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DETERMINATION OF THE STRUCTURE OF CLAY AND CEC BY CHEMICAL ANALYSIS METHOD

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This work is based on the structural characterization of Algerian clay. Natural clay before and after treatment was characterized using IR, TEM, and XRD techniques and has to undergo complete characterization by chemical analysis. Thus, this work reports, for the first time, a simple method is used to prepare the clay we use. The chemical composition of the clay is of particular concern in this study and that can be used for determining the chemical formula of Montmorillonite, which can be used as an active ingredient in the pharmaceutical industry with a CEC equal to 121 meq/100g of clay.

Keywords: Chemical composition; Clay; CEC; Montmorillonite; Structural formula; X-ray diffraction

1. Introduction

Clay minerals are present on the surface of the Earth and are the principal constituents of soil [3]. The primary constituents of clay are silicon and aluminum magnesium, which form its framework. These Si ions occupy the centers of tetrahedral structures, and other metal cations occupy the centers of octahedrals, in addition to water molecules [11]. If the two centers of the octahedral layer are occupied by a trivalent metal ion like Al^{3+} or Fe^{3+}, this clay is said to be di octahedral. On the other hand, if all the cavities of this similar octahedral layer are occupied by divalent metal ions, such as Mg^{2+} or Fe^{2+}, we will say that this clay is tri octahedral. Structurally, to a first approximation, they can be like hydrated sheet silicates with a layered structure made up of various sets of connected tetrahedral and octahedral layers. The color of the clay depends on the concentration of iron oxide. Kaolinite sheets are neutral, in dioctahedral and aluminous form, of composition: Al4 (OH)8(Si4O10) is half mesh [5]. The amount of oxygen in a tetrahedron is four and the amount of oxygen and hydroxyls in an octahedron is six [6]. The total negative charge of fundamental structural layers caused by the cationic substitutions in tetrahedrons and octahedrons of some phyllosilicates is balanced by cations trapped in the interlayer space like Mg^{2+} and K^{+}, Ca^{2+}, and Na^{+}. In the trioctahedral sheet of a

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Montmorillonite all tow sites are occupied by Mg^{2+} cations; the unit formula is: $(Na, Ca)_{0.3}(Al,Mg)_2Si_4O_{10})(OH)_2$-$xH_2O$. A distinction between dioctahedral and trioctahedral phyllosilicates can be made on the basis of reflection 060. Montmorillonite is important in environmental applications and the pharmaceutical industry [7]. Smectites are the dominant percentage in clay [1]. The various minerals such as montmorillonite, illite, and kaolinite are part of the smectite group [2]. The chemical analysis of clay minerals is presented in terms of elemental oxides and brings of different cations in tetrahedral, octahedral, and intercalary sites according to Pauling's rules [8]. The crystal structure of clay is made up of ionic planes. The actual a and b unit cell dimensions are, respectively, a = 5.223; b = 9.018 Å, for Illite; *and* a = 5.149; b = 8.93 Å for kaolinite. The tetrahedral and the octahedral develop along the a and b axes; the stacking of sheets is done along the c axis.

2. Experimental procedure

2.1. The Method Treatment of Clay

The clay used in this article is natural Algerian clay. Clay was washed several times with deionized water and completely dispersed in water.

After standing for 5 hours, the dispersion was centrifuged for one hour to thirty minutes at 3000 rpm. The size of the clay particles obtained was less than 2 mm and then dried at 100 ° C for one day. The purified clay is crushed beforehand and sieved to a size of less than 20 µm, and then the mixture is stirred for three hours at room temperature, from 22 to 24 °C, after placing the mixture to stand for one day. After this step, the clay is dispersed in a quantity of hydrogen peroxide H_2O_2 (30%) and then heated to 80 ° C. overnight, to remove the organic matter.

The particle size fraction is all of the Montmorillonite concentrated in the finest clay fraction equal to 2 µm.

2.2. The structural formula method

The method of structural formulas is a well-known procedure for the calculation of structural formulas of minerals **[9].** And remains a standard method for the determination of the layer charge of phyllosilicates. There are several methods to calculate the structural formula of phyllosilicates **[10].**

In our case, we have calculated our structural formulas on the basis of 44 anionic charges per unit cell or 22 anionic charges per half-cell **[11].**

The fine grain size of the clay and **2 µm** are chemically analyzed and characterized by the appropriate methods used in this study. With effective processing, the space becomes large between the layers, which allows the passage of sufficiently large charges as $\mathbf{K^+}$ is selectively incorporated into the interlayer space, reducing the smectite layer to form an illite layer.

2.3. Method to calculate the CEC

The number of variable charges is a function of the degree of division of the crystallites clay, so that the CEC increases as the size of the particles **[12].**

The charges induced are either positive or negative and depend on the pH of the medium. The CEC can vary from 1 to more than 100 cmol kg^{-1} depending on the organic matter and clay, as well as the nature of these two constituents.

In this work, the clay was well treated by the elimination of organic matter **[13]** where the charge deficit is compensated by the cations of Na $^{+}$, k,$^{+}$ and Ca $^{++}$.

$$Natural\ Clay + Na^{+} + K^{+} + Ca^{++} = Treated\ Clay + Quartz \quad (1)$$

The meq / 100 g of clay or the centimole of positive charge per kilogram knowing that:

$$\mathrm{CEC} = (\mathrm{Charge}/weight)\ (\mathrm{meq}/100\ \mathrm{g}) \quad (2)$$

3. Results and Discussion

3.1. Characterization

The physicochemical properties of natural and treated clay are presented in Tables 1 and 2.

The comparison of the chemical compositions of natural and treated clay showed a difference in sodium, potassium, and calcium load intercalated between the layers of clay which were subsequently treated.

Table 1

Chemical composition of natural and the treated Clay

Oxide Metal	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**Na_2O**	**K_2O**	**CaO**	**H_2O**
Treated Clay	57,2	15,37	4,86	3,36	0,52	1,53	1,51	14,5
Naturel Clay	60,7	15,85	4,49	2,48	1,42	2,24	3,53	6,92

Table 2

The basic calculation for a half-unit formula for number of cation 12 equivalents of natural Clay

Metal Oxyde	**Weight % Natural clay**	**Molecular weight (g/mole)**	**Number of cation ×1000**	**Number of oxygen**	**Number of cation 12 equivalent**
Na_2O	1,42	61,9789	22,9110229	11,4555115	**0,01955576**
MgO	2,48	40,3044	61,5317434	61,5317434	**0,21008227**
Al_2O_3	15,85	101,96	155,453119	233,179678	**0,53074952**
SiO_2	60,7	60,08	1010,31957	2020,63915	**3,44944273**
K_2O	2,24	94,2	23,7791932	11,8895966	**0,02029679**
CaO	3,53	56,0774	62,9487102	62,9487102	**0,21492009**

Fe_2O_3	4,49	159,69	28,1169766	42,175465	**0,09599725**
H_2O	6,92	18	384,444444	192,222222	**0,32814347**
				∑2636,04207	

Table 3

The basic calculation for a half-unit formula for number of cation 12 equivalents of treated Clay.

Metal Oxyde	**Weight % Natural clay**	**Molecular weight (g/mole)**	**Number of cation ×1000**	**Number of oxygen**	**Number of cation 12 equivalent**
Na_2O	0,52	61,9789	8,38995206	4,19497603	**0,00698256**
MgO	3,36	40,3044	83,3655879	83,3655879	**0,27752497**
Al_2O_3	15,37	101,96	150,74539	226,118086	**0,50183308**
SiO_2	57,2	60,08	952,063915	1904,12783	**3,16943139**
K_2O	1,53	94,2	16,2420382	8,12101911	**0,01351748**
CaO	1,51	56,0774	26,9270687	26,9270687	**0,08964051**
Fe_2O_3	4,86	159,69	30,4339658	45,6509487	**0,10131501**
H_2O	14,58	18	810	405	**0,67412476**
				∑2703,50552	

Therefore, from tables 2 and 3, we deduce the structural formula of natural and treated clay.

The determination of the tetrahedral (Al and Si) and octahedral (Al, Mg, and Fe) composition indicates the variable chemical composition of these materials and is clearly visible in the structural formulas of natural and treated clay.

The structural formulas of natural and treated clays show that they have tetrahedral loads of between **0.4 and 0.55** per half mesh in our case study.

The structural formula of natural and treated clay is given as follows in the formula:

The first structural formula is for natural clay is as follows:

$$[Si_{3.45}\,Al_{0.55}]\,(Al_{0.02}\,Fe^{III}_{0.095}\,Mg_{0.21})Ca_{0.21}\,Na_{0.019}K_{0.02} \qquad (3)$$

With the same method, the structural formula of the treated clay was determined according to the structure:

$$[Si_{3.6}\,Al_{0.4}]\,(Al_{0.1}\,Fe^{III}_{0.1}\,Mg_{0.27})Ca_{0.089}\,Na_{0.0069}K_{0.013} \qquad (4)$$

3.2. X-ray diffraction

The mineralogical composition of the natural and treated Clay was determined with X-ray diffraction (XRD) with a Siemens D5000 diffractometer using Cu Kα radiation at radiation (λ= 1.5406 Å).

The XRD patterns were recorded in the range of 0°–60° 2θ at a scanning speed of 1.2 °2θ.min^{-1}.

Results of the X-ray diffraction analysis for natural and treated clay are shown in Fig 1. It clearly shows that the d-spacing of clay increased from d=15.22 Å, 2ϴ = 5.8° to d=17.31 Å, 2ϴ= 5.1°, which could be attributed to the natural and Treated clay.

Quartz 2ϴ = 27° and calcite 2ϴ = 20° are the major impurities.

Their flection at d=4.13 and 7,07 Å, 2 ϴ =21.5°- 12.5° is characteristic of kaolinite; and their flection in d=3.55 Å, 2ϴ =25° is characteristic of illite respectively, and the major clay minerals were identified by XRD, (Fig 1).

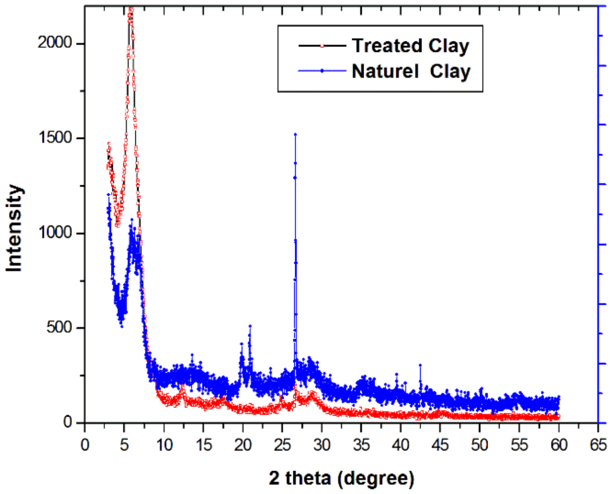

Fig. 1. XRD pattern for natural clay and Treated clay

3.3. Infrared spectroscopy study

The IR spectra of the natural and treated clay were recorded over the spectral range of 400–4,000 cm^{-1}. The IR techniques have been used by many researchers for the identification of the structure of natural clay minerals **[15].**

The characteristic vibrations of hydroxyl groups, the silicate anions, and the octahedral captions are present in the IR spectra of the studied samples, as shown in Fig. 2. The peak positions agree with the values given in the literature **[16].** In the region of 3750–3500 cm^{-1}, a number of sharp peaks at 3325 and 3150 cm^{-1} are observed; the region above 3100 cm^{-1} wavenumber contains information about the silanols.

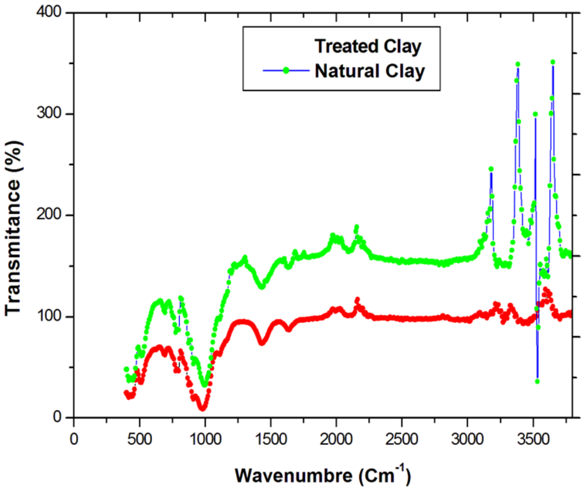

Fig. 2. FTIR spectra of natural and treated clay

The characteristic vibration peaks of Montmorillonite are at 3325 cm^{-1} (O–H stretching), 1000 cm^{-1} (Si–O stretching) Indicating the presence of Kaolinite, 800 cm^{-1} (Al–O–Si stretching), 750 cm^{-1} (Si–O–Al bending), this tow bands indicating the presence of Illite and 470 cm^{-1} (Si–O–Si bending).

3.4. Transmission electron microscopy (TEM)

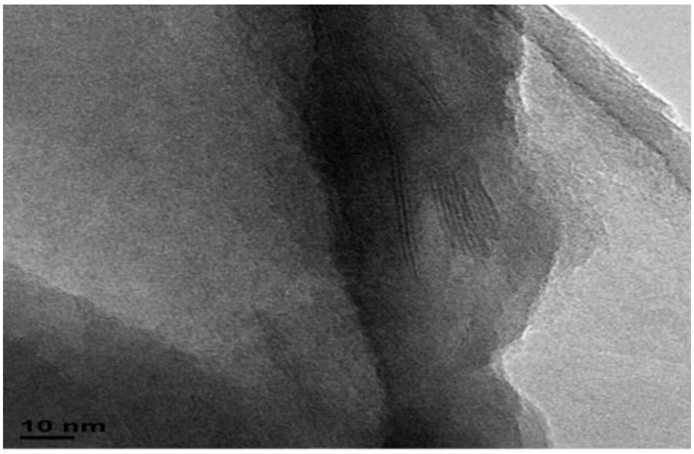

Fig. 3. Transmission electron microscopy (TEM) of naturel Clay

The TEM micrograph of natural and treated clay is shown in Figs. 1 and 2. It shows the laminated clay layers and the average layer thickness of 10 nm. This is a characteristic of the nano clay of natural and treated clay. The difference between treated clay and natural clay was more clearly observed when the clay was examined by TEM.

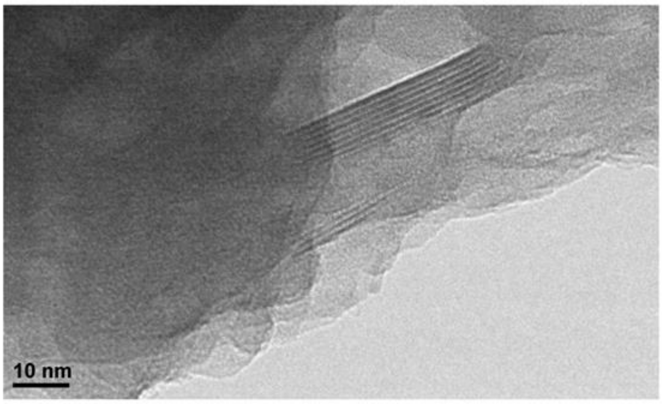

Fig. 4. Transmission electron microscopy (TEM) of Treated Clay

The figures of the treated clay showed that a homogeneous distribution of the layers appears in the form of many visible parallel sheets.

Table 4

Structural formula and CEC of Natural and treated clay

Mineral	Natural Clay	Treated Clay
Structural formula	$[Si_{3.6}\ Al_{0.4}]\ (Al_{0.1}\ Fe^{III}_{0.1}\ Mg_{0.27})Ca_{0.089}\ Na_{0.0069}K_{0.013}$	$[Si_{3.45}\ Al_{0.55}]\ (Al_{0.02}\ Fe^{III}_{0.095}\ Mg_{0.21})Ca_{0.21}\ Na_{0.019}K_{0.02}$.
CEC meq/100g of Clay	56	121

The CEC of the natural and treated clay is calculated by the equation 2. This value of 56–121 meq|100 g corresponds to the exchange capacity of the interlayer sites, and I determined the Structural formula of natural and treated clay respectively which are presented in Table 4.

6. Conclusions

In this work, the structural characterization of original clays from Algeria using the chemical composition that gives the physicochemical properties of natural and treated clay is used for determined the Structural formula of clay. These are shown in Table 1. The result of this work shows that the cations K^+, Na^+, and Ca^{++} introduced into the interfoliar sites in the clay studied with varying amounts increase the CEC of the clay from 56 to 121 meq/100g of clay, as shown in Table 4. The treated clay has shown that a homogeneous distribution of the layers appears in the form of numerous visible parallel sheets was observed by TEM.

The structural formulas of natural and treated clays show that they have tetrahedral loads of between **0.4 and 0.55** per half mesh in our case study. The treated clay has a high degree of purity in which it can be used as an active principle in the pharmaceutical industry, as an adsorbent and catalyst.

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