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Properties and Characterization of Two Clays Raw Material from Mountain District (West of Côte d'Ivoire) for Use in Low-Carbon Cements

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Abstract

This work was devoted to the study of the physico-chemical properties of two clay minerals from the Mountain District (West Côte d'Ivoire) referenced ME1 and ME2. These samples were characterized by the experimental techniques, such as X-ray diffraction (XRD), Infrared spectroscopy (IR), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Differential Thermal Analysis and Thermogravimetry (DTA-TG), Brunauer, Emett and Teller method (BET), laser particle size analysis and Scanning Electron Microscope (SEM). The main results of these analyses reveal that the two clay samples mainly contain quartz (52.91% for ME1 and 51.72% for ME2), kaolinite (36.60% for ME1 and 41.6% for ME2) and associated phases, namely goethite and hematite (13.47% for ME1 and 11.00% for ME2). The specific surface values obtained for samples ME1 and ME2 are 34.78 m^2/g and 29.18 m^2/g respectively. The results obtained show that the samples studied belong to the kaolinite family. After calcination, they could have good pozzolanic activity and therefore be used in the manufacture of low-carbon cements.

Keywords

Quartz, Kaolinite, Mountain District, Low-Carbon Cements

1. Introduction

Cement based materials are the most widely used in the building industry around the world [1]. However, cement manufacture requires significant energy consumption [2] and consequently produces a large quantity of carbon dioxide (CO_2, a greenhouse gas) [3]. This gas comes essentially from the decarbonation of the limestone ($CaCO_3$) used to make the clinker that is the main component of cement. To reduce CO_2 emissions during cement production, it would be wise to use alternative cementitious materials to partially replace clinker. By combining clinker with industrial co-products such as silica fume, blast furnace slag and fly ash, it is possible to achieve the technical and environmental performance sought in cementitious materials. However, the availability of these industrial co-products may be limited both globally and locally. The use of calcined clay now appears to be a promising alternative solution, as these raw materials are relatively abundant and available in many parts of the world (particularly Côte d'Ivoire). They are obtained by calcination (at temperatures below 1000˚C), a process that consists of dehydroxylation, without emission of CO_2 [4].

Several studies carried out on calcined clays have shown that they can act as pozzolans or supplementary cementing materials [5]. It has also been shown that, after calcination, kaolin has the best pozzolanic activity of all clay minerals [6]. Consequently, cements with added calcined kaolin or metakaolin have better mechanical properties and durability [7] [8].

The present work is devoted to the physico-chemical characterization of two clay raw materials from the Man region (west of Côte d'Ivoire) with a view to their use in low-carbon cements. The aim is to determine the chemical and mineralogical composition of these two clays.

2. Materials and Methods

2.1. Raw Materials

The clays in this study, referenced ME1 and ME2, were sampled in the village of Delobly, located in the Montagnes district, in the west of Côte d'Ivoire. The coordinates of the sampling site are around 6˚52'13.2"N, 7˚24'07.5"W.

2.2. Experimental Methods

The chemical composition of the two clays' raw materials was determined by plasma emission spectrometry (ICP-AES) using the Anton Paar device.

The crystalline phases in the different samples were identified by X-ray diffraction on unoriented preparations of powder with a particle size of less than 100 μm. Diffractograms were obtained using the Bruker D8 ADVANCE diffractometer and then processed using the EVA (short for Evaluation) Brukers AXS software.

The chemical analysis results combined with those of the X-ray diffraction made it possible to evaluate the semi-quantitative mineralogical composition according to Equation (1):

$$T(a) = \sum M_i \times P_i(a) \tag{1}$$

$T(a)$: content (oxide %) of chemical element "a"; M_i: content (%) of mineral" i" in the material studied and containing the element "i"; $P_i(a)$: proportion of the element “*a*” in the mineral “*i*”.

The thermal behavior of the samples (Differential Thermal Analysis and Thermogravimetric DTA/TGA) was recorded simultaneously using the NETZSCHSTA device from room temperature to 1200˚C, with a temperature rise of 5˚C/min.

The Perkin Elmer Spectrum 1000 brand Fourier transform spectrometer was used to perform the samples infrared spectra.

The microstructure of the clays was observed using an FEI Quanta FEG 450 brand scanning electron microscope.

The particle size distribution of the samples was determined using a Mastersizer 3000 laser granulometer (Malvern).

The specific surface area of the clay samples was determined by the BET (Brunauer-Emmet-Teller) method. After degassing the samples at 150˚C for 16 hours, measurements were taken using a Micromeritics Flow Sorb II 2300 instrument.

3. Results and Discussion

Table 1 shows the results of the chemical analysis of the two raw clay materials.

Table 1. Chemical compositions (wt%).

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	TiO_2	SiO_2/Al_2O_3
ME1	64.94	14.47	12.11	0.41	0.27	0.33	0.17	2.30	4.8
ME2	71.21	16.47	9.94	0	0.29	0	0.16	1.89	4.4

The results obtained show that these clays are mainly composed of silica, alumina and iron oxide. The high silica and alumina contents indicate that these clays can be classified in the aluminosilicate group [9]. The SiO_2/Al_2O_3 ratio, which is an indicator of the clay mineral content of a sample, is 4.8 and 4.4 respectively for ME1 and ME2 instead of between 1 and 2 for pure kaolinite [10]. This difference in value can be explained by the presence silica in free form in significant quantities in both samples [11]. The iron oxide content is in both clays provides for the presence of oxy-hydroxides, namely goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and/or oxides such as hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) [12]. Low levels of K_2O and Na_2O are also observed. The high alumina content and low alkaline element content indicate the possibility of using these clays as a raw material for making refractory product [13].

Figure 1 shows the X-ray diffractograms of the ME1 and ME2 clays obtained on a fraction of grain size less than or equal to 100 µm. The main reflections were indexed with kaolinite ($Si_2Al_2O_5(OH)_4$), quartz (SiO_2), goethite (FeOOH) and hematite (Fe_2O_3) crystallographic phases.

The DTA-TG thermograms of the two samples ME1 and ME2 shown in **Figure 2(a)** and **Figure 2(b)** respectively exhibit six thermal phenomena, four of which are endothermic and two exothermic.

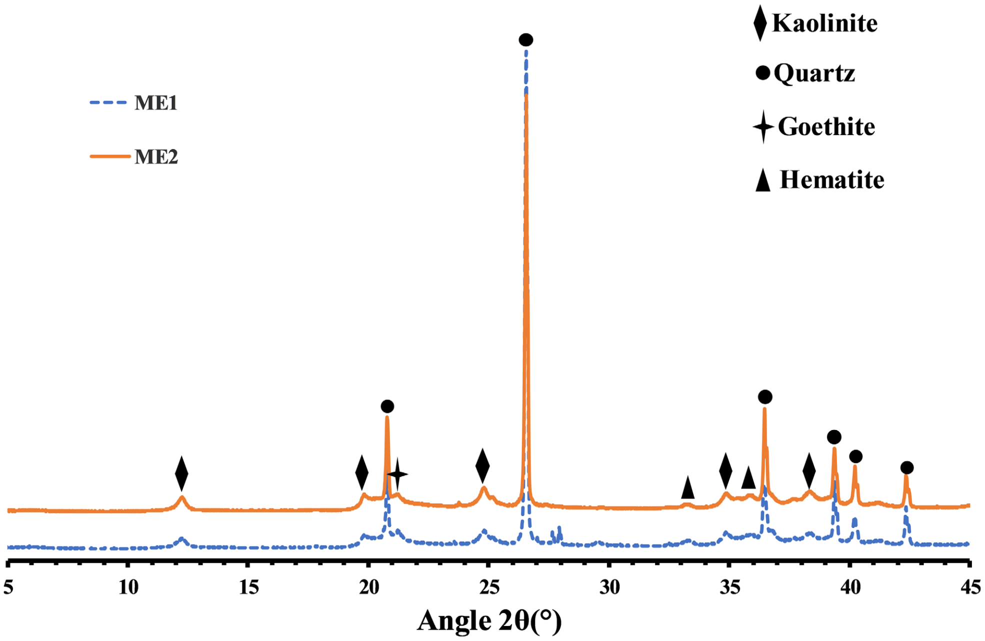

Figure 1. X-ray diffractograms of clay samples.

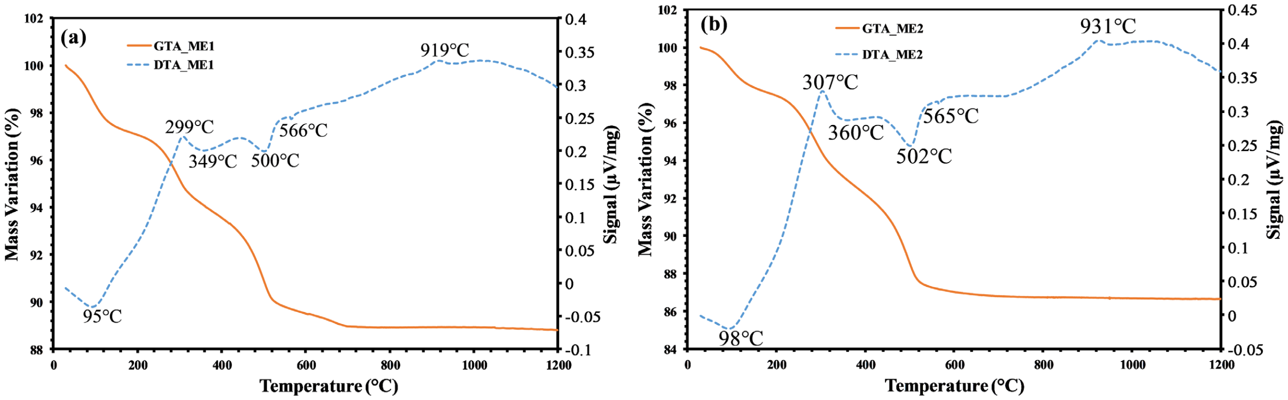

Figure 2. Differential thermal and thermogravimetric analyses of samples ME1 and ME2 respectively.

The endothermic peak around 96˚C with a mass loss of around 1.8% represents the evaporation of adsorbed hygroscopic water. The departure of this water does not modify the structure of the material [14].

Around 300˚C, the exothermic peak observed reflects the combustion and/or oxidation of the organic matter present in the samples.

Between 345˚C and 360˚C, another endothermic peak is observed, associated with a mass loss of around 1.15%. This peak corresponds to the transformation of goethite into hematite [15] according to the Equation (2):

$$\underset{\text{Goethite}}{2\text{FeOOH}} \Rightarrow \underset{\text{Hematite}}{\text{Fe}_2\text{O}_3} + \text{H}_2\text{O} \qquad (2)$$

The intense endothermic peak at around 500˚C with a mass loss of between 3.44% and 3.50% characterizes kaolinite dehydroxylation. Dehydroxylation is due to the departure of hydroxyls from the kaolinite structure in the form of water, leading to the formation of “metakaolin”, which has a disorganized structure [15]. This reaction is expressed according to Equation (3):

$$\underset{\text{Kaolinite}}{Si_2Al_2O_5(OH)_4} \Rightarrow \underset{\text{Metakaolinite}}{Si_2Al_2O_7} + 2H_2O \tag{3}$$

The endothermic peak at around 566˚C corresponds to the allotropic transition of quartz ($\alpha \rightarrow \beta$).

Finally, the exothermic peak without mass loss at around 900˚C reflects the structural reorganization of metakaolinite into a spinel phase and the formation of amorphous silica [16] according to the following Equation (4):

$$2\underset{\text{Metakaolinite}}{\left[Si_2Al_2O_7\right]} \Rightarrow \underset{\text{Spinelle}}{Si_3Al_4O_{12}} + \underset{\text{Silica}}{SiO_2} \tag{4}$$

The chemical analysis results combined with those of X-ray diffraction were used to determine the mineralogical composition of the samples. The results are recorded in **Table 2** as well as those for specific surface areas.

Table 2. Mineralogical composition and Specific surface areas of ME1 and ME2.

Mineralogical composition (wt%)			
Samples	**Kaolinite**	**Quartz**	**Associated phases (Goethite & Hematite)**
ME1	36.60	52.91	13.47
ME2	41.67	51.72	11.60
Specific surface areas (m^2/g)			
ME1	34.78		
ME2	29.18		

The results show that both samples are rich in kaolinite and quartz. It can be deduced that quartz is the source of free silica, which is in agreement with the calculation of the SiO_2/Al_2O_3 ratio carried out above. The high quartz content, which favours the use of these raw materials in ecomaterial formulations (bricks, tiles, etc…), also plays the role of degreasing kaolinite [17]. The high kaolinite is an advantage for obtaining metakaolin. Consequently, they could be used in eco-cement.

The specific surface area value obtained for sample ME1 is between 10 and 30 m^2/g, which corresponds to the range for the specific surface of kaolinite-type clays [18], while the ME2 is slightly above the upper limit of this range. This difference can be explained by the slightly higher iron content in ME2 than in ME1 (**Table 1**). Indeed, according to some authors [19]-[21], the specific surface area of kaolinitic clays increases with the amount of iron.

Figure 3 shows the infrared spectra of ME1 and ME2 samples. These show broadly the same vibrational bands.

The presence of bands in the region from 3700 to 3600 cm^{-1} confirms the presence of clay minerals in our two samples. These correspond to the elongation vibrations of kaolinite's OH bonds [22]. The absorption bands at 1097 and

1032 cm^{-1} are attributed to the Si-O and Si-O-Si vibrations of kaolinite, respectively [1]. The absorption near 912 cm^{-1}, observed represents to Al-OH stretching vibrations of kaolinite [1]. The bands around 779 and 536 cm^{-1} on the two spectra are attributed with the Si-O-Al bonds of the kaolinite [1]. The presence of quartz in our samples is indicated by bands around 685 and 469 cm^{-1} corresponding to the elongation of Si-O-Si bonds. The band at 1610 cm^{-1} is due to absorbed hygroscopic water [1].

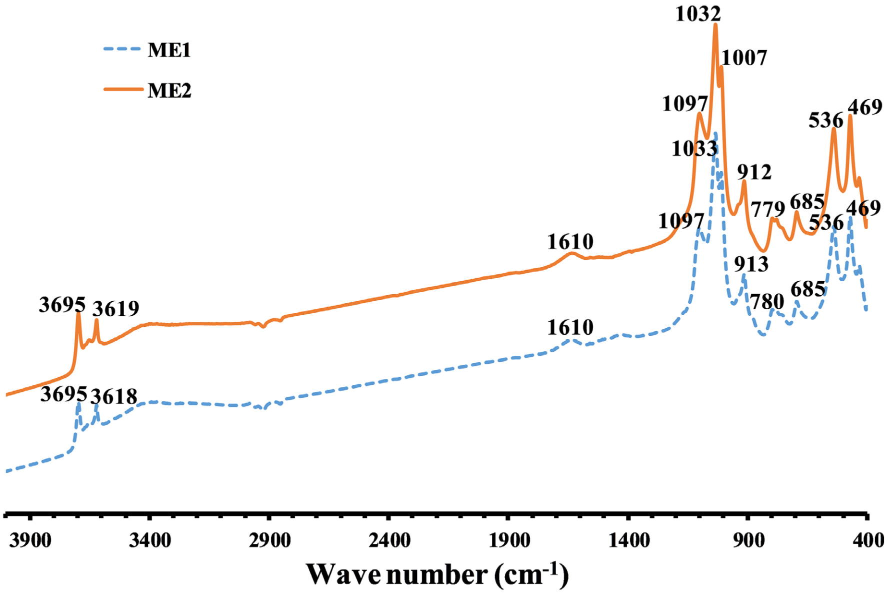

Figure 3. Infrared spectra of ME1 and ME2 samples.

The particle size distribution curves for the two samples are shown in Figure 4. These show an order of magnitude in the order of the meshes corresponding to 90%, 50% and 10% of the passage of the particles respectively noted d90, d50 and d10 (Table 3). Analysis of the table shows that our samples are characterized by relatively clean grains, with 90% of the particles passing through having an average diameter of less than 56 microns and 50% having an average diameter of less than 5 microns. Figure 4 also shows the presence of three populations in our samples, centered on 3, 9 and 39 microns.

The scanning electron microscope (SEM) microstructure of our samples is shown in Figure 5. This shows a porous microstructure and a disordered morphology. The latter is explained by the high quartz content in our samples, which can screen the kaolinite platelets [23].

Table 3. Values of d10, d50 and d90.

	Particle size (µm)		
	d10	**d50**	**d90**
ME1	1.15	3.12	43.50
ME2	1.35	4.90	55.03

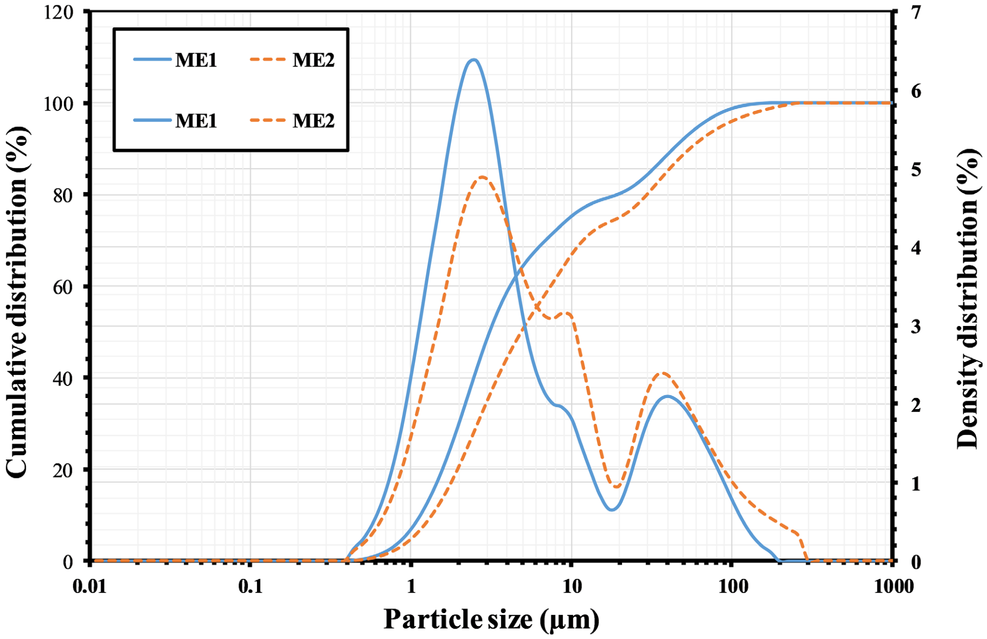

Figure 4.The particle size curves of ME1 and ME2 samples.

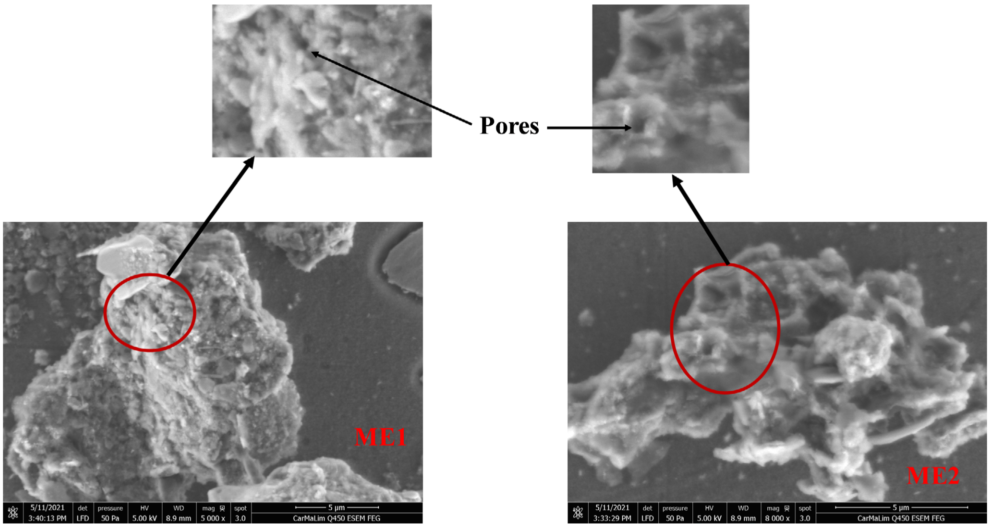

Figure 5. SEM images of the two clays samples.

4. Conclusions

Using a material requires knowledge of its physico-chemical properties, we therefore set out to characterize two clay minerals from west Côte d'Ivoire with a view to their use in low-carbon cements. Mineralogical and structural analyses showed that the samples contain kaolinite, quartz, goethite and hematite. The particle size analysis of our samples showed that they were very fine. The specific surface values obtained confirm that our samples belong to the kaolinite family of clay minerals.

At the end of our study, we can say that samples ME1 and ME2 belong to the kaolinite family and, after calcination, could have good pozzolanic activity with a view to substituting clinker in the manufacture of low-carbon cement.

For the continuation of this work, we count:

- Studying the characteristics of calcined samples ME1 and ME2 in order to assess their pozzolanic activity;
- Producing compressed earth bricks (CEB) from our samples in order to study their properties.

Conflicts of Interest

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

References

[1] Kouakou, L.P.M.-S., Kouamé, A.N., Doubi, B.I.H.G., Méité, N., Kangah, J.T., Zokou, E.P., *et al.* (2022) Characterization of Two Clay Raw Materials from Côte D'ivoire with a View to Enhancing Them in Eco-Construction. *Journal of Minerals and Materials Characterization and Engineering*, **10**, 198-208. https://doi.org/10.4236/jmmce.2022.102016

[2] Verma, Y., Mazumdar, B. and Ghosh, P. (2020) Dataset on the Electrical Energy Consumption and Its Conservation in the Cement Manufacturing Industry. *Data in Brief*, **28**, Article 104967. https://doi.org/10.1016/j.dib.2019.104967

[3] Balde, M.Y., Sidibe, D., Bakam, É.S.S., Njiomou, C.D. and Blanchart, P. (2023) Formulation of Geopolymer Cements from Two Clays Containing Kaolinite and Muscovite: Effect of Temperature on the Physicomechanical Properties of the Products. *Journal of Materials Science and Chemical Engineering*, **11**, 34-45. https://doi.org/10.4236/msce.2023.1112004

[4] Scrivener, K.L., John, V.M. and Gartner, E.M. (2018) Eco-Efficient Cements: Potential Economically Viable Solutions for a Low-CO_2 Cement-Based Materials Industry. *Cement and Concrete Research*, **114**, 2-26. https://doi.org/10.1016/j.cemconres.2018.03.015

[5] Sabir, B.B., Wild, S. and Bai, J. (2001) Metakaolin and Calcined Clays as Pozzolans for Concrete: A Review. *Cement and Concrete Composites*, **23**, 441-454. https://doi.org/10.1016/s0958-9465(00)00092-5

[6] Alujas, A., Fernández, R., Quintana, R., Scrivener, K.L. and Martirena, F. (2015) Pozzolanic Reactivity of Low Grade Kaolinitic Clays: Influence of Calcination Temperature and Impact of Calcination Products on OPC Hydration. *Applied Clay Science*, **108**, 94-101. https://doi.org/10.1016/j.clay.2015.01.028

[7] Avet, F. and Scrivener, K. (2018) Investigation of the Calcined Kaolinite Content on the Hydration of Limestone Calcined Clay Cement (LC^3). *Cement and Concrete Research*, **107**, 124-135. https://doi.org/10.1016/j.cemconres.2018.02.016

[8] Jaskulski, R., Jóźwiak-Niedźwiedzka, D. and Yakymechko, Y. (2020) Calcined Clay as Supplementary Cementitious Material. *Materials*, **13**, Article 4734. https://doi.org/10.3390/ma13214734

[9] Kouamé, N.A. (2021) Stabilisation, par le ciment, de blocs de terre argileuse incorporant des tourteaux de karate. Thèse de Doctorat, Université Félix Houphouët-Boigny.

[10] Atta, A.Y., Ajayi, O.A. and Adefila, S.S. (2007) Synthesis of Faujasite Zeolites from Kankara Kaolin Clay. *Journal of Applied Sciences Research*, **3**, 1017-1021.

[11] Sanou, I. (2017) Influence du mélange ciment-pouzzolane sur quelques propriétés physiques et mécaniques des adobes. Thèse de Doctorat, Université Joseph KI-ZERBO.

[12] Sei, J., Jumas, J.C., Olivier-Fourcade, J., Quiquampoix, H. and Staunton, S. (2002) Role of Iron Oxides in the Phosphate Adsorption Properties of Kaolinites from the Ivory Coast. *Clays and Clay Minerals*, **50**, 217-222. https://doi.org/10.1346/000986002760832810

[13] Sagbo, E., Laibi, A., Senou, M., Josse, R., Mensah, J., Borschneck, D. and Noack, Y. (2015) Physico-Chemical and Mineralogical Characterization of some Clays from Coastal Sedimentary Basin of Benin Used in Ceramic. *Research Journal of Chemical Sciences*, **5**, 1-19.

[14] Gouré Doubi, B.I.H. (2013) Etude de la consolidation des matériaux «géomimétiques» à base d'argile latéritique: Effet des acides et des phases ferriques. These de Doctorat, Université de Limoges.

[15] Manoharan, C., Sutharsan, P., Dhanapandian, S. and Venkatachalapathy, R. (2012) Characteristics of Some Clay Materials from Tamilnadu, India, and Their Possible Ceramic Uses. *Cerâmica*, **58**, 412-418. https://doi.org/10.1590/s0366-69132012000300021

[16] Hu, P. and Yang, H. (2013) Insight into the Physicochemical Aspects of Kaolins with Different Morphologies. *Applied Clay Science*, **74**, 58-65. https://doi.org/10.1016/j.clay.2012.10.003

[17] Laibi, A.B., Gomina, M., Sorgho, B., Sagbo, E., Blanchart, P., Boutouil, M., *et al.* (2017) Caractérisation physico-chimique et géotechnique de deux sites argileux du Bénin en vue de leur valorisation dans l'éco-construction. *International Journal of Biological and Chemical Sciences*, **11**, 499-514. https://doi.org/10.4314/ijbcs.v11i1.40

[18] Ma, Y., Zhu, J., He, H., Yuan, P., Shen, W. and Liu, D. (2010) Infrared Investigation of Organo-Montmorillonites Prepared from Different Surfactants. *Spectrochimica Acta Part A*: *Molecular and Biomolecular Spectroscopy*, **76**, 122-129. https://doi.org/10.1016/j.saa.2010.02.038

[19] Sei J. (1998) Etude de matériaux de dimensionalité réduite. Relation structure-propriétés dans des kaolinites naturelles de Côte d'Ivoire. Thèse de Doctorat, Université de Montpellier II.

[20] Soro N. (2003) Influence des ions fer sur les transformations thermiques de la kaolinite. Thèse, Université de Limoges.

[21] Arias, M., Barral, M.T. and Diaz-Fierros, F. (1995) Effects of Iron and Aluminium Oxides on the Colloidal and Surface Properties of Kaolin. *Clays and Clay Minerals*, **43**, 406-416. https://doi.org/10.1346/ccmn.1995.0430403

[22] de Almeida Azzi, A., Osacký, M., Uhlík, P., Čaplovičová, M., Zanardo, A. and Madejová, J. (2016) Characterization of Clays from the Corumbataí Formation Used as Raw Material for Ceramic Industry in the Santa Gertrudes District, São Paulo, Brazil. *Applied Clay Science*, **132**, 232-242. https://doi.org/10.1016/j.clay.2016.06.009

[23] Konan, K.L. (2006) Interaction entre des materiaux argileux et un milieu basique riche en calcium. Thèse de Doctorat, Universite de Limoges.