Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2019, Volume 10, Issue 7, Page 582-589

http://www.jmaterenvironsci.com

Mineralogical and morphological characterization of a clay from Niger

O.D.M. Abdoulaye [1], B.K. Yao [1*], A.M. Ahmed [2], K. Adouby [1], D.M.K. Abro [1], P. Drogui [3]

[1]Laboratoire des Procédés Industriels de Synthèse, de l'Environnement et des Energies Nouvelles (LAPISEN),
Institut National Polytechnique Félix Houphouët-Boigny de Yamoussoukro BP 1093, Côte d'Ivoire
[2]Université Boubakar BÂ de Tillabéri, BP 175, Niger
[3] Institut National de la Recherche Scientifique (INRS Eau Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec City, Canada

Received 22 April 2019,
Revised 24 July 2019,
Accepted 25 July 2019

Keywords
- ✓ *Clay Characterization,*
- ✓ *X-rays diffraction,*
- ✓ *EDS*
- ✓ *SEM*
- ✓ *ICP-AES*

benjamin.yao@inphb.ci;
Phone: +22507 80 05 19;
Fax: +225 30 64 04 06.

Abstract

A clay of the Tahoua region (sedimentary basin of Iullemmeden, Niger) was characterized in order to evaluate its ability to be used as catalysts manufacturing for oil cracking. Analysis of the clay fraction by X-ray diffraction (XRD), infrared (IR) and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) was performed for this purpose. The results showed that this clay is composed of an irregular interlayer mineral composed of three (3) different Smectite/Illite/Chlorite sheets and 46.3% of kaolinite quantified by FITYK software with diffraction intensities correction factors. The pseudo-hexagonal morphology characteristic of kaolinite and illite was also revealed by SEM coupled with EDS. Moreover, Inductively Coupled Plasma – atomic Emission Spectroscopy (ICP-AES) investigations indicated the presence of free quartz in the sample. The specific surface area (SSA) and the Cation-exchange capacity (CEC) was also determined and are respectively 15.26 m^2/g and 6.36 meq/100g. The loss on ignition value is 16.1%.

1. Introduction

Last decades , catalysts have become more and more used in the petroleum refining industry [1]. A catalyst is a substance that increases the rate of a chemical reaction, without being neither consumed nor produced [2, 3]. Catalytic cracking catalysts are solids and possess acidic properties. They are composed of a supporting matrix which is the major component and zeolite. The matrix are consisted of different constituents such as aluminosilicates and additives that are solid compounds added to improve its properties (combustion promoters, metal oxides ...) [4, 5, 6]. The matrix of modern catalysts for catalytic cracking are generally made of 60 to 85 wt% of synthetic and natural components and 40 to 15 wt% of zeolite. The natural component is clay such as kaolinite, bentonite, etc. The synthetic component is amorphous silica or alumina silica [7].

Due to their abundance in nature, their specific surfaces, the presence of electrical charges on their surfaces and especially the cation exchange capacity interfoliar, clays are increasingly inciting much interest for catalytic application in the petroleum refining industry especially [1, 8]. Clays are widely used as catalyst and catalyst supports for a wide range of processes namely catalytic cracking, hydrocracking, reforming, isomerization, hydrogenation and alkylation. The most generally used in the manufacture of catalysts are kaolin and montmorillonite [1]. In fact, catalysts giving mainly high octane gasoline in petroleum industry have been produced from clays composed of halloysite, montmorillonite and kaolinites [9], so that the quantity of kaolin used annually for production of petroleum cracking catalysts was estimated at more than 200,000 tons [10].

The refractory nature of kaolin is also suitable for many applications [11]. Therefore, many clayey catalysts are used at high pressures and high temperatures. Then, the understanding of the clay composition and nature are necessary for their valorization.

The objective of this work is to determine the mineralogical and morphological characteristics of a clay from Tahoua (Niger) for its possible use in the manufacture of industrial catalysts.

2. Material and Methods

2.1. Sampling

The crude clay sample studied (sample B) in this work was collected in Tahoua region (14º 53’ 40’’ N, 5º 15’ 52’’ E) of Niger (Figure 1).

Figure 1: Location of sampling site

The extraction of the clay fraction lower than 2 microns (sample A1) was realized according to the protocol of Médard Thiry et *al.* (2013) [12] . A carbonate test is performed to facilitate the suspension of the clayey particles. After saturation of sample A1, with ethylene glycol for 12 hours and drying, sample A2 is obtained. Then, the sample were heated in an oven at 500 °C for 4 hours to obtain the A3 one.

2.2. Experiments

The X-Ray Diffraction (XRD) diagrams for all samples was recorded through a D8 ADVANCE Bruker diffractometer piloted by EVA software for minerals identification. FITYK software was used for the quantification of the clay fraction based on Thorez J (1976) intensities correction factors [13].

Infrared (IR) spectroscopy was performed in Attenuated Total Reflectance (ATR) mode with a Fourier Transform Bruker Alpha spectrometer equipped with a diamond crystal in the range of wavelengths from 400 cm^{-1} to 4000 cm^{-1}[14]. The specific surface (SSA) *S* was also determined by isothermal adsorption of acetic acid [15] given by equation (1):

$$S(m^2g^{-1}) = Q_0 \times s \times A \qquad (1)$$

where *A* is Avogadro's number (= 6,02 x 10^{23} mol^{-1}), the capacity Q_o is the maximum adsorption capacity (mol / g) and *s* is the area occupied by an acetic acid molecule (i.e. 21 $Å^2$) [16].

The measurement of the cation exchange capacity (CEC) which indicates the exchange of cations between the clay and the free ions in aqueous solution is performed by colorimetric quantitative analysis [16, 17].

The elementary chemical composition of the crude sample and the clay fraction A1 was conducted through ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy).

Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS) experiments were also performed.

Results and discussion

The test of carbonate content of the sample B gives a negative result indicating an easy extraction of clay fractions lower than 2 µm, A1.

3.1. X-Ray Diffraction

Figure 2 depicts the XRD pattern recorded with the crude clay (B). In Figure 2, the intense peak appearing around 26.78 ° is characteristic of quartz [19, 20]. The presence of smectite is indicated by the peak located at 6° [21, 22]. Others peaks at 12.5° and 25°are relative to kaolinite [19, 23, 24]. Figure 3 shows the results of mineralogical composition studies by XRD of the sample clay fraction (A1), treated with ethylene glycol (A2) and heated to 500 °C (A3).

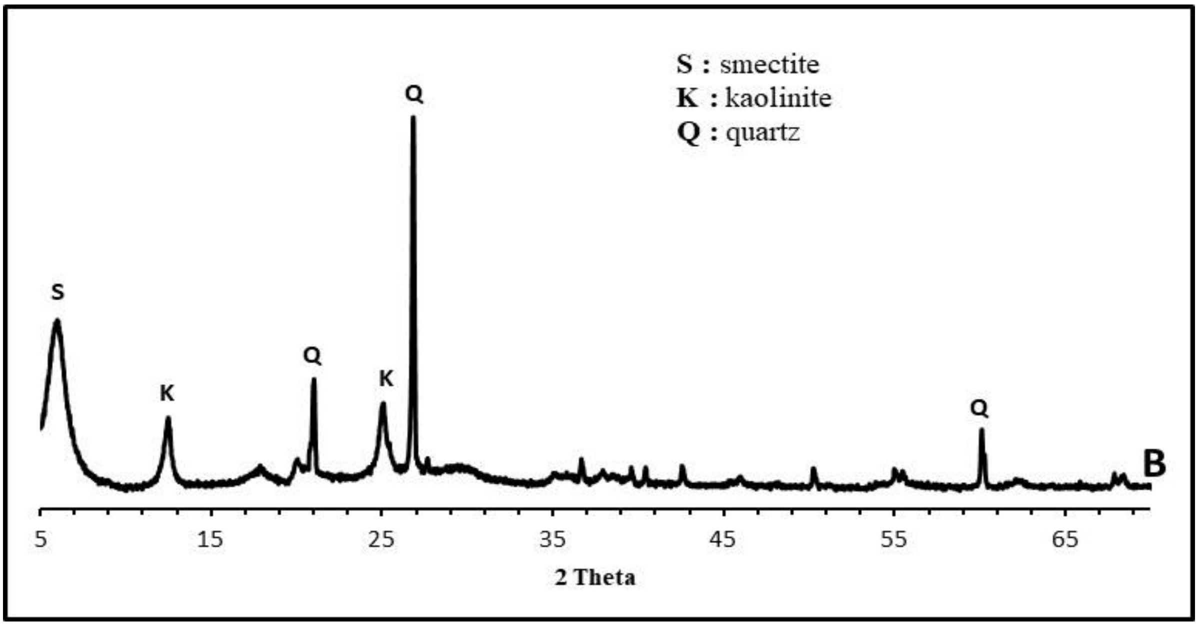

Figure 2: X Ray diffraction diagrams of the crude clay (B)

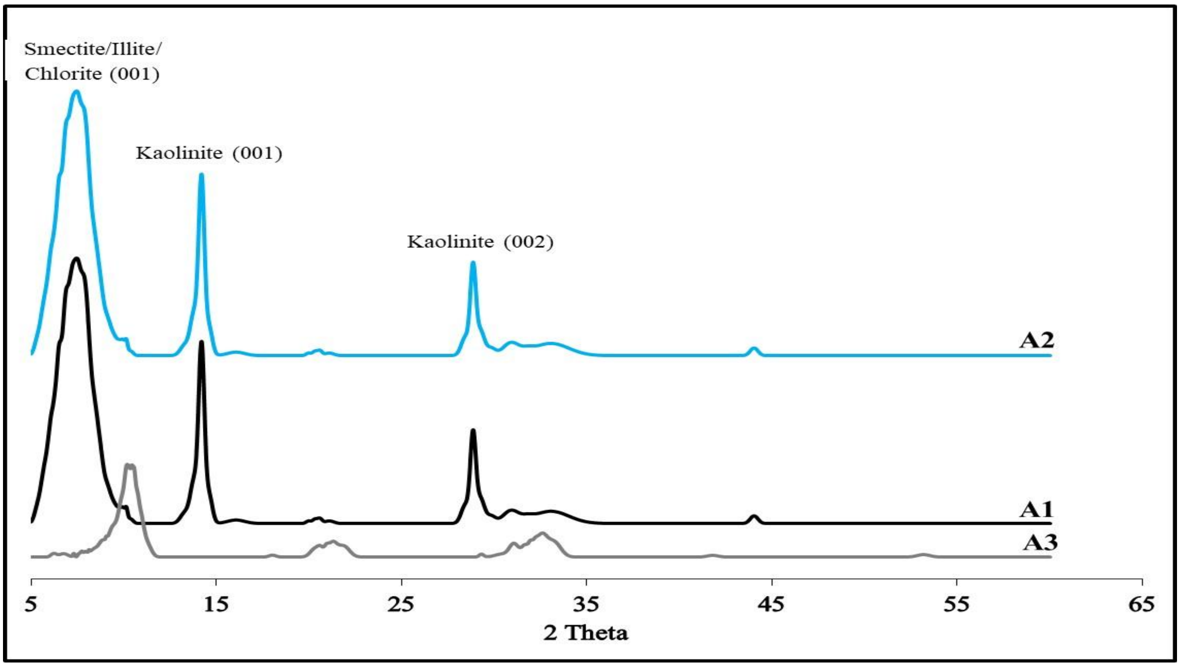

Figure 3: X-Ray Diffraction diagram of the clay fraction (A1), treated with ethylene glycol (A2) and heated at 500°C (A3).

Comparing XRD diagrams, from B to A1, it is noticed that the peaks related to quartz disappear due to purification indicating the efficiency of the purification method used. Quartz (SiO_2) is identified as an impurity [11]. Besides, spectra A1 and A2 show characteristic peaks of kaolinite, smectite and illite. Then, the clay fraction is composed of an irregular interlayer mineral of three (3) different Smectite/Illite/Chlorite sheets and a single mineral Kaolinite ($Al_2Si_2O_5(OH)_4$) as reported by Mouna and co-workers [19, 23, 24, 25].

The heat treatment causes kaolinite dehydrolysis. The two Kaolinite characteristic peaks previously present in the sample A1 and in the sample treated with ethylene glycol A2, disappear after heat treatment at 500°C (A3). Similar results proving the presence of kaolinite in the sample were obtained by other authors [24, 25].

The quantification of the clay fraction based on intensities correction factors gives 46.3 wt.% and 53.7 wt % for kaolinite and interbedded smectite/illite/chlorite respectively [13]. This This kaolin content suggests possible uses for the manufacture of catalysts.

3.2. Infrared Spectroscopy (IR)

The infrared spectrum of the clay fraction A1 is depicted in Figure 4. The absorption bands between 600 and 1200 cm^{-1} correspond with the interatomic bonds Si-O and Al-O and indicate the alumino-silicate nature of sample [26]. The bands at 468 and 525 cm^{-1} are respectively attributed to the deformation vibrations of Si-O-Mg and Si-O-Al bonds [8]. The bands located at 700; 810 and 935 cm^{-1} are related to the deformation vibration Al-Al-OH groups of smectite [27]. In the spectrum kaolinite presence is indicated by four absorption bands namely 695 cm^{-1} , 910 cm^{-1}, 1112 cm^{-1} and 1012 cm^{-1}[28].

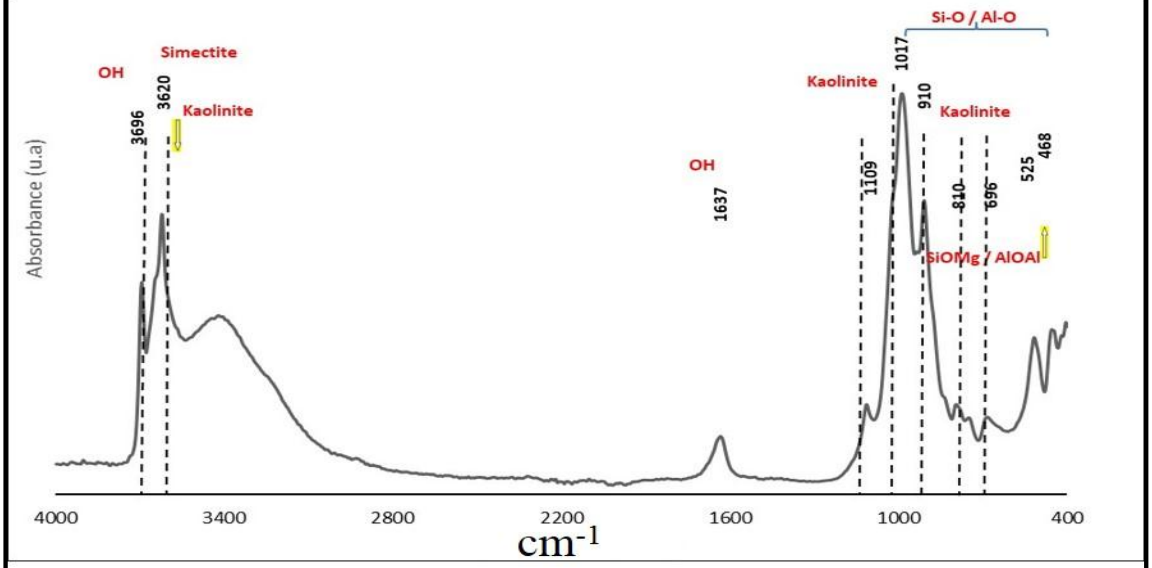

Figure 4: IR spectrum of the clay fraction

Besides, the bands around 1017 and 1109 cm^{-1} are characteristic of Si-O bond and the deformation bonds of hydroxyl appears at 1637 cm^{-1}[29, 30].

The adsorption bands at 3620 and 3696 cm^{-1} are characteristic of phyllosilicates such as smectite, illite and kaolinite. These bands also reflect the presence of the hydroxyl OH groups of clayey minerals [28]. Thus, the infrared results are in a good agreement of those of XRD.

3.3. Chemical composition

The results of the elemental chemical analysis of samples B and A1 conducted with ICP-AES are shown in Table 1. According to Table 1, silica is predominant into the tested samples (B, A1). The ICP-AES analysis also indicate that the sample studied is low in leachable metals (Pb, As, Zn). High concentrations of these metals in the natural kaolin negatively affect catalyst performance. Thus, the chemical composition of the clayey fraction makes it an excellent raw material for producing zeolite for catalysis after further purification to improve its catalytic properties.

Table 1: Chemical composition of samples

Samples	Weight % of the elements									
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**MgO**	**TiO_2**	**CaO**	**Na_2O**	**K_2O**	**P_2O_2**	**MnO**
B	56.1	19.3	3.22	1.57	1.66	0.97	0.064	0.6	0.21	0.0093
A1	49	23.5	4.1	2.19	1.35	1.76	0.45	0.93	0.3	0,008

The Silica to Alumina ratio of different samples and the loss on ignition are given in Table 2.

Table 2: SiO_2 / Al_2O_3 Ratio and loss on ignition

Samples	SiO_2 / Al_2O_3	loss on ignition %
B	2.91	15.1
A1	2.09	16.1

SiO_2/Al_2O_3 ratios of 2.91 and 2.09 obtained respectively for samples B and A1, are higher than those of standard kaolinite reported to be in the range of 1.73 and 1.8. Likewise, the loss on ignition (LOI) values are relatively high compared to standard kaolinite i.e. 14% [31]. LOI represents the weight of hydroxyl, organic materials and other volatile component contained in the clay samples [32]. These SiO_2/Al_2O_3 ratios and LOI values are probably due to an abundant quartz contents and interbedded mineral smectite/illite/chlorite [20] and the presence of free quartz in the samples studied [19, 29]. The pH of the clay fraction (A1) is 7. Thus, A1 is neutral according to pedological referential [34].

Clays are phyllosilicates characterized by cation exchange capacity (CEC). The CEC of this clay fraction (A1) being 6.36 meq/100g is within the Kaolinite range [18]. However, Maman and coworkers (2017) found higher CEC values respectively 8.2 and 8.4 mEq / 100g for two kaolinite samples studied. Then, This CEC value can be explained by the abundance of quartz impurity [35, 36].

The specific surface area determined is 15.26 m^2/g. This value agreed with SSA of kaolinite [37, 38]. An acid activation can increase this specific surface area for a good catalyze [39].

3.4. Scanning Electron Microscopy and Energy Dispersive Analysis (SEM-EDS)

SEM images of the clay fraction are shown in Figure 5. This SEM imaging of clay fraction (A1) depicts a typical structure of conventional kaolinite. The weakly resolved structures are probably due to the presence of other crystalline structures as impurities in the sample [23]. The pseudo-hexagonal and stratified structure of kaolinite is observed in Figure 5 (a) [10, 24].

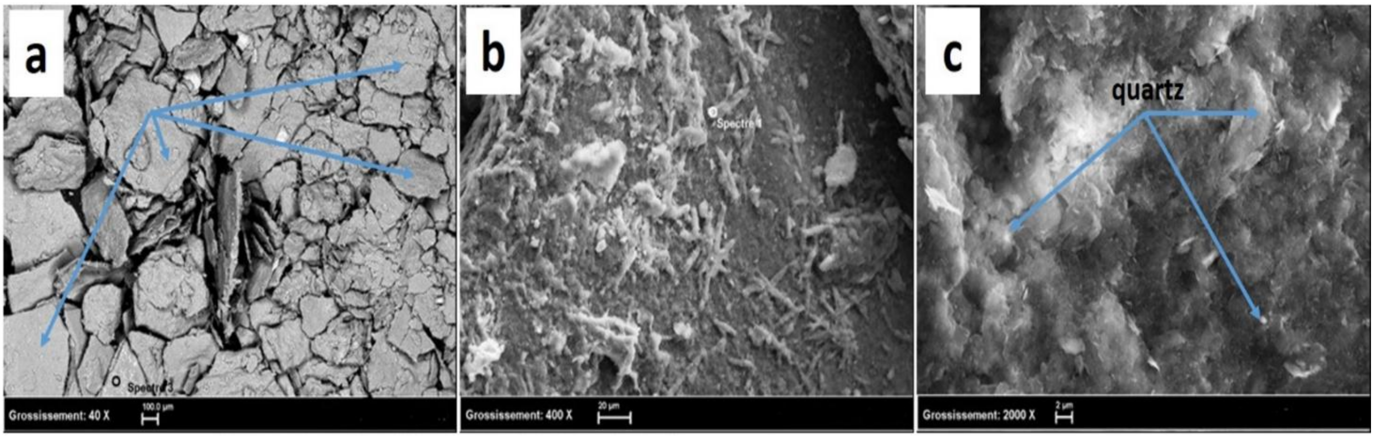

Figure 5: SEM Images of clay A1 at different magnifications 100 µm (a), 20 µm (b) and 2 µm (c).

Micrographs (b) and (c) on Figure 5 show that clay particles form rod-shaped with irregular contours. This morphology is characteristic of kaolinite and illite poorly crystallized [33]. In fact, these results confirm the XRD, IR and ICP-AES analyzes. The Energy Dispersive Spectrum of sample A1 is presented in Figure 6 below.

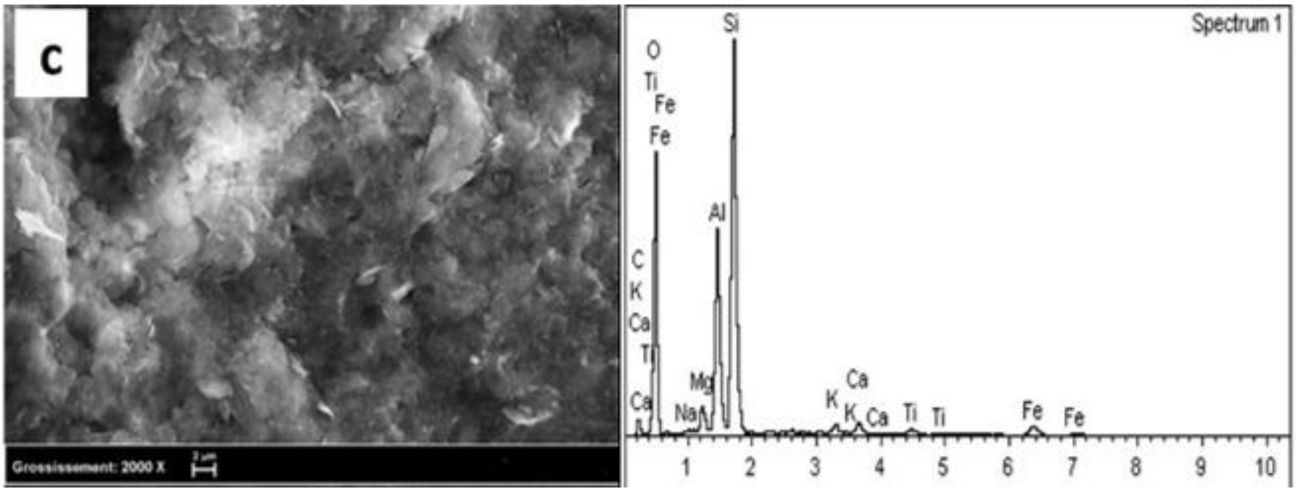

Figure 6: Energy Dispersive Spectrum of the clay fraction.

Small quartz grains are observed in Figure 6 as predicted by elemental analysis. Then the amount of quartz in the clay is characteristic of Tahoua clay. However, the mineralogical and morphological characteristics of this clay are suitable for catalysts manufacture.

Conclusion

The study undertaken here has dealt with the mineralogical and morphological characterization of a clay from Tahoua region in Niger. This clay is mainly composed of kaolinite 46.3 wt%, three different Smectite / illite / chlorite sheets with a high quartz proportion of about (49%). The kaolin character of the sample studied is confirmed by the X-Ray Diffraction and Infrared spectroscopy. The 6.36 meq / 100g CEC values, the specific surface area of 15.26 m^2 / g, the SiO_2/Al_2O_3 ratios of 2.09 and the loss on ignition value namely 16.1% of the clay fraction are closed to the standard values despites the presence of free quartz as impurity. The pseudo-hexagonal and stratified structure of kaolinite was also observed by Scanning Electron Microscopy. Altogether, the characteristics of the clay from Tahoua in Niger is a good candidate as a support in the manufacture of industrial catalysts for a petroleum catalytic cracking operation.

References

1. E.A. Emam, Clays as Catalysts in Petroleum Refining Industry, *ARPN J. Sci. Technol*. 3 (2013) 356–375.
2. W.Z. Ostwald, Referate Zeit, Über den Wärmewert der Bestandteile der Nahrungsmittel“. "À propos de la valeur calorifique des constituants de l'aliment". *Phys. Chem*. 15 (1894) 705–706.
3. J.J. Berzelius, Quelques Idées sur une Nouvelle Force Agissant Dans les Combinaisons des Corps Organiques, *Ann. Chim. Phys*. 61 (1836) 146–151.
4. A.A. Avidan, Chapter 1 Origin, Development and Scope of Fcc Catalysis, *Studies in Surface Science and Catalysis, Elsevier* 76 (1993) 1–39. https://doi.org/10.1016/S0167-2991(08)63824-0
5. J. Scherzer, Octane-Enhancing, Zeolitic FCC Catalysts: Scientific and Technical Aspects, *Rev. Eng*. 31 (1989) 215–354. https://doi.org/10.1080/01614948909349934
6. P. Leprince, “Petroleum Refining. 3. Conversion Processes”, p. 33. ISBN 2-7108-0730-0 *Editions Technip.* (1998) 688.

7. S. Al-Khattaf, M. Rahat Saeed, Abdullah Aitani, Michael T. Klein, Catalytic Cracking of Light Crude Oil to Light Olefins and Naphtha over E-Cat and MFI: Microactivity Test versus Advanced Cracking Evaluation and the Effect of High Reaction Temperature, *Energy & Fuels* 32, 5 (2018) 6189-6199, DOI: 10.1021/acs.energyfuels.8b00691S.

8. O. Bouras, Proprietes adsorbantes d'argilespontees organophiles :synthese et caracterisation, *Ph. D. Thesis. Univ. Limoges.* (2003) 162.

9. E.N. Njoka, O. Ombaka, J.M. Gichumbi, D.I. Kibaara, O.M. Nderi, Characterization of clay from Tharaka Nithi County in Kenya for industrial and agricultural applications, *Afr. J. Environ. Sci. Technol*. 9 (2015) 228-243.

10. H.H. Murray, Applied Clay Mineralogy, Volume 2 1st Edition Occurrences, Processing and Applications of Kaolins, Bentonites, Palygorskitesepiolite, and Common Clays, *Elsevier*. Hardcover ISBN: 9780444517012 eBook ISBN: 9780080467870 (2006).

11. I.B. Messaoud, N. Hamdi, E. Srasra, The suitability of thermally activated red illite/kaolinitic clay as raw material for geopolymer binders, *J Mater Env. Sci*. 9 (2018) 946–954

12. M. Thiry, N. Carrillo, C. Franke, N. Martinea, Technique de préparation des minéraux argileux en vue de l'analyse par diffraction des Rayons X et introduction à l'interprétation des diagrammes, Ecol. Min. Fr. No : RT131010MTHI (2013) 39.
13. J. Thorez, Pratical identification of clay mineral, *Edition G. Lelotte, Dison, Belgique* (1976) 90
14. B.J. Dçebska, B. Guzowska-Świder, Spectral Databases, Infrared, *Encycl. Anal. Chem*. (2006).
15. J. Avom, J.K. Mbadcam, M.R.L. Matip, P. Germain, Adsorption isotherme de l'acide acétique par des charbons d'origine végétale, *Afr. J. Sci. Technol*. 2 (2001) 1-7.
16. E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, *J. Am. Chem. Soc*. 73 (1951) 373–380.
17. I. Mantin, R. Glaeser, Fixation des ions cobaltihexammines par les montmorillonites acides, *Bull. Groupe Fr. Argiles*. 12 (1960) 83–88.
18. C. Bardon, Recommandations pour la détermination expérimentale de la capacité d'échange de cations des milieux argileux, *Rev. Inst. Fr. Pétrole*. 38 (1983) 621–626.
19. S. Barama, Développement et synthèse de deux séries de catalyseurs à base de bentonite et d'oxydes mixtes. Application à la déshydrogénation oxydante du méthane, Ph. D. Thesis. Univ. Sci. Tech. *Houari Boumediene*. (2011) 314.
20. O. Zaki, A. Abdoulaye, D.L. Nomao, P. Rumori, G.T. Palomino, I. Amadou, Caractérisation des Sols de Périmètres Irrigués de l'Ouest du Niger par Diffraction de Rayons X, *J. Soc Ouest-Afr Chim*. 26 (2008) 89-97. http://www.soachim.org/files/volume_26/10-O%20Zaki%20et%20al.pdf

21. L. Bouna, Fonctionnalisation des mineraux argileux d'origine Marocaine par TiO2 en vue de l'elimination par photocatalyse de micropolluants organiques des milieux aqueux, *Ph. D. Thesis. Univ. Toulouse.* (2012) 298. http://ethesis.inp-toulouse.fr/archive/00002107/01/bouna.pdf

22. J.R. Mache, Mineralogie et proprietes physico-chimiques des smectites de Bana et Sabga (Cameroun). Utilisation dans la décoloration d' une huile végétale alimentaire *Ph. D. Thesis. Univ. Liège.* (2013) 145. http://www.ages.ulg.ac.be/pdf/theses/these_jr_m.pdf

23. A. Rabani, Utilisation des matériaux argileux du Niger dans la dépollution des eaux contaminées par les insecticides pyréthrinoïdes, *Ann. Univ Abdou Moumouni*. 15 (2013) 14–26.
24. M.A. Maman, A. Rabani, F. Habbachi, F. Menai, A. Abdoulaye, A. M'nif, Characterization of two clay minerals of the Niger River Valley: Téra and Boubon, *J. Tun. Chem. Soc*. 19 (2017) 52-58.
25. M. Gourouza, A. Zanguina, I. Natatou, B. Anne, Caractérisation d'une argile mixte du Niger, *Sci. Struct. Matière*. 1 (2013) 29-39
26. P.Cambier, Application de la spectrométrie d'absorption infrarouge à l'étude des minéraux argileux du sol, (1975). http://www.documentation.ird.fr/hor/fdi:16827

27. V.C. Farmer, J.D. Russell, The infrared spectra of layer silicates. Spectrochim, *Spectrochim. Acta*. 20 (1964) 1149–1173.
28. P. Pialy, Etude de quelques matériaux argileux du site de Lembo (Cameroun): minéralogie, comportement au frittage et analyse des propriétés d'élasticité, Ph. D. Thesis. Univ. Limoges. (2009) 147.
29. V.C. Farmer, Infrared spectra of minerals. Mineralogical society, *Mineralogical society. ISBN-13: 978-0903056052* (1974).
30. J. Fripiat, Application de la spectroscopie infrarouge à l'étude des minéraux argileux, *Bull. Groupe Francais Argiles*. 12 (1960) 25–41. https://www.persee.fr/doc/argil_0429-3320_1960_num_12_7_967

31. A. Qlihaa, S. Dhimni, F. Melrhaka, N. Hajjaji, A. Srhiri, Caractérisation physico-chimique d'une argile Marocaine [Physico-chemical characterization of a morrocan clay], *J Mater Env. Sci*. 7 (2016) 1741–1750.

32. A. Ksakas, K. Tanji, B. El Bali, M. Taleb, A. Kherbeche, Removal of Cu (II) Ions from Aqueous Solution by Adsorption Using Natural Clays: Kinetic and Thermodynamic Studies, *J Mater Env. Sci*. 9 (2018) 1075–1085.

33. M. Koneshloo, Caractérisation physico-chimique d'une argile marocaine, Ph. D. Thesis. *Ecol. Nat. Sup. Min. Paris*. (2007).

34. D. Baize, M.C. Girard, Référentiel pédologique. *Quae*. ISBN : 978-2-7592-0186-0 (2009) 435.

35. S. Mahmoudi, A. Bennour, A. Meguebli, E. Srasra, F. Zargouni, Characterization and traditional ceramic application of clays from the Douiret region in South Tunisia, *Appl. Clay Sci*. 127–128 (2016) 78–87. https://doi.org/10.1016/j.clay.2016.04.010

36. A.V.O. Akowanou, M.P. Aina, S.E.R. Mahunon, B.K. Yao, Characterization of Clays from the "Sè" Region in the South of Benin Used to Make Ceramic Water Filters, *Am. J. Appl. Chem*. 5 (2017) 90. https://doi.org/10.11648/j.ajac.20170506.11

37. M H. Mohamed, Contribution à l'amélioration du procédé de fabrication de la céramique Etude sur site : unité Maghreb céramique de Touggourt, *Magister Mem. Univ. Kasdi Merbah Ouargla*. (2007)

38. S. Azizian, Kinetic models of sorption: a theoretical analysis, *Science*, 276 (2004) 47–52, https://doi.org/10.1016/j.jcis.2004.03.048

39. G. Derafa, Synthèse et caractérisation de montmorillonite modifiée : Application à l'adsorption des colorants cationiques» *Magister Mem. Univ. FERHAT ABBAS- SETIF-1*. (2018) 197

(2019) ; http://www.jmaterenvironsci.com