

The Effect of Chlorhydric Acid Activation on the Physico-Chemical and Rheological Properties of A Kaolinite

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Abstract : *The kaolinite (Douala, Cameroun) (named D0M) was activated with HCl 0.5M at 25°C for 24h (named D05M) to obtain optimum parameters for imparting a maximum power toward facial mask. The natural and activated samples were characterized by scanning electron microscopy (SEM), X-ray Dispersive Energy Spectroscopy (XDE), X Fluorescence (XF), X-ray diffraction (XRD), by Fourier Transform Infrared Spectroscopy (FTIR), thermogravimetric analysis (TGA), Nitrogen adsorption-desorption, pore size distribution (PSD), and rheological properties of the samples were determined. The results show that the acid activation implore the specific surface area from 55.05 m²/g to 61.23 m²/g, whereas total pore volume is 0.228ml/g before acid activation and 0.248 ml/g after activation. The essential elements such as calcium, Magnesium and sodium not change considerably; the superficial properties are not modified. Rheological analyzes show that viscosity increase with acid activation and be more benefit as facial mask application.*

Keywords: kaolinite, physico-chemical, rheological properties.

Introduction

Because of their high specific surface area, optimum rheological characteristics and/or excellent sorptive capacity,

clays (kaolinite) always played a major role in human life. Clay materials are used and their value recognized in many economic branches pharmaceutical and cosmetic products, agriculture, civil engineering and environmental studies (Blachier et al., 2014, Carretero et al., 2010, Viseras et al., 2007, Konta, 1995). Kaolinites generally are 1:1 layered, hydrated aluminum silicates, at raw state, kaolinite may also contain other clay and non clay minerals as impurities. kaolinites are treated by the inorganic acids such as HNO₃, HCl and H₂SO₄ to remove some of the impurities and thereby to obtain more adsorptive materials (Noyan et al., 2007). In this study, the analysis of the structural, textural and rheological properties of natural and activated clay from Douala is made. The morphological analysis has been performed by scanning electron microscopy (SEM). The

chemical composition has been determined by X-ray Dispersive Energy Spectroscopy (XDE) and by X Fluorescence (XF). The different crystalline and superficial phases were studied by using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Gravimetric Analysis (TGA). Textural properties were analyzed by Nitrogen adsorption-desorption and rheological properties are also made. This clay is usually used by the local population as cosmetic facial mask, but an understanding the physico-chemical and porous properties of this kaolinite and the effects of its acid activation could permit to understand the others applications.

2. Material and methods

2.1. Material

The kaolinite analyzed in this study originate from the littoral of Cameroon, in the areas of Douala. Clay fraction (<2 μm) were separated by sedimentation and has been identified as D0M following the work. Twenty five gram aliquots of this clay were added to 25 ml of 0.5M HCl held at 25°C. After leaching for 24h the mixture was filtered off, washed several times with distilled water and dried at 105°C overnight. The crystalline phase obtained named D05M following the study were analysed. SEM and XDE observations were carried out with a Beckman Coulter SA 3100 microscope. The chemical analysis of the mineral components (minor and traces) has been done by XF, on a AE380 Fluorimeter XRD data were obtained by using a Siemens X: DRON-3 diffractometer with CuKα1 radiation ($\lambda = 1.4505 \text{ \AA}$), U=30kV and I=30mA. The detection limit for a given crystalline phase is estimated around 1% in mass. Infrared spectra were recorded using a Perkin Elmer 100 Fourier Transform Infrared spectrometer (4000–650 cm⁻¹) equipped with a detector cooled at 77 K, working in diffuse reflectance mode. The amount of clay was 70 mg dispersed in 370 mg KBr. Nitrogen adsorption-desorption isotherms at 77 K were recorded on a step-by-step automatic home-built setup. Pressures were measured using 0–10 mbar and 0–1000 mbar Beckman Coulter SA 3100-type pressure sensors provided by Edwards. Prior to adsorption, the samples were out gassed between 18h at 110°C and under a residual pressure of 0.3Pa. Nitrogen N55 (purity >99.9995%) that was used for experiments was provided by Alphagaz (Italy). Specific surfaces areas were determined from adsorption data by applying

the Brunauer–Emmet–Teller (BET) equation. Micropore volume areas were obtained using the *t* -plot method. Pore size distributions were calculated based on the desorption branch by using the Barrett–Joyner–Halenda method. The rheological values are obtained on the Rheological AR 2000 ex with 60mm of stray diameter.

3. Results and discussion

3.1. Morphology and chemical composition

SEM micrographs of clays of 1000µm size shows the particles of different sizes and forms, dispersed over the large matrix in more or less compact plates This indicates the presence of particles of quartz (SiO₂) (fig 1a). Scanning electronic of acid activated clays reveal the small corroded particles (fig 1b). This structural modification can be explained by the destruction of the crystal structure of kaolinite during acid activation, the same observation was described by several authors (Hussein et al., 2001, Hymore, 1996). The major elements of these two clays were identified by XDE (Table1). Oxygen is the most abundant element, consequently the other elements existing in the form of oxide. Si and Al are the two most important components after Oxygen, because the clays are generally alumino-silicates. The exchangeable cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺), very important in cosmetics products are not destroyed after acid activation. The analysis of trace elements by XF (see Table 2) show the other traces elements like Co, Zr, Rb, Sr, Zn, Mo and Pb.

Elements (ppm)	Fe	Co	Zn	Pb	Rb	Sr	Zr	Mo
DOM	4747	222	146	30	43	44	150	13
D05M	4498	/	62	22	38	40	156	20

3.2. Structure and superficial phases

The nature of different phases is identified by XRD, as shown in Figure 2a and 2b for the raw and acid activated Doukala clays respectively.

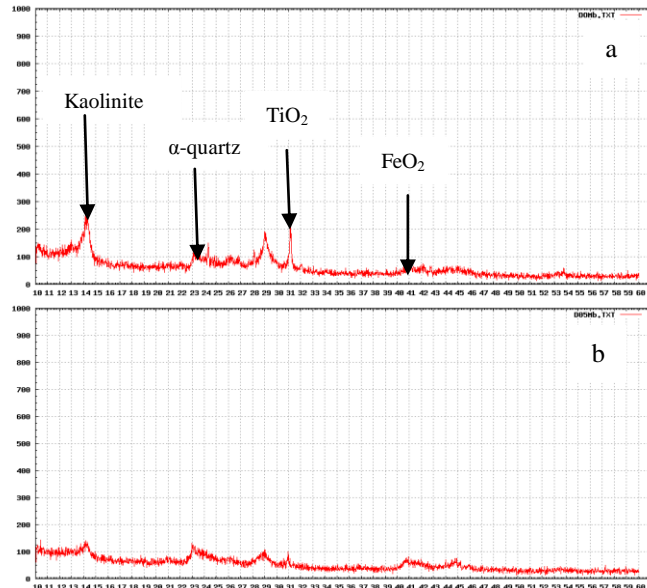


Fig. 2. DRX diffractograms of raw (a) and acid activated (b) clay

The infrared spectra of raw and acid activated Doukala clays are shown in Figure 3. The adsorption bands of the two samples are similar; many superficial groups have Si and Al, as indicated previously by the XDE observations. The bands around of 3693 Cm⁻¹ is assigned to the OH stretching vibration of kaolinite, the band around 3621 Cm⁻¹ is characteristic of the OH stretching of kaolinite and of AlAlOH or AlMgOH groups of smectite. The band between 1633-1639 is characteristic of the deformation vibration γOH of water or Si-O, Si-O-Al. The signal around 679 Cm⁻¹ (Si-O-Al) and 908 Cm⁻¹ (deformation δOH of AlAl–OH), the amorphous silica at 796 Cm⁻¹. These bands are not modified by the acid treatment.

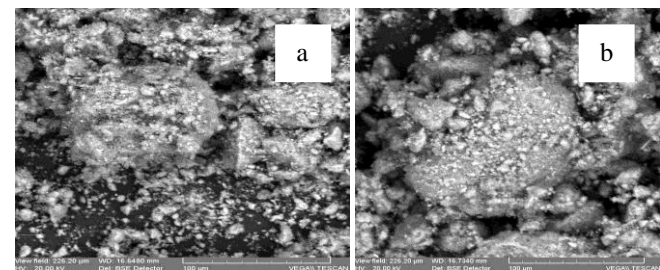
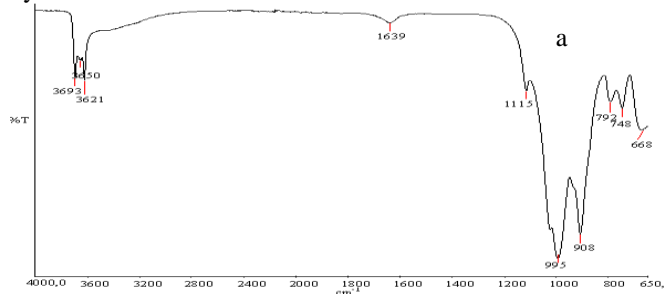


Fig.1. SEM of raw (a) and acid activated (b) clay, size 1000µm.

Table1. Majors elements of raw and acid activated clays determined by XDE.

Elements % weight	Si	Al	Fe	Cl	Na
DOM	20,469	18,195	2,570	0,286	0,167
D05M	21.908	18.606	2.174	0.330	0.079

Elements % weight	K	Mg	Ti	Ca	O
DOM	1,039	0,513	1,500	0,341	57,388
D05M	0.968	0.355	1.477	0.357	58.105

Table2. Composition in trace elements of raw and acid activated clays determined by XF

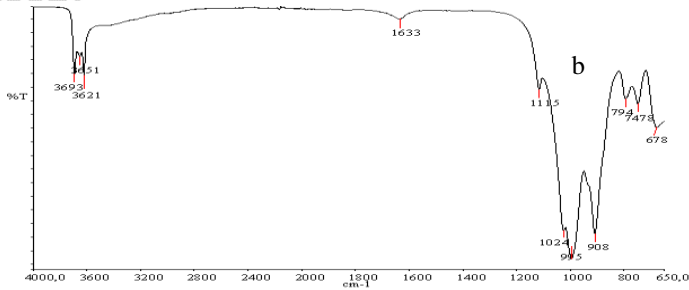


Fig. 3. Infrared spectra of raw (a) and acid activated (b) clay
The thermoponderal curves of raw and acid activated Douala clays are presented in Figure 4. We observe on the curve two mass loss of different importance. The first around 100°C is from adsorbed water. The weak slope of the curve indicates that the water is at the surface of the material, indication of presence of a clay type 1:1 (non-swelling clays). The second largest weight loss between 250° and 600°C corresponds to the dehydroxylation of the clay. The acid treatment reduced by more than 25% weight loss between 30 and 200°C, the acid treatment make that the surface of the clay become more hydrophobic. Table 3 illustrates these losses of weight.

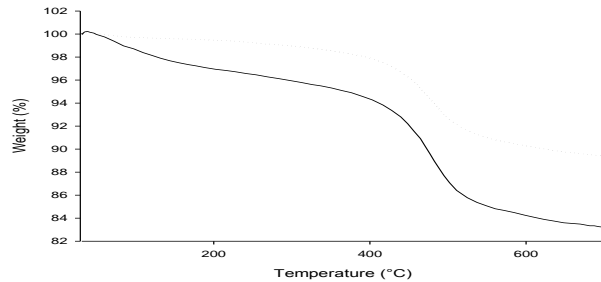


Fig. 4. Thermoponderal curves of D0M (—) D05M (···)

Table 3. Relative proportions of weight loss between 30-200°C and 200-600°C determined by TGA

Weight loss (%)	Temperature variations (°C)	
	30-200	200-600
D0M	19,4	80,6
D05M	5,1	94,9

3.3. Texturals properties of clays

The objective of this part of work is to define the interstitial spaces between clay platelets and the vacant sites.

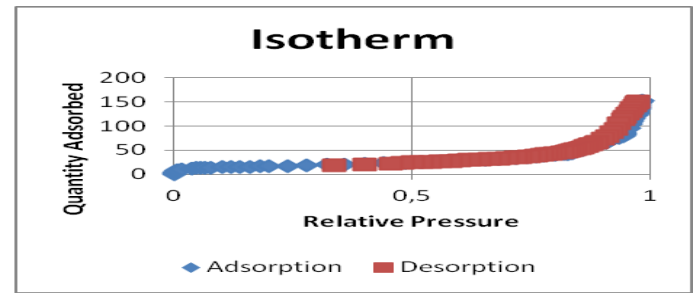
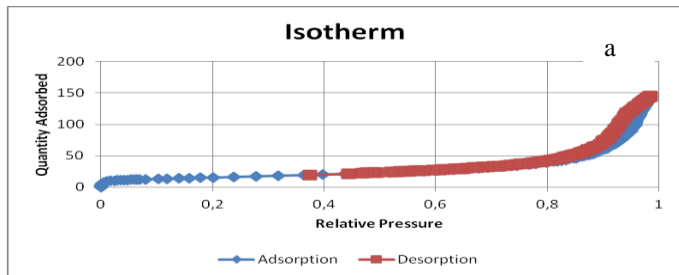


Fig.5 Adsorption/desorption isotherms D0M(a) and D05M(b)

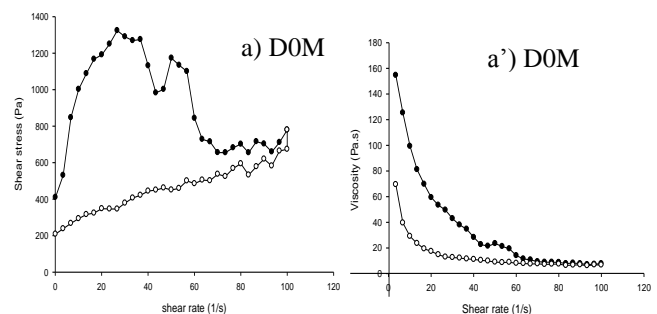
The nitrogen adsorption–desorption isotherms obtained for the both clays display very similar shapes (Figure 5). The two isotherms are close in shape to type IV because hysteresis occurs during the desorption branches, according to the IUPAC (International Union of Applied Chemistry) classification. This behavior can be attributed to mesoporous structures (Srasra et al., 2000).

Table 4. Pore size distribution and specific surface of clays

Pores size distribution (nm)	D0M		D05M	
	Pore volume (ml/g)	Percentage (%)	Pore volume (ml/g)	Percentage (%)
< 6	0,014	6,200	0,015	6,100
6 – 8	0,008	3,500	0,008	3,300
8 – 10	0,009	3,900	0,009	3,700
10 – 12	0,012	5,100	0,012	4,800
12 – 16	0,021	9,000	0,020	8,100
16 – 20	0,021	8,800	0,020	8,200
20 – 80	0,130	57,300	0,145	58,500
> 80	0,015	6,300	0,019	7,500
Total volume(ml/g)	0,228		0,248	
Specific surface (m ² /g)	55,050		61,230	

3.4- Rheological properties of clays

The main rheological parameters of suspensions are viscosity, shear rate, the yield stress, thixotropy. The figure 6 shows a linear relationship between shear stress and shear rate, and the relationship between viscosity and shear rate. Viscosity analysis curves of raw and acid activated do not recover their initial viscosity after shearing.



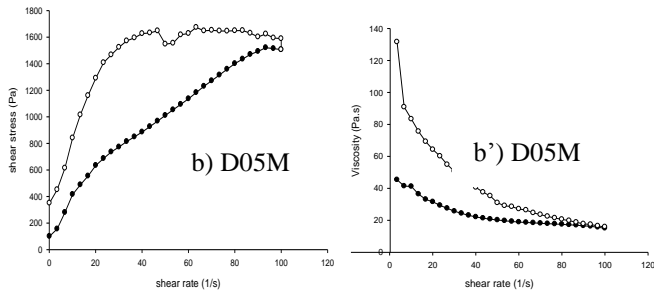


Fig 6. Flow curbs (a, b) and viscosity (a', b') of Douala clays untraited (D0M) and acid activated (D05M) ascendant (●) and descendant (○).

The oscillation dynamic tests are also significant tools to reveal the microscopic structure of viscoelastic materials (Agguzi et al., 2013). In general, the material can respond to this type of deformation through two mechanisms: conventional storage energy and viscous dissipation energy. Quantitatively, these responses can be represented as storage modulus (G') or stored energy per unit volume, and loss modulus (G'') or energy dissipated per unit strain rate per unit volume. The storage modulus is proportional to the extent of the elastic behavior of the system and the loss modulus is proportional to the extent of the viscous behavior of the system. Figure 7 presents the evolution of the elastic and viscous depending on the frequency modules. Acid activation increase elasticity.

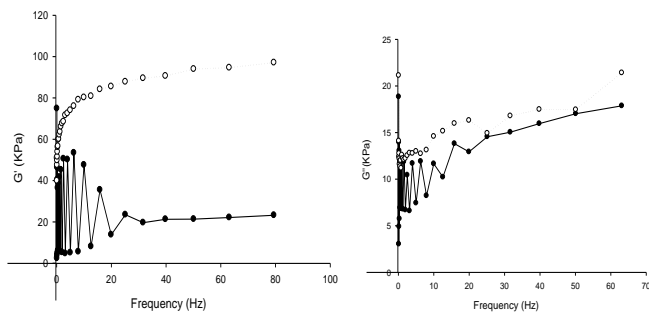


Fig 7. Storage modulus (G') and loss modulus (G'') D0M(●) and D05M (○).

4. Conclusion

This work was focused on effect of acid activation on mineralogy, structural, textural and rheological properties of kaolinite from Douala usually used by the local population as beauty mask. Acid activation with 0.5 M of HCl increase the specific surface area, but does not alter the proportions of Oxygen, Silic b') D05M Iron, Potassium and Titanium and exchangeable b') D05M both clay are plastic fluid with yield stress and thixotropic behavior.

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