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THE PILLARING OF NATURAL TUNISIAN CLAYS FROM JEBEL NAHLI FOR EVENTUAL INDUSTRIAL APPLICATIONS

R. Rekik Ellouze[1]*, J. Gharsalli[2], F. Turki[1], T. Mhiri[1] and H. Zouari[2]

[1] *Laboratoire de l'Etat Solide, Faculté des Sciences de Sfax, B. P. 1171, 3000 Sfax, Tunisie*
[2]*Laboratoire de Géoressources, CERTE - Borj Cedria, B.P. 27, 8020 Soliman, Tunisie.*

*: e-mail: rellouze78@yahoo.fr

Abstract : The different properties developed by the clays such as; their capacities of exchanges cationic and their properties of surface were showed by several works. These properties confer to the clay important adsorption properties. They can acquire other properties by various modifications which can be through chemical, physical and/or thermal view. These new properties may open the ways of unsuspected applications: adsorption and catalysis.

In this work, we have studied the pillaring of the upper Cretaceous natural Tunisian clays taken from Jebel Nahli with polyhydroxymetallic precursor [$Al_{13}O_4$ $(OH)_{24}(H_2O)_{12}$ $^{7+}$]. Several techniques are used, in this study: XRD, infra red spectroscopy, thermogravimetric analysis, textural measures and scanning electron microscopy. The results show that the pillaring of smectitic clays with Aluminum oxides polycations has allowed obtaining microporous materials, rigid, with a large interlayer spacing and a high thermal stability.

Keywords: Natural clays, micropourous materials, Pillared clays, Thermal stability, Tunisia

I. INTRODUCTION

Clays are layered minerals with important cation exchange capacity (CEC) due to their negative layer charge. This charge was compensated by cations such as Na^+ and Ca^{++}, intercalated in the interlayer region. The material, exhibit poor acidity depending on the kind of exchangeable cation and its hydration state. Their thermal stability was limited to temperature lower than 200°C [1]. A net improvement of their acidity, surface and thermal stability, necessary for a number of industrial applications, could be achieved via pillaring processes. The pillaring process was based on the intercalation properties of the clay matrix and involves exchange of the interlayer cations with polyhydroxymetallic precursor such as Keggin ions, ($Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$), which upon calcinations converted to robust metal oxide pillars between the clay layers, keeping them apart at a definite [2].

The kind of clay modification which have the great stability of the pillaring bidimensional network [3] led to the award of the appropriate catalysts for a number of reactions such as hydrocarbon cracking, isomerization, alkylation, cyclization, dehydration of alcohols to ethers, the conversion of primary amines to secondary amine or catalysts of fine chemicals reactions such as stereoselective epoxidation of allylic alcohols.

The most studied pillaring clays were intercalated by hydroxyaluminun polycations and determined by spectroscopy NMR MAS (Magic Angle Spinning) ^{27}Al and ^{29}Si [4]. Many authors suggested that the Al intercalated existed in the form of a polycationics complex [5, 6]. Brindley et al. [7, 8] have published their first works on the intercalation of smectites by complexes respectively of aluminium and chromium. The diffractometrics results showed spacing of 14.8 Å (100°C) that increased until to 17 Å after treatment with ethylene glycol and heating at 500°C.

For their part, Lahav et al. [9] have confirmed, thanks to XRD analysis, the intercalation of Aluminium polycations with basal spacings of about 18 Å at room temperature, and which transformed into oxide Al_2O_3 after calcinations at 500°C. Singh and Kodama [10] have prepared Aluminum pillared montmorillonits with 28Å through several successive treatments by the same pillared solution based on aluminum. In catalysis application field, a wide variety of catalysts, depending on the pillar, have been implemented and used in various chemical reactions such as oil cracking or the fine chemical synthesis [11-14].

In adsorption application field, some studies [15-19] were oriented towards exploring the possibilities of setting some heavy metals (Cu, Ni, Zn, Cr) and the arsenic on several types of pillaring clays.

In this paper we investigate properties of the pillaring of Tunisian natural clays from Jebel

Nahli located in the Northeast of Tunisia [20], for eventual applications. Clay samples were selected according to their mineralogical character (clays rich in smectites). Indeed, we studied the behaviour of clays after their pillaring with Aluminum oxide polycations.

2. EXPERIMENTAL

2. 1. Preparation of clay

The experiments were performed on clay samples rich in smectites: NHA11, NHA14, NHA15, NHA16 and NHA20 (from Jebel Nahli). The upper Cretaceous Tunisian clay materials taken from Jebel Nahli were treated with hydrogen peroxide and HCl (N/10) to removes the carbonates and organic matter. These samples are then placed in suspension and the fraction lower than < 2 µm had extracted by settling according to Stoke's law [21]. The preliminary treatment of purified clays, by sodium homoionisation, to replace all the exchangeable cations of various kinds by sodium cations all the same. We symbolized, by Na-clay the homoionic sodic clays.

Thus we dispersed the purified clay sample in a certain distilled water volume with proportions (0.4% w/w), that we were submitting to a good stirring for 3 to 4 hours for complete homogenization of the suspension. The clay samples became homoionic sodic through five successive treatments with NaCl (1 M). This was followed by several successive washing with distilled water.

2. 2. Preparations of pillaring Solution

Pillaring solution were prepared by titration of ($AlCl_3.6H_2O$) solution with 0.5 M concentration and a solution of sodium hydroxide of 0.225M with a discontinuous rate (1.5 $mL.min^{-1}$) with an OH/Al ratio equal to 1.8. The maturation of pillaring solution was obtained after 48h (Table 1).

Pillaring solution	**PCBA**
Polycation formula	$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$
Symbol	$Al_x(OH)_y$
Molar ratio	OH/Al = 1.8
Final concentration $[Me]_f$ (mol. L^{-1})	0.1
Aging time (hours)	48 h

Table 1. Characteristics of the prepared pillaring solution [22, 23].

2. 3. Pillaring clay process

The clay-Na suspensions with concentrations generally equal to 0.5% (w/w) [22], homogenized for one hour were titrated dropwise (8.1 mL.min-1) using a peristaltic pump, by the pillaring solution (PCBA) under rapidly and permanently agitation. At the end of the titration, we let the clay into contact with metal polycations for about 4 hours in order to ensure proper insertion. After several washes with distilled water and vacuum filtration, the complex were dried, and heated to a temperature of 500°C for 3 h for obtaining pillared clays.

The operating conditions adopted for the preparation of complex clays-$Me_x(OH)_y$ [22, 23] were presented in Table 2.

Table 2. The preparation Conditions of pillared clays.

Matrix	**Clay $Al_x(OH)_y$ [22, 23]**
Me / Na-clay ($mmol.g^{-1}$)	4
$[Me]_f$ ($mol.L^{-1}$)	0.1
The suspension concentration (weight %)	0.4
Maturation time (hours)	4 h

2. 4. Technical Characterisations

The clays minerals data were obtained by analyzing the < 2µm fraction through X-ray diffraction. Oriented slides were prepared from the concentrated clay suspension by pipetting onto glass and allowing them to dry at room temperature. The identification of clay minerals was made according to the position of the (001) series of basal reflexions on the X-ray diagrams and semi-quantitative estimations were based on the area of the main diffraction peak [24-26].

XRD patterns were obtained using a SIEMENS D500 diffractometer with CuK_α radiation. Infrared spectra were obtained on a Perkin-Elmer model 1600 FTIR spectroscopy using the Kbr-pellet method.

Thermogravimertric analyses (TGA) were performed from room temperature to 800°C using a SETERAM thermobalance, with a heating rate of 300°C/h. The Brunauer, Emmett, and Teller [27] (BET) method was also performed, using adsorption of an inert gas (nitrogen), to determination of the surface area with Micromeritics ASAP 2420.

Finally, the morphology and the grain boundaries were investigated by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3. 1. X-ray Diffraction

The mineralogical analysis of the upper Cretaceous Tunisian clay samples taken from Jebel Nahli, have indicated that the clay fraction was formed by a high content of smectites {NHA11 (86 %), NHA14 (89 %), NHA15 (79 %), NHA16 (65 %) and NHA20 (75 %)} with the presence of kaolinite (Table 3).

Table 3. Mineralogical composition of the clay samples of Jebel Nahli.

Samples	**Kaolinite%**	**Smectite%**
NHA1	14	86
NHA2	11	89
NHA3	21	79
NHA4	15	85
NHA5	25	75

After pillaring, the X-ray difractograms showed a displacement of (001) reflection to about 17.5 Å. In fact, the clays pillaring with a solutions aged (48 h), clearly showed large equidistance ranging from about 16Å to 17.5Å, confirming the reality of polycationics species formation (Figs. 1-3).

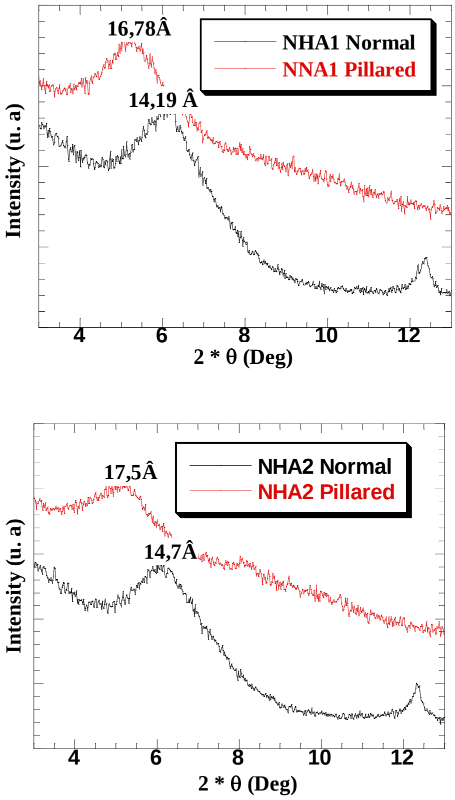


Fig. 1. X- ray diffraction patterns on oriented slides of NHA1 and NHA2 samples (normal and pillared).

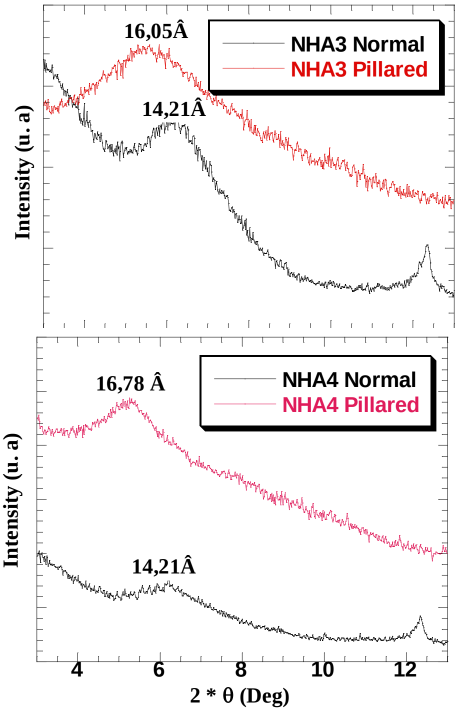


Fig. 2. X- ray diffraction patterns on oriented slides of NHA3 and NHA4 samples (normal and pillared).

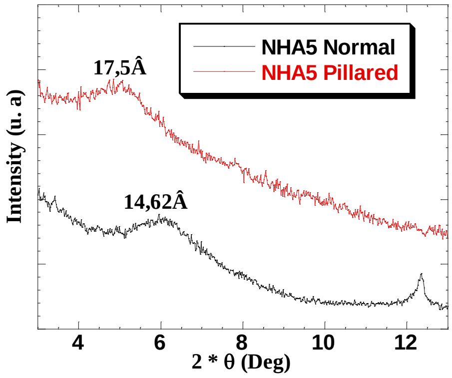


Fig. 3. X- ray diffraction *patterns* on oriented slides of NHA5 sample (normal and pillared).

This phenomenon was explained by the intercalation of big Aluminum oxides pillars between layers of clay is realized through their adsorption by cation exchange against the purified clay (Na-clay) for which it manifested the maximum selectivity. It seems that the polycations $Al_x(OH)_y$ whose size was identified by XRD were likely to provide significant expansions [23].

- Influence of the report Me / Na-clay: While treating the suspension (clay-Na) with the pillaring solution in excess, all Na^+ ions easily exchangeable were replaced completely by Al-polycations. However, when the same amount of suspension was treated with a pillaring solution of lower concentration, the exchange sites were only partially occupied by polycations and the interlayer space was heterogeneous. In this case the quantity of polycations was insufficient, Na-clay adsorbs only what was offered as metallic polycations. The remaining interlamellar sites remained occupied by the Na^+ ions [23]. That was why we must respect the report Me / Na-clay.

3. 2. Infrared spectroscopy

The examination of infrared spectra reveals absorption bands that we presented as follows [28, 29] (Fig. 4).

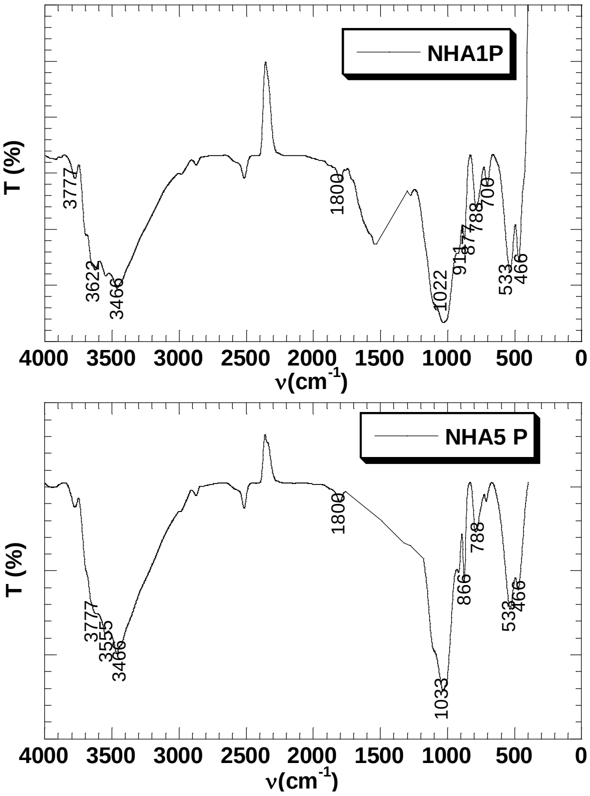


Fig. 4. The infrared spectra of the pillared clay samples: NHA1 and NHA5

Groups OH: The spectra show two absorption bands between 3200-3800 cm^{-1} and between 1600-1700 cm^{-1}.

-The band between 1600-1700 cm^{-1} was attributed to the deformation vibrations of OH group of water content and the vibrations of liaison of adsorbed water.

-The band ranging between 3200-3800 cm^{-1} characterized the Smectite and corresponds to the stretching vibrations of OH groups of the octahedral layer coordinated either 1 Al + 1 Mg (3640 cm^{-1}) or 2 Al (3620 cm^{-1}).

- The valence vibrations of H_2O molecules were characterized by the 3400 cm^{-1} band

- Band centred around 1630 cm^{-1} was attributed to deformation vibrations of adsorbed H_2O molecules between the layers.

The Si-O bonds were characterized by the following absorption bands:

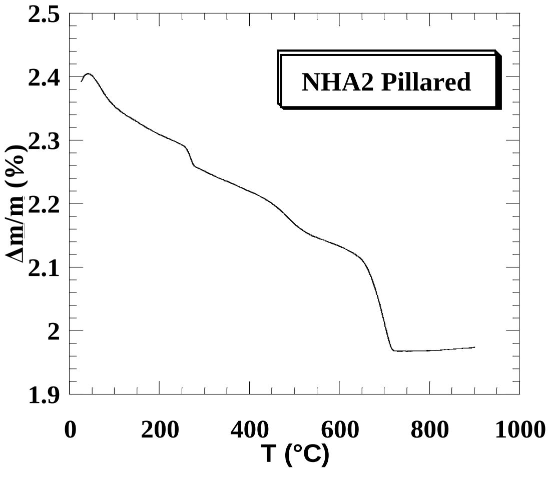
- Intense band between 900-1200 cm^{-1} and centred around 1040 cm^{-1} corresponded to the valence vibration of Si-O liaison.
- Bands located at 525, and 468 cm^{-1}, were assigned respectively to deformation vibrations of Si-O-Al and Si-O-Mg.

Bonds M (VI) -OH (M = Al, Mg, Fe): The sharing of the OH group between the atoms Fe and Al in octahedral position may moved Al-OH vibrations at low frequencies around 815 and 915 cm^{-1}. Thus, Mg-O and Mg-OH vibrations (combined with that of SiO) were located respectively at 530 cm^{-1} and 560 cm^{-1}.

The results obtained by infrared spectroscopy showed that the pillared clays spectra were similar to those of natural clays [20]. This proved that they preserved theirs structural network even after the insert of metallic oxides polycations.

3. 3. Thermogravimetric analysis

The different results of thermogravimetric analysis (TGA) of some pillared clays were represented by the curves in figures (5). The profile of the thermogravimetric curves (TGA) was comparable to those obtained on many other clay minerals and clearly indicated their high thermal stability even at extremely high temperatures. It showed a mass losses located between ambient and 200°C, 200 and 400°C, 400 and 500°C to 650-750°C.



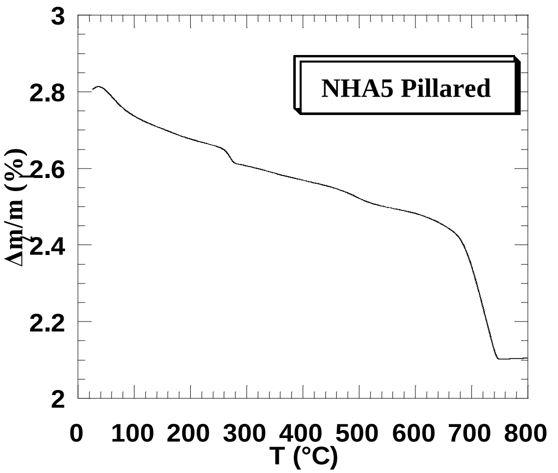


Fig. 5. Thermogravimetric curves of pillared clay samples: NHA2 and clay NHA5

- The first mass loss corresponded to the departure of water hydrated [30, 31].
- We note also other mass losses corresponded to the deshydroxylation, at once, of polycations (400 to 500 ° C) and clay layers (smectites) (600 to 750 ° C) [23, 31].

Despite the mass losses, the clays safeguarded the intercalated structure with a structural rearrangement of pillar and it's surrounding.

3. 4. BET

The pillared clays showed BET surfaces ranging from 200 to 300 m^2 / g, significantly higher than that of the original purified clay (Na-clay), indicating the insert reality. The thermal stability of these microporous materials was confirmed, once again, by the textural measures since the surfaces BET are higher than $200 m^2.g^{-1}$ for all pillared clays prepared (Table. 4).

Table 4. Variation of BET surface before and after the clays pillaring

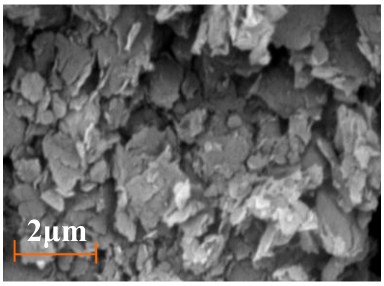
Samples	BET surface (m^2/g) of Na+-clays	BET surface (m^2/g) of the pillaring clays
NHA1	60.3	209
NHA2	63.7	216
NHA3	68.4	224
NHA4	68.2	218
NHA5	64.4	216

While, several previous studies on Aluminum-pillared clays showed that these microporous solids subjected to thermal treatments (calcination at 550°C) under different atmospheres (air, vacuum or argon) preserved their porosity, since the specific surface remain above 200 $m^2.g^{-1}$ [23].

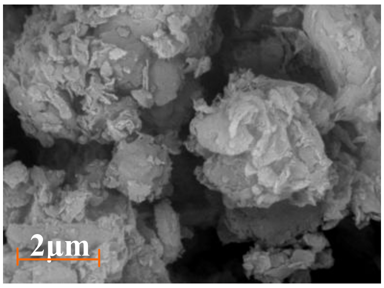
3. 5. Scanning Electron Microscopy

The scanning electron microscopy investigations showed the general organization and morphologies of pillared clay samples. The SEM photos of pillared clays presented aggregates, whose particle size varies from 1μm to several micrometers (Fig. 6. a, b and c). Also, they demonstrate the structure in petaloid particle of these clays. Moreover, they indicated no changes after pillaring.

a) NHA1



b) NHA2



c) NHA4

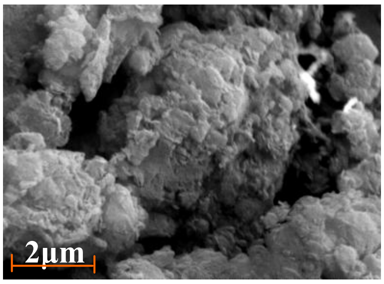


Fig. 6. SEM photo of NHA1, NHA2 and NHA4 pillared clays

4. CONCLUSION

In this work, It has been shown that clays intercalated with Al-polycations, presented specific surface areas and high thermal stabilities could be obtained under certain optimal preparation conditions related to the ratio (OH/Al), the aging time and the final concentration of pillaring solution and especially the amount of the interlayer in the solution (Me / Na-clay).

The diffractometric analyses showed a very important interlayer distances d(001) between 16 and 17,5 Å depending on the nature of the clay samples. These reticular distances decreased very little, according to the dehydration and dehydroxylation of the metallic pillars that were transformed, subsequently in oxide Al_2O_3.

Textural measurements indicated that the pillaring of clays by metallic polycations created a very important microporous network. This led to pores opening and a great evolution of the surface area exceeding 200 m^2 g^{-1} even after calcination at high temperature (500°C).

Thermogravimetric analysis (TGA), for its part, confirmed the high thermal stability of pillared clays. The calcination of these new materials, at high temperature, caused only the dehydroxylation, at once, of metallic pillars that transformed into clusters of metallic oxides and the layers of clay.

References

[1] T. J. Pinnavaia, Intercalated clay catalysts. Science 220 (1983), 365–371.

[2] T. J. Pinnavaia, S.D. Landau, M.S. Tzou, and I.D. Johnson, Layer cross-linking in pillared clays. J. Am.Chem.Soc.107 (1985), 7222–7224.

[3] J. Bovey, and W Jones, Characterization of Al-pillared acid-activated clay catalysts. Journal Of Materials Chemistry, 5 (1995), 2027-2035.

[4] D. Plee, F. Borg, L. Gatineau and J. J. Fripiat, High-resolution solid-state 27Al and 29Si nuclear magnetic resonance study of pillared clays. J. Am. Chem. Soc., 107 (1985), 2362-2369.

[5] J. Y. Bottero, J. M. Cases, F. Fiessinger, and J. E. Poirier, Studies of the hydrolysed aluminium chloride solution: Nature of aluminium species and composition of aqueous solutions. J. Phys. Chem., 84 (1980), 2933-2939.

[6] D. Plee, L. Gatineau, and J. J. Fripiat, Pillaring processes of smectites with and without tetrahedral substitution. Clays Clay Miner., 35 (1987), 81-88.

[7] G. W. Brindley, and R. E. Semples, Preparation and properties of some hydroxyaluminum beidellite. Clay. Miner., 12 (1977), 229-237.

[8] G. W. Brindley, and S. Yamanaka, A study of hydroxy-chromium montmorillonites and the form of the hydroxy-chromium polymers. Amer. Mineral., 64 (1979), 830- 835.

[9] N. Lahav, U. Shani and J. Shabtai, Cross-linked smectites I. Synthesis and properties of hydroxy-aluminum montmorillonite. Clays Clay Miner., 26 (1978), 107-115.

[10] S. S. Singh, and H. Kodama, Reactions of polynuclear hydroxyaluminum cations with montmorillonite and the formation of a 28 Å-pillared complex. Clays Clay Miner., 36 (1988), 397-402.

[11] H. M. Yuan, L. Zhonghui, and M. Enze, Acidic and hydrocarbon catalytic properties of pillared clay, Catal. Today, 2 (1988), 321-338.

[12] B. M. Choudary, A. D. Prassad, V. Bhuma, and S. Swapna, Chromium pillared clay as a catalyst for benzylic oxidation and oxydative deprotection of benzyl ethers and benzylamines: a simple and convenient procedure. J. Org. Chem., 57 (1992), 5841-5844.

[13] B. M. Choudary, S. Shobha Rani, and N. Narender, Asymetric oxidation of sulfides to sulfoxides by chiral titanium pillared montmorillonite catalyst. Catal. Lett., 19 (1993), 299-307.

[14] R. Issadi, N. F. Garin, C. E. Chitour, and G. Maire, Catalytic behaviour of combined palladium acid catalysts: use of Al and Zr-pillared montmorillonite as supports. Appl. Catal. A: general, 207 (2001), 323-332.

[15] N. Frini, M. Crespin, N. Trabelsi, D. Messad, H. Van Damma, and F. Bergaya, Preliminary results on the properties of pillared clays by mixed Al-Cu solutions. Appl. Clay Sci., 12 (1997), 281-292.

[16] J. Barrault, C. Bouchoule, K. Echachoui, N. F. Srasra, M. Trabelsi, and Brown, G., The X-ray identification and crystal structures of clay minerals. Ed. Mineral. Soc., (1961) 544 p.

[17] A. Bakhti, Z. Derriche, A. Iddou, and M. Larid, A study of the factors controlling the adsorption of Cr(III) on modified montmorillonites. Eur. J. Soil Sci., 52 (2001), 683-692.

[18] T. Vengris, R. Binkiene, and A. Sveikauskaite, Nickel, copper and zinc removal from waste water by a modified clay sorbent, Appl. Clay Sci., 18 (2001), 183-190.

[19] V. Lenoble, O. Bouras, V. Deluchat, B. Serpaud, and J. C. Bollinder, Arsenic adsorption onto pillared clays and iron oxides. J. Colloid Interface Sci., 255 (2002), 52-58. Environ. Technol., 17, 1169-1180.

[20] R. Ellouze, Etude minéralogique,physico-chimique et technologique de quelques argiles de la region du Nord-Est de la Tunisie. Thèse de Doctorat, Faculté des Sciences de Sfax, (2010), 215p.

[21] G. Galehouse, Les facteurs de la pédogenèse. (Lelotte, Dison, Belgium), (1971), 730 pp.

[22] O. Bouras, Synthèse et caractérisation des montmorillonites pontées à base de bentonites algériennes. Thèse de magister, Institut de Chimie Industrielle, Université de Blida (1992) (Algérie).

[23] H. Khalaf, O. Bouras, and V. Perrichon, Synthesis and characterisation of Al pillared and cationic surfactant modified Algerian bentonite. Microporous Mater., 8 (1997), 141-150.

[24] G. Brown, and G. W. Brindley, X-ray diffraction procedures for the clay mineral identification. In G. W. Brindley and G. Brown, (Eds), Crystal Structures of clay minerals and their X- ray Identification. Mineralogical Society, London, Monograph, 5: (1980) 305-359.

[25] R. C. Reynolds, Interstratified clay minerals, In Brindley G.W and Brown G (Eds), Crystal Structures of Clays Minerals and their Identification, Mineralogical Society, London, Monograph, 5: (1980) 249-303.
[26] D. M. More, and R. C. Reynolds, X-ray diffraction and the identification and analysis of clay minerals, Oxford University Press, Oxford, (1989).

[27] S. Brunauer, P. H. Emmett, E. Teller, Absorption of gases in multimolecular layers. Journal of the American chemical, 60: (1938) 309 - 319.

[28] V.C. Farmer, Infrared spectroscopy. Pp. 285–337 in: Data Handbook for Clay Materials and other Non-metallic Minerals (H. van Olphen and J. J. Fripiat, editors). Pergamon Press, Oxford, UK (1979).

[29] P. Salerno, O. M. B. Asenjo and S. Mendioroz, Influence of preparation method on thermal stability and acidity of Al–PILCs. Thermochimica Acta, 379 (2001), 101-109.

[30] F. Jamoussi, and E. Srasra, Mineralogy and geochemistry of smectitic clays of Gafsa area (South of Tunisia) and their industrial applications, Mineralogy Petrology Acta 35-A (1992), 135- 145.

[31] H. Ben Rhaim, D. Tessier, and A. Ben Haj Amara, Mineralogy of the < 2µm fraction of three mixed-layer from southern and central Tunisia. Clay Minerals, 35 (2000), 375-381.