Characterization of two clay minerals of the Niger River Valley: Téra and Boubon

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Abstract: This work presents some results of a characterization by X-ray diffraction (XRD), infrared spectroscopy (IR), Scanning Electronic Microscopy (SEM), Thermo gravimetric analysis (TGA) and differential thermic analysis (DTA) of two samples of clay minerals collected from Téra and Boubon in the valley of the Niger River.
The results reveal that these samples contain a significant amount of kaolinite ranging from 60.99 to 61.61 %. We note also, the presence of Illite at low quantities.

Keywords: clay minerals, kaolinite, XRD, IR, SEM

INTRODUCTION

Clay minerals are materials that are abundant in the world. They are used in some commercial applications, in engineering and/or in industrial processes [1,2]. They are also used in some traditional applications.The main field of use includes ceramics, paper, paint, plastics, drilling fluids, chemical carriers, liquid barriers, decolorization, and catalysis [3-5]. In other applications, clay minerals are used for the purification of wastewater by removing heavy metals or organic pollutants. Heavy metals are non -biodegradable and tend to accumulate in living organisms, thus causing different disorders [6-10]. Clay minerals are also used like natural barriers against radioactive waste [11]. Hence, an important effort is required to characterize clay as valuable national resource.

The valley of the Niger River is rich in clay minerals. They are mostly used for making some potteries, in construction, and in the field of health. However, despite previous studies carried out on samples of this region, a lack of database that characterize these clay materials is noted [12,8]. The purposes of this work, is to study clay minerals collected at Toula Namari-Goungou, Saga and Say, Niger. These clay minerals were used so far to remove pesticides from wastewater [8].

Samples of clay minerals were collected from the Niger River valley, Téra and Boubon. Samples were characterized by various physicochemical methods. Subsequently samples presenting the best properties may be used for the removal of heavy metals. Clay minerals after sieving were subjected to different physicochemical analyzes. Fractions less than 2 microns were examined by X-ray diffraction (XRD), infrared and scanning electron microscopy (SEM). Obtained X-ray diffractogrammes were compared according to the extraction processes.

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[†] This paper is dedicated to the memory of Prof. Abdoulaye Alassane

Table I: Samples

Sample	Geographical location (GPS)	Sampling site
T10	N 13° 35' 42.5" / E 01° 55' 57.5"	Boubon
LP11	N 14° 00' 13.0" / E 00° 45' 41.3"	Téra

MATERIALS AND METHODS

Clay mineral samples were collected from the region of the Niger River (Tillabéry region) at a depth of 0 to 30 cm. The geographical locations of sampling sites are shown in the figure 1. The GPS coordinates of each sample are indicated in Table I. After drying in laboratory (35°C - 40°C), they were crushed and sieved to 2 mm. The clay fraction lower than 2 µm was extracted by using two methods: chemical and ultrasonic. The first method is the protocol developed by Robert and Tessier [13]. In this method, 100 mL of distilled water was added to 20 g of the crude clay, sieved at 2 mm. The mixture was left for an hour and then 25 mL of hydrogen peroxide was added to remove organic matter. The mixture was covered and left at room temperature for 24 hours. To completely destroy organic matter, the sample was carried on a sand bath at 60°C for 3 hours. A solution of sodium chloride 0.1 N was then added to saturate the mixture. The dispersion was done with graduated cylinder. The suspension was then collected by siphoning. Examination reveals that it contains particles lower than 2 microns. During the ultrasonic method, 20 g of the samples of clay were put in an ultrasonic device. They were then submitted to ultrasonic waves at 35 kHz for 5 min. The suspensions were collected after dispersion [14]. The clay fraction lower than 2 microns, of each sample was dried and crushed. The powder was subjected to the X-ray diffraction. The diffractometer used is a Panalytical X'PERT Pro Philips, equipped with a cobalt anticathode (monochromatic Kα radiation; λ = 1.5418 Å) operating under a voltage of 40 kV and a current emission of 40 mA. The rotational speed was $0.02°.s^{-1}$.

The infrared spectra of the samples were recorded on an FTIR Perkin-Elmer spectrometer. Specimens for measurement were prepared by mixing 0.02 g of the sample powder with 0.18 g of KBr and pressing the mixture into a pellet. The average over 20 scans was collected between 4000 cm^{-1} and 400 cm^{-1} for each measurement with a resolution of 2 cm^{-1}.

The samples were also subjected to a mineralogical analysis by a scanning electronic microscopy coupled with an EDAX probe. The apparatus used is a Hitachi S-350 at 20 kV.

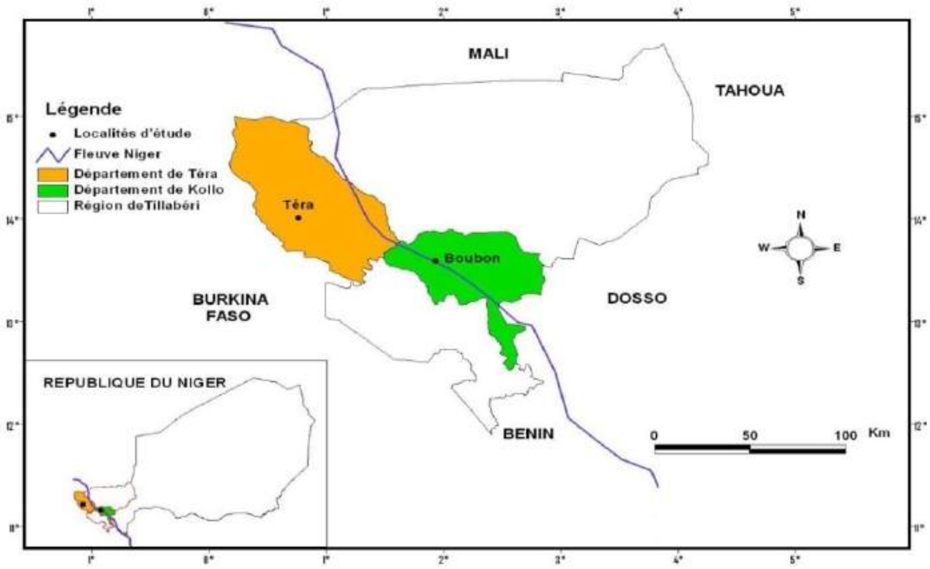


Figure 1: Location of sampling site of Boubon and Téra

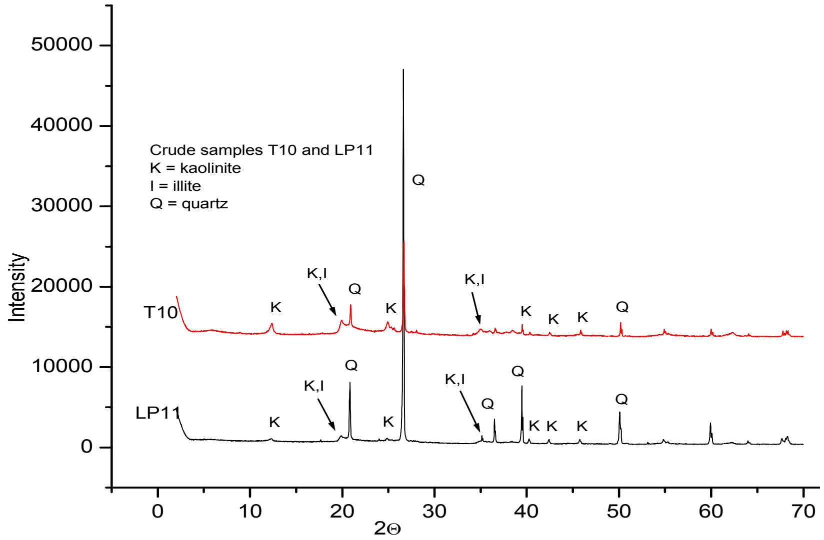


Figure 2: Diffractograms of crude samples LP11 and T10

RESULTS AND DISCUSSIONS

1. X-ray diffraction

The X-ray diffractograms of crude samples T10 and LP11 are shown in figure 2. Characteristic peaks of kaolinite around 12° (7.1 Å) and quartz between 26°; 27° (3.34 Å) were observed for both samples. Illite was found in the samples LP11 and T10 at 19.93°, 34.98°.

Besides crude sample characterization, chemical and ultrasonic methods were utilized to obtain the two samples clay fractions. The X-ray diffraction results obtained for the two (2) purification methods are shown in the figures 3a and 3b.

In figure 3a, the characteristic peak of kaolinite was observed at 12.35° (7.1 Å). Other peaks were observed at 19.8°, 24.9°, 34.9°, 38.4° and 45.6°. The principal peak of quartz is at 26.6° (3.34 Å). In figure 3b, kaolinite appears at 12.36° (7.1 Å), 19.8°, 24.8°, 34.9°, 38.4° and 45.5°. The two samples, LP11 and T10 contain principally kaolinite and quartz. After purification of the crude samples, the X-ray diffraction of their clay fractions obtained by chemical extraction and ultrasonic method confirms the presence of kaolinite in these samples.

For further investigation needs, the clay minerals were also submitted to two other treatments; one with ethylene glycol and the other heated at 550°C during 2 hours [15,16]. The results are shown in figures 4a and 4b.

The treatment by heat induces kaolinite dehydrolysis. The two (2) Kaolinite characteristic peaks were present in the normal sample (LP11N, Figure 4a; T10N, Figure 4b) and in the sample

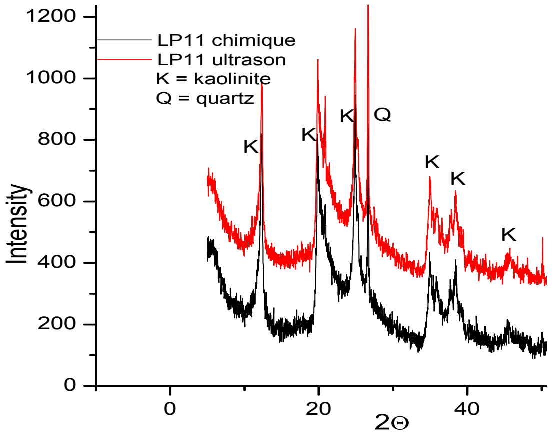


Figure 3a: Diffractogram of LP11 sample

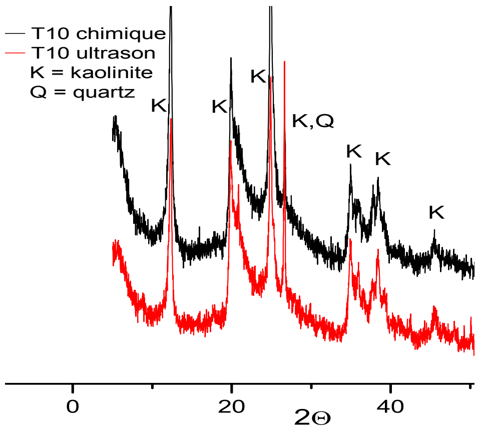
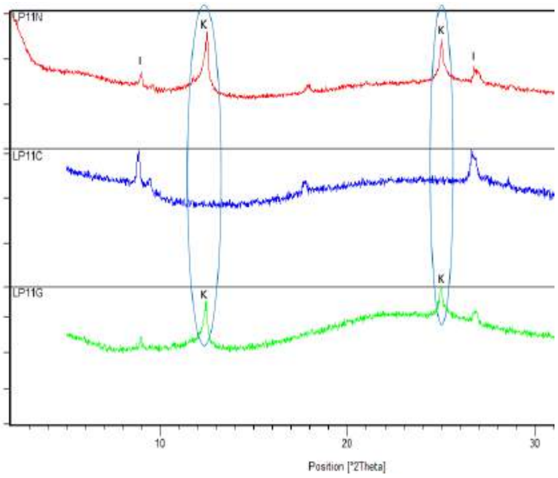


Figure 3b: Diffractogram of T10 sample



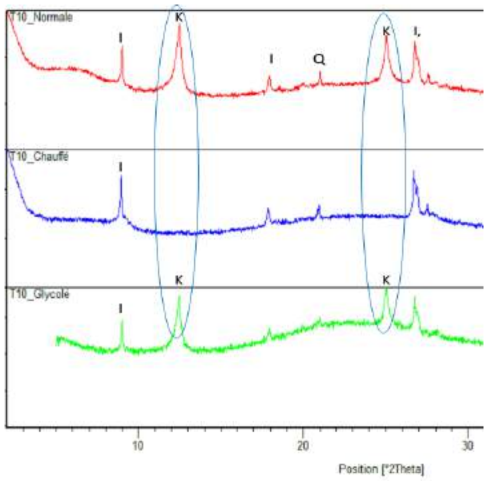


Figure 4a: Diffractograms of LP11N (normal), LP11C (heated), LP11G (ethylene glycol)
Figure 4b: Diffractograms of T10N (normal), T10C (heated), T10G (ethylene glycol)

treated with ethylene glycol (LP11G, Figure 4a; T10G, Figure 4b), but kaolinite peaks disappear after heating treatment at 550°C (LP11C, Figure 4a; T10C, Figure 4b). Similar results were obtained by others authors [15,17,12] and this proves the presence of kaolinite in the samples.

2. Infrared analysis

The infrared analyses of crude samples are shown in figures 5a and 5b. The wide band at 3462 cm^{-1} and 3450 cm^{-1} respectively in samples LP11 and T10 is characteristic of O-H (H_2O) bond. Another absorption peak of O-H band (inter layer water) was noted at 1626 cm^{-1} and 1632 cm^{-1}. The characteristic vibration and elongation bond of Si-O is also observed at 1034 cm^{-1} and 914 cm^{-1}. Moreover, the vibrations bands of Si-O-Mg appear at 470 cm^{-1} and the deformation bonds of Si-O-Al appear at 538 cm^{-1}. The peak at 3450 cm^{-1} and 640 cm^{-1} reveals the presence of kaolinite as obtained by others authors [18,19]. The infrared results are in conformity with the results of X-ray diffraction.

3. Thermo gravimetric analysis - differential thermic analysis

Thermic analysis graphs of clay fractions were giving in figures 6a and 6b. There are two endothermic peaks on these figures. Between 50°C and 100°C, the elimination peak of physisorption water and an intense one between 400°C and 600°C for the kaolinite dehydrolysis. There are also exothermic peaks between 850 and 1000°C. These peaks correspond to kaolinite structure reorganization. The losses of mass were observed between 400°C and 600°C for the two samples on ATG graphs. Similar results are observed by many authors [12,8].

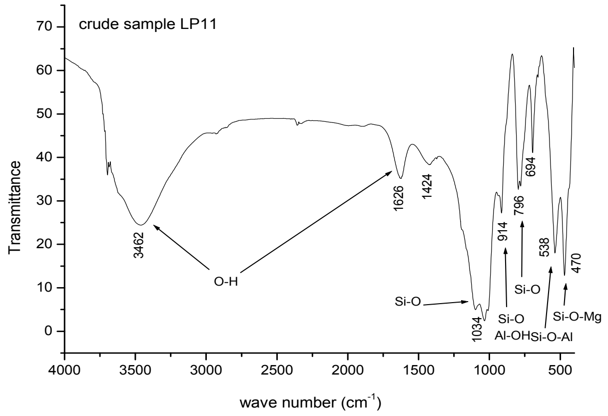


Figure 5a: LP11 crude infrared

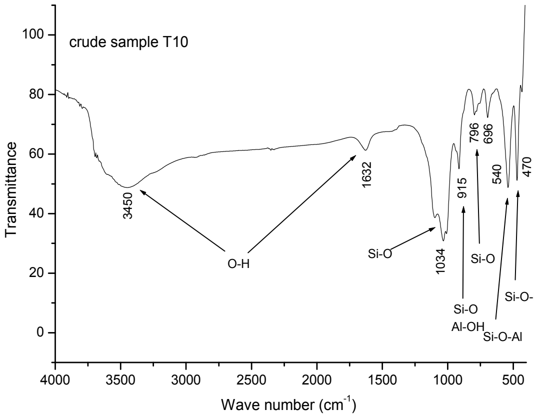


Figure 5b: T10 crude infrared

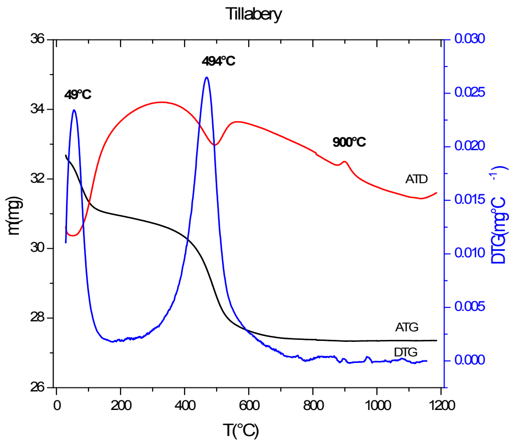


Figure 6a: T10 thermic analysis curve

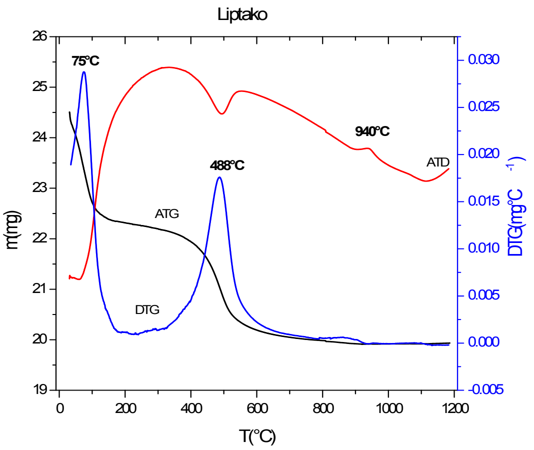


Figure 6b: LP11 thermic analysis curve

4. Chemical analysis

The results of chemical analysis on the crude samples are shown in Table II. It indicates the values for pH-KCl, exchangeable bases, organic carbon and cation exchange capacity. A high acidity of sample T10 (pH = 3.5) was observed compared to sample LP11 (pH = 6.4). This is probably due to an important amount of SiO_2 in this clay mineral. The exchangeable base results of sample T10 do not follow the order $[Ca^{2+}] > [Mg^{2+}] > [K^{+}] > [Na^{+}]$ like LP11. Similar result was obtained for samples taken in the same region [12]. The cation exchange capacity of the two samples varies from 8.2 to 8.4 $cmol.kg^{-1}$. These values agreed with kaolinite cation exchange capacity [17].

5. Mineralogical analysis and microscopic electronic scan

The scanning electron micrograph of samples LP11 and T10 were obtained by using a Hitachi microscope S-350. The results are shown in the figures 6a and 6b. It reveals the stratifying structure of the two clay minerals. These micrographs prove that these samples are phyllosilicates. The results of microanalysis using the EDAX probe of the two samples are summarized in Table III. All of these samples contain more than 60 % kaolinite. These analyses are also in conformity with the results of X-ray diffraction and infrared.

CONCLUSION

The characterization of two clay minerals, LP11 and T10, obtained from the valley of Niger River, Téra and Boubon, was done by using X-ray diffraction, infrared and scanning electronic microscopy. The scanning electronic microscopy shows morphology of argillaceous structure of these samples. The X-ray diffraction of the samples treated chemically and by ultrasonic method confirms the result obtains using crude samples. The kaolinite characteristic peaks appear at 12.35° (7.1 Å) and 25° (3.56 Å) then disappears when heated at 550° C. In the infrared analysis, the peaks at 3450 cm^{-1} and 640cm^{-1} reveals the presence of kaolinite. Thermic and mineralogical analysis shows that all these samples contain

Table II: Chemical analysis of the crude sample LP11 and T10

Sample	pH-KCl (1:2.5)	Org. Carbone % CO	Exchangeable bases				CEC-Ag cmol/kg
			Na^{+}cmol/kg	K^{+}cmol/kg	Ca^{2+}cmol/kg	Mg^{2+}cmol/kg	
LP11	6.4	0.11	0.4	0.9	5.0	2.5	8.2
T10	**3.5**	**0.33**	**0.6**	**0.1**	**3.9**	**3.2**	**8.4**

Table III: Microanalysis results using EDAX

Samples	Al_2O_3	SiO_2	Fe_2O_3	K_2O	SiO_2/Al_2O_3	% kaolinite
%mass (LP11)	27.51	49.58	12.03	1.91	1.80	60.99
% mass T10	30.87	53.27	8.99	0.73	1.73	61.61

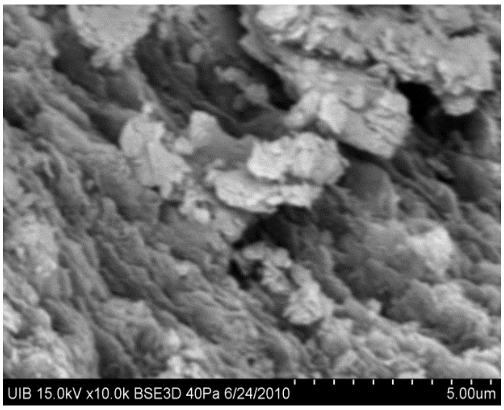


Figure 7a: Scanning electron micrograph of LP11

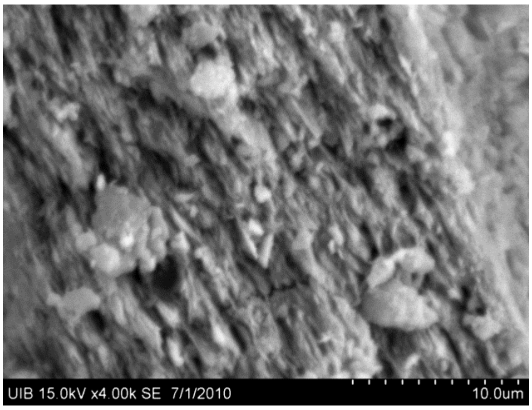


Figure 7b: Scanning electron micrograph of T10

principally kaolinite. As shown by their K_2O percentages, the samples LP11 (1.91%) and T10 (0.73%) contain a few amount of Illite.

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