Moroccan Journal of Chemistry
ISSN: 2351-812X
http://revues.imist.ma/?journal=morjchem&page=login
Ainane & al. / Mor. J. Chem. 9 N°2 (2021) 210-220

Study of dependence between two types of most abundant natural clays in Bejaad province (Central Morocco) using a statistical approach

***A. Ainane*[(a)], *M. Taleb*[(b)], *F. El-Hajjaji*[(b)], *B. Hammouti*[(c)], *A. Chetouani*[(c)], *T. Ainane*[(a)]**

[(a)]*Superior School of Technology (EST-Khenifra), University of Sultan Moulay Slimane, PB 170, Khenifra 54000 Morocco.*

[(b)]*Laboratoire d'Ingénierie d'Electrochimie, Modélisation et d'Environnement (LIEME), Faculté des sciences/Université Sidi Mohammed Ben Abdellah, Fes, Morocco.*

[(c)]*LC2AME-URAC18, Faculté des Sciences, Université Mohammed Premier, B.P. 717, 60000, Oujda, Morocco.*

* *Corresponding author:*
t.ainane@usms.ma

Received 20 July 2020,
Revised 03 Feb 2021,
Accepted 04 April 2021

Abstract

This work proposes the studying of characterization analysis of two natural Moroccan clays (RC and GC) in the same location from Bejaad (Province of Khouribga, Morocco) and to know the relationship dependence between them. The values obtained during the determination of a few parameters (density, pH, conductivity, dry matter - moisture content, organic matter-mineral matter) show that the two materials RC and GC studied have the same physical-chemical properties. The all characterization of the two clays was carried out by XRD, XRF, FTIR, SEM/EDX and TGA. The results obtained show that the two materials have very irregular and microporous structures, a heterogeneity of the pore forms and they are contain a mixture of Kaolinite, Illite, Quartz, Calcite, and Dolomite, with the presence of Hematite only in clay RC. On the other hand, The statistical approach applied to determine the dependence relationship between the two clays was based on two tests: Student's t-test (Comparison of two means for physical-chemical parameters) and Pearson's test (contingency table for XRF analysis) in order to prove that the two materials studied are the same chemical and physical-chemical characteristics.

Keywords: *Characterization; natural clay; characterization; statistic; dependence relation.*

1. Introduction

Clays occupy a predominant place in all sedimentary rocks, they are made up of a mixture of minerals and crystalline impurities, often hydrated, in lamellar or fibrous form **[1-2]**. There are a number of varieties of clays such as sandy, limestone or marl clays and bituminous **[3]**. Moreover, clays content is an important parameter governing the hydrodynamics soil parameters and fundamental to address agricultural management and environmental development, it was found to be a dominant factor in controlling aggregate stability which is used as an indicator of soil structure. Clay minerals affect properties that influence aggregation: surface area, charge density, cation exchange capacity (CEC), dispersivity and expandability, etc. **[4-6]** Also, clays are used as raw materials in many industrial fields such as ceramics, paper, paint, petroleum industry, clarification of various effluents, catalysis, etc. **[7-10]** Their applications are tightly dependent on their structure, composition, and physical properties. Knowledge of these properties is important for understanding the technology of several industrial applications. In Morocco, clay deposits and occurrences have been recorded in different lithological successions ranging in age from Cretaceous to Quaternary **[11]**. In the Central Morocco as well as in the Meseta domains, Tertiary sediments appear to be the main host of lithogenic clays, where Kaolinite and Illite is the dominant clay minerals in this region and restricted environments **[12]**. This material clays have been detailed in several studies according to its distribution, occurrences, genesis and paleoenvironmental significance. The objective of this study is the identification and the physical-chemical characterization of two natural clays from central Morocco sampled in the "Bejaad" region, Khouribga Province by advanced analysis techniques (XRD, XRF, FTIR, SEM / EDX) and to know the relationship of dependence between them according to in-depth statistical studies (Student's test and Pearson's test) which will make it possible to establish a database with the various properties studied making their later use more rigorous and more rational.

2. Materials and methods

2.1. Origin of clay rocks and Sample preparation

The two samples of clay rocks which were the subject of this study, noted (RC) and (GC), come from the territorial commune of Boukhriss (Bejaad, Central Morocco) and under the coordinates geographic: 32°47'01.7''N 6°13'52.3''W (Figure 1).

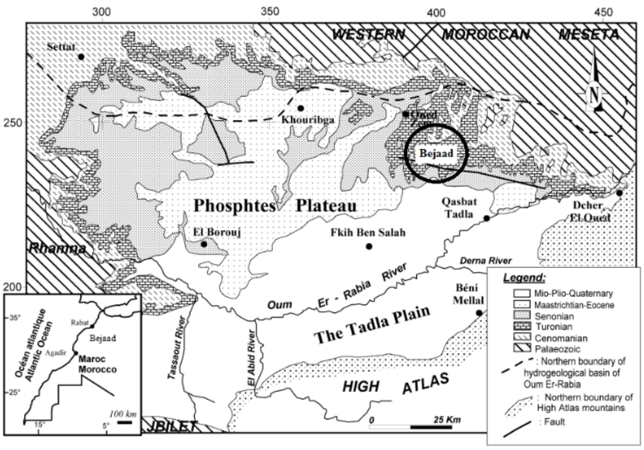

Figure 1. Geological MAP and location of the studied clays.

The samples in the form of blocks are crushed and ground, the homogeneous powders obtained are washed with distilled water, the latter is removed by centrifugation at 3000 rpm for 10 min. After drying, the samples are ground and sieved to a smaller particle size of 200 µm.

2.2. Physico-chemical property

Several techniques have been used in this work to determine the physicochemical property of materials (RC) and (GC) namely: density, pH, electrical conductivity, humidity, dry matter, organic matter and mineral matter.

2.3. Physico-chemical characterizations

The X-ray diffraction was performed at a wavelength of 1.549 Å, at 40 kV and 40 mA using a Bruker CCD-Apex equipment with a X ray generator (Cu Ka and Ni filter).

Oxide content analysis was determined by using the X-ray fluorescence spectrometer (XRF, Model X Rays Siemens Type SRX 3000), equipped with a Rh anode X-ray tube.

A Fourier transform infrared (FT-IR) spectrum was recorded using a Bruker Alpha in transmission mode.

The morphology of the investigated PGFs was examined using a scanning electron microscope coupled with the X microanalysis (MEB-EDX, Model FEI Type Quattro S).

Thermogravimetric analyses (TGA) were conducted with a Du Pont thermogravimetric analyzer, with 10 mg samples from room temperature to 900 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.4. Statistical study

Student's t-test

Among the most commonly used statistical significance tests applied to small data sets (samples of populations) is the series of Student's tests. One of these tests is used for the comparison of two means, which is commonly applied to many cases **[13-15]**. this test is used to compare the two-corresponding means of each physical-chemical propriety of clays (RC and GC).

Hypotheses of test:

$$H_0: \quad \bar{x}_A = \bar{x}_B$$
$$H_a: \quad \bar{x}_A \neq \bar{x}_B$$

This test assumes:

(a) A normal (gaussian) distribution for the populations of the random errors;

(b) there is no significant difference between the standard deviations of both population samples.

The two means and the corresponding standard deviations are calculated by using the following equations (X=A or=B):

$$\mu_X = \bar{x}_X = \frac{1}{n}\sum_{i=1}^{n} n_i . x_i$$

$$s_X = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x}_X)^2$$

Then, the pooled estimate of standard deviation $\hat{s}$ is calculated:

$$\hat{s} = \sqrt{\frac{\upsilon_A s_A^2 + \upsilon_B s_B^2}{\upsilon_A + \upsilon_B}}$$

With, υ_X degree of freedom of each sample.

Finally, the statistic texp (experimental t value) is calculated:

$$t_{exp} = \frac{\bar{x}_A - \bar{x}_B}{s.\sqrt{\frac{1}{n_A} + \frac{1}{n_B}}}$$

texp value is compared with the critical (theoretical) t_{th} value corresponding to the given degree of freedom ν (in the present case $\nu = \nu_A + \nu_B - 2$) and the confidence level chosen. Tables of critical t values can be found in any book of statistical analysis, as well as in many quantitative analysis textbooks. If $t_{exp} > t_{th}$ then H_0 is rejected else H_0 is retained.

Pearson's test

In statistics, a contingency table (also known as a cross tabulation or crosstab) is a type of table in a matrix format that displays the (multivariate) frequency distribution of the variables **[16-18]**. Pearson's chi-squared test (χ^2) is a statistical test applied to sets of categorical data to evaluate how likely it is that any observed difference between the sets arose by chance. It is the most widely used of many chi-squared tests. The Chi-Square test of independence is used to determine if there is a significant relationship between two nominal variables. In this work, we will use the test to know the dependence of two clay materials used according to their chemical compositions determined by FRX. The frequency of each category for one nominal variable (RC and GC clays) is compared across the categories of the second nominal variable (Different determined oxides). The data can be displayed in a contingency table where each row represents a category for one variable and each column represents a category for the other variable.

Hypotheses of test:

H_0: Dependence between the two variables.

H_a: No dependence between the two variables.

First we have to calculate the expected value of the two nominal variables. We can calculate the expected value of the two nominal variables by using this formula:

$$E_{i,j} = \frac{\sum_{k=1}^{c} O_{i,k} \sum_{k=1}^{r} O_{k,j}}{N}$$

Where

- $E_{i,j}$: expected value.
- $O_{i,k}$: Sum of the ith column.
- $O_{k,j}$: Sum of the kth row
- N: total number

After calculating the expected value, we will apply the following formula to calculate the value of the Chi-Square test of Independence:

$$\chi^2 = \sum_{i=1}^{r} \sum_{j=1}^{c} \frac{(O_{i,j} - E_{i,j})^2}{E_{i,j}}$$

- χ^2: Chi-Square test of Independence.
- $O_{i,j}$: Observed value of two nominal variables.
- $E_{i,j}$: Expected value of two nominal variables.

Degree of freedom is calculated by using the following formula:

$$DF = (r-1)(c-1)$$

Where

- DF: Degree of freedom.
- r: number of rows.
- c: number of columns.

Hypothesis testing for the chi-square test of independence, where a test statistic is computed and compared to a critical value. The critical value for the chi-square statistic is determined by the level of significance (typically 0.05) and the degrees of freedom. The degrees of freedom for the chi-square are calculated using the previous formula. If the observed chi-square test statistic is greater than the critical value, the null hypothesis can be rejected.

3. Results and discussions

3.1. Physico-chemical property

All the values obtained during the determination of the physico-chemical properties of the two clay rocks are presented in Table 1. The first reading of the results shows that the physico-chemical property of the two materials studied are similar. In general: The density for the two samples are high, the pH values are respectively 7.22 for (RC) and 7.23 for (GC), reveal the neutrality of the porous media studied. The humidity (water content) values are low, which explains the non-hygroscopic nature of the samples as well as the organic matter contents are low which correspond to the mineral composition of the materials. The low values of colloidality and the electrical conductivity explain the weak ionization of the particles entering into the constitution of two materials and the porosity of the two media is important and it is worth 0.72. The results obtained give a general point of view on porous clay media before insertion into practical applications of later work.

Table 1. Physical-chemical parameters of RC and GC porous media.

Parameters	RC	GC
Density (g/cm^3)	1.42	1.44
pH	7.22	7.23
Conductivity (mS/m)	302	298
Dry matter content (%)	98.17	98.14
Moisture content (%)	1.83	1.86
Organic content (%)	8.35	6.74
Mineral content (%)	91.65	93.26
Swelling index (%)	48.17	48.14
Colloidality (%)	7.7	7.6
Porosity	0.72	0.72

3.2. Physico-chemical characterizations

The purpose of the X-ray crystallography study started as part of this work was to determine the mineralogical composition of the two media studied. Figure 2 shows the diffractograms of the (RC) and (GC) samples. According to the XRD diagrams obtained, these two types of materials have identical clay mineralogical compositions: Reflections characteristic of phyllosilicates have been detected at 10 Å, 7 Å, 5.1 Å, 4.5 Å, and 3.5 Å for the two samples, hence, the first 3 peaks correspond to the basal distance d_{001} and d_{002} kaolinite, while the other two peaks correspond respectively to the reflections d_{001} and d_{002} Illite **[19-20]**. Quartz is also present in both samples as an associated mineral. It manifests with a high intensity peak towards the reflection 3.2 Å with four low intensity peaks associated with 4.2 Å, 2.3 Å, 2.1 Å and 1.9 Å **[21]**. The presence of the characteristic carbonate lines in the two samples associated with the 1.8 Å reflection confirms the presence of calcite and at the 2.4 Å and 2.1 Å reflections of the presence of dolomite **[22]**. The presence of hematite in the RC sample towards the reflections 3.58 Å, 2.55 Å, and 2.37 Å **[23]**. Spectral analysis by DRX indicates that the two clay rocks (RC) and (GC) contain a mixture of: Quartz (SiO_2), Calcite ($CaCO_3$), Dolomite ($CaMg(CO3)_2$), Kaolinite (($Al_2Si2O_5(OH)_4$) and Illite $(K,H_3O)((Al,Mg,Fe))_2$ $(Si,Al)_4O_{10}$ $[(OH)_2,(H_2O)]$, which implies that these environments are heterogeneous. Table 2 shows the content of the chemical elements present in each sample. Silicon oxide SiO_2 and aluminum oxide Al_2O_3 are the major constituents for both (RC) and (GC) clays. The highest amount of SiO_2 was detected for (GC) green clay, around 52.17%, while the percentage in red clay is around 33.40%. These percentages are justified by the presence of free silica. Aluminum oxide Al_2O_3 is present with a percentage of 17.03% for (RC) and 29.06% for (GC). The iron oxide Fe_2O_3 is present in the two samples with a remarkable quantity

for the red clay (RG) with a percentage of 32.47% and a low percentage of 1.61% for the green clay (GC) which explains the red color of the first one. The oxide compositions: Na_2O, K_2O, MgO, CaO and TiO_2 in the two samples reach moderate percentages between 1% and 4%, thus the others remaining: P_2O_5 and SO_3 present low percentages on the order of ppm. Loss on ignition (PAF) corresponds to the departure of water H_2O, carbon dioxide CO_2 from the decomposition of carbonates and organic matter in the sample to be analyzed, the values obtained are 8 35% for red clay (RC) and 6.74% for green clay (GC) and they reflect the sum of the two contents of water and organic matter presented in Table 2

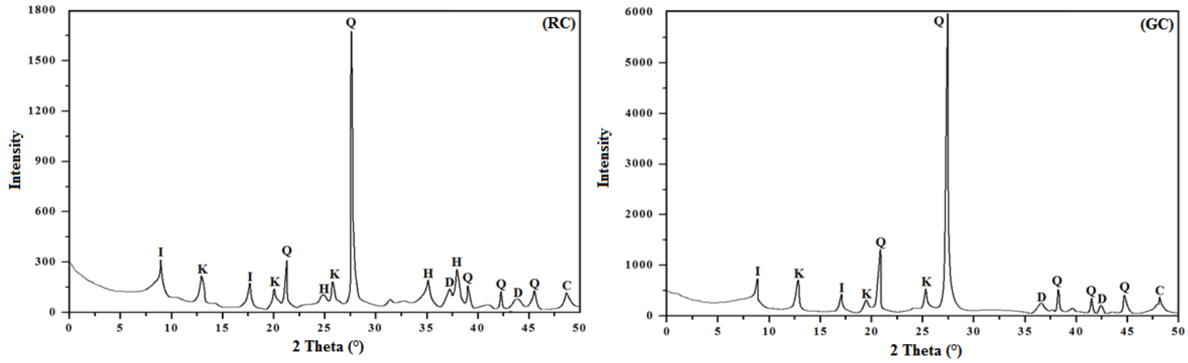

Figure 2. X-Ray diffraction diagram of RC and GC.

(K = Kaolinite, I = Illite, Q = Quartz, C = Calcite, D = Dolomite, H = Hematite)

Table 2. Chemical composition of RC and GC.

	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	MgO	TiO_2	CaO	P_2O_5	SO_3	PAF
RC	33.40	17.03	32.47	3.27	3.60	1.24	0.69	0.68	0.10	0.01	8.35
GC	52.17	29.06	1.61	4.06	3.85	1.27	1.00	0.58	0.11	0.01	6.74

Fourier transform infrared spectroscopic analysis (IRTF) consists in measuring the quantities of radiation absorbed by the sample as a function of the incident wavelength.The analyzes by IRTF Spectroscopy are represented in the spectra of Fig. 3. The examination reveals adsorption bands which appear as follows: The band which spreads at 1025 cm^{-1} corresponds to the vibrations of valence of the Si-O bond, and it is characteristic of the aluminosilicate.The bands observed at approximately 920 and 3620 cm^{-1} are attributed to the valence vibrations of the OH group and the elongation of Al_2OH (interaction between OH and Al), also the vertices at 698 cm^{-1} are characteristic of the Al-OH and Si-O bonds. The bands observed at 475 and 540 cm^{-1} are respectively attributed to the deformation vibrations of the Si-O and Si-O-Al bonds. The band observed at 1517 cm^{-1} is attributed to the C-O bond vibrations of calcium carbonate $CaCO_3$. The band observed at 1455 cm^{-1} in the first spectrum of (RC) is attributed to the bending vibrations of the group O-Fe-O which proves the presence of Hematite **[24-26]**. The scanning electron microscope (SEM) pictures illustrated in Fig. 4 and 5 respectively for (RC) and (GC), revealed the nature of the morphology of the two samples at a resolution of 5 to 200 µm. The results obtained show, on the one hand, very irregular and microporous structures and, on the other hand, a heterogeneity of the pore shapes over the entire surface. In addition, microanalyses by dispersive X-ray analysis (EDX) of the surfaces of the samples (RC) and (GC) give chemical compositions presented as a function of percentages by mass which are described in Table 3. The data obtained confirm the results found by X-ray diffraction (XRD) and X-ray fluorescence (FRX), hence the high percentages of silicon (Si) and aluminum (Al) which are consistencies with nature. alumino-silicate of argillaceous rocks, thus the presence in a relatively important quantity of iron (23.27%) in the sample (RC)

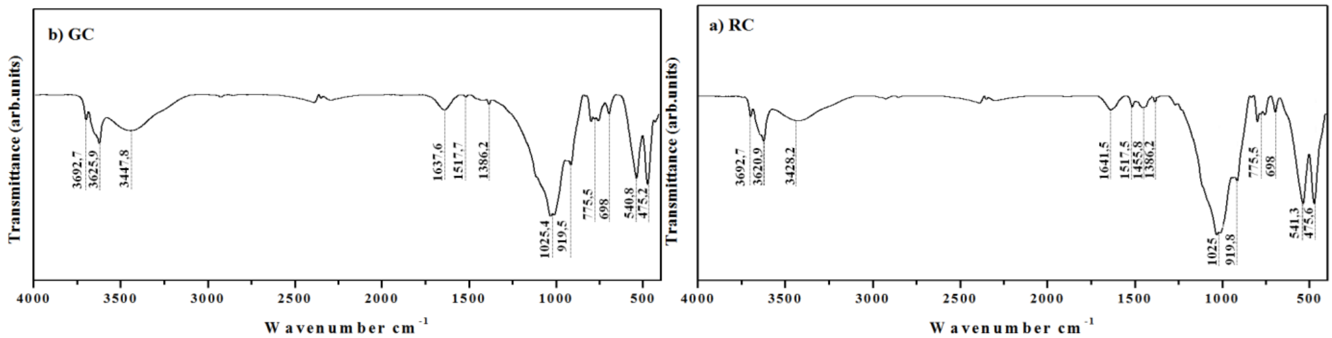

Figure 3. IRTF spectra of two RC and GC samples..

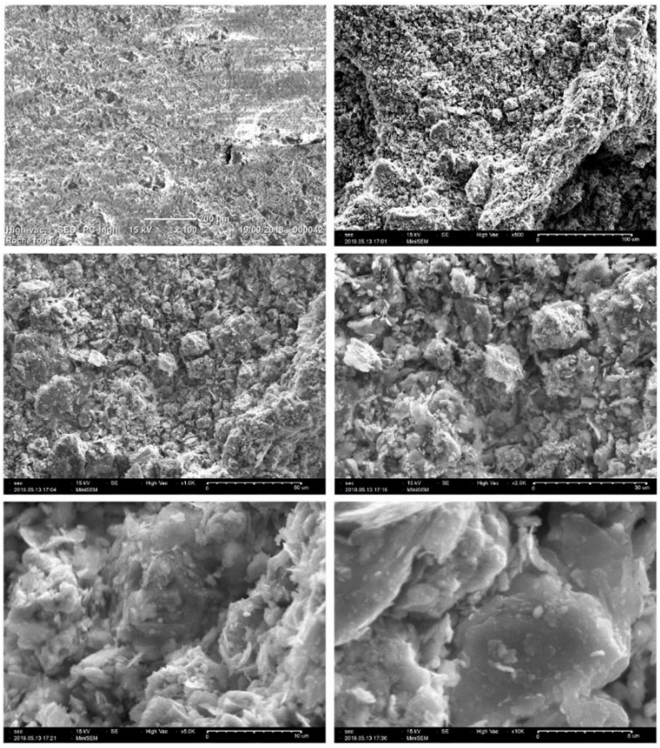

Figure 4. SEM of RC (Resolution of 200 µm to 5 µm).

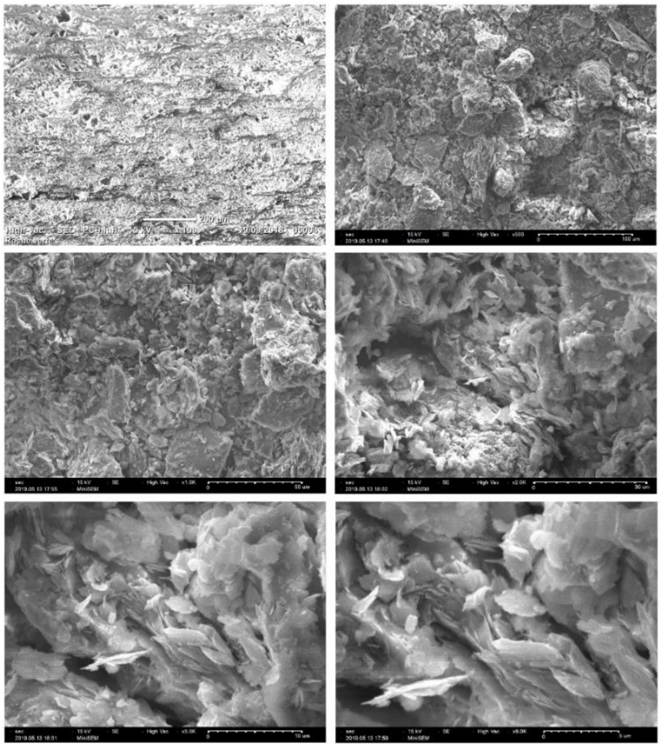

Figure 5. SEM of GC (Resolution of 200 µm to 5 µm).

Table 3. EDX microanalysis of RC and GC surfaces.

	RC	GC
C	8.41	-
O	36.34	48.76
Mg	2.87	-
Al	10.74	18.70
Si	15.49	27.26
K	2.87	5.28
Fe	23.27	-
Total	100	100

Thermogravimetric analysis consists in continuously monitoring the variation in the mass of a sample as a function of temperature. The temperature rise is 10 ° C / minute. The result of this study is given in FIG. 5. The curves show that the two clay samples have three stages of mass loss: The first stage situated in the lower region of 200 ° C. corresponding to the dehydration of the surface and the removal of organic matter from the two samples. The percentage of mass loss is of the order of 0.38%. The second level extends between 430 to 670 ° C corresponding to the dehydroxylation of the sheets of clay rock, particularly kaolinite, it is worth around 1.01% for RC and 1.04% for GC. The third stage which ranges between 700 to 800 ° C corresponding to the dehydroxylation of the illites. The percentage of mass loss due to this elimination is around 3.21% for RC and 3.24% for GC **[27-30]**

.

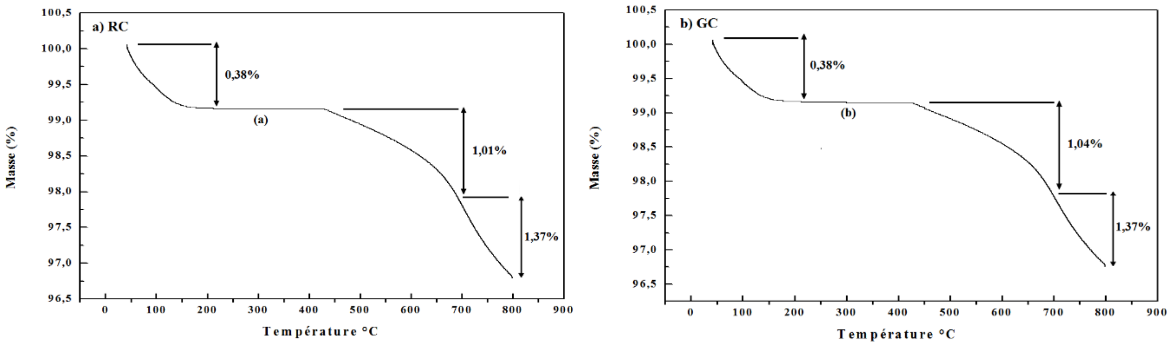

Figure 6. Thermogravimetric analysis of two RC and GC samples.

3.3. Statistical approach to study of dependence between two clays

As described above, the use of statistical approaches gives a general view on the dependence of the two abundant clay materials of the Bejaad region (Morocco). Tables 4 and 5 give the statistical parameters obtained during the realization of Student's test for the physical-chemical properties and Pearson's test for the composition of the oxides of the two clays RC and GC.

Table 4. Statistical parameters of Student's test for Physical-chemical proprieties of two clays.

Parameters	$\bar{x}_{RC}$	$\bar{x}_{GC}$	s_{RC}	s_{GC}	t_{exp}	t_{th}	**p-value**	**Hypothesis retained**
Density (g/cm3)	1.42	1.44	0.01	0.02	-2.12	4.30	0.16	H_0
pH	7.22	7.23	0.01	0.01	-4.24	4.30	0.05	H_0
Conductivity (mS/m)	302	298	5	3	0.68	4.30	0.56	H_0
Dry matter content (%)	98.17	98.14	0.11	0.32	0.09	4.30	0.93	H_0
Moisture content (%)	1.83	1.86	0.11	0.32	0.09	4.30	0.40	H_0
Organic content (%)	8.35	6.74	1.22	1.52	-0.83	4.30	0.54	H_0
Mineral content (%)	91.65	93.26	1.22	1.52	-0.83	4.30	0.49	H_0
Swelling index (%)	48.17	48.14	2.21	1.30	0.01	4.30	0.99	H_0
Colloidality (%)	7.7	7.6	0.05	0.11	0.82	4.30	0.49	H_0
Porosity	0.72	0.72	0.03	0.01	0.00	4.30	1.00	H_0

In the results of the Student's test, all the experimental values of t_{exp} are lower than the critical values t_{th} at the significance level α=0.05, which proves to retain the null hypothesis H_0, and to reject the alternative hypothesis Ha, which explains that the two materials have the same physical-chemical properties such as: pH, conductivity, dry matter content/ moisture content, organic/mineral content, swelling index, colloidality, porosity. The calculated statistical

parameters of the 2nd test of Pearson applied to the XRF analysis in the form of a contingency table, gives an experimental value above the critical value at the significance level alpha=0. 05, which proves to retain the null hypothesis H_0, and reject the alternative hypothesis Ha, which explains that the two materials have similar chemical compositions. The set of statistical results performed according to two models shows that the two clay materials RC and GC have the same properties and characteristics at a 95% confidence level.

Table 5. Statistical parameters of Pearson's test for XRF analysis of two clays.

Parameters	Values
χ^2_{exp}	35.53
χ^2_{th}	18.31
DF	10
p-value	0.00
alpha	0.05
Phi of Pearson	0.42
Contingency coefficient	0.38
V of Cramer	0.42

4. Conclusion

In this work we determined, by different physicochemical analysis techniques, the physicochemical properties and the textural analysis of the two clays RC and GC. The results obtained show that: The properties of the two samples are remarkable: high densities, neutral media and low moisture and organic matter contents. Textural analyzes show that the composition of the two samples has a clay character, from where they contain a mixture of illite and kaolinite, as well they contain associated minerals such as quartz and calcite, and hematite for the sample (RC). The morphological texture of two samples is porous, while the structures are heterogeneous and the samples (RC) and (GC) are stable under ambient conditions.

References

[1] S.P. Pletnev, Main Types of Aptian–Cenomanian Sedimentary Rocks on Guyots of the Magellan Mountains, Pacific Ocean. *Russian Journal of Pacific Geology*, *13*(5), (2019) 436-445.

[2] M.H.R. Khan, J. Liu, S. Liu, A.A. Seddique, L. Cao, A. Rahman, Clay mineral compositions in surface sediments of the Ganges-Brahmaputra-Meghna river system of Bengal Basin, Bangladesh. *Marine Geology*, *412*, (2019) 27-36.

[3] J. Schieber, C. Miclăuș, A. Seserman, B. Liu, J. Teng, When a mudstone was actually a "sand": Results of a sedimentological investigation of the bituminous marl formation (Oligocene), Eastern Carpathians of Romania. *Sedimentary Geology*, *384*, (2019) 12-28.

[4] W.J. Likos, X. Song, M. Xiao, A. Cerato, N. Lu, Fundamental challenges in unsaturated soil mechanics. In *Geotechnical Fundamentals for Addressing New World Challenges*, Cham. (2019). 209-236.

[5] M. Fazeli Sangani, G. Owens, A. Fotovat, Transport of engineered nanoparticles in soils and aquifers. *Environmental Reviews*, *27*(1), (2019) 43-70.

[6] Y. Tao, Z. Zou, L. Guo, Y. He, L. Lin, H. Lin, J. Chen, Linking soil macropores, subsurface flow and its hydrodynamic characteristics to the development of Benggang erosion. *Journal of Hydrology*, (2020) 124829.

[7] C.Y. Teh, P.M. Budiman, K.P.Y. Shak, T.Y. Wu, Recent advancement of coagulation–flocculation and its application in wastewater treatment. *Industrial & Engineering Chemistry Research*, *55*(16), (2016) 4363-4389.

[8] H. Bahmanpour, S. Awhadi, J. Enjili, S. Eslamian, K. Ostad-Ali-Askari, Optimizing absorbent bentonite and evaluation of contaminants removal from petrochemical industries wastewater. *International Journal of Constructive Research in Civil Engineering (IJCRCE)*, *3*(2), (2017) 34-42.

[9] S.S. Gaur, P. Dhar, S. Sakurai, A. Kumar, V. Katiyar, Cellulose nanocrystal/clay based macroion nanogel as support for stable platinum catalyst for electrochemical oxidation of methanol in alkaline medium. *Applied Clay Science*, *182*, (2019) 105277.

[10] N.K. Soliman, A.F. Moustafa, Industrial solid waste for heavy metals adsorption features and challenges; a review. *Journal of Materials Research and Technology*, *9*(5), (2020) 10235-10253.

[11] S. Elidrissi, L. Daoudi, N. Fagel, Palygorskite occurrences and genesis in calcisol and groundwater carbonates of the Tensift Al Haouz area, Central Morocco. *Geoderma*, *316*, (2018) 78-88.

[12] S. Elidrissi, F.E. Omdi, A. El Azhari, N. Fagel, L. Daoudi, New application of GIS and statistical analysis in mapping the distribution of quaternary calcrete (Tensift Al Haouz area, Central Morocco). *Catena*, *188*, (2020) 104419.

[13] Z. Ali, S.B. Bhaskar, Basic statistical tools in research and data analysis. *Indian journal of anaesthesia*, *60*(9), (2016) 662-668.

[14] Z. Zhang, Univariate description and bivariate statistical inference: the first step delving into data. *Annals of translational medicine*, *4*(5), (2016) 1-10.

[15] J. Ho, T. Tumkaya, S. Aryal, H. Choi, A. Claridge-Chang, Moving beyond P values: data analysis with estimation graphics. *Nature methods*, *16*(7), (2019) 565-566.

[16] P.M. Kroonenberg, A. Verbeek, The tale of Cochran's rule: My contingency table has so many expected values smaller than 5, what am I to do?. *The American Statistician*, *72*(2), (2018) 175-183.

[17] Q. Zhang, Independence test for large sparse contingency tables based on distance correlation. *Statistics & Probability Letters*, *148*, (2019) 17-22.

[18] M. Baak, R. Koopman, H. Snoek, S. Klous, A new correlation coefficient between categorical, ordinal and interval variables with Pearson characteristics. *Computational Statistics & Data Analysis*, (2020). 107043.

[19] S. Han, Y. Liu, C. Yin, N. Jiang, Fast synthesis of submicron ZSM-5 zeolite from leached illite clay using a seed-assisted method. *Microporous and Mesoporous Materials*, *275*, (2019) 223-228.

[20] K. Dou, Y. Jiang, B. Xue, C. Wei, F. Li, Carbothermal Reduction Nitridation of Fly Ash, Diatomite and Raw Illite: Formation of Nitride Powders with Different Morphology and Photoluminescence Properties. *Crystals*, *10*(5), (2020) 409.

[21] S.M. Awadh, Z.M. Yaseen, Investigation of silica polymorphs stratified in siliceous geode using FTIR and XRD methods. *Materials Chemistry and Physics*, *228*, (2019) 45-50.

[22] Y. Fang, H. Xu, A new approach to quantify the ordering state of protodolomite using XRD, TEM, and Z-contrast imaging. *Journal of Sedimentary Research*, *89*(6), (2019) 537-551.

[23] N. Thüns, B.M. Krooss, Q. Zhang, H. Stanjek, The effect of H2 pressure on the reduction kinetics of hematite at low temperatures. *International Journal of Hydrogen Energy*, *44*(50), (2019) 27615-27625.

[24] A. Am, F. Ouzidan, T. Ainane, L. El Kouali, M. Talbi, Adsorption of cationic dye onto Moroccan natural rock. *Mediterranean Journal of Chemistry*, *9*(1), (2019) 37-44.

[25] A. Am, R. Mounir, K. Ifrhalane, F. Amegrissi, M. Elkouali, M., Talbi, A. Ainane, T. Ainane, Physico-chemical characterization of a limestone rock used as a building material in the SIDI LAMINE region-Province of Khénifra (Morocco). *Journal of Analytical Sciences and Applied Biotechnology*, *2*(1), (2020) 63-66.

[26] T. Ainane, A. Abourriche, M. Kabbaj, M. Elkouali, A. Bennamara, M. Charrouf, M. Talbi, Valorization of natural clay from agadir (Morocco): characterization and study of the isotherms adsorption of Methylene blue. *J. Chem. Pharm. Res*, *6*(4), (2014) 599-606.
[27] D. Gournis, V. Georgakilas, M.A. Karakassides, T. Bakas, K. Kordatos, M. Prato,F. Zerbetto, Incorporation of fullerene derivatives into smectite clays: a new family of organic− inorganic nanocomposites. *Journal of the American Chemical Society*, *126*(27), (2004) 8561-8568.
[28] R.R., Desai, J.A., Erwin Desa, V.K. Aswal, Hydration studies of Bentonite clay. In *AIP Conference Proceedings*. 1447 (2012) 197-198.
[29] P.B. Arab, T.P. Araújo, O.J. Pejon, Identification of clay minerals in mixtures subjected to differential thermal and thermogravimetry analyses and methylene blue adsorption tests. *Applied Clay Science*, *114*, (2015) 133-140.
[30] D. Martín, P. Aparicio, E. Galán, Time evolution of the mineral carbonation of ceramic bricks in a simulated pilot plant using a common clay as sealing material at superficial conditions. *Applied Clay Science*, *180*, (2019) 105191.