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Contribution to the Study of Useful Natural Materials from Niger: Physicochemical Characterization of Natural Nigerien Clay

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ABSTRACT

This paper concerned the physicochemical characterization of a natural Nigerien clay from the Goulbi valley, Djirataoua, department of Madarounfa, Maradi province, Niger republic. Sample clay was characterized using X-rays diffraction spectrometry, infrared spectrometry, laser granulometry, and atomic absorption spectrometry. The results obtained showed that Djirataoua clay is acidic (pH = 5.5) with a low percentage of humidity (3.298%) and a small swelling index (2.141%). This clay contains mainly of quartz (67.67%) and relatively small fractions of other probable minerals.

1. Introduction

Clays have been used by man early [1]. Their use, for example in the manufacture of bricks of clay, mud, clay tablets or containers, has contributed as much as agriculture to the development of the first civilizations [2]. Today, they are used as minor constituents (paints, plastics, cosmetics, pharmaceuticals, etc.) as well as the main raw material, for example for the production of ceramic materials of great diffusion [3-5]. Several studies on the characterization of clays in Africa and the rest of the world have been carried out [6-8]. This confirms the interest given to this material.

The Niger potentialities in clay are reported previously [7, 9]. The Maradi region of Niger, in particular the Goulbi valley, has enormous potentialities of uncharacterized clays. Even if the Djirataoua clay is already used by a factory in the square (BRIMA: Maradi brickworks) for the manufacture of ceramic bricks, no scientific studies have been carried out on the characterization of this material. It is therefore important to characterize this clay in order to make it an optimal valorization. This study is, therefore, part of this framework. Indeed, this paper is a contribution the study of Djirataoua clay through its physicochemical characterization. This will make it possible to optimize the production of the ceramic bricks from this clay.

2. Experimental Methods

2.1 Preparation of Clay Sample

The sample was taken from Djirataoua located at department of Madarounfa, Maradi province, Niger republic.

The sample taken has undergone the following unit operations:

- Crushing the rocks of the sample into pieces by a mortar,
- Drying in the oven for 24 h (T = 101 °C),
- Grinding of the pieces of the clay sample in a grinder,
- Screening of the powder of the sample (212 µm sieve).

2.2 Determination of pH

Determination of pH is necessary to quantify the contribution of acidity when the solid is in contact with the solution. A 10% (m/v) solution of clay (5 g in 50 mL of distilled water) is prepared with distilled water; the mixture is left to stand for 4 hours at room temperature, to allow the ions to pass into solution. The solution of clay obtained is homogenized by a magnetic agitator. Reading is done directly on a HANNA pH meter [6].

2.3 Humidity Ratio

Measurement of the humidity ratio consists of determining the mass of water removed by drying a wet material until a constant mass is obtained at a temperature of 105 ± 5 °C for 24 hours, the mass of the material after parboiling is considered as the mass of solid particles (ms). The determination of the humidity content was calculated from the ratio of the mass of the water (m_{water}) to the mass of the solid particles (ms). This gives the water content of the sample analyzed (Eq.(1)) [6]:

$$H (\%) = (m_{\text{water}}/m_s) * 100 = (mt - ms/ms) * 100 \quad (1)$$

where, m_{water} : masse of water (g)
ms: mass of the dry sample (g)
mt: mass of the wet sample (g).

2.4 Swelling Index

By suspending, the clay can fix a significant amount of water, which has the effect of displacing each other, thus leading a swelling.

We fill a 100 mL graduated cylinder with 50 mL of distilled water and we add 0.5 g of clay. After 45 min, we add another 0.5 g of clay. After 2 h, the swelling volume is noted. The index of swelling is measured by the following formula (Eq. (2)) [10]:

$$\text{Swelling Index (\%)} = (\text{swelling volume} * 50) / (50 - \text{humidity}) \quad (2)$$

2.5 X-Ray Diffraction Study

5 mL of distilled water are added to a test portion of 1 g of clay and the mixture is placed under magnetic stirring for 8 hours until a homogeneous viscous suspension is obtained. A few drops of this suspension are taken and spread on the surface of three plates and we dried them during 24 hours:

- a normal blade (without any treatment)

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- a glycol blade (treated with ethylene glycol)
- a slide which is subsequently heated for 2 hours in a fur at 500 °C.

The powder obtained after sieving with a 212 μm sieve and the three blades under analysis by X-ray diffraction using a BRUKER D8 ADVANCE diffractometer.

2.6 FTIR Analysis

An amount of powder (1 mg) obtained after sieving with 212 μm sieve is mixed with KBr (100 mg). The mixture is pressed with a PERKENELMER pelletizer at a pressure of 5 Pa and pellets are thus obtained. We realized a reference pellet with only KBr under the same conditions. The pellets obtained were analyzed by using an infrared BRUKER VERTEX 80v spectrometer (KBr pellet is used as reference to avoid interference phenomenon).

2.7 Laser Granulometry

The size of particle clay powder obtained, after sieving with 212 μm , was determined by using a MICROTAB 3500S laser granulometer.

2.8 Extraction of Clay Fractions

2 g of well-ground clay is weighed and introduced into a Teflon beaker, and then 30 mL of concentrated HCl, 10 mL of concentrated HNO_3 and 10 mL of concentrated H_2SO_4 are added slowly and in the order. The resulting mixture is heated in a sand bath until it turns yellowish-white. After scraping the reddish edge of the beaker with a glass rod in order to bring down the remainder glued to the beaker's walls, the mixture is heated until the SO_3 is released completely from the mixture. The mixture is then allowed to cool a little and stirred with the glass rod. To the mixture obtained, 10 mL of HCl and 10 g of NH_4Cl are added in order, and the whole is heated in a sand bath until the mixture dries out. The mixture is then allowed to cool a little, and then 20 mL of HCl and 200 mL of distilled water are added. The mixture is then heated with stirring until everything goes into solution except silica. It is filtered using 0.45 μm filter and washed with distilled water. The solid obtained is allowed to dry and finally the % SiO_2 is calculated by using the following formula (Eq.(3)),

$$\% \text{SiO}_2 = \text{dried mass of solid obtained} / \text{initial mass of test sample} \quad (3)$$

The filtrate obtained, poured into a 1 L volumetric flask and completed with distilled water to the gauge line, is analyzed by atomic absorption using an analyst 200 precisely spectrometer.

3. Results and Discussion

Table 1 shows an acidic value of pH. This value is between 3.5 (pH value of Boubon clay) and 6.4 (pH value of Tera clay) found by Maazou et al. [9]. These authors have explained this acidity by the presence of an important amount of SiO_2 in their clay. However, Qlihaa et al. [6] during their study about the physicochemical characterization of a Moroccan clay from Missouri (Boulemane province) obtained a basic value of pH (8.5). These authors have explained this basic pH by the presence of basic soluble salts in clay as carbonates and bicarbonates. The pH value of Djirataoua clay is also lower than that found by Amin N.C. et al [11] for UB1 and UB2 clay samples studied [11] and by Antonine Poitevin [12]. This author has obtained pH values near by the neutrality (between 7.12 and 7.30).

Djirataoua clay has a ratio of humidity relatively low, but higher than that found by Qlihaa et al [6] who obtained 1.41% in their study about Missouri clay and explained the result by the non-hygroscopic character of the studied clay.

Otherwise, a value of swelling index lower than that found by Qlihaa et al. [6] (47.54%) was obtained in this work (2.141%). This result showed that Djirataoua clay can fix less water than that studied by Qlihaa et al. [6].

Table 1 pH, humidity ratio, and swelling index

Djirataoua Clay	pH	Humidity ratio (%)	Swelling index (%)
	5.5	3.298	2.141

Percentage of SiO_2 , and concentrations in some metallic elements were determined in Djirataoua clay sample (Table 2). These results revealed the presence of Quartz in preponderant quantity in this clay. This percentage is in the interval of the limit admissible for the use of clay in ceramic reported by Kornmann 2005 [13] and Wetschondo Osomba 2012 [14]. This value is higher than those obtained by several previous studies [6, 8, 9, 15, 16]. However, Tchamo Leussa [17] has obtained, for calcinated MH clay, a percentage of SiO_2 comparable to that measured in this study. Amin et al

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[11] have also obtained percentage of SiO_2 , for both UB1 and UB2 clays, lower than our value. It is important to note that Gourouza et al. [7] have obtained, during their previous study about another Nigerien clay (from Koundigué, Tahoua region, Niger republic), a percentage of SiO_2 lower than ours. Our result was also confirmed by X-rays diffraction spectra (Figs. 1-4) where quartz (SiO_2) was detected mostly.

Table 2 % of SiO_2 and concentration of some metallic elements in the Djirataoua clay sample

Djirataoua clay	SiO_2 (%)	Fe (mg/L)	Cd (mg/L)	Zn (mg/L)	Mn (mg/L)	Cu (mg/L)	Ni (mg/L)
	67.67	8.581	0.049	1.626	5.4	0.186	0

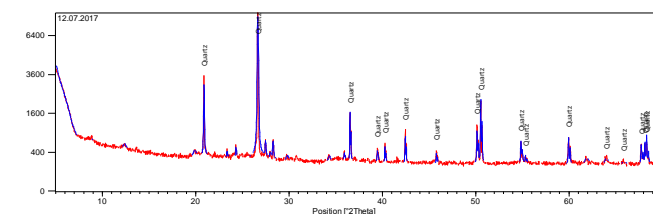


Fig. 1 X-rays diffraction spectrum of clay sample sieving with 212 μm sieve

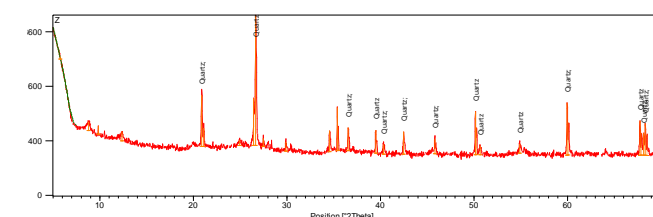


Fig. 2 X-rays diffraction spectrum of clay sample sieving with 212 μm sieve and deposited on a glass blade

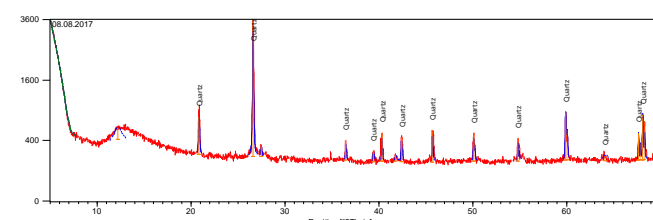


Fig. 3 X-rays diffraction spectrum of clay sample sieving with 212 μm sieve deposited on a glass blade and heated

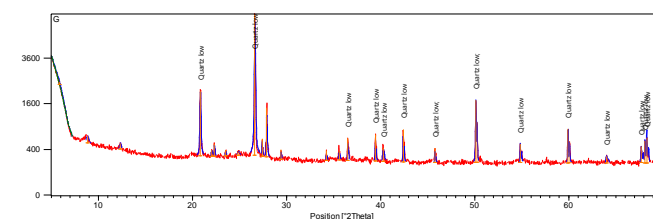


Fig. 4 X-rays diffraction of clay sample sieving with 212 μm sieve deposited on a glycolated glass blade

Table 2 shows that iron is the most important metallic element almost the metallic elements analyzed. That is confirmed by the presence of a relatively intense peak at $2\theta = 27.858^\circ$ and a small peak at $2\theta = 34.577^\circ$ in the X-rays diffraction spectrum of clay treated by ethylene glycol probably attributable to giniite. Manganese is also present in our clay in a relatively important quantity. That could be explained by a peak appeared at $2\theta = 34.170^\circ$ in the X-rays diffraction spectrum of clay treated by ethylene glycol (Fig. 4). This peak can be attributable to helvite; 2 peaks appeared at $2\theta = 29.570^\circ$ and $2\theta = 12.283^\circ$, respectively which can be probably attributable to franklinfurnaceite; a peak observed at $2\theta = 8.752^\circ$ probably relative to wisnerite. However, zinc, copper and cadmium are detected in very low content. Nickel has not detected.

Otherwise, the most intense peak ($2\theta = 26.637^\circ$) of clay analyzed has been explained, by Qlihaa et al. [6] to be relative to quartz's one. That confirmed our result when the most intense peak is obtained to a same 2θ that found by Qlihaa et al. [6]. It is important to note the absence of the most intense peak at $2\theta = 29.782^\circ$ relative to calcite [6]. This confirmed the result found in this study where no effervescence was observed by reacting our clay with concentrated HCl. A peak at $2\theta = 12.3579^\circ$ which was identified to be kaolinite's one by Qlihaa et al [6] was also observed in the spectrum of X-rays diffraction of Djirataoua clay. The same comments

was done with the small peak appeared at $2\theta = 8.7012^\circ$ which is identified as relative to illite's one [6].

The concentration in minor elements such as cadmium, zinc, copper, and nickel is lower than those obtained by Amin et al. for UB1 and UB2 clays [11].

Results obtained, when analyzing Djirataoua clay by laser granulometry, are drawn in Fig. 5 (without using ultrasound) and Fig. 6 (using ultrasound). They showed that all clay particle sizes were between 0.817 and 176 μm (without using ultrasound: Fig. 5), and between 0.486 and 124.4 μm (using ultrasound: Fig. 6). 50% of clay particles have sizes lower than 15.84, and 9.71 μm , respectively without using and using ultrasound.

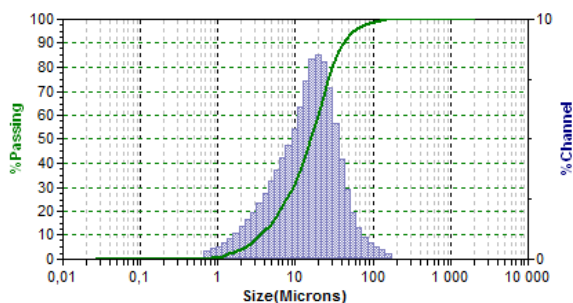


Fig. 5 Particle sizes of Djirataoua clay sample sieving with 212 μm sieve without using ultrasound

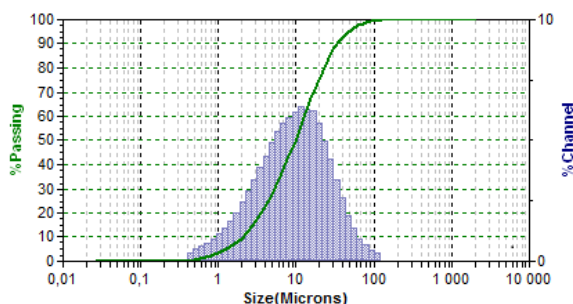


Fig. 6 Particle sizes of Djirataoua clay sample sieving with 212 μm sieve using ultrasound

We have obtained 10% of clay particles with sizes $<2 \mu\text{m}$ in the present study, while El Ouahabi [18] has obtained in his previous study the same particle sizes with a high percentage (4–49%). This author detected that until 93% of sand fraction has sizes higher than 20 μm , while we found only 25% of particle exceeded these sizes in the present study.

The infrared analysis of Djirataoua clay sample (Fig. 7) revealed the presence of characteristic bands at 470.60, 513, 540.03, 667.3, 698.19, 748.33, 798.48, 842.84, 916.13, 954.70, 1024.14, 1035.71, 1109, 1386.73, 1600.82, 1662.54, 3473.59, 3597.02, 3624.03, 3701.17, 3706.96, 3710.82 cm^{-1} .

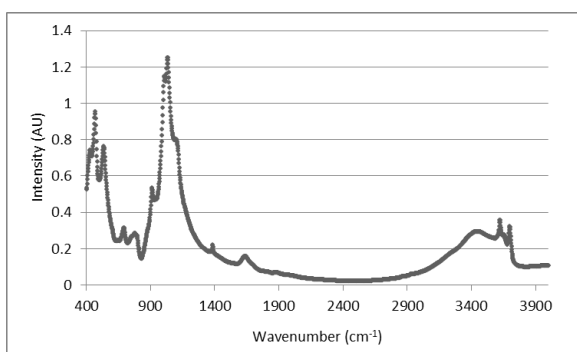


Fig. 7 Infrared spectrum of the clay sample from Djirataoua

The bands 3473.59, 3597.02, 3624.03, 3701.17, 3706.96, 3710.82 cm^{-1} are between 3200 and 3800 cm^{-1} , so it can be relative to elongation vibrations of internal OH groups as reported by Qlihaa et al [6]. The bands appeared at 1600.82 and 1662.54 cm^{-1} can be attributed to the valence vibrations of the OH group of the water of constitution [6]. The bands 916.13, 954.70, 1024.14, 1035.71, 1109 cm^{-1} can be relative to valence vibrations of Si-O [19]. The bands 748.33, and 798.48 cm^{-1} can be attributed to Si-O-Al [20, 21]. However, the band 798 cm^{-1} may correspond to quartz [22]. Otherwise, the band at 748.33 cm^{-1} is nearby to 750 cm^{-1}

identified as due to illite's presence [23]. The band 667.3 cm^{-1} is in the interval 663–677 cm^{-1} , identified as relative to vibrations of Al-O-Si and Al-OH of kaolinite [24, 25].

It is important to note the absence of a band at 872.6 cm^{-1} corresponding to the presence of calcium carbonate. This confirms the absence of CO_2 release when a few drops of concentrated HCl were poured onto a sample of our clay. This result is also confirmed by Amin et al. [11] because no bands at 1470 and 876 cm^{-1} attributable to C-O elongation of calcite have been detected. It is the same for the bands at 2985, 2875, 2512, and 1795 cm^{-1} relative to calcite which have not appeared in the IR spectrum of the clay sample from Djirataoua studied in this work [11].

4. Conclusion

The clay of Djirataoua has been studied in this work and concerned the physicochemical characterization of a sample of this material. The results obtained showed that this clay is acidic with a low percentage of humidity and a low swelling index. This clay contains mainly quartz with relatively small proportions of other minerals.

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