

Mineralogical, structural and physicochemical characterization of a green clay from Tanout Quarry in Zinder region (Niger), used in the brickyard.

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Abstract:

This work aims to identify the mineral phases, the chemical composition, the textural characteristics (specific surface, pore volume and pore size) and physicochemical characteristics of a green clay of Tanout from Zinder region (Niger) in order to judge on its possible use in water treatment. The methodology is based on mineralogical analyzes (X-ray fluorescence, X-ray diffraction, thermogravimetric analysis, scanning electron microscopy), textural (adsorption of N₂ at 77 K by the Brunauer-Emmett-Teller method) and physicochemical (preliminary analyses). The results obtained show that green clay is mainly composed of SiO₂ (56.1%), Al₂O₃ (14.3%) and Fe₂O₃ (8.06%) with trace elements including, among others, Zr (1400.2 ppm), Sr (780.34 ppm), Cu (430 ppm), V (560 ppm) and Zn (190 ppm). It consists essentially of Montmorillonite and Kaolinite with impurities such as quartz and microclines. This clay has an important degree of crystallinity with specific surfaces of 437.8 m².g⁻¹ and 3840 m².g⁻¹ calculated according to the BET and Langmuir methods respectively and a microporous surface of 463.1 m².g⁻¹, with pore volume varying from 0.0124 to 0.2439 cm³.g⁻¹ and pore size varying from 1.847 to 6.399 nm calculated according to the methods (Barrett-Joyner-Halenda, Dubinin-Radushkevich, Dubinin-A, Horvath-Kawazoe and Saito-Foley). It has slit-shaped micro-pores, cylindrical-shaped mesopores with a neutral pH in aqueous medium, a high cation exchange capacity, low humidity rate and density. These characteristics make it a promoter material that can be used in water treatment.

Keywords: Green clay, Mineral phases, Structural, Tanout, Zinder.

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I. Introduction

Characterization is the most appropriate method for the recovery of clay materials regardless of their field of application. However, several techniques exist allowing a perfect understanding of the mineralogical, chemical, textural and structural composition of a clay material such as X-ray diffraction, X-ray fluorescence, thermogravimetric analysis, adsorption of nitrogen by the BET method. Indeed, the interest given in recent years to clay materials is due to their textural and mineralogical properties, their natural abundance¹ and their applicability in several fields. They are generally used in the ceramic industry, the cement industry, metal alloy², adsorption.... In addition, the field of adsorption is very attractive for the recovery of clay materials. In Niger, this area remains stationary where we note the studies carried out in Tahoua region and in Tillabéry region on the adsorption of fluoride ions and copper ions respectively^{3,4}. It is in this context, in the research and development of materials of natural origin, a green clay from a quarry in the municipality of Tanout was characterized in order to assess its characteristics and to judge its possible use in this domain.

II. Material And Methods

Sampling

The green clay sample was taken from a quarry located south of the urban township of Tanout in Zinder region of Niger (Figure 1). This clay is generally used in the brickyard for the construction of individual dwellings. This quarry has the following geographical coordinates: 08.52363° longitude and 14.57447° latitude. The sample taken is named Arg3-B.

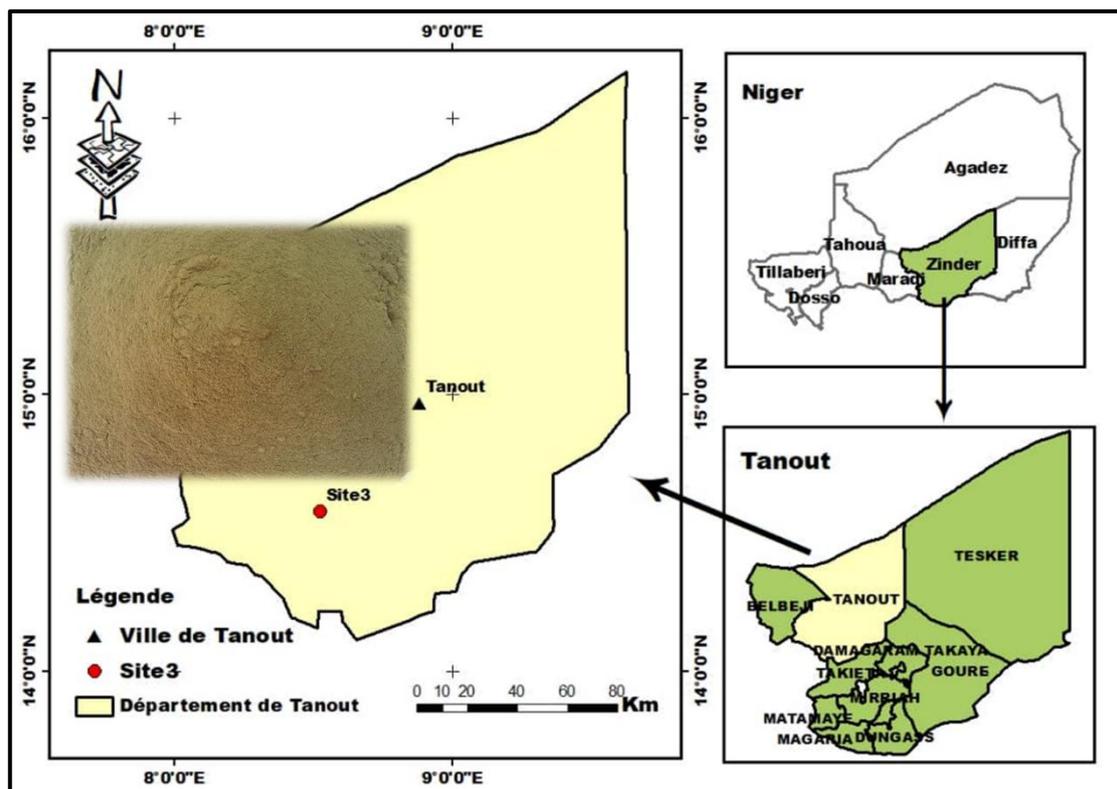


Figure1: Presentation of the study area and the sampling site

Crushing, grinding and sieving

The green clay used in this study was crushed, then ground using a jaw crusher and sieved using a 200 μm grain size sieve (Figure 2). This step eliminates a number of impurities such as quartz and reduces the clay into millimetric fragments. These operations were carried out at the Second Year Chemistry Laboratory (SYCL) of the AMU.



Figure 2: Crushing, grinding and sieving green clay

Process for extracting the clay fraction < 2 μm

The extraction of the clay fraction is a process which makes it possible to eliminate certain accessory minerals (quartz, carbonates, feldspar, etc.) and to extract the fine fraction rich in clay minerals. The method used was developed by *M. Robert and D. Tessier* in⁵. The clay fractions resulting from this analysis were named Arg3-FNa⁺ and Arg3-FSNa⁺.

Green clay pH

The pH was determined to quantify the contribution of acidity when the solid is in contact with the solution. The technique consists in bringing 1g of green clay into contact with 100 ml of distilled water under magnetic stirring at room temperature for 2 hours. After filtration, the pH of the filtrate was measured. Thus,

increasing masses of green clay (1, 3 and 5 g) were brought into contact with 50 ml of distilled water under magnetic stirring at room temperature, then the mixture was left to stand for 24 hours in the purpose of verifying the effect of the clay mass on the pH. Finally, the pH of Arg3-B was measured *AFNOR in*⁶.

Cation exchange capacity (CEC) by conductimetry

The conductometric method has been used to determine the cation exchange capacity of green clay^{6,7}. The technique consists of putting 1 g of green clay in 100 ml of distilled water under magnetic stirring at room temperature for 2h 30'. After adding 150 ml of a 1 M BaCl₂ solution while adjusting the pH to that of green clay, the suspension was left under stirring for 2h 30'. Then the suspension was filtered and washed to a negative AgNO₃ test, then oven-dried overnight at 60°C. After grinding, 0.5 g of treated clay was brought into contact with 50 ml of distilled water under magnetic stirring at room temperature for 2 hours followed by conductometric titration with a 0.02 M MgSO₄ solution. At each addition of 0.5 ml of MgSO₄ solution, the conductivity value was noted after stabilization. Finally, the curve of conductivity as a function of the volume of MgSO₄ poured was plotted and the equivalent point which corresponds to the intersection of two half-lines tangent to the curve was determined. The CEC was calculated by the following formula :

$$CEC (meq. 100g^{-1}) = 2Cx \frac{V}{m} \times 100 \quad (1).$$

Humidity rate

The evaluation of the humidity rate can be indicative of the hydrophilic behavior of adsorbent materials. The technique consists in weighing the empty crucible by noting its weight P, then the hollowed one containing 2 g of clay by noting its weight P₁. The assembly was brought to an oven at 105°C for 24 hours, then cooled in a desiccator for 30' while again weighing its weight P₂. The humidity rate of green clay was calculated by the following formula⁸.

$$H(\%) = \frac{P_1 - P_2}{P_1 - P} \times 100 \quad (2)$$

Density

Density is the set of solid and pore fractions. In the case of this study, it was determined by the test-tube method. This density was calculated by the following formula :

$$\rho (g. cm^{-3}) = \frac{P_2 - P_1}{V} \quad (3).$$

pH at point of zero charge (pH_{PCN})

The pH_{PCN} corresponds to the pH value for which the net charge of the solid surface is zero. The technique consists of putting 50 mg of clays in 50 ml of distilled water with a pH between 2 and 12 (adjusted by solutions of HCl and 0.01M NaOH) with magnetic stirring at room temperature for 24 hours. Afterwards, the final pH of the suspension was measured and the graph pH_f – pH_i as a function of pH_i was drawn. The isoelectric point corresponds to the intersection of the curve and the straight line which passes through the origin⁹. This parameter was determined for green clay and its clay fractions < 2 μm.

Loss on ignition (LOI)

The green clay was subsequently heated to 1000°C for 2 hours to determine the LOI. The latter was determined gravimetrically by heating 1 g of powdered clay in a cleaned weighed crucible to 1000°C. Then the crucible and contents were weighed to obtain the difference in weight before and after heating. The following formula was applied to determine the LOI.

$$LOI = \left(\frac{a-b}{a} \right) \times 100 \quad (4).$$

With: a = weight of the crucible + 1 g of the sample before heating, b = weight of the crucible + 1 g of the sample after heating. The analysis was carried out at the National Geoscience Research Laboratories (NGRL) in Kaduna (Federal Republic of Nigeria).

X-ray fluorescence spectrometry (XRF)

To determine the chemical composition of our samples (Arg3-B and Arg3-FNa⁺), an energy dispersive X-ray fluorescence spectrometer (EDXRF) of the "Minipal 4" model was used. The analysis was carried out at the Kaduna NGRL.

X-ray diffraction (XRD)

For the determination of the mineralogical composition of green clay and its clay fraction < 2 μm, an Empréan diffractometer DY674 (2010) with copper anode manufactured by Panalytical (Holland) was used at the Kaduna NGRL. The condition for the radiation to be in phase is expressed by Bragg's law: $n\lambda = 2d_{hkl} \sin\theta$ (5). In the tube, the current was 40 mA and the voltage was 45 kV. The ICDD (International Center for Diffraction Data) PDF (Powder Diffraction File) 4 (2015) and COD (2016) databases make it easy to find and match the diffractogram to identify mineral phases and compounds.

Thermogravimetric Analysis (TGA)

A quantity of raw green clay was subjected to a temperature range from 28.13°C to 950°C with a constant rate of 10°C per min under a nitrogen flow. The analysis was carried out at the Block B Multipurpose Laboratory of the Federal University of Technology, Mina (Federal Republic of Nigeria). The device used in this study is of the PerkinElmer MES-TGA TGA4000 brand, manufactured in the Netherlands.

Scanning electron microscopy (SEM)

The morphology of the raw green clay sample and its clayey fraction was observed by using a Phenom ProX type scanning electron microscope at the Laboratory of the Department of Engineering Chemistry of Ahmadu Bello University (ABU) of Zaria (Federal Republic of Nigeria). In an experimental way, the samples were placed on a double adhesive tape, then sprayed. Afterwards, they were deposited in a sputter coater (quorum-Q150R Plus E) with 5 nm gold.

Measurement of specific surface (SS) by the Brunauer, Emmett and Teller (BET) method

It is quite conclusive to evaluate the SS, pore volumes and microporous sizes of our green clay sample. Because it is the quality and extent of these surfaces that will largely determine the adsorption capacities of this clay material. The SS of green clay was determined at the Block B Multipurpose Laboratory of the Federal University of Technology, Mina (Federal Republic of Nigeria). These measurements were taken using a Quantachrome Nova 4200e device manufactured in the United States. The analysis was carried out after degassing the green clay sample at 300°C for 3 hours in order to desorb the water and any impurities present in the pores of the clay material.

III. Results

Preliminary analyzes of Arg3-B

Table no 1 summarizes the results of the preliminary analysis carried out on the raw green clay (pH, CEC, humidity rate and density)

Table no 1: Results of preliminary analyzes of Arg3-B

Clay	pH	CEC (meq.100 g ⁻¹)	H (%)	ρ (g.cm ⁻³)
Arg3-B	6.985	119.44	3.945	1.204

This table shows that Arg3-B has a neutral pH in an aqueous medium, an average humidity level with a low density. However, an increase in the mass of this clay leads to a lesser regression of this pH (Figure 3). It has a high CEC of the order of 119.44 meq.100 g⁻¹. This CEC, which is the number of cations that can be substituted for the compensating cations to compensate for the negative charge of 100 g of clay, varies according to the materials.

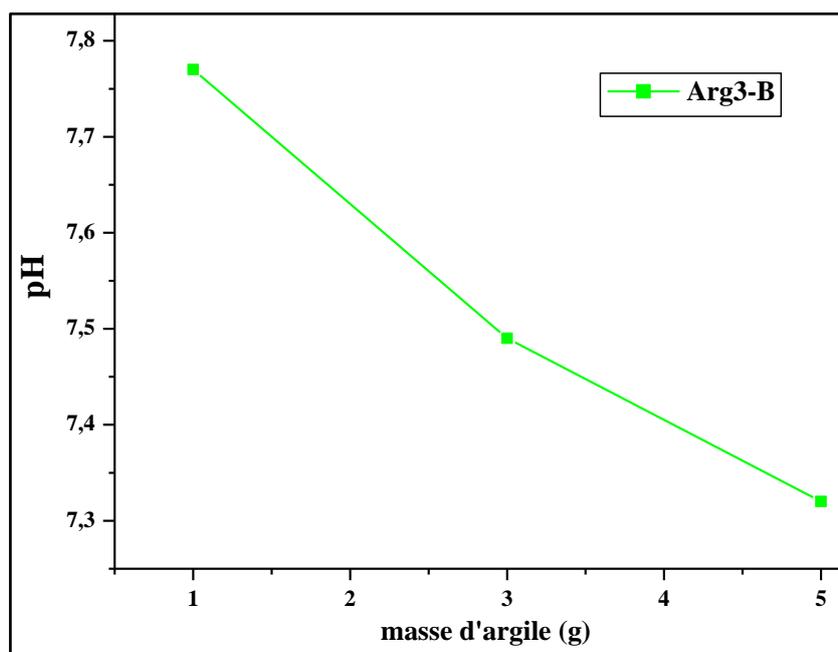


Figure 3: Variation of pH of Arg3-B as a function of mass

pH at point of zero charge (pH_{PCN})

Figure 4 presents the different values of pH_{PCN} or isoelectric point of raw green clay and its clay fractions. The values are 8.54 for Arg3-B, 9.06 for Arg3-FSNa⁺ and 5.58 for Arg3-FNa⁺. There is a considerable decrease in the pH_{PCN} of Arg3-FNa⁺ and a slight increase in the pH_{PCN} of Arg3-FNa⁺ compared to that of Arg3-B. These values characterize the acidity or the alkalinity of the surface of the studied material and they are very important factors in the phenomenon of sorption especially when the electrostatic forces are implicated in the mechanism of adsorption. So, for pH values lower than the pH_{PCN} found in this study, the surface charges of green clay and its clay fractions are positive, when they are higher they become negative and when they are equal the charges are negative. balance, so the surfaces become electrically neutral (there are as many positive as negative charges).

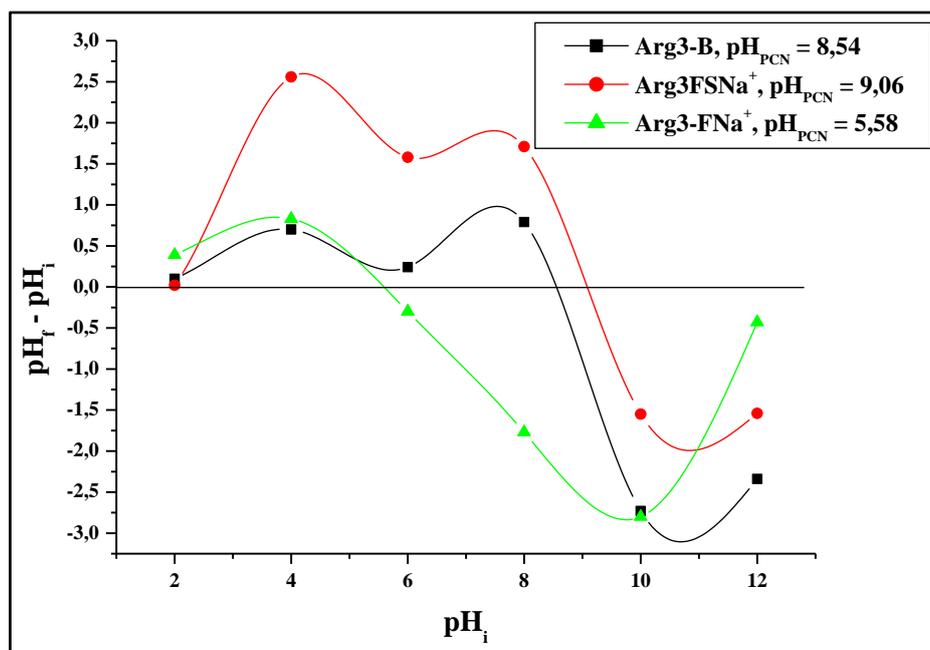


Figure 4: pH_{PCN} of Arg3-B, Arg3-FSNa⁺ and Arg3-FNa⁺

X-ray fluorescence spectrometry (XRF)

Table no 2 summarizes the results of X-ray fluorescence analysis of raw green clay and its soda clay fraction for major oxides and loss on ignition and Table no 3 for trace elements.

Table no 2: Percentages of the major oxides of Arg3-B and Arg3-FNa⁺ and those of the loss on ignition

Oxides (%)	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	CaO	MgO	TiO ₂	MnO	P ₂ O ₅	SO ₃	Fe ₂ O ₃	LOI	SiO ₂ /Al ₂ O ₃
Argiles													
Arg3-B	56.1	14.3	1.21	0.79	1.09	0.6	1.9	0.14	ND	ND	8.06	14.9	3.923
Arg 3- FNa ⁺	53.1	18.13	0.9	0.04	1	0.11	1.2	0.091	ND	0.106	6.01	19.2	2.92

ND: not detected

Table no 3: Trace element of Arg3-B and Arg3-FNa⁺ in ppm

Minor elements	V	Cr	Ni	Zn	Cu	Ga	Sr	Y	Zr	Hf	Ba	Ce	Eu	Re	Pb
Argiles															
Arg3-B	560	320	ND	190	430	ND	780.34	<0.001	1400.2	38.31	<0.001	60	0.33	0.031	ND
Arg3-FNa ⁺	380	320.01	<0.001	200.21	300	3	570.34	ND	520	40.34	1000	20	0.24	0.02	ND

ND: not detected

Analysis of Table no 2 shows that silica and alumina are the major constituent oxides in Arg3-B. The percentage of silica in this clay slightly exceeds 50%. This leads to a SiO₂/Al₂O₃ ratio equal to 3.923. So Arg3-B has a significant amount of silica. It contains quite a considerable percentage of iron oxide (Fe₂O₃). It is also important to note the presence of K₂O and TiO₂ in significant quantities in this clay. Thus, the low percentages of CaO and MgO show that Arg3-B contains slightly calcium and magnesium carbonates. The low percentage of Na₂O < 1% shows that this clay contains a negligible amount of alkaline feldspars. The LOI, which is likely to estimate the rate of organic matter and carbonates contained in this clay, shows a high rate of organic matter,

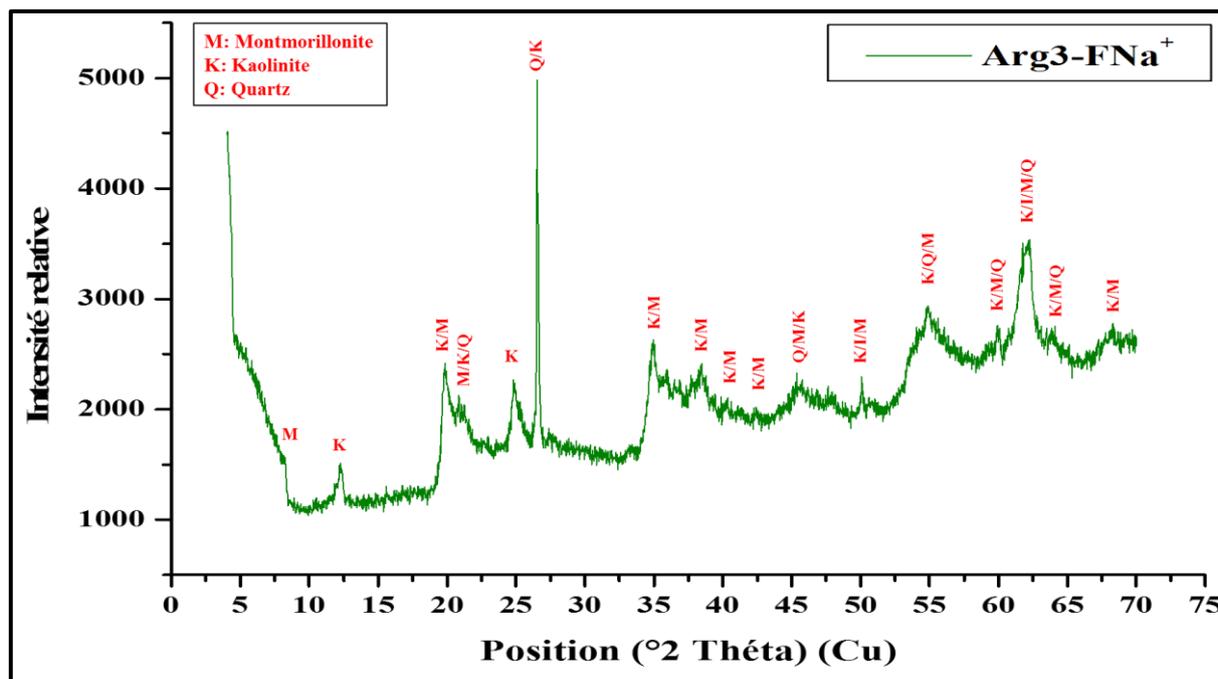


Figure 6: Diffractogram of Arg3-FNa⁺

Thermogravimetric Analysis (TGA)

Figure 7 presents the result of the thermogravimetric analysis carried out on green clay (Arg3-B). The analysis of this figure (TGA curve) shows 6 mass losses at different temperatures. The first appears between 28.15 and 230.98°C (2.445%), the second between 230.98 and 242.62°C (1.008%), the third between 272.14 and 448.19 °C (68.897%), the fourth between 448.19 and 566.33°C (3.003%), the fifth between 576.69 and 591.49°C (0.773%) and the last between 719.31 and 884.81°C (0.499 %). The same curve shows a perceptible increase in weight between 242.62 and 272.14°C, between 566.33 and 576.68°C and between 591.49 and 719.31°C. The derivative of the ATG curve (DTG) shows five endothermic peaks (at 104.28°C, at 235.16°C, at 366.79°C, at 582.97°C and at 706.62°C) and four exothermic peaks (at 246.11°C, at 570.12°C, at 596.15°C and at 729.23°C).

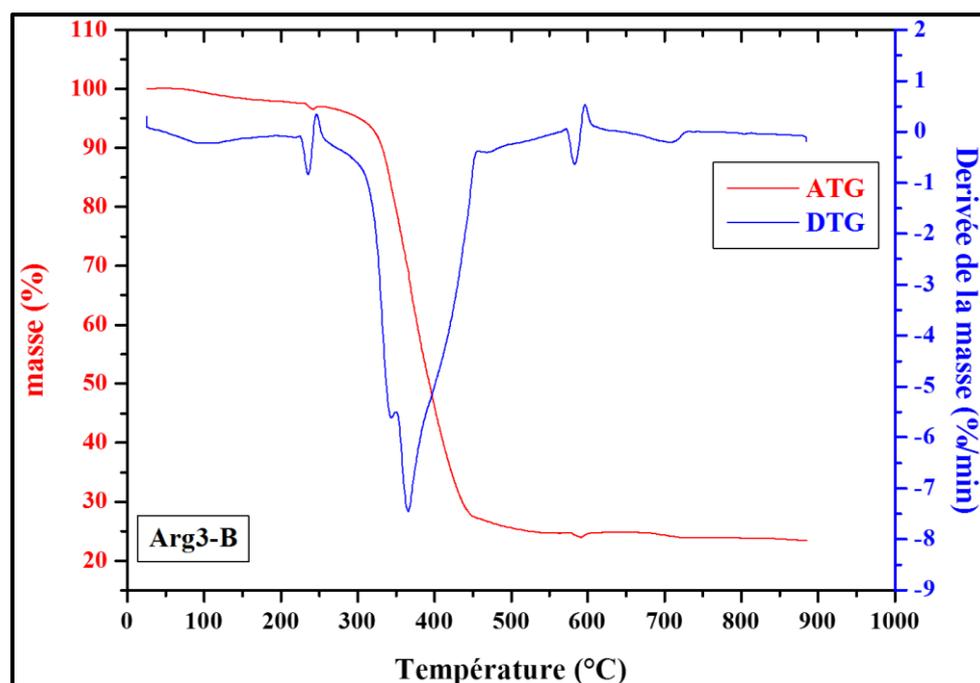


Figure 7: TGA and DTG curve of Arg3-B

Measurement of SS by the Brunauer, Emmett and Teller (BET) method

The SS of Arg3-B calculated according to the methods are presented in Table no 4 present.

Table no 4: Different surfaces of Arg3-B

Characteristic	Sizes	Arg3-B
Specific surface (m ² .g ⁻¹)	at P/P0 = 0.3	258.5
	BET	437.8
	Langmuir	3840
	Cumulative (BJH)	479.5
	Cumulative (DH)	509.1
	External (t-method)	437.8
	Micropores (DR)	463.1
	Cumulative (DFT)	99.55

This table shows a variability of the SS according to the methods used. At one point (P/P0 = 0.3), Arg3-B exhibits a significant SS, but much lower than that found by BET. An exceptional value was obtained by the Langmuir method of around 3840 m².g⁻¹. Regarding the cumulative SS according to the methods (BJH and DH), the difference is not significant, but it greatly exceeds that of BET and remains below that of Langmuir. The external SS determined by t-method is the same as that of BET, while the microporous one determined by DR method slightly exceeds it. As for the DFT method, it shows a value of the SS which is much lower than the values found for the other methods.

The results of the Arg3-B pore volumes calculated according to the different methods are given in Table no 5.

Table no 5: Pore volumes of Arg3-B

Characteristic	Sizes	Arg3-B
Volume (cm ³ .g ⁻¹)	BJH (cumulative)	0.2386
	DH (cumulative)	0.2439
	DR (micropore)	0.1646
	HK (micropore)	0.0659
	SF (micro-pore)	0.0124
	DFT (cumulative)	0.1208

The interpretation of this table shows that the cumulative pore volumes according to the BJH and DH methods do not show a significant difference, but they greatly exceed that calculated according to the DFT method. While the microporous volumes according to the shapes of the pores by the HK and SF methods show a very significant difference. That of HK (0.0659 cm³.g⁻¹) corresponding to the slot shape is much higher than that of SF (0.0124 cm³.g⁻¹) corresponding to the cylindrical shape. But, they are lower than that calculated according to the DR method.

Table no 6 summarizes the results of the pore size distribution calculated according to the different methods.

Table no 6: Pore size of Arg3-B according to the different methods

Characteristic	Sizes	Arg3-B
Pore size (nm)	Meandiameter BJH	2.141
	Averagediameter DH	2.141
	Pore width DR	6.399
	Pore diameter DA	2.96
	Pore diameter HK	1.847
	Pore diameter SF	3.469
	Pore diameter DFT	2.647

It can be seen from this table that the average pore size diameter according to the BJH and DH methods by adsorption is the same, with a good pore width calculated according to the DR method and a micropore diameter according to the DA method similar to that calculated by the DFT method which is the best method

allowing a much more precise approach to pore size. Because it includes the size of micropores and narrow mesopores which other methods cannot determine. Thus, the microporous diameter size according to the HK and SF methods which take into account the pore shape, shows a large difference in pore size between these two methods. That of SF (3.469 nm) greatly exceeds that of HK (1.847 nm).

Scanning electron microscopy (SEM)

Images from SEM of green clay and its clayey fraction to observe the morphology and organization of aggregates of clay particles are presented in Figure 8. The micrographs show that, this clay has morphologies showing irregularly shaped crystals distributed in a random way. However, there is a significant change in morphology between Arg3-B and its sodium clay fraction (Arg3-FNa⁺). Given the diversity of minerals identified contained in these clay particles by XRD and the low resolution of the SEM image of this green clay, the structural identification of the morphologies specific to the basic clay minerals (Montmorillonite and Kaolinite) remains very difficult. But, it shows the degree of crystallinity of this clay.

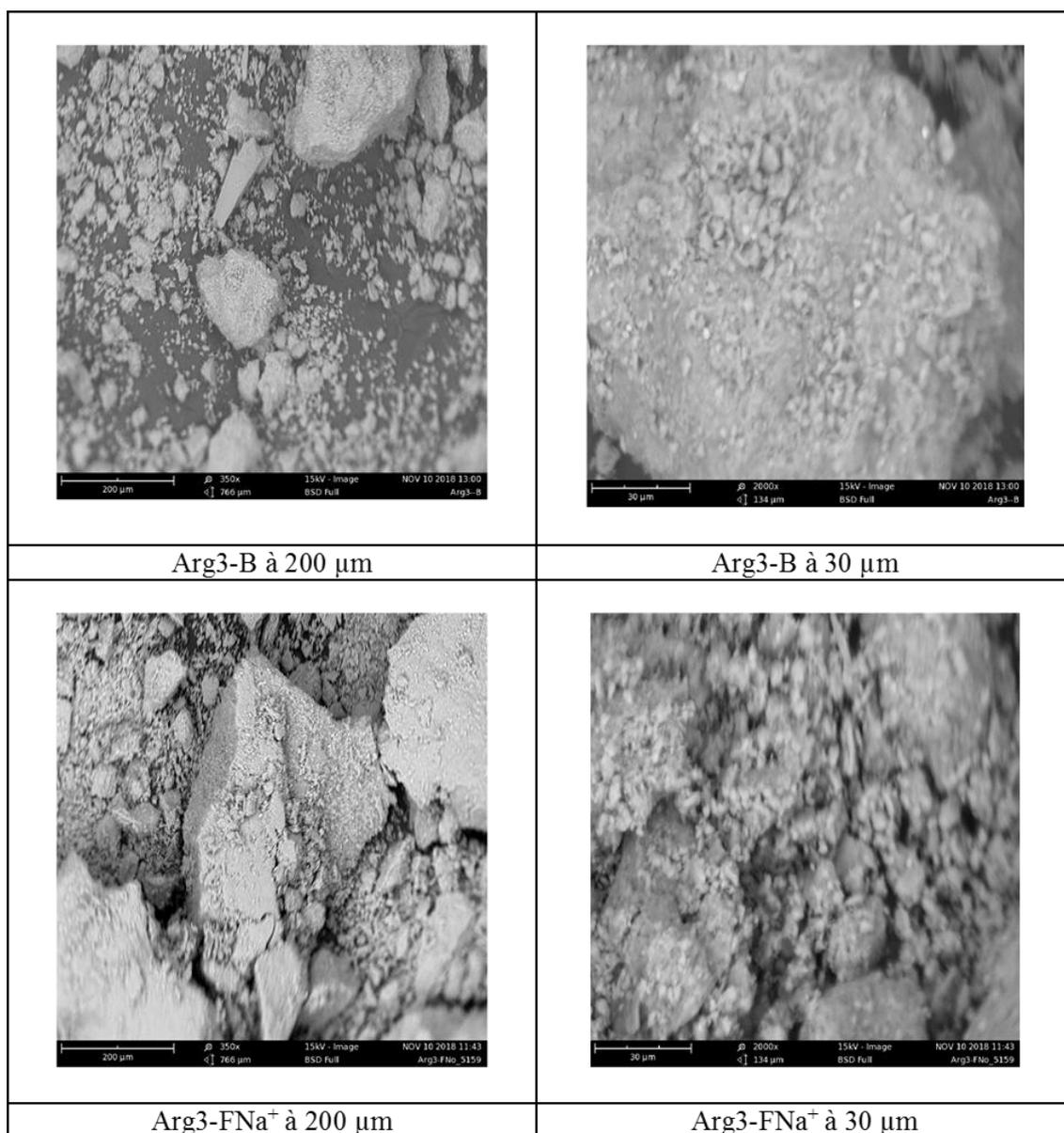


Figure 8: SEM images of Arg3-B and Arg3-FNa⁺

IV. Discussion

Preliminary analyzes of green clay (Arg3-B)

The neutral pH value obtained for Arg3-B, shows that it has surfaces which are made up of acidic and basic groups capable of reacting with the hydroxyl groups and the hydronium groups of the water, which will cause an ionic balance in the environment. The value obtained is lower than those obtained by *Qlihaa and al, Zahaf, Bouzid, Amin and al.*^{1,6,7,10}. This difference could be due to the low levels of alkaline and alkaline-earth cations that Arg3-B has, which is confirmed by the results of the X-ray fluorescence analysis. On the other hand, the value obtained is higher than those obtained by *Maman and al* on the LP11 and on the T10 of Tillabéryregion in Niger⁴, those found by *Mache* on the smectites of Sabga and Bana in Cameroon¹¹ and those found by *Dominique* on the clays of Kasangulu and Kingabwa in Congo¹². The humidity rate recorded for Arg3-B could be due to the arid nature of the area where this clay was taken and shows its non-hygroscopic character, which is also confirmed by the results of the ATG-DTG. It appears from the literature that the CEC of between 3 to 15 meq.100 g⁻¹ corresponds to kaolinite, from 10 to 40 meq.100 g⁻¹ to illite, from 80 to 150 to smectites¹³. So the CEC of our determined green clay which is 119.44 meq.g⁻¹ belongs to the interval of 80 to 150 meq.g⁻¹, which lets us suggest that it contains a significant amount of minerals belonging to the smectite family. The density obtained is below that obtained by *Bouzid*⁶. This could be due to the geological formation or the experimental conditions (mesh, method) which differ, or our clay does not contain a dense element (such as quartz) likely to increase this density.

pH at the point of zero charges (pH_{PCN})

The pH_{PCN} value of green clay obtained in this study is almost similar to those in the literature for smectitic clays¹⁴. This leads us to predict that this clay still contains significant quantities of minerals belonging to the smectite family. This corroborates the hypothesis put forward above in the case of the CEC. The increase in pH_{PCN} of Arg3-FSNa⁺ would be mainly due to the elimination of certain impurities carrying positive charges which are likely to decrease this pH_{PCN} in the raw state. However, the decrease in pH_{PCN} observed in the cases of Arg3-FNa⁺ would probably be due to the adsorption of Na⁺ by the negative charges of this clay fraction.

X-ray fluorescence spectrometry (XRF)

The percentage of silica recorded could be mainly attributable to clay minerals and quartz. So green clay has free silica content. It appears from the literature that SiO₂/Al₂O₃ ratios between 2 and 5.5 generally correspond to materials of type 2/1, more precisely montmorillonite^{15,16}. So this lets us already suggest that Arg3-B could contain montmorillonite in large quantities. The fairly large percentage of Fe₂O₃ recorded in green clay could be due to the existence of minerals that can contain iron in large quantities, because according to the literature, iron is found in the form of oxide-hydroxides, namely goethite, and/or oxides such as hematite and magnetite^{17,18}. So, drawing inspiration from this result from the literature, we can say that, this clay could contain goethite and / or hematite and magnetite. These types of minerals are generally attributable to montmorillonites. The titanium content recorded could be attributable to kaolinites, as it appears from the literature that titanium is found in the form of rutile or anatase in kaolinitic clays⁵. This leaves us to suggest that the green clay in addition to montmorillonite, could contain kaolinite. The low percentages of CaO and MgO recorded let us predict that the green clay is devoid of carbonated elements. The percentage of LOI of Arg3-B obtained, lets us suggest that green clay could also contain a significant amount of kaolinite, because this ratio is close to those obtained by several authors who have worked on kaolinites^{5,12}.

The presence of the trace elements found (V, Cr, Zn, Cu, Sr, Zr, Hf, Ce, Eu and Re) in this study differs from the results found by *Gourouza*¹⁹ in Niger in the clays of the Tahoua region, where he concludes the total absence of these elements. This could be due to the difference in the geological formations where these samples were taken. But, more than 40 trace elements were found by *Amin and al.*¹⁰ in Ivory Coast in UB1 and UB2 clays. This is in agreement with the results of the present study. And he concludes that UB1 contains kaolinite and illite and UB2 contains montmorillonite and illite. This leaves us to suggest that our clay could contain all these minerals. *Mache* also found a certain number of trace elements in the smectites of Sabga and Bana in Cameroon¹¹. This is in agreement with the hypotheses put forward above that our clay contains minerals belonging to the smectite family.

The decrease in silica in the clay fraction compared to the raw state, would be due to the fact that this silica could only come from the constituent minerals of this clay except that of quartz. This shows that the green clay is becoming more and more aluminous. This difference could be due to the different substitution reactions likely to occur during the clay fraction extraction processes. On the other hand, the decrease in the percentage of Fe₂O₃ of the clay fraction compared to that of the raw clay, could be attributable to the various impurities eliminated that may contain iron. In addition, the increase in the percentage of LOI exceeding that of the raw

clay, this shows that the extraction of the clay fraction has been well carried out and that it contains only fractions rich in clay minerals which are susceptible to adsorb large quantities of water, of which after calcination this water is easily desorbable, which could give it a high SS.

X-ray diffraction (XRD)

In general, the XRD analysis showed that the green clay analyzed contains a mixture of clay minerals with impurities. The main constituent minerals are montmorillonite and kaolinite associated with impurities such as quartz and microclines. This proves the heterogeneous nature of green clay, which is in perfect agreement with the various observations made at the SEM and the results of X-ray fluorescence. It appears from the literature that clay minerals of the kaolinitic type are always associated with impurities. such as quartz, and smectitic types associated with microclines^{5,6,20,21}. In the soda argillaceous fraction, the main constituent minerals are montmorillonite and kaolinite which appear with very intense peaks, but with the persistence of certain low intensity peaks characteristic of quartz. These results are in agreement with those of several authors who reported the presence of quartz in the clay fractions^{1,5,22}. So these different observations confirm the significant elimination of quartz during the extraction of the clay fraction, these results also confirm those of X-ray fluorescence.

Thermogravimetric analysis

In the case of Arg3-B, the 1st mass loss could be attributable to the dehydration of the adsorbed water of Kaolinite or montmorillonite, but, the 2nd and 3rd could be attributable to the dehydration of the bound water to the interfoliar cations of the montmorillonite, causing for the 2nd a structural reorganization of the network with increases in the weights perceptible on the TGA curve and an exothermic peak on the DTG curve. The 4th could be attributable to the dehydroxylation of montmorillonite or kaolinite which is transformed into metakaolinite also causing a structural reorganization of the network. As for the last two, they could be attributable to the dehydroxylation of montmorillonite, each causing a structural reorganization of the network perceptible on the TGA curve and exothermic peaks on the DTG curve or a change in the oxidation state of the constituent elements of the clay. green. These hypotheses lead us to believe that this clay contains montmorillonite and kaolinite, which is in agreement with the results of XRD and X-ray fluorescence.

Measurement of SS by the Brunauer, Emmett and Teller (BET) method

The SS obtained by the different methods of Arg3-B except those of Langmuir, single point and DFT, do not reach that of a pure montmorillonite ($880 \text{ m}^2 \cdot \text{g}^{-1}$), but largely exceed that of pure kaolinite (between 10 and $30 \text{ m}^2 \cdot \text{g}^{-1}$). These SS obtained not reaching that of a pure montmorillonite could be due to the presence of kaolinite and impurities contained in Arg3-B which are likely to attenuate the normal development of the SS of a montmorillonite. These results are in agreement with those of the XRD which showed the presence of Kaolinites and impurities in Arg3-B. Similarly, values exceeding those of kaolinite could be due to the presence of montmorillonite and impurities that could increase these SS. This is always confirmed by the results of the XRD. This lets us suggest that Arg3-B mainly contains montmorillonite. In addition, the values obtained in this study greatly exceed those found by many authors^{7,11,19,20,22 - 26}. These obtained strong SS could make Arg3-B a high performance adsorbent material capable of adsorbing both anions and cations. Thus, the differences observed between the different methods, especially that of Langmuir ($3840 \text{ m}^2 \cdot \text{g}^{-1}$) and of BET ($437.8 \text{ m}^2 \cdot \text{g}^{-1}$) could be attributable to the different assumptions that each of the methods is based on. The strong SS of Langmuir would probably be due to the three assumptions that this model uses (the adsorption is localized and only gives rise to the formation of a monolayer; all the sites are equivalent and the surface is uniform; no interaction between the adsorbed molecules). This stipulates that there is no distinction between the different pores of this clay material (micro, meso and macropore), so as Arg3-B is made up of several types of minerals (montmorillonite and kaolinite) with impurities (microclines, quartz and other elements), this could lead to the adsorption of a large amount of nitrogen gas in the various pores contained in Arg3-B, which will undoubtedly lead to the exceptional enhancement of the SS of Arg3-B exceeding largely this daughter of BET. These strong SS could increase the performance of Arg3-B. Results for Langmuir's SS for clay materials are somewhat lacking to our knowledge in the literature.

Pore volume

The total pore volumes found by the methods (BJH and DH) are greater than those obtained by Bouna, by Célini and by Meriam^{22,24,26} respectively on montmorillonite, on crude and soda TAG and on clays of the Morocco. This could be due to the fact that Arg3-B consists of several minerals likely to increase the pore volume, which is confirmed by the SS obtained in this study which largely exceed those of these authors. Similarly, the micropore volume of Arg3-B exceeds those of Mache, Bouna, Haffane and al, Meriam and Gourouza and al.^{11, 22, 25 - 27}. The assumption is the same as before.

Distribution of pore sizes

The results obtained by the various methods show that the pore sizes of Arg3-B are on the one hand less than 2 nm characteristic of microporous materials, and on the other hand greater than 2 nm but not reaching 50 nm characteristic of microporous materials. mesoporous materials according to the UIPCA classification. This suggests to us that Arg3-B could contain micropores and mesopores. But, according to the DFT method which gives the results of micropores and mesopores, shows a large peak at a diameter size of less than 2 nm confirming the presence of micropores and two peaks at diameter sizes greater than 2 nm confirming the presence mesopores. These hypotheses could also be confirmed by the obtained microporous SS largely exceeding that of BET. In addition, the diameter sizes obtained by the HK and SF methods and according to the pore width, let us think that this clay could contain slit-shaped micropores and cylindrical-shaped mesopores, because the values obtained according to these two methods are respectively less than 2 nm and greater than 2 nm. This further shows that Arg3-B could contain more micropores than mesopores. This hypothesis could be supported on the one hand by its high microporous SS and on the other hand by its high microporous volume. The diameter size values obtained in this study are lower than those of *Bound*²². This could probably be due to the multiplicity of minerals and impurities contained in Arg3-B on the one hand or to the large SS developed by this clay on the other.

Scanning electron microscopy (SEM)

The rather irregular morphologies observed on the SEM images of Arg3-B could be largely attributable to smectitic type materials (montmorillonite)²⁸. Similarly, small particles of hexagonal shape and sometimes reduced to diamonds could be attributed to kaolinites^{28,29}. The rough deposits noticeable on the crystals could be free silicas in this clay material and *Bellaroui* and *Mokhtari* impurities *in*³⁰. These hypotheses are in agreement with the results of XRD, X-ray fluorescence and TGA-DTG.

V. Conclusion

In conclusion, the green clay analyzed by the different techniques consists of montmorillonite and kaolinite associated with impurities such as microclines and quartz. It exhibits a high degree of crystallinity with large specific surface areas, slit-shaped microporous and cylindrical-shaped mesoporous volumes and large pore sizes. It is also neutral with trace elements and a basic isoelectric point. These characters give this clay very powerful intrinsic characteristics allowing its use as an adsorbent.

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