

# Characterization of Tataouine's Raw and Activated Clay

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## Abstract

This study deals with the mineralogical and thermal analysis of red clay taken from the south of Tunisia (Tataouine area) which will be used in industrial and environmental fields. In that purpose the study had recourse to several quantitative and qualitative research instruments: chemical analysis, mineralogical study and thermal analysis. The analyses were carried out by different methods such as: (i) X-ray diffraction (XRD), (ii) infrared spectroscopy (IR), (iii) thermogravimetric analysis (TGA), (iv) differential thermal analysis (DTA) and (v) cation exchange capacity (CEC). The data collected from these techniques show that illite and kaolinite are the major clay phases. The accessory minerals detected in powdered rock is calcite.

The raw clay has undergone an acid activation using the sulfuric acid. The acid activation of south of Tunisia clay increase the specific surface area by adsorption of methylene blue from 117 m<sup>2</sup>/g to 163 m<sup>2</sup>/g. The experimental investigation is performed in accordance with the methodology of the factorial design of experiments. The different factors or parameters used in this methodology are: the temperature (T), the contact time (t), the liquid/solid ratio (R), and the acid concentration (C). The optimal conditions, obtained by the statistically designed experiments, for the best results of methylene blue adsorption were:  $60 \,^{\circ}$ C, a contact time of 1.5 h, a liquid/solid ratio of 7 and acid concentration of 20%. These parameters are applied in the preparation of the sample used in characterization study. The effect of the reaction conditions on the solid structure is investigated by comparison with the raw clay sample.

**Keywords:** Clay; Characterization; Activation; XRD; IR; TGA; DTA; CEC

## Introduction

In recent years, many laboratories around the world were interested by the study of clays. This interest is justified by their abundance in nature (covering about 42% of the earth's crust), the importance of the specific surface areas developed, the presence of electric charges on the surface and above the exchangeability of interlayer cations. The latter one, also known as compensating cations, is the main element responsible for the hydration, swelling and plasticity.

Clay's activation is a process of improving the adsorption properties of the clay by subjecting it to thermal or chemical treatment. In chemical activation, is generally used sodium carbonate or strong acids such as sulfuric acid. Acid activation was the subject of many studies [1-4], treating either, the various reaction mechanisms, or the effect of attack on the physicochemical characteristics of clay. The supreme goal of the clay activation, as by the sulphuric acid attack [5,6], it is the increase in porosity by peripheral dissolution of clay, in order to increase the number of the active sites: Indeed, the structural cations of clay (Al<sup>3+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>) are replaced during activation by protons H<sup>+</sup>. It leads to a high capacity of adsorption.

Adsorption is a reversible and interfacial physicochemical phenomenon causing the accumulation of solute's molecules in the solid-liquid interface (or solid-gas). Often the adsorption of organic molecules is characterized by soils in the laboratory using the technique called "batch". This technique consists to agitate suspensions of adsorbents in aqueous solutions containing the adsorbate, in a closed container, until to reach adsorption equilibrium.

The MB adsorption method is currently used to measure the specific surface area of biosorbent particles in aqueous suspension. This method has been widely adopted for solids of variable nature such as iron oxides [7], clays [8], activated carbon [9,10], zeolites and silica [11]. The method has also been used to assess average pore size and pore size distribution in charcoals, silica, and alumina [12].

The work presented in this manuscript, aims to apply an acid activation on our natural clay, to characterize the raw and activated clay and to compare by emphasizing the results and shows the effect of activation.

#### Experimental

#### Material

In the present work, red clay was selected from site of 'Tataouine', located in the south of Tunisia was used as raw material. It has a BET surface area equal to 44.87  $m^2/g$  and 117  $m^2/g$  by adsorption of methylene blue. The received material contains many impurities. This content of impurities was decreased or removed completely by applying a purification protocol. This was achieved by dispersing the crude lumps in distilled water. The mixture was stirred vigorously and sieved several times through a different mesh sieves with the addition of more water. Then dispersed particles were collected, after allowing coarser mineral particles to settle. Finally, water was siphoned off, and it was dried in air at around 60°C.

#### Acid-activation

Acid-activation was carried out with sulphuric acid in a jacketed glass reactor equipped with a reflux condenser, a thermometer and a stirrer. At the end of each experiment, the solid content was immediately filtered, washed with water until the washing water was neutral and dried.

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All samples were prepared according to central composite orthogonal design (CCOD) [1]. Temperature (53.8-96.2°C), contact time (0.57-6.93 h), liquid/solid mass ratio (3.38-7.62) and acid concentration (13.8-56.2%) are chosen as numerical procedure variables for optimization for methylene blue adsorption.

The table 1 shows the variation interval of activation's factors (T, t, R et C).

 $\Delta Z_j$  means the half extent of its range of variation:  $\Delta Z_j = \frac{Z_j^{\text{max}} - Z_j^{\text{min}}}{2}$ 

The table 2 presents the matrix of acid-activation experimental design and the specific surface area (SMB) by adsorption of methylene blue.

The optimal conditions, obtained by the statistically designed experiments, for the best results of methylene blue adsorption were: a temperature of 60°C, a contact time of 1.5 h, a liquid/solid ratio of 7 and acid concentration of 20%. These parameters are applied in the preparation of the sample used in the characterization study.

#### Characterization

The chemical analyses of the raw material and activated clay were carried out by X-ray fluorescence. The specific surface area was calculated by adsorption of methylene blue method. The value

j	Variables	$Z_j^{\min}$	$Z_j^{\max}$	$\Delta Z_{j}$
1	T (°C)	60	90	15
2	t (h)	1.5	6	2.25
3	R (g/g)	4	6	1.5
4	C (% mass.)	20	50	15

Table 1: Study variables and their variation ranges

Essai (i)	T (°C)	t (h)	R (g/g)	C (%)	S <sub>MB</sub> (m²/g)
1	60	1.5	4	20	146.67
2	90	1.5	4	20	146.43
3	60	6	4	20	155.04
4	90	6	4	20	138.70
5	60	1.5	7	20	162.98
6	90	1.5	7	20	144.84
7	60	6	7	20	144.04
8	90	6	7	20	131.92
9	60	1.5	4	50	146.27
10	90	1.5	4	50	139.24
11	60	6	4	50	142.45
12	90	6	4	50	136.95
13	60	1.5	7	50	156.16
14	90	1.5	7	50	154.17
15	60	6	7	50	135.35
16	90	6	7	50	130.17
17	75	3.75	5.5	35	147.65
18	53.8	3.75	5.5	35	139.93
19	96.2	3.75	5.5	35	130.09
20	75	0.57	5.5	35	148.51
21	75	6.93	5.5	35	133.35
22	75	3.75	3.38	35	152.65
23	75	3.75	7.62	35	139.02
24	75	3.75	5.5	13.8	153.85
25	75	3.75	5.5	56.2	144.68

Table 2: Experimental design and results of methylene blue adsorption.

Compounds	CaO	SiO2	AI2O3	Fe2O3	SO3	K2O	MgO	Na2	LI
Raw clay	5.91	45.46	15.61	9.64	3.86	1.79	3.26	0.28	11.56
Activated clay	0.95	58.63	20.37	9.93	0.6	1.94	0.4	0.03	8.05

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Table 3: Chemical analysis (wt %) and loss in ignition of raw and activated clay.

of the cation exchange capacity (CEC) is determined by the method using complex of copper ethylenediamine [13]. The mineralogical compositions were identified by Philips Panalytical X'Pert PRO X-ray powder diffractometer. The Infra Rouge spectra were obtained using a Perkin Elmer FTIR (the sample was diluted with potassium bromide: 50 mg of sample mixed with 350 mg of KBr). To obtain the DTA/ TGA curves, a differential calorimeter apparatus TG-DTA 92 SETARAM with an argon flow was used: the finely ground sample was introduced into a platinum crucible and placed in the furnace along with the reference sample (the temperature was increased from room temperature to 1000°C at a rate of 10°C/min, maintained at this temperature for 10 min then reduced again) [14].

#### **Results and Discussion**

#### Chemical analysis

The table 3 shows the chemical analysis and the loss on ignition of raw and activated clay.

The high loss on ignition is attributable to the presence of substantial volatiles, existing in clay minerals (mainly hydrous species), dolomite (carbonate), and organic matter [14].

The chemical analysis of raw moldier shows that the major elements are  $SiO_2$  and  $Al_2O_3$ , which are both associated with the kaolinite structure [15].

The ratio of  $SiO_2$  increase at activated sample: this increase is due to the formation of amorphous silica during activation. We note also a clear reduction in the calcium portion. Indeed, the composition of raw clay on CaO is 5.91 and for the activated sample is 0.95. So we can conclude that Ca<sup>2+</sup> is a major exchangeable cation.

The increase of  $K_2O$  after activation is probably due to the existence of illite clay mineral: potassium is not involved in the cation exchange [16].

The ratio  $\frac{SiO_3}{Al_2O_3 + Fe_2O_3 + MgO} = 1.59$  for the raw clay and 1.9 for the activated clay: this value is between 1 and 2, indicating that the clay is a mixture of 1/1 and 2/1 dioctahedral phyllosilicates [14]: our clay is a mixture of kaolinite and illite.

The overall structural formula of the clay is calculated:  $[Al_{_{0.95}}Fe_{_{0.56}}Mg_{_{0.38}}][Si_{_{3.52}}Al_{_{0.48}}]O_{_{10}}(OH)_2Ca_{_{0.49}}Na_{_{0.042}}K_{_{0.18}}$ 

#### X-Ray diffraction (XRD)

The diffractograms obtained shows that our clay is a well crystallized material.

Figure 1a and 1b show the X-ray diffraction pattern of respectively raw and activated clay. The raw clay sample contains illite as the major clay mineral associated with kaolinite; the peak at 9.97 Å is the wider peak which characterized the illite clay mineral, the two peaks at 7.14 and 3.33 Å are the characteristics peaks of kaolinite clay mineral. Accessory minerals such as calcite was detected in our natural clay, occur at 4.94 Å.

For the activated clay sample, we note: the disappearance of characteristic peak of kaolinite at d=7.14 Å: this disappearance is due to





the high temperature used during the acid activation [1]. We also noticed the disappearance of characteristic peak of calcite: this is explained by the cation exchange that occurs between the cations  $Ca^{2+}$  of clay and  $H^+$  of the sulfuric acid which is proved by the chemical composition by the reduction of fraction of CaO of activated clay sample.

The two reflections at 9.97 and 3.33 Å correspond respectively to the phyllosilicate phase 1/2 of illite and 1/1 of kaolinite are still. However, there was a decrease in intensity which can be attributed to a change in the internal structure of the clay during the activation.

#### Infrared spectroscopy (IR)

The figure 2a and 2b below shows the IR spectrum of raw and activated clay.

The IR spectrum of raw and activated clay shows that the stretching band of the hydroxyl group of water of hydration H-O-H is around  $3444 \text{ cm}^{-1}$ , while the deformation is around  $1637 \text{ cm}^{-1}$ .

The band of stretching vibration of Al-Al-OH is at 3632  $cm^{-1}$  and the strain is at 911  $cm^{-1}$  indicates that this clay is dioctahedral [17].

The band at 1021 cm  $^{\cdot 1}$  is characteristic of vibration of Si-O of clay, while the deformation bands appear respectively at 525 cm  $^{\cdot 1}$  for Al-O-

Si and at 470 cm<sup>-1</sup> for the group Si-O-Si which increase on activated sample comparing with the raw sample's one: this result is confirmed by the chemical analysis.

The band that appears at 1385 cm<sup>-1</sup> corresponds to the presence of carbonate (calcite (CaCO<sub>3</sub>) or dolomite (Ca,Mg((CO<sub>3</sub>)<sub>2</sub>)) [18]. But, this band is reduced relative to that of natural clay: this is explained by the fact that cation exchange between Ca<sup>2+</sup> cations of the clay and H<sup>+</sup> from the acid.

## Thermal analysis (DTA-TGA)

Both DTA and TGA characterizations are carried out simultaneously with the same device.

The DTA and TGA curves of raw and activated clay are shown respectively on figure 3a and 3b.

The interpretation of the DTA-TGA curves of the raw clay sample (Figure 3a) leads to the following results: An endothermic peak at 160°C, due to the removal of moisture and interlayer water of the clay minerals (water of hydratation) [14]. The endothermic peak at 580°C can be attributed to the elimination of constitution water resulting from the loss of hydroxyl groups from the clay structure (dehydroxylation of kaolinite). Weight loss is observed up to 799°C, in accordance with the









decomposition of dolomite in the sample (decarbonation of clay).

For the activated clay (Figure 3a): the peak corresponding to the loss of the water of hydration is at 150°C and more significant than the raw clay's one. An endothermic peak appears at 520°C which correspond to the dehydroxylation of kaolonite with a high intensity compared with the raw clay's one. An endothermic peak appears at 600°C which attributed to the decarbonation of clay with a low intensity because of the decrease of the amount of CaO confirmed by the chemical composition and the IR spectrum.

#### Cation exchange capacity (CEC)

The value of the cation exchange capacity (CEC) of raw and activated clay is established by the method using the complex of copper ethylenediamine.

This low value shows that the clay studied is kaolinite: it is because

the cation exchange capacity of kaolinite is generally between 3 and 15 meq/100 g of clay [19].

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We note, from the table 4, the value of the cation exchange capacity of the activated clay is decreased compared to the raw clay. Indeed, this decrease is due to activation and shows that a portion of exchangeable cations were replaced during the activation by H<sup>+</sup> from sulfuric acid. Indeed, the surfaces of clay particles are negatively charged, and to balance these loads, the clay particles attract positive ions contained in the solutions that are exchangeable ions [20].

## Determination of pH

The pH of clay is determined by the traditional method suggested by Oboth and coll [21] (Figure 4).

The knowledge of the pH change of a clay/water suspension is important for the environmental and industrial applications. Therefore, we have investigated the chemical behavior of clay/water suspension in natural and activated sample.

The table 5 shows that the pH of raw clay is 7.78 which give it a basic character. However; the pH of activated clay gives it an acidic character. Indeed, it has generally been observed [22], that high solution pH tends to disperse clay systems. This phenomenon is undoubtedly related to the dissociation of H<sup>+</sup> ions as the pH increases and the resultant increased negative charge on clay particles which increased repulsion between particles and the probability of the dispersion being stable. The reverse occurs at low pH where positive charges dominate the edges of particles and lead to enhanced flocculation by edge-to-face attraction. Low pH also affects the stability of the clay particles. Van Olphen [23] indicated that acid attacks clay particles at edges, thereby releasing Al<sup>3+</sup> ions.

CEC (meq/100g of clay)					
Raw clay	6.22				
Activated clay	5.11				





pH			
Raw clay	7.78		
Activated clay	2.6		

Table 5: pH of raw and activated clay.

# Determination of isoelectric pH

The isoelectric pH is a method used to know the nature of the surface charge. To determine the isoelectric pH of our clay, we used the method developed by TJ Bondosz Keling and King in 1997 [21].

After activation of clay, the isoelectric pH decreases from 7.96 to 3.68. The acid treatment of the crude clay moves the PIE to acidic pH, which is directly related to the chemical modification of groups on the surface of these solids. The activated clay has indeed a negative charge on its surface for pH>IEP. Thus, clay minerals that are usually characterized as aluminum silicates exhibit negative charges in aqueous media, which results from the substitutions within the crystal lattice of Al<sup>3+</sup> for Si<sup>4+</sup> or Mg<sup>2+</sup> for Al<sup>3+</sup> [24]. As a result, negative charges are developed in the lattice to compensate for the so-called exchangeable cations, that is, Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> entering the crystal structure. If such clay minerals come into contact with water, some of these cations can easily dissociate, leading to a negatively charged surface. The electro neutrality of the system requires that the charged surface be surrounded by oppositely charged ions. The cloud of ions around the particle is described by the double-layer model, developed by Gouy, Chapman, Stern and Grahame [25].

#### Conclusion

The main objective of present study is chemical, mineralogical and thermal analysis of raw and activated clay taken from the region of Tataouine (southern Tunisia). Activated clays are obtained by acid activation using sulfuric acid and for different operating conditions.

Different techniques have been used to characterize raw clay and activated. We confirm that the red clay of Tataouine is a clay type illite kaolinite with a specific surface area BET equal to 44.87  $m^2/g$  and 117  $m^2/g$  by adsorption of methylene blue. After activation, this values increases to 163  $m^2/g$ .

The influence of activation conditions for an experimental design has allowed highlighting changes in the specific surface area measured by adsorption of methylene blue according to the activation parameters.

Our study allowed us to define the optimal conditions for the largest surface area and which are: Activation time: 1.5 hours; activation temperature: 60°C; weight ratio: 7 and concentration of acid: 20%.

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