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Physico-Chemical charaterisation of Sabon-Karré's Clay.

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Abstract

Clay samples taken at Sabon-Karré in the region of Tahoua (Niger Republic) have undergone a series of mineralogic, chemical and physico-chemical analysis. The analysis show that the clay minerals are mainly formed of smectite (72 %) associated with kaolinite (19 %) and illite (2%).The interstratified Illite / Smectite represents 7 %. The clay phase < 2µm represents 26, 78% of the rock mother. The ICP-AES chemical analysis shows that this clay is in majority composed of SiO_2, Al_2O_3, Fe_2O_3 MgO, Na_2O, and does not present any harmful elements. The granulometery laser shows that 26, 78% of these particles have a diameter inferior to 2µm. The samples'thermic behavior shows that losses of water humidity and interfoliar water occur between 30 and 130 °C the loss of constitution water at 530°C. The clay decarbonation occurs between 900 and 1000°C. These results compared to those of literature enable to state that the Clay of Sabon-Karré is bentonite.

Key words : clays, processing, characterization, water.

1. Introduction

Bentonites are natural aluminosilicates phyllithe frequently used as reiforcing agent of hydraulics' works, waters treatment, clarification of vegetable oil and wine, the manufacturing of cosmetic products supports of catalysers [1, 2]. They are either used at natural level, or treated by various methods in order to improve certain of their caracteristics [3]. Some developping countries like China, India have developped semi-handicraft technologies on the basis of natural and local materials. (calcinated bone, gyps, clay…) at a cheaper price allowing the purification of drinking waters in rural households. The work that we are presenting here, physico-chemical caracterisation of Sabon-Karré's clay enters in this perpectives. In fact, Niger has a surface area 1.267.000 km^2 out of which the saharan zone represents 65% of the national territory. In some zones, the enthusiasm to find water permitted to relegate to the second plan its quality. The water supply rate is inferior to 20 %. The rural populations still get drinking water from ponds during the rainy seasons, and from wells during the dry season. Flowing waters forming these ponds during their run, cherish many organic and mineral wastes for home usage, these populations only use decantation to clarify the water. Compared to the modesty of the potential in drinkable water in Niger, it is advisable to better manage this commodity by promoting and popularizing purification technologies of surface waters and polutted sheets, but also by recycling exhausted waters for agricultural need.

2. Experimental

Clay samples were taken at Sabon-Karré in the region of Tahoua (Niger) which GPS co-ordinates are: height 348 m; Latitude 13° 58' 29'' N; Longitude 5° 42' 55'' E. These samples underwent physico-chemical characterization tests using different qualitative and quantitative analysis methods.

2.1. Granulometery laser

The representative sample has been grounded using an agate and siftered using a sifter of 125 µm diameter. A portion of the fraction inferior to 125 µm has been dispersed into 100 ml of pure water and treated by ultrasound for 30 mn.

2.2. Analysis by X rays diffraction

The rough clay (the entire rock) as well as the clay fraction (particles of size inferior to 2 µm) have been identified by powder X rays diffraction and over orientated agregates (natural condition, saturation at ethylen-glycol, heated at 490°C for four hours). The samples have been caracterized using a Brüker D5000, X-ray diffractometer in a $\theta/2\theta$ mode (Scanning range of 3 to 15° or 3° to 30°, with a scan speed of 0,02° per second, using a Cu, 40 kV – 30 mA anticathode).

2.3. Infrared Spectrometer I (IR)

Infrared analysis has been done by the mean of an universal ATR (Attenuated Total Reflectance) PERKIN ELMER spectrometer prototype with sampling accessory.

2.4. Thermal analysis

The thermal analysis has been made by the mean of a Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA).

2.5. Chemical analysis

The elementary analysis has been done by the mean of a Varian Liberty 220 ICP/AES spectrometer. The choice of analytical rays has been done in such manner to avoid spectral interfaces in the emission of inductive plasma.

2.6. Capacity of cationic exchange

To determine the Capacity of Cationic Exchange (CCE) of ours sample, we used the method of hexammine cobalt (III).

2.7. Nitrogen adsorption- desorption isotherms

The isotherms of nitrogen adsorption–desorption have been measured over a Thermofinnigan device; model Sorptomatic 1990 at 77K.

3. Results and Discussion

3.1. Laser granulometery

The laser obtained granulometery curve (figure 1), shows that 26, 78 % of particles have a diameter inferior to 2µm. The clay being formed of less 2µm fraction, we can conclude that within the samples taken at Sabon-Karré, the clay fraction represents 26, 78 % of the pristine rock (Figure 1).

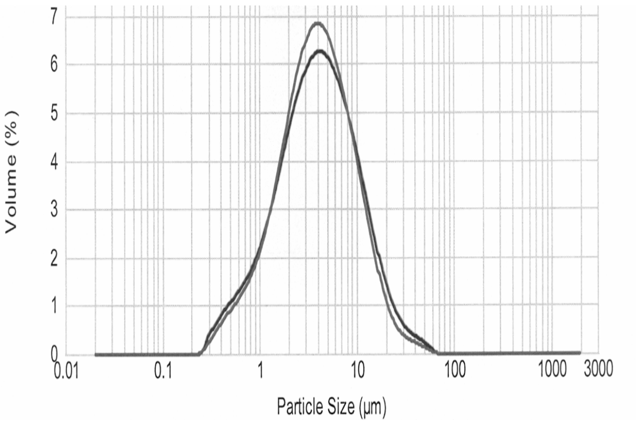


Figure 1. Laser granulometry of Sabon-Karré clay.

3.2. Analysis by X-rays diffraction.

Taking in consideration only the spectrum of an orientated preparation dried at free air, some clay minerals are not dissociable (example : the peak at (001) of the kaolinite corresponds to 7,15 Å coincides with the (002) peak of chlorite). That is the reason why four spectra are recorded (figure 2). The spectrum 1 is recorded under normal essay conditions (measurement of orientated preparation dried at free air). The spectrum 2 is recorded after a treatment at ethyle-glycol. This treatment is aimed to swell the smectitic layers by introducing ethylene glycol molecules of big size within the interstitial space. Spectrum 3 is recorded after a treatment at hydrazine. The objective here is to distinguish the kaolinite in presence of chlorite by « pumping » minerals of kaolin family. The spectrum 4 is recorded after heating the sample for 4 hours at 490°C. At this temperature the kaolinite is destroyed; the vermiculites and the smectites dehydrated.

The X-rays analysis at normal essay conditions of the total rock shows peaks at *d* (001): 7, 14 Å and d (002): 3, 56 Å characteristics of kaolinite. The peaks at *d* (001): 14, 59 Å; d (003): 4, 96 Å are caracteristics of smectite. With the essay using the sample treated at ethylene glycol, we observe the same peaks of kaolinite at about 7,15 Å and 3,57 Å, but those of smectite have shifted to 8, 5 Å and 17 Å. With the treatment at hydrazine, the peaks of smectite disappear. We therefore observe the ordinary *d* (001) diffraction: 10, 33 Å of the kaolinite and *d* (001): 7, 16 Å and the disorganized kaolinite. By heating at 490°C during 4 hours the peaks of the kaolinite disappear. On the other hand, a peak at *d* (001): 9, 86 Å of the smectite is observed.

On the spectrum of fraction less than 2 µm diameter (figure 3), in addition to the peaks of the kaolinite and the smectite, appeared the peaks of the illite, which implies the presence of an interstratified Illite / Smectite [5-6].

The spectra of normal essays have been decomposed by using profiles of peak Pearson types VII for all clay phases. The peaks related surfaces represent the relative abundance of different mineral clays and amounted to: pumped up (Smectite 72%, Illite/Smectite 7 %) and non-pumped up clays (kaolinite 19 % and Illite 2 %).

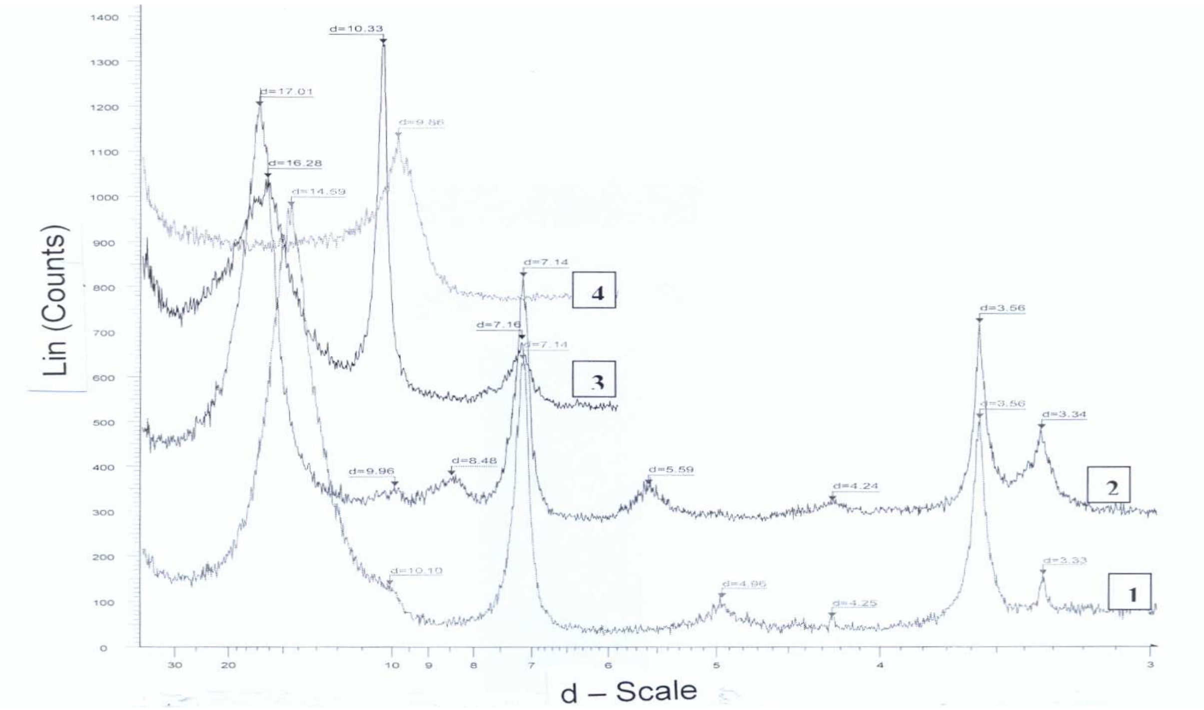


Figure 2 : X-ray diffraction of total rock.

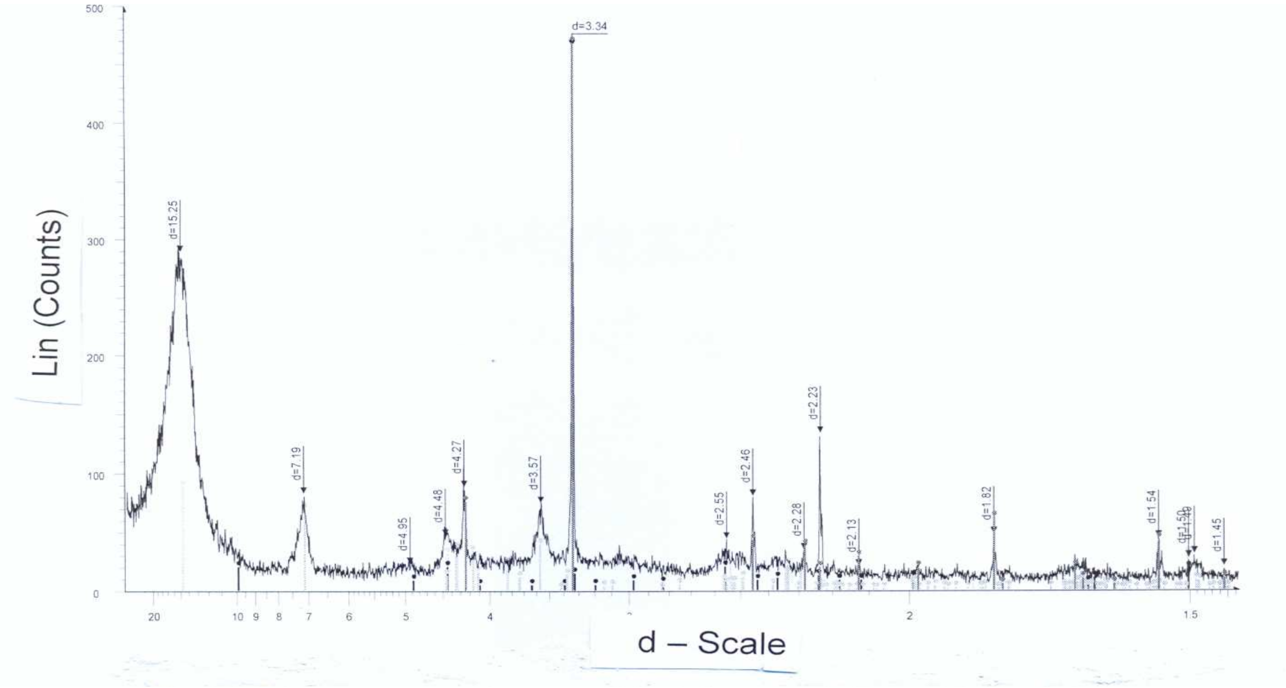


Figure 3 : X-Ray Diffraction of fraction less than 2µm diameter.

3.3. Infrared Spectrometry (IR)

On the IR spectrum of Sabon-Karré clay, we observe several bands between 4000-650 cm^{-1}. The band at 3620 cm^{-1} is attributed to hydroxyls groups being situated between octahedral and tetrahedral layers. The bands at 3620 cm^{-1} and 911 cm^{-1} confirm the dominant presence of di-octahedral smectite with (Al, Al-OH). The absorption bands at 1110 cm^{-1} and 1000 cm^{-1} show the presence of (Si-O) links of kaolinite. The one at 1024 cm^{-1} is attributed to montmorillonite [7]. The band at 796 cm^{-1} shows the presence of quartz [8-9].

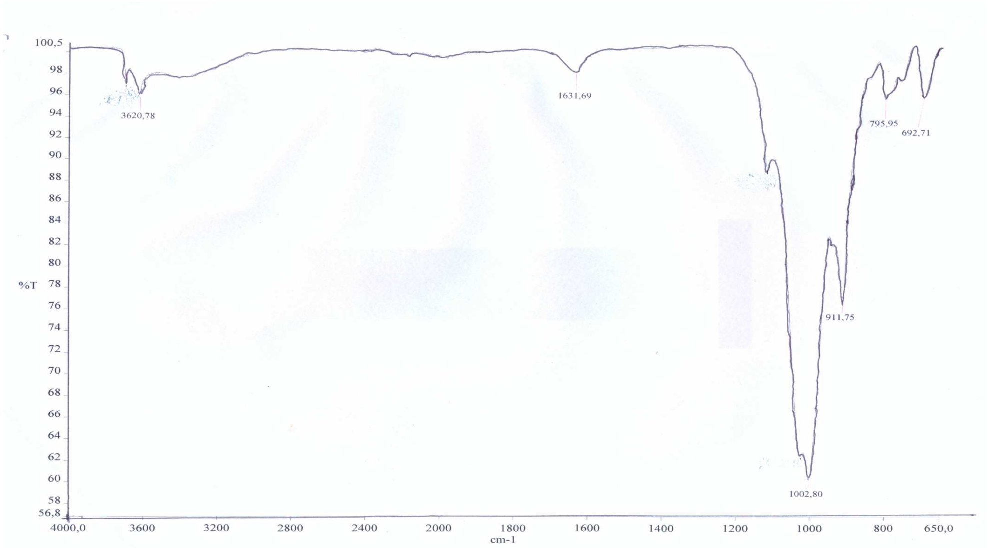


Figure 4 : IR Spectrum of Sabon Karré clay.

3.4. Thermal analysis

That ATD curve (figure 5.a) presents three peaks, the first one endothermic, very intense at low temperature (30-130°C), a second one, endothermic and less intense between 450-550°C and an exothermic peak between 900-1000°C. These peaks are caracteristic montmorillonite [9]. The ATG curve (figure 5.b) allows to follow the loss in mass of samples. Three losses in mass have been observed. The losses humidified water and interstitial water occur at between 30 and 130 °C, and the loss of water of constitution at 530°C. The decarbonatation of the clay occurs at between 900 and 1000°C [10]. The intensity of the first endothermic peak confirms the presence of a swelling phase (smectite) interstratified with a non-pumping phase illite) [11].

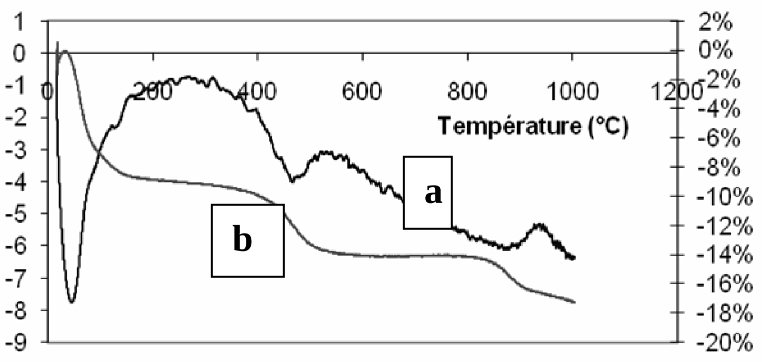


Figure 5 : Thermal spectrum DTA (a) and TGA (b) of Sabon Karré clay.

3.5. Chemical Analysis

The elementary chemical analysis has been done with the help of spectrometer Varian Liberty 220 ICP/AES. The choice of analytical rays has been made so as to avoid spectral interfaces which are major problems in the emission of spectrometry in Inductive Coupled Plasma. The results of the chemical analysis of the total rock are reported in table II.

Table II. Chemical composition of total rock.

Oxydes	**%**
SiO_2	54,59
Al_2O_3	15,77
Fe_2O_3	3,80
MgO	5,58
Na_2O	3,00
K_2O	0,09
CaO	0,07
MnO	0,02
TiO_2	0,007

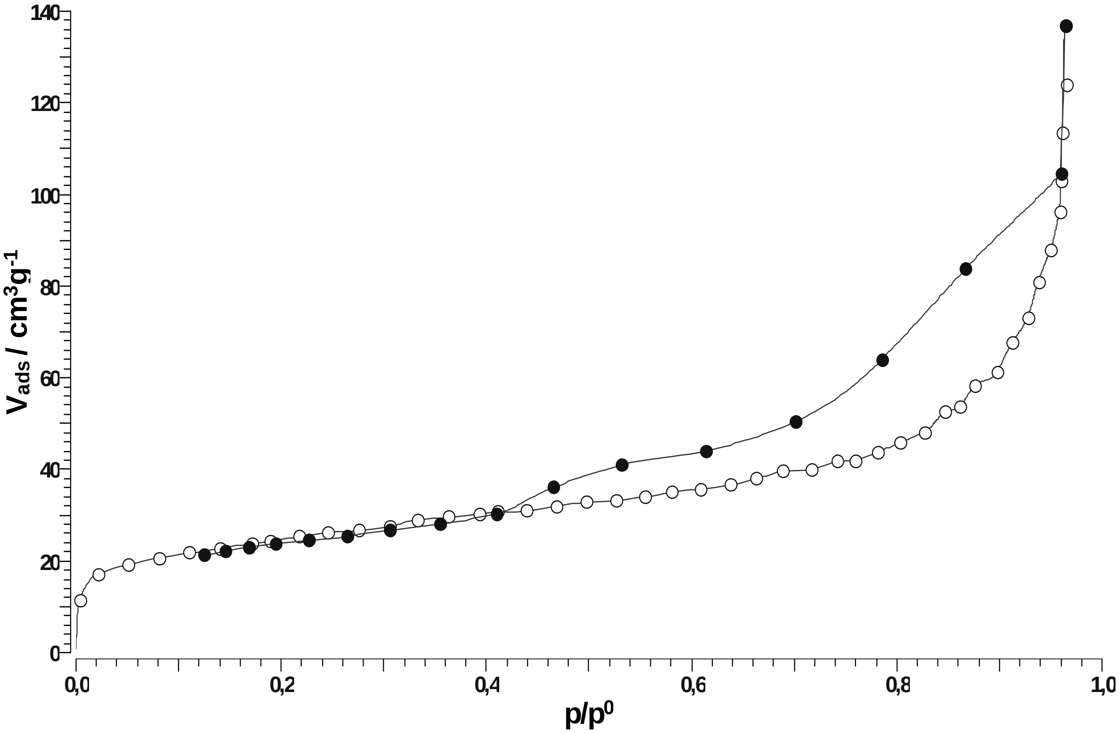
The loss in heat of the total rock is of 17 %.
The SiO_2 / Al_2O_3 ratio which is of 3.4 is higher than the classical value of 2.7 bentonites. This difference can be due to the presence of free silica [9].

3.6. Cationic Exchange Capacity

The Cationic Exchange Capacity (CEC) is a measurement of the ions quantity likely to be kept by exchange over a solid, in presence of an excess of exchange ions in solution. It corresponds to the necessary charge to reach the electroneutrality of the solid.
This exchange capacity can be cationic or anionic (CEA), depending on the surface of the medium, be it positively or negatively charged. Determining the CEC of a solid consists in measuring a parameter characterising a state of equilibrium between the sample and a given experimenral. To determine the CEC of our sample we have used the method of hexamminecobalt chloride (III). The cationic exchange capacity has been obtained at 69.89 meq/100g of the equilibrium. This shows that the medium possesses relatively big numbers of exchange sites [12]. This value of the CEC enters in the range of certain commercial bentonites CEC [9]. The raw clays present values which have relatively elevated cationic exchange capacity, but which still remain inferior to the given values of pure smectites [13]. The weak values of the cationic exchange capacity of raw clays are due to various factors such as bad crystallinility of the smectite and the presence of kaolinite and illite within the clay fraction [13-14].

3.7. Nitrogen adsorption and desorption isotherms

The volume of pores at p/p° = 0.95 is of 0.136 cm^3/g. The specific area is of 85.83 m^2/g. The full points on the graph (figure 6) materialize the isotherm of desorption and the empty points isotherm adsorption. The BET (figure 7) method have been used to determine the specific area of the sample which gas has been extracted primarily degasified under emptiness at 300°C during 6 hours. The t – plot method (figure 8) has been used to determine the specific area developped by mesopores and the volume developped by micropores of the sample. These values are respectively of 48.38 m^2/g and 0.0191 cm^3/g. The B.J.H method (figure 9) has been used to determine the cumulative volume of the sample's mesopores. It is of 0.2091 cm^3/g.



Figue 6. Nitrogen adsorption and desorption isotherms.

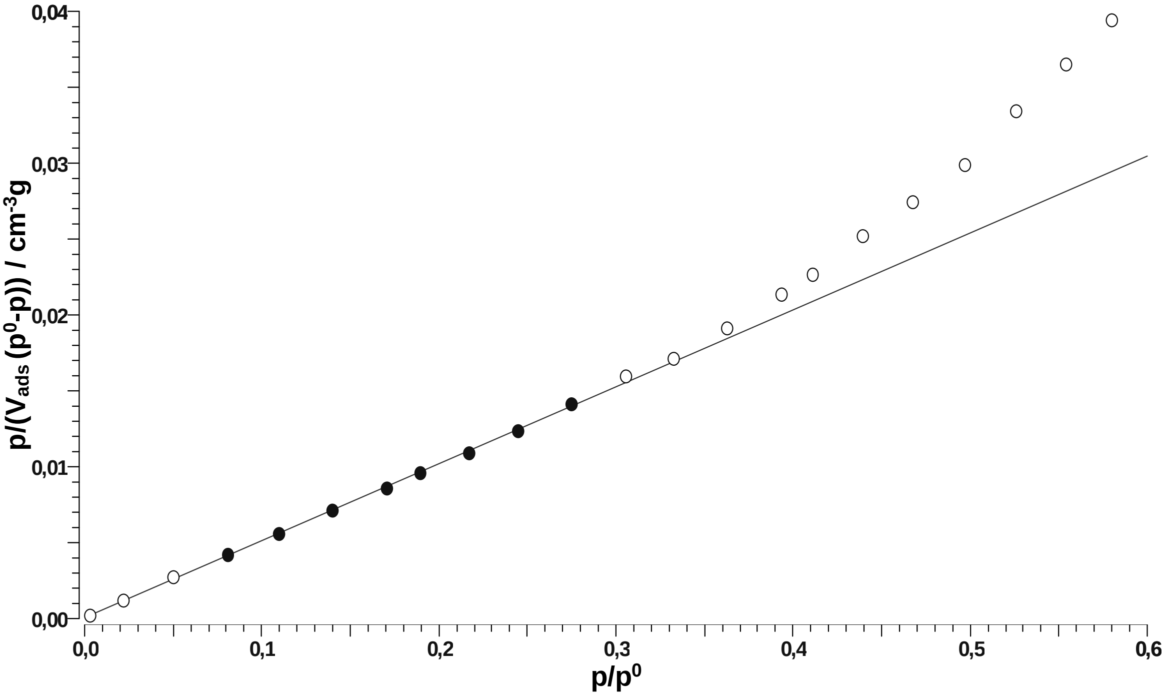


Figure 7. B.E.T method of Sabon Karré Clay.

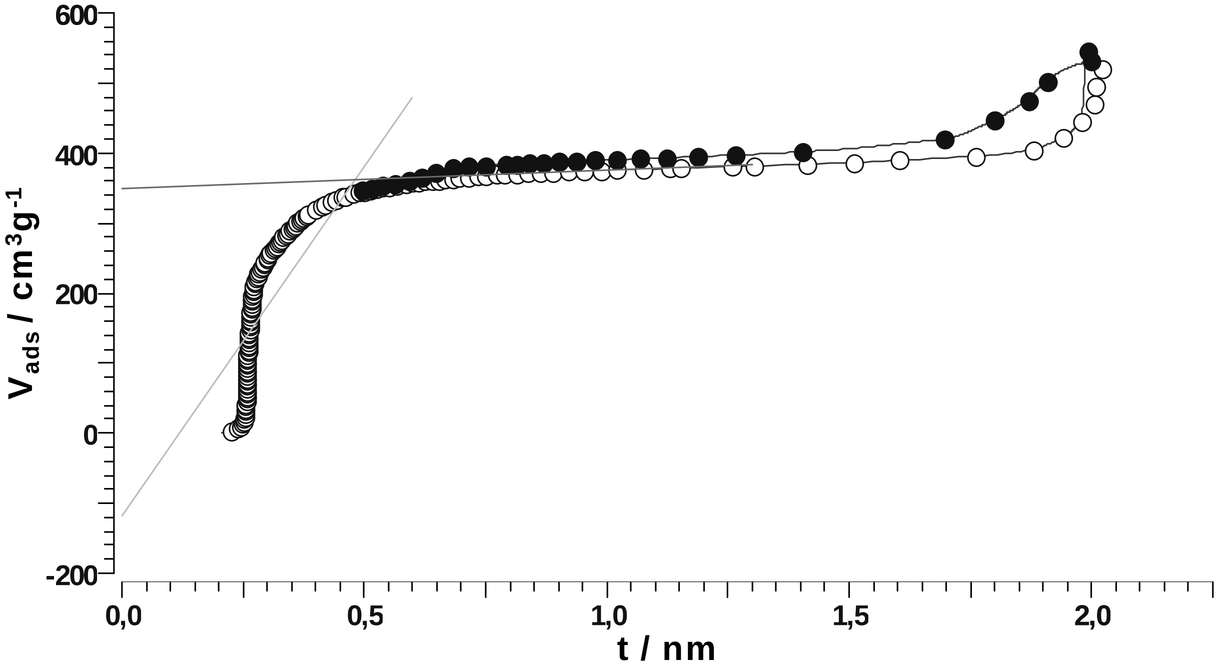


Figure 8. t-plot method of Sabon Karré clay.

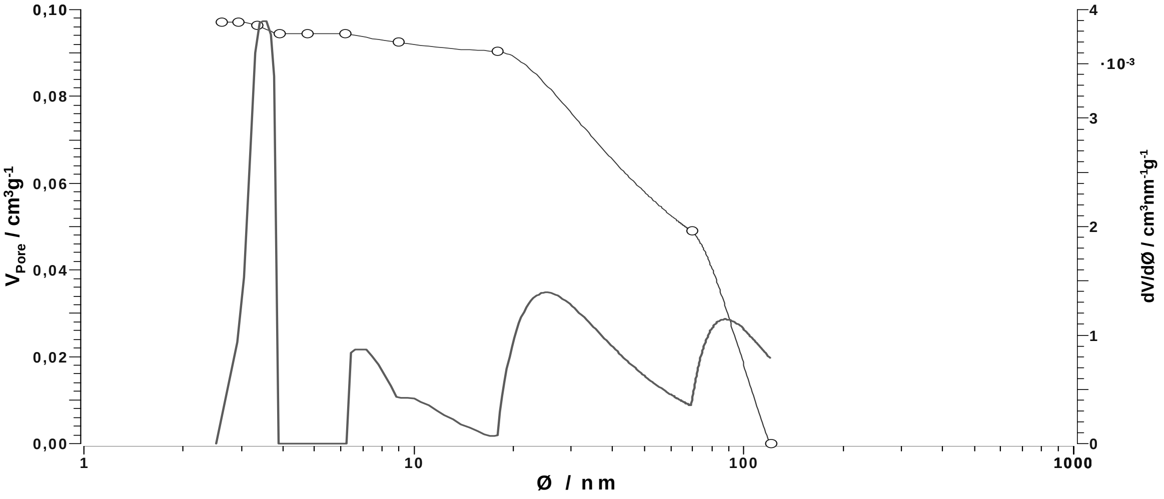


Figure 9. B.J.H method of Sabon Karré clay.

Conclusion

Different analysis techniques used in this work (The X-Ray Diffraction, The IR spectrometry, the Cationic Exchange Capacity (CEC) value as well as the specific area measurements) allowed the characterization of the Sabon Karré clay. These analysis show that the clay is of smectitic type. It contains kaolinite and very little illite. The values of Cationic Exchange Capacity and the specific surface of this clay are relatively high. From an application point of vue, the clay of Sabon-Karré is sweetable for use in the field of treatments of waste and drinkable waters as part of village hydraulics.

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