBN	51.47	18.50	2.66	6.16	2.86	1.72	1.14	0.25	0.34	17.19
RBN-1	53.80	19.10	1.8	5	1.5	1.65	1	0.35	0.2	15.60
RBN-2	56.40	19 .22	2	3.11	1.56	3.12	1	0.45	0.56	12 ,58

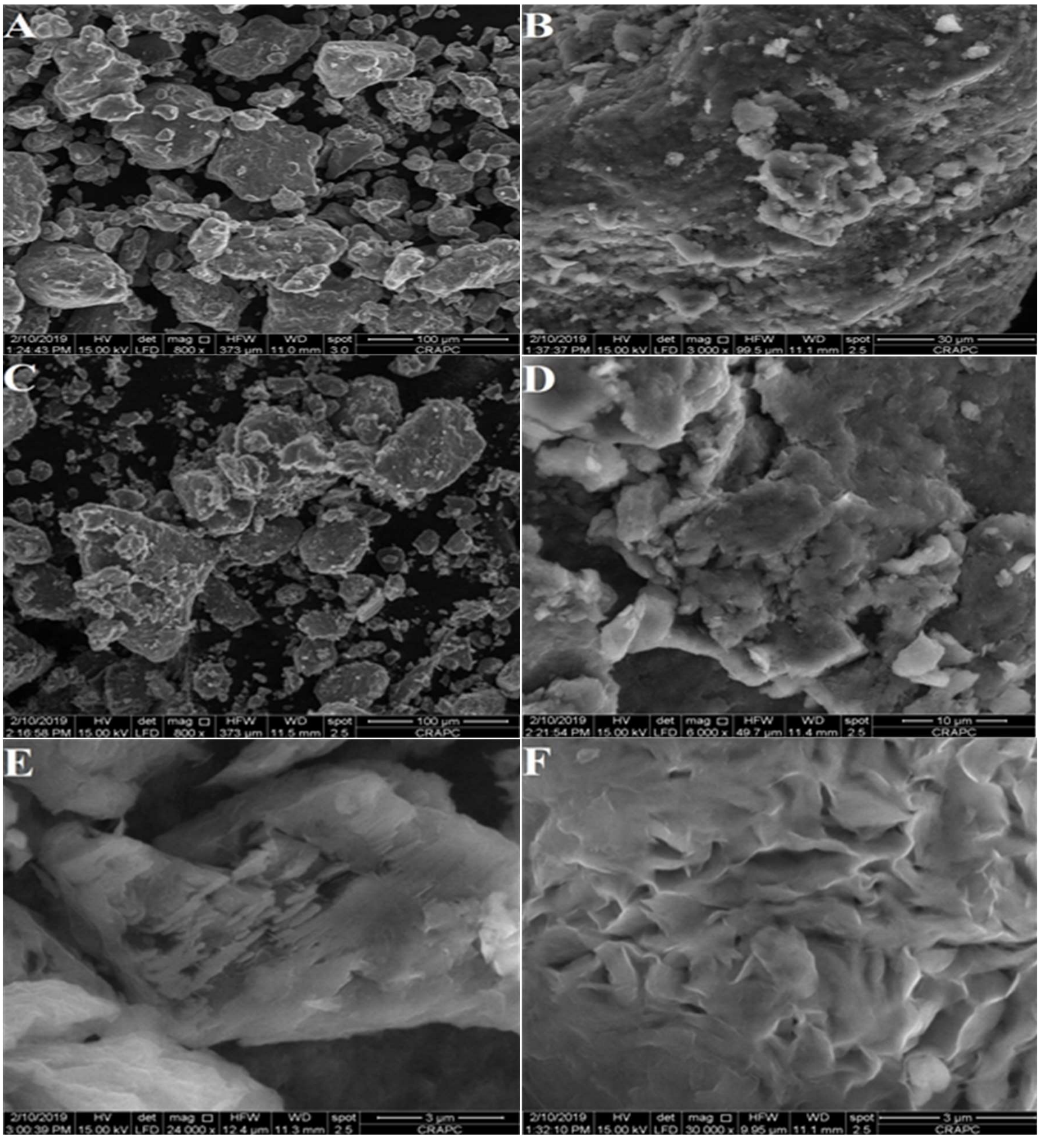

Fig. 6: SEM images of RBN (A, B), RBN-1(C, D) and RBN-2 (E, F)

D. Cation exchange capacity (CEC) and specific surface area (SSA)

CEC and SSA values of natural and purified bentonite samples (RBN , RBN-1. RBN-2) are illustrated in Table 3. Significant increases in CEC and SSA were observed (Fig.7 A and B, respectively). The cation exchange capacity CEC ranged from 61.76 to 70.36 and to 88.20 meq/100 g for RBN-1 and RBN-2 , respectively . These results could be related to the mineralogical changes that occurred in the clay minerals. Also, this increase in CEC is caused by the complete conversion of natural bentonite to Na + bentonite and therefore replacement of the pre-existing interlayer cations with sodium cations occurs and gives the maximum CEC value of 88,20 meq. / 100g.
Purified bentonite RBN-2 has a specific surface area of 677.7 m2/g), greater than the raw bentonite RBN (474.64 m2 / g) and RBN-1 (540.70 m2 / g).
This significant increase in SES is due to the total removal of impurities and the high purity and high montmorillonite content obtained by purification (method -2).

Table 3
CATION EXCHANGE CAPACITY (CEC) AND SPECIFIC SURFACE AREA (SSA) VALUES OF RAW AND PURIFIED SAMPLES

Sample	RBN	RBN-1	RBN-2
CEC (meq/100g)	61.76	70.36	88.20
SSA (m^2/g)	474.64	540.70	677.71

E. Particle size analysis

RBN-1 sample showed a broad particle size distribution with high volume percentages centered at 5 µm and 11 µm, which were attributed to quartz, feldspar and other impurities [10]. (Fig. 8).
In the case of RBN-1, we did not see a big change in the particle size distribution compared to RBN; this may be explained by the mineralogical composition of RBN-1, which may be the same with the RBN.
After beneficiation by NaCl, the volume percentage of the fine particle size increased dramatically compared to RBN and RBN-1 samples, and two maxima (one centered at 0.3 µm and the other centered at 1.5 µm) were attributed to the purity of RBN-2 clay (100% of montmorillonite) [10].

IV. CONCLUSION

In this study, Algerian bentonite samples underwent physical and chemical purifications in order to evaluate the efficiency of tow methods and their characteristics were analyzed using different methods. Raw bentonite clay is composed of montmorillonite (59%) associated with variable proportions of quartz, feldspar and calcite. The chemical compositions indicated that SiO_2 (51.47%), Al_2O_3 (18.50%) and MgO (6.16%) are major elements while Ti_2O_3 is less abundant (0.25%).The efficiency of chemical treatment (by NaCl) is clearly approved, because it allows a better increase in the content of montmorillonite. Moreover, this method leads to a total disappearance of impurities and especially of quartz and feldspar. Physicochemical characterizations showed that purified bentonite by method-2 (chemical purification by NaCl) has a higher values of cation exchange capacity (CEC) and specific surface area (SES).

On the basis of bulk mineralogical composition, chemical and physical properties of Algerian bentonite indicate that the purification by chemical procedure is more efficient and the treated bentonite (by NaCl) could be potential materials for industrial applications.

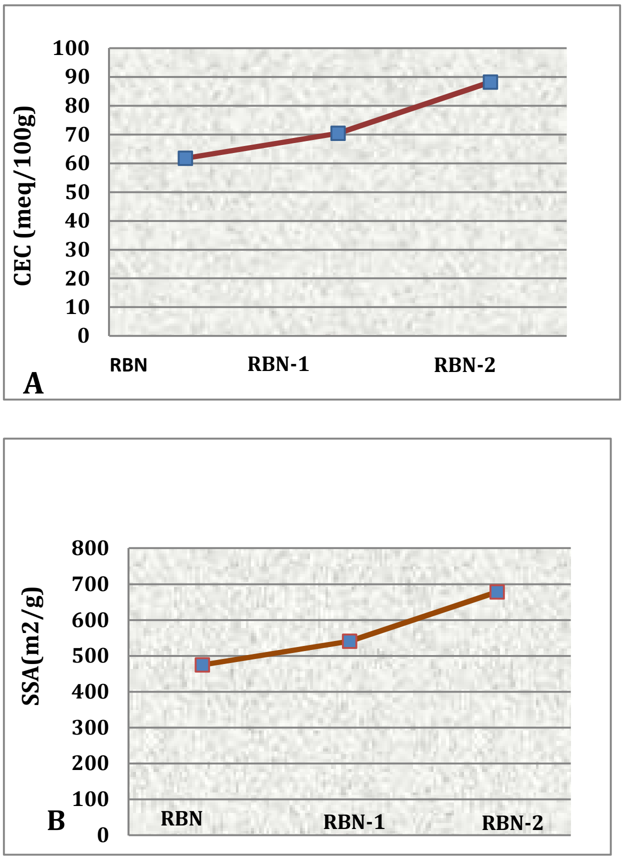

Fig. 7: **A**, variation of CEC values in RBN, RBN-1 and RBN-2; **B**, variation of SES values in RBN, RBN-1 and RBN-2

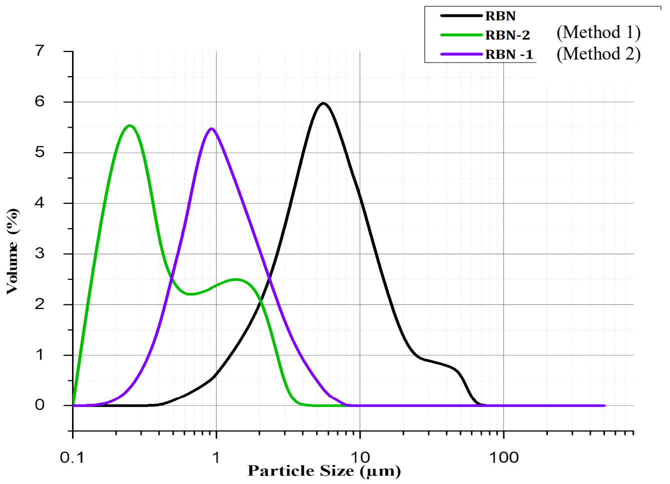

Fig. 8: Distributions of particle sizes for RBN, RBN-1 and RBN-2 bentonite clay

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