Physico-Chemical and Mineralogical Characterizations of Two Togolese Clays for Geopolymer Synthesis

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Abstract

Geopolymers are an alternative to Portland cement, well known for their contribution to greenhouse gas emissions. Finding materials that can validly replace Portland cement is a challenge. It is in this logic that this work was undertaken with the objective of characterizing two local clay resources of Togo as raw materials for geopolymers. The physico-chemical properties of these clays were determined by characterization using X-ray diffraction (XRD), Fourier transform infrared (FTIR), thermogravimetric (TGA) and elemental analysis (ICP-OES). The results show that these clays contain kaolinite and therefore can be used in the formulation of geopolymers. The characterized clays underwent heat treatments transforming the crystalline phases into more reactive amorphous phases and then were activated by an alkaline solution in order to formulate the geopolymer materials. These elaborated materials were analyzed by Fourier transform infrared to identify the types of bonds formed. The results of these analyses show that these two local clays are well suited to be used in synthesizing geopolymers. Our future work will focus on the constraints of consolidation as well as the mechanical properties of these geopolymer materials.

Keywords

Clay, Kaolinite, Physico-Chemical Characterization, Geopolymer

1. Introduction

Geopolymers are a kind of inorganic material, initially reported by Davidovits in

1978 [1]. According to Davidovits, the geopolymer consists of polymeric Si-O-Al-O framework, with SiO_4 and AlO_4 tetrahedron linked alternately by sharing all the O atoms [1]. The geopolymers are obtained by reacting aluminosilicate precursors with alkaline solutions. Those precursors are commonly metakaolin obtained by the thermal decomposition of kaolin [2] [3], coal fly ash [4], and metallurgical slags [5]. Geopolymers are environmentally friendly materials that can be used as building materials with a prospect of replacing Portland cement emitting more CO_2 [2]. Geopolymer mortar has good chemical and fire resistance as well as relatively high mechanical resistance [6].

Clay is one of the oldest materials used by man. Geologically, clay is a sedimentary rock, composed mainly of aluminosilicates. Clay is used in the manufacture of fired bricks, ceramics and porcelain, in cosmetics or in medicine. Clays are also used in paper industry, paint, petroleum industry, clarification of various effluents, catalysis, etc. [7]. Applications of clays are dependent on their composition and structure.

Few studies have been conducted on Togolese clays and their potential in the ceramic industry [8] [9] and clay resources are not exploited enough. The most important use of clay in Togo remains traditional pottery, yet the country has sufficient clay reserves to supply a ceramic industry [9].

The present study aims at valorizing local clays in ecological materials. More specifically, it will involve carrying out a physicochemical and mineralogical characterization of two clay resources and their use in geopolymer synthesis.

2. Material and Methods

2.1. Clay Samples

The clays come from two different sites. The first clay, called clay A comes from a site located in southern Togo at Afagnan (6°29'39"N; 1°37'56"E) and the second clay called clay B from a site in northern Togo at Bandjeli (9°25'05"N; 0°37'12"E). The samples were dried at 105°C for 24 hours then ground to 75 μm and stored for analysis.

2.2. Clay Characterization

Physico-chemical and mineralogical characterizations were carried out on the clay samples.

Chemical composition was determined by inductively coupled plasma—optical emission spectrometry (ICP-OES, Agilent 5110 Dual View). This elementary analysis of the solid phases by ICP-OES required beforehand, a step of mineralization by alkaline fusion of the samples to solubilize them completely.

Structural characterization is carried out by X-ray diffraction (XRD) using the Bruker D8 diffractometer. The range of analysis is from 5° to 70° and the crystalline phases presented in the clay samples were identified with QualX software version 2.24 using the COD 1906 INO database.

Fourier transformed infrared (FT-IR) was performed using Bruker VERTEX

70 spectrometer. The samples were finely ground, mixed with 95% KBr by weight and pressed to obtain transparent pellets in the infrared. The range of absorption bands is between 400 and 4000 cm^{-1}.

Thermal analysis (TGA) of the clay samples was performed by a TG 209 F1 ASC-Netzsch apparatus in a dry environment with a heating rate of 10°C/min from room temperature to 1000°C.

2.3. Geopolymer Synthesis and Characterization

The mass ratio of the solid material and liquid activator for the geosynthetic reaction is optimized as 1.25. The solid material is calcined clay at 750°C and the liquid activator is 12 M NaOH solution. Thus, the activator was added to the calcined clay powder according to above mentioned ratio and stirred for 5 min.

The mixture was then cast into cylindrical mold at room temperature to allow the fabrication of the molded samples. The molded samples were allowed to mature at room temperature for 24 hours and cured at 70°C for 24 hours in an oven to increase their mechanical strength. FTIR and mechanical strength were measured on final samples named geopolymer A (GPA) and geopolymer B (GPB).

3. Results and Discussion

3.1. X-Rays Diffraction

The mineralogical composition of clay samples is determined by XRD analysis of the bulk clay samples. The results are shown on **Figure 1** and **Figure 2**. The diffractogram of clay A (**Figure 1**) shows mainly kaolinite mineral (more than 90%) and a minor phase of anatase (TiO_2). The clay B (**Figure 2**) is composed of a predominance of quartz and the presence of illite (19%) and kaolinite (6%).

3.2. Chemical Composition

The chemical composition of clay samples and their loss on ignition (LOI) are listed in **Table 1** in oxide form. The results show that SiO_2 and Al_2O_3 are the most abundant oxides in the studied samples whereas K_2O, Fe_2O_3, MgO, Na_2O, TiO_2, and P_2O_5 are present in weak quantities.

SiO_2 and Al_2O_3 are mainly associated with the illite and kaolinite. The SiO_2 content should be associated with the presence of quartz. The SiO_2/Al_2O_3 ratio in clay A is 1.25. The highest SiO_2/Al_2O_3 ratio in clay B (3.72) is an indication of quartz presence [10] [11]. The presence of potassium K_2O in clay B indicates the existence of illite.

The sum of exchangeable bases (CaO, K_2O, Na_2O and MgO) in clay B was higher (6.89) than Clay A sample (0.63%), indicating that clay B is richer in fluxing agents than clay A.

The loss on ignition determined on the clays shows a greater loss in clay A (15.7%) than in clay B (6.6%). This difference can be related to the organic matter combustion and to the dehydroxylation of the clay minerals. The loss on ignition is explained by the TGA analysis. This chemical composition is confirmed by the mineralogical composition.
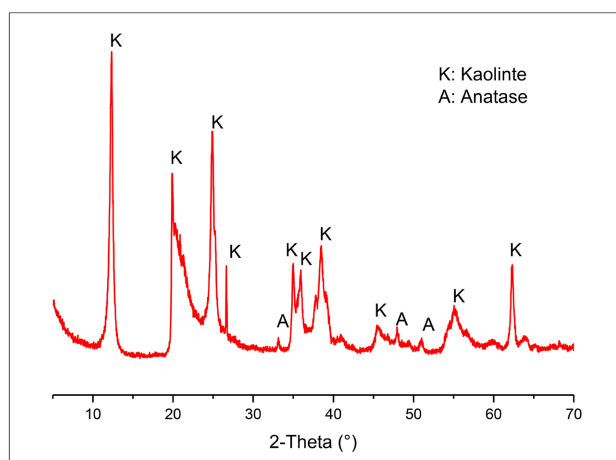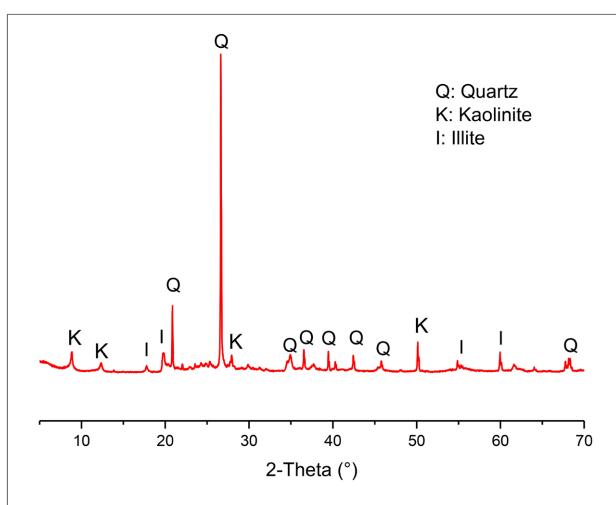
Figure 1. XRD of clay A.

Figure 2. XRD of clay B.

Table 1. Chemical composition of the studied clays (wt%).

	LOI (%)	Al_2O_3 (%)	SiO_2 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	P_2O_5 (%)	TiO_2 (%)	Na_2O (%)
Clay A	15.70	34.90	43.80	0.14	3.60	0.24	0.15	0.04	1.39	0.10
Clay B	6.60	17.50	65.10	0,09	2.99	4.32	1.44	0.03	0.81	1.04

3.3. Thermal Analysis

The thermal analysis of the different clays can help to determine the rate of kaolinite from the dehydroxylation reaction and the favorable temperature ranges for the geopolymerization reaction.

The thermogravimetric analysis of the studied clays are shown on **Figure 3** and **Figure 4**.

The first mass loss, which appeared at the temperature between 25°C and 180°C in clay A and from 25°C to 275°C in clay B, is due to the removal of water physisorbed on the surfaces of particles and to dehydration of interlayer cations
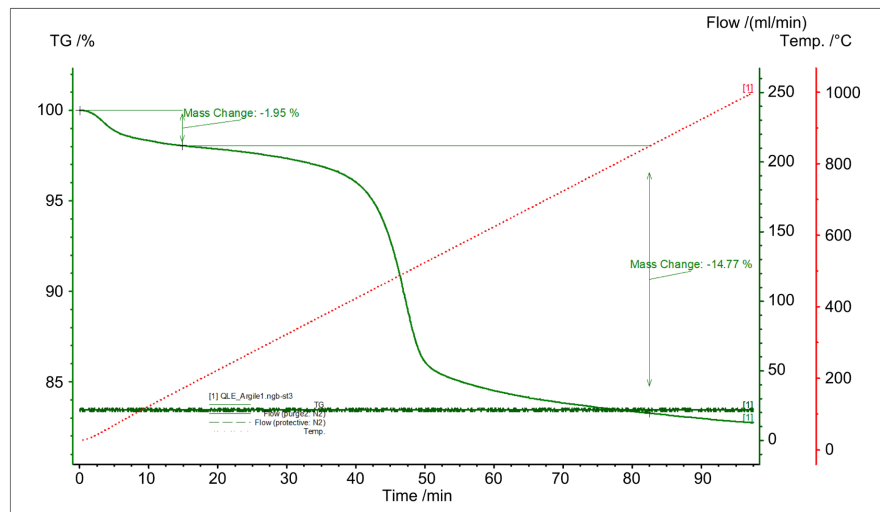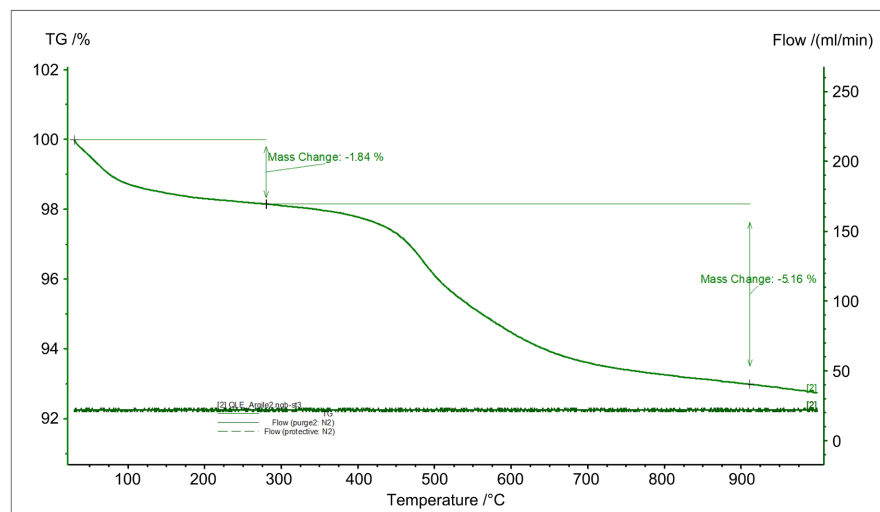
Figure 3. TGA of clay A.

Figure 4. TGA of clay B.

of clay minerals. At these temperatures the weight loss was 1.95% in clay A and 1.84% in clay B.

The second mass loss occurs between 300°C and 800°C in clay A and between 300°C and 900°C in clay B. This mass loss is attributed to the dehydroxylation of kaolinite. The relative mass losses observed are respectively 14.77% and 5.1% for clay A and B. The high mass loss in clay A is due to the presence of a large amount of kaolinite [12] while the low mass loss in clay B is due to a small amount of kaolinite and the presence a micaceous phase [10] [11].

3.4. Formulation of Geopolymers and Infrared Characterization

The FTIR of clay A (**Figure 5**) confirmed the presence of kaolinite mineral. The bands detected at 3700 - 3625 cm^{-1} are related to the stretching of hydroxyl groups in the kaolinite [11] [13] [14]. Bands at 1115 and 1000 cm^{-1} correspond to the vibration of Si-O-Al bonds [15] [16], and the peak at 903 cm^{-1} to the vi-

bration of Al-OH bond [17]. In the FTIR of clay B (**Figure 6**), in addition to the bands characteristic of kaolinite mineral, peaks at 785 and 702 cm^{-1} which are attributable to the O-Si-O bonds vibrations of Quartz [13] and peak at 3620 cm^{-1} attributable to hydroxyl groups of illite are observed [18].

The clay samples calcined at 750°C (AC, BC) and the formulated geopolymers (GPA, GPB) also were analyzed by FTIR.

The FTIR of clay A calcined AC at 750°C (**Figure 7**) showed the disappearance of the two peaks of the hydroxyl group. The characteristic peaks of Si-O-Si bonds initially located between 1000 and 1050 cm^{-1} seem to transform into a single broad peak located around 1080 cm^{-1} characteristic of silica sites inducing the formation of metakaolinite [12]. It's also observed, in clay B calcined at 750°C BC, the disappearance of the Si-O bonds between 950 and 1200 cm^{-1}. The band located at 798 cm^{-1} highlights the persistence of quartz after the heat treatment (**Figure 8**).
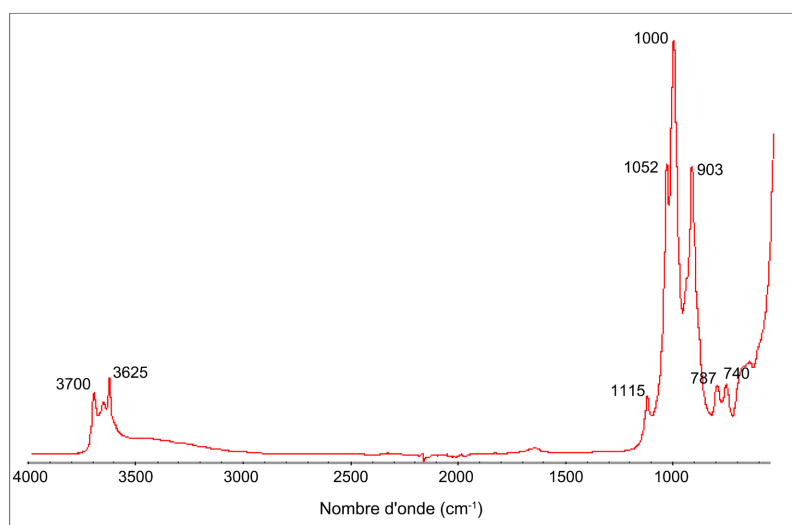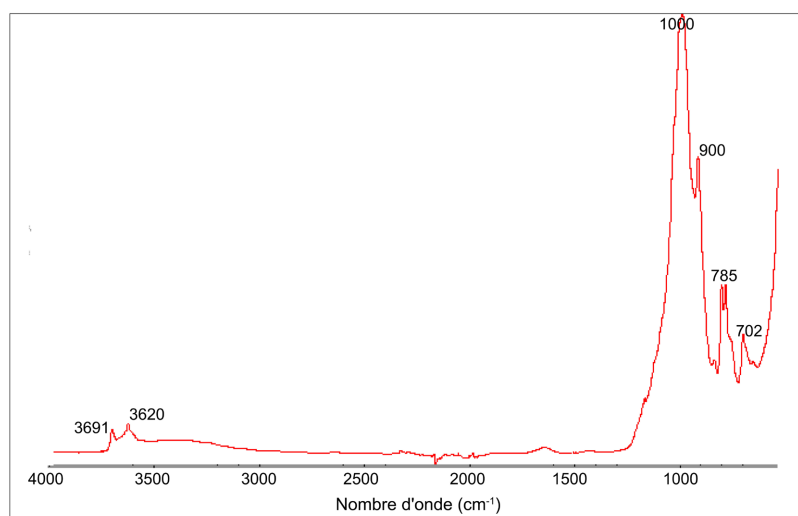

Figure 5. FTIR of clay A.
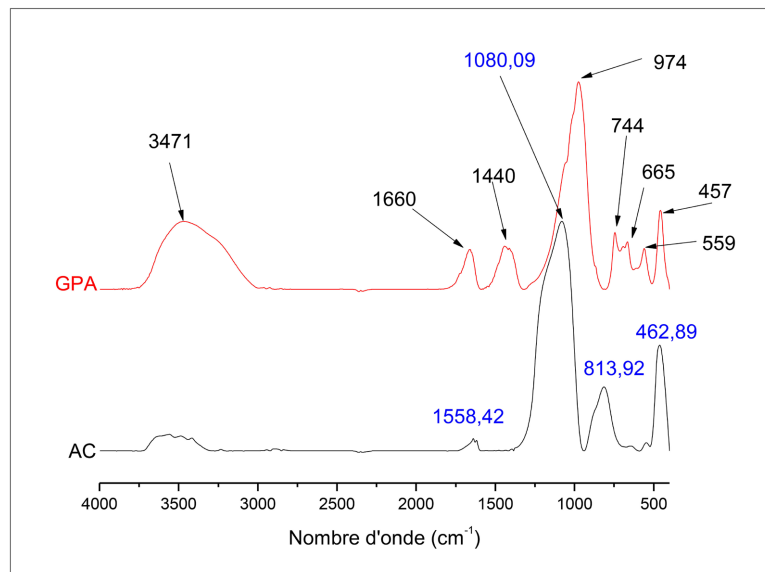

Figure 6. FTIR of clay B.

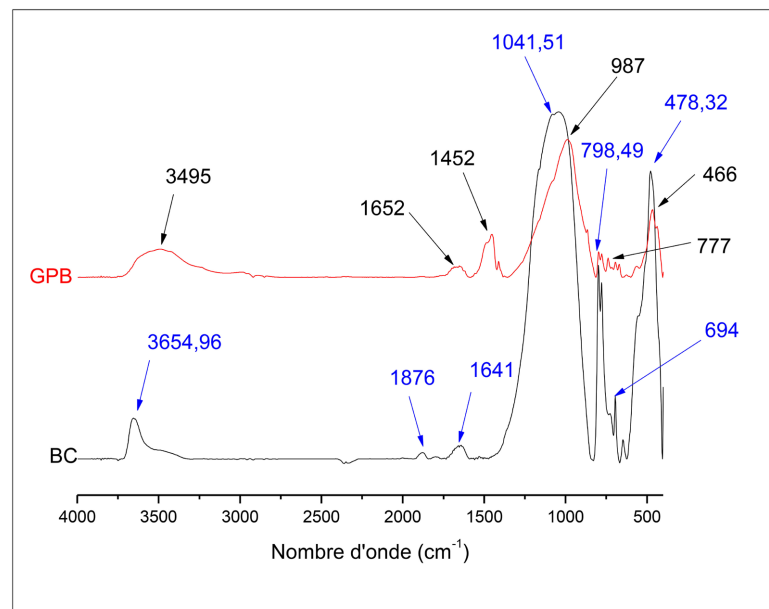**Figure 7.** FTIR of calcined clay A (AC) and geopolymer A (GPA).

Figure 8. FTIR of calcined clay B (BC) and geopolymer B (GPB).

The FTIR of geopolymers GPA and GPB are compared to the FTIR of calcined clay samples AC and BC. The displacement of some peaks detected 1080 cm^{-1} to 974 cm^{-1} in geopolymer GPA and 1041 cm^{-1} to 987 cm^{-1} in geopolymer GPB. These peaks are attributed to the asymmetric vibrations of the Si-O-Al and Si-O-Si bond of the AlO_4 and SiO_4 tetrahedra of the geopolymers [15] [19]. The displacement of the peaks attributed to Si-O-Al and Si-O-Si bonds proves the polycondensation in alkaline media by incorporation of aluminum into the Si-O-Si structure [15] [19]. The peaks at 974 and 987 cm^{-1} respectively for the geopolymer materials GPA and GPB are attributed to the Si-O-X bonds (X = Si, Al, K or Na). The spectra show also peaks at 3471 cm^{-1} (GPA) and 3495 cm^{-1}

(GPB) in broader bands as well as peaks at 1660 cm^{-1} (GPA) and 1652 cm^{-1} (GPB) which reflect the vibrations of hydroxyl group of water on the surface of the geopolymer [20].

It's also observed peaks at 777 cm^{-1} and at 738 cm^{-1} on FTIR of geopolymer GPB which shows the presence of quartz after the synthesis indicating the non-reactivity of quartz.

Furthermore, the peaks at 1440 cm^{-1} (GPA) and at 1452 cm^{-1} (GPB) are due to the asymmetric stretching mode of carbonates O-C-O [21]. During hardening, the geopolymers were normally exposed to CO_2 from the atmospheric air, which leads to the formation of carbonate [21] in alkaline medium.

4. Conclusion

The chemical, mineralogical and thermogravimetric characterization of the clays showed that clay A is mainly constituted of kaolinite and clay B is a mixture of quartz, illite and kaolinite. The presence of kaolinite in these clays makes them raw materials for the synthesis of geopolymers. The synthesis of geopolymers with these clays calcined at 750°C shows that the studied clays can be transformed into ecological cement. Further study should improve the physico-chemical and mechanical properties of the formulated geopolymers.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Davidovits, J. (1994) Geopolymers: Man-Made Rocks Geosynthesis and the Resulting Development of Very Early High Strength Cement. *Journal of Materials Education*, **16**, 91-139.

[2] Rozek, P., Krol, M. and Mozgawa, W. (2019) Geopolymer-Zeolite: A Review. *Journal of Cleaner Production*, **230**, 557-579.
https://doi.org/10.1016/j.jclepro.2019.05.152

[3] Wang, H., Li, H. and Yan, F. (2005) Synthesis and Mechanical Properties of Metakaolinite-Based Geopolymer. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **268**, 1-6. https://doi.org/10.1016/j.colsurfa.2005.01.016

[4] Swanepoel, J.C. and Strydom, C.A. (2002) Utilization of Fly Ash in a Geopolymeric Material. *Applied Geochemistry*, **17**, 1143-1148.
https://doi.org/10.1016/S0883-2927(02)00005-7

[5]   Duxson, P. and Provis, J.L. (2008) Designing Precursors for Geopolymer Cements. *Journal of the American Ceramic Society*, **91**, 3864-3869. https://doi.org/10.1111/j.1551-2916.2008.02787.x

[6]   Zhang, P., Zheng, Y., Wang, K. and Zhang, J. (2018) A Review on Properties of Fresh and Hardened Geopolymer Mortar. *Composites Part B: Engineering*, **152**, 79-95. https://doi.org/10.1016/j.compositesb.2018.06.031

[7]   Achiou, B., El Omari, H., Bennazha, J., Albizane, A., Daoudi, L., Saadi, L., Ouammou, M., Younssi, S.A., El Maadi, A. and Chehbouni, M. (2016) Physicochemical and Mineralogical Characterizations of Clays from Fez Region (Basin of Saiss, Morocco) in the Perspective of Industrial Use. *Journal of Materials and Environnemental Science*, **7**, 1474-1484.

[8]   Koriko, M., Zounon, D., Degbe, A., Tchegueni, S., Bafai, D.D., Fiaty, K., Tchangbedji, G. and Drogui, P. (2021) Caractérisations physico-chimiques et minéralogiques de l'argile d'Aklakou utilisée dans la poterie en vue de son application dans la formulation des agrégats légers. *International Journal of Advanced Research*, **9**, 706-712. https://doi.org/10.21474/IJAR01/13471

[9]   Tchangbédji, G., Tchakpele, K., Assih, T., Atiode, A.S., Ouro-Djobo, S. and Martin, F. (2004) Caractérisations chimique et minéralogique de quelques variétés d'argiles du Togo. *Journal de la société ouest africaine de chimie*, **17**, 155-166.

[10] Jarraya I., Fourmentin S. and Benzina M. (2010) Adsorption de Cov par un matériau argileux Tunisien organo-modifié. *Journal de la Société Chimique de Tunisie*, **12**, 139-149.

[11] Felhi, M., Tlili, A., Gaied, M.E. and Montacer, M. (2008) Mineralogical Study of Kaolinitic Clays from Sidi EL Bader in the Far North of Tunisia. *Applied Clay Science*, **39**, 208-217. https://doi.org/10.1016/j.clay.2007.06.004

[12] Tironi, A., Trezza, M.A., Irassar, E.F. and Scian, A.N. (2012) Thermal Treatment of Kaolin: Effect on the Pozzolanic Activity. *Procedia Materials Science*, **1**, 343-350. https://doi.org/10.1016/j.mspro.2012.06.046

[13] Boulingui, J.E., Nkoumbou, C., Njoya, D., Thomas, F. and Yvon, J. (2015) Characterization of Clays from Mezafe and Mengono (Ne-Libreville, Gabon) for Potential Uses in Fired Products. *Applied Clay Science*, **115**, 132-144. https://doi.org/10.1016/j.clay.2015.07.029

[14] Gourouza, M., Zanguina, A., Natatou, I. and Boos, A. (2013) Characterization of a Mixed Clay Niger. *Revue CAMES—Sciences et Structure de la Matière*, **1**, 29-39.

[15] Ogundiran, M.B. and Kumar, S. (2015) Synthesis and Characterisation of Geopolymer from Nigerian Clay. *Applied Clay Science*, **108**, 173-181. https://doi.org/10.1016/j.clay.2015.02.022

[16] Essaidi, S.R.N., Samet, B., Baklouti, S. and Rossignol, S. (2013) Effect of Calcination Temperature of Tunisian Clays on the Properties of Geopolymers. *Ceramics-Silikaty*, **57**, 251-257.

[17] Saikia, J.B. and Parthasarathy, G. (2010) Fourier Transform Infrared Spectroscopic Characterization of Kaolinite from Assam and Meghalaya, Northeastern India. *Journal of Modern Physics*, **1**, 206-210. https://doi.org/10.4236/jmp.2010.14031

[18] Abdoulaye, O.D.M., Yao, B.K., Ahmed, A.M., Adouby, K., Abro, D.M.K. and Drogui, P. (2019) Mineralogical and Morphological Characterization of a Clay from Niger. *Journal of Materials and Environmental Sciences*, **10**, 582-589.

[19] Prud'homme, E., Autef, A., Essaidi, N., Michaud, P., Samet, B., Joussein, E. and Rossignol, S. (2013) Defining Existence Domains in Geopolymers through Their Physicochemical Properties. *Applied Clay Science*, **73**, 26-34.

https://doi.org/10.1016/j.clay.2012.10.013

[20] Soleimani, M.A., Naghizadeh, R., Mirhabibi, A.R. and Golestanifard, F. (2012) Effect of Calcination Temperature of the Kaolin and Molar Na_2O/SiO_2 Activator Ratio on Physical and Microstructural Properties of Metakaolin Based Geopolymers. *International Journal of Medical Science and Education*, **9**, 43-51.

[21] Bernal, S.A., Provis, J.L., Rose, V. and Mejía De Gutierrez, R. (2011) Evolution of Binder Structure in Sodium Silicate-Activated Slag-Metakaolin Blends. *Cement and Concrete Composites*, **33**, 46-54. https://doi.org/10.1016/j.cemconcomp.2010.09.004