The Effect Of Fine Dry Grinding On The Physicochemical Properties And Textural Morphology Of Tunisian Smectite Clay

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ABSTRACT

A montmorillonite clay from Zaghouan (Tunisia) was fine grounded in a mortar. The period of grinding was varied from 2 to 20 mn. The crystalline structure, textural morphology, FTIR spectra and metals extraction by a 0,1 M HCl acid solution were studied. We found that the crystalline peaks of momtmorillonite were gradually reduced with the increase of grinding time, and after 20 mn of fine grinding, the montmorillonite transformed into an amorphous phase. From FTIR spectra, it was found that a prototropic effect occurs after 20 minutes of fine dry grinding. The extraction rate of the metals contained in the mineral by HCl acid solution was rapidly increased by the mechanochemical treatment. Analysis by N_2 adsorption-desorption showed a zigzag of the S_{BET} and the azote adsorption. AFM and SEM images showed an increased presence of sub-micrometric rounded particles at the surface of the treated samples than for the untreated one.   © 2006 Trade Science Inc. - INDIA

INTRODUCTION

Montmorillonite is a kind of 2:1 type layered clay minerals. It has been widely used for the preparation of organo-clay composites due to its high cation ex-change capacity, swelling ability and high surface area. The synthesis of organo-clay composites has received considerable attention due to their interesting properties and wide application. Organo-clays are commonly synthesized by solid-liquid reaction

by adsorption process. During the last two decades, there has been interest in the preparation of organo-clay material by solid-solid reaction[1-4]. The so-called solid-solid reaction is a mechanochemical solid state adsorption of organic molecules by clay. These reactions are carried out by a grinding of clay mineral with the corresponding organic species. It was reported that the mechanochemical adsorption of organic molecules by smectite clay increased in the first minutes of grinding, but after some period of treatment it decreased[1-2]. It's obvious that the prolonged grinding has an effect on the physico-chemical structure and the adsorption properties of smectite clay. In our laboratory, we are interesting in the preparation of organo-clay composites by mechanochemical route. The aim of this study is to evaluate the effect of a fine grinding on the adsorption properties of local smectite clay. In fact, the study of the effect of mechanical treatments on clay minerals has been limited to some clay minerals such as Kaolinite, tac and pyrophyllite[5-11]. Dry grinding of Kaolinite causes a decrease in the degree of crystallinity, and leads to the formation of reactive surfaces or changes in the physicochemical behavior. Mechanochemical treatment of pyrophyllite causes some delamination in the first stages of grinding, followed by structural degradation on prolonged grinding[12-13]. Several techniques have been used; XRD, FTIR, N_2 adsorption desorption, SEM, AFM and atomic absorption.

EXPERIMENTAL

The starting material was natural raw smectite clay from the region of Zaghouan in Tunisia. It contains predominantly montmorillonite mineral with accompanying minerals (calcite, quartz and illite). The clay fraction (<2μm) was separated by sedimentation technique, transformed into the sodium form with 1M NaCl solution. After washing, sedimentation and dialysis, the fine sediment was freeze-dried.

The cation exchange capacity[14] of the sample was 90 meq/100 g.

The clay (250 mg) was mechanically treated in an agate mortar for 1, 3, 7, 10, 15 and 20 mn. Different samples are denoted Gi, where i is referring to time of treatment in mn. The structural properties of the starting and mechanically treated clay were determined by X-ray diffraction analysis. The X-ray diffractograms (XRD) were obtained on a Panalytical diffractometer using Cu Kα radiation. Diffraction data were collected in the range from 2º to 70º. The IR spectra were obtained with a Nicolet spectrophotometer, model 560, with a scanning range between 400 and 4000 cm^{-1}, samples were prepared as tablets diluted in KBr, keeping constant the sample/KBr ratio and the total weight of sample. The nitrogen adsorption-desorption isotherms were measured with an automatic adsorption instrument (Autosorb I) using a volumetric technique. Prior to the analysis, the samples were outgassed at 150 °C for 2h. The nitrogen adsorption-desorption data were recorded at liquid nitrogen temperature (77 K). Specific surface area was determined by applying the Brunauer-Emmett-Teller (BET) method[15]. The t-plot method[15] was applied to calculate the micropore volume. The total volumes were estimated to the liquid volumes of adsorbate (N_2) at a relative pressure of 0.99, assuming that all the accessible pores had been filled with condensed nitrogen in the normal liquid state, The distribution of the clay particles were checked by topological AFM images (Nanoscope II) in contact mode and in a region of 500×500 nm². Surface morphology analysis was made with a Philips Fei Quanta 200 Scanning Electron Microscope. Fe^{3+}, Al^{3+}, and Mg^{2+} concentrations were checked by an atomic absorption spectrophotometer AAS (Vario 6).

RESULTS AND DISCUSSION

X-Ray diffraction

The X-ray diffractogramms of the untreated and treated samples are given in figure 1. Significant broadening and decrease of 00l peak were observed with increasing grinding time. This observation supports previous work[5-13]. On the contrary, the d_{060} peak only decreased after a prolonged grinding of 20 mn. Since the intensity of the d_{001} diffraction diminishes more rapidly than that of the d_{060} diffraction as function of grinding time. It seems that tangential forces predominate over perpendicular ones and the gliding of particles of 2:1 layers in the ab plane is more
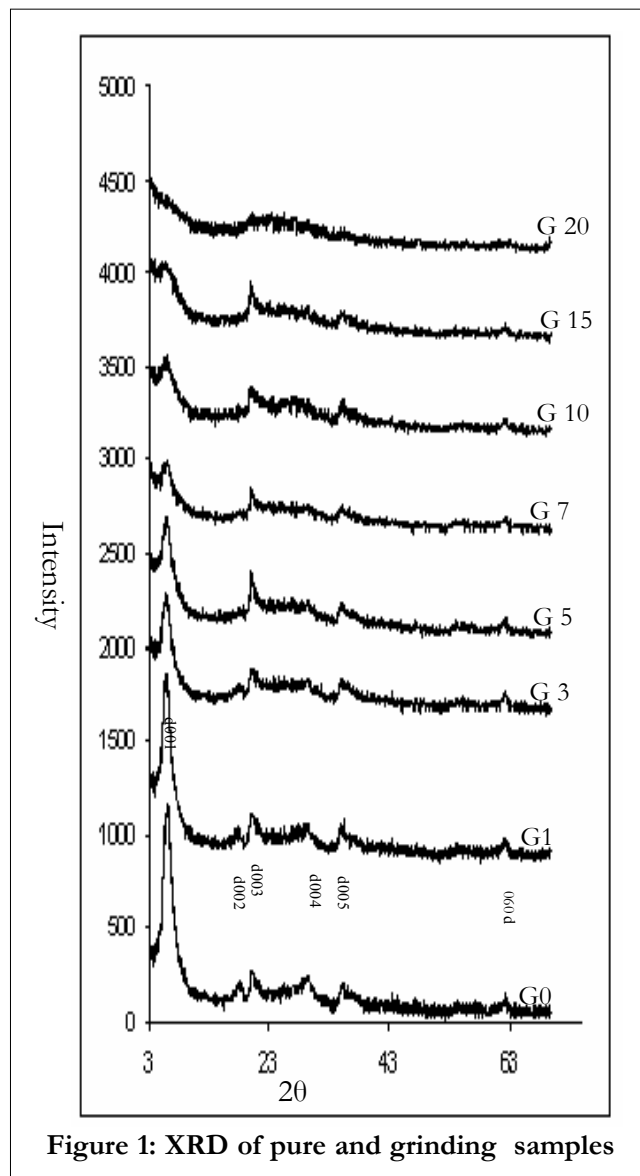
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Figure 1: XRD of pure and grinding samples

probable destructed than their structural. It is interesting to note that the treatment of a quantity of 1g of clay did not affect the crystalline structure of material. This difference in structure is due to the fact that the force and pressure applied to sample inversely increase with the quantity.
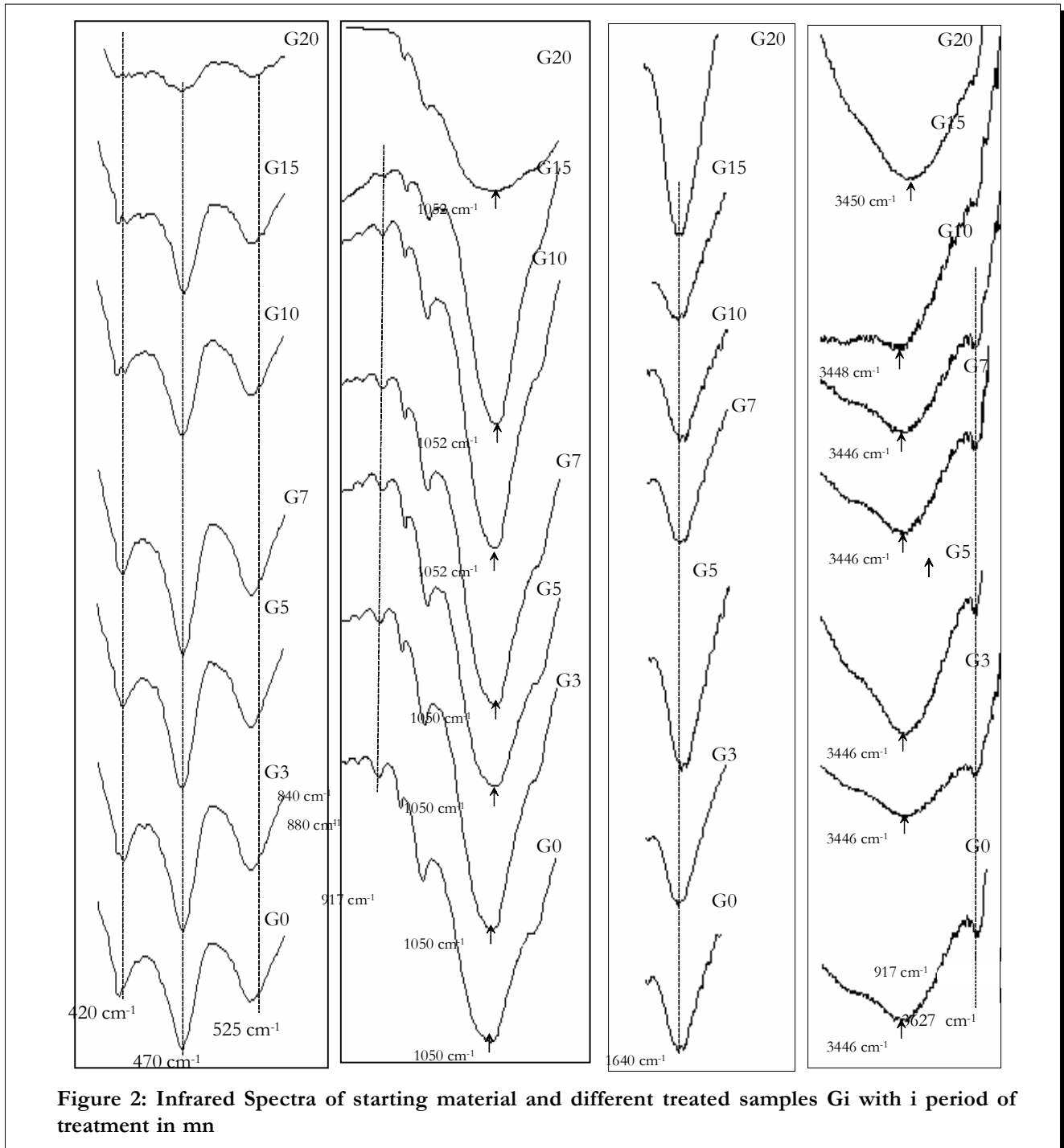
IR study

Infrared spectra of starting and the mechanically treated samples are given in figure 2. The IR spectrum of the natural sample showed the following bands ; ν_{OH} of $H_2O \sim 3446 cm^{-1}$; and δ_{OH} at 1640 cm^{-1}) [16]. The Al-Al-OH stretching frequency is observed at 3627 cm^{-1} , while the bending frequency is at 917 cm^{-1}. This can be considered as characteristic of

dioctahedral clay[17], and more precisely a dioctahedral smectite[18]. The bands at 420, 470, 525 cm^{-1} are assigned respectively to Si-O-Fe, Si-O-Si and Al-O-Si deformation. The bands appeared at 880 and 840 cm^{-1} corresponding respectively to Fe-Al-OH and Mg-Al-OH bending frequencies. After mechnochemical treatment, changes in the intensity and the width of different bands are observed. This indicates a gradual disturbance of the crystal structure. The intensity of the bands at 420, 470 and 525 cm^{-1} decreased and the width became extent, this indicates the destruction of Si-O-Fe and Al-O-Si links. The band due to both structural tetrahedral and octahedral (917 cm^{-1}; AlAlOH deformation) gradually decreased.

This suggests that the structural damage preferentially affects the $Al(Mg)O_6$ octahedral packed between silica tetrahedral layers, and that cohesion forces between octahedral and tetrahedral are progressively diminished. However, the intensity of the band of deformation of water increased in intensity after 20 mn of treatment, this indicates that the material adsorbs atmospheric water. A distinct prototropic Effect was reported in the IR spectrum of G20 especially in the region of 1500 - 4000 cm^{-1}. This is represented by a weakening of some structural O-H bondings (located in the octahedral sheet) [5-7]. In addition, the OH stretching of water OH bands, which are localised in our case at 3446 cm^{-1} and the band at 3627 cm^{-1} corresponding to OH stretching of structural hydroxyl groups became one band localised at 3450 cm^{-1}. Both these spectroscopic features prove the prototropic effect by the decrease of the peaks due to structural OH, and by the formation of OH group of variable nature (represented by wide band at 3450 cm^{-1}), which result from the recombination of the split protons. Moreover, in contrast to Kaolinite[10-11], the prototropic effect in montmorollinite did not take place from the first stage of grinding.

Ions metals release

The washing of different samples with an aqueous solution did not release any metals. However, after the washing with a 0.1N HCl solution, a release of metals is observed. TABLE 1 shows the

Figure 2: Infrared Spectra of starting material and different treated samples Gi with i period of treatment in mn

percentage of the amounts of Fe^{3+}, Mg^{2+} and Al^{3+} released, It can be observed that the prolonged grinding has for effect the breakdown of the layer, especially the exposed functional group such as AlOH, SiOFe, MgAlOH. After 20 mn of grinding the percentenge of released metals attains respectively 20, 25 and 28 % for aluminium, magnesium and iron .

TABLE 1: Mg^{2+}, Al^{3+} and Mg^{2+} extracted from the structure after grinding

Samples	Dissolved Al_2O_3 %	Dissolved MgO %	Dissolved Fe_2O_3 %
G0	0	0	0
G2	2	3	2.5
G5	15	7	9
G10	18	10	15
15G	20	25	28
G20	11.92	3.1	3.83

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Adsorption and textural study

Figures 3 and 4 show the nitrogen adsorption-desorption isotherms for different samples. The isotherms are type II of the BDDT classification[19]. These isotherms represent unrestricted monolayer-multilayer adsorption, however, in the zone of low values, all samples present Langmuir adsorption isotherms (type I). However the isotherm of G20 approaches type III isotherm. Moreover, there is an increase of adsorbed nitrogen volume around $P/P0$ > 0.1, which decreased upon grinding to 10 mn, this

increase in nitrogen adsorption must be due to reduction of the dimension of particles clay during the grinding process, thus creating a greater interparticle space, and consequently, pores of larger diameter. However a prolonged period of grinding has for effect the agglomeration of clay particles, thus a decrease of nitrogen adsorption. All samples present H_2 hysterisis, which is a characteristic of slit shaped pores, however for G20, the hysterisis became more closed. Figure 4 shows the t-plot for different grinding samples, the existence of positive intercepts in the
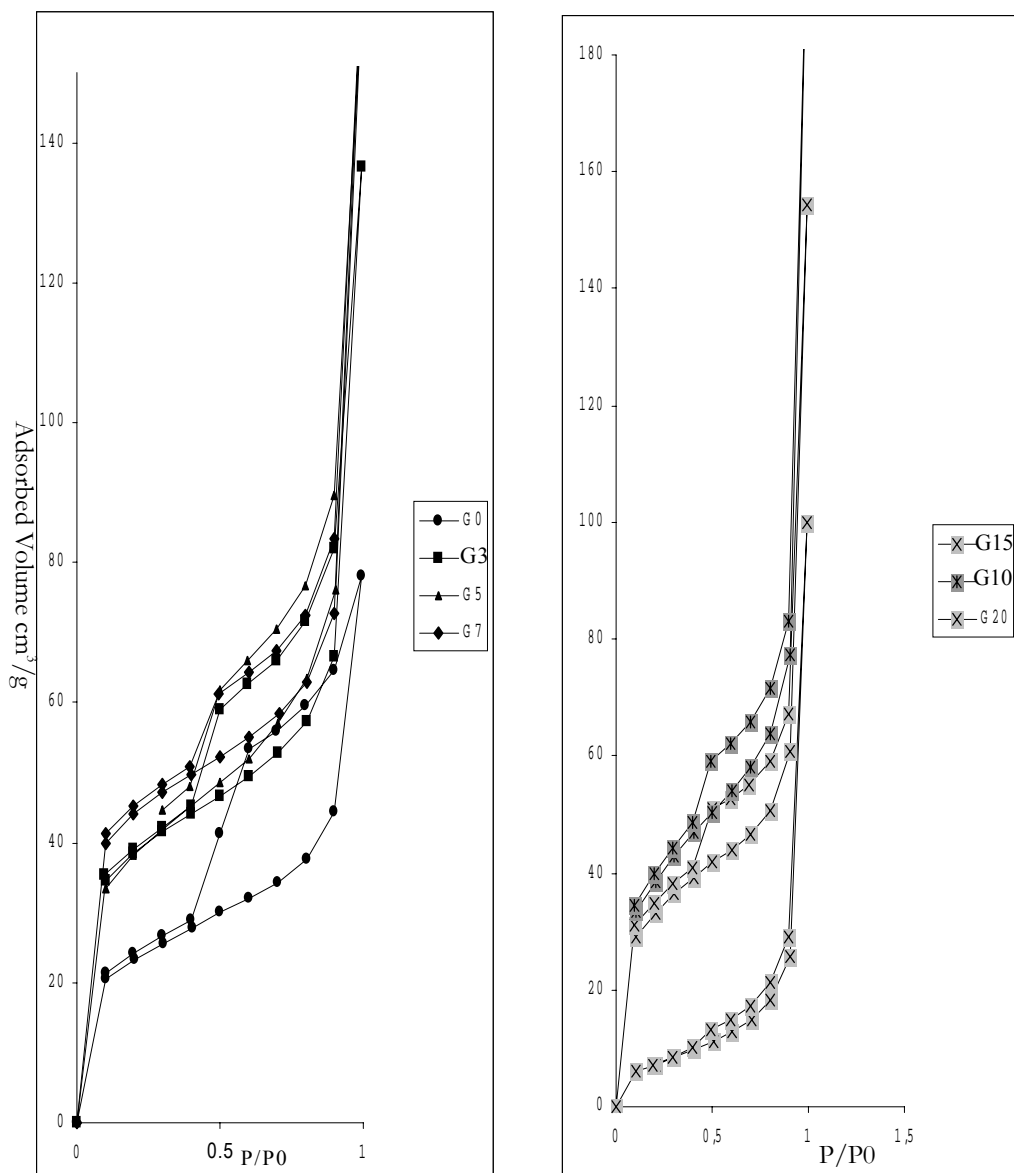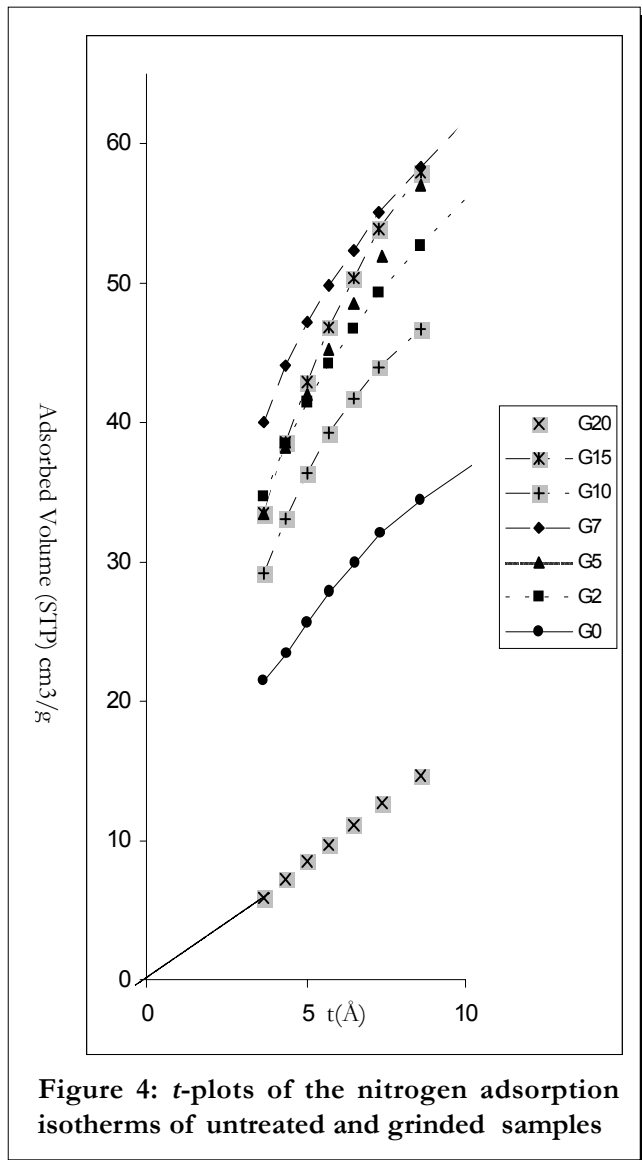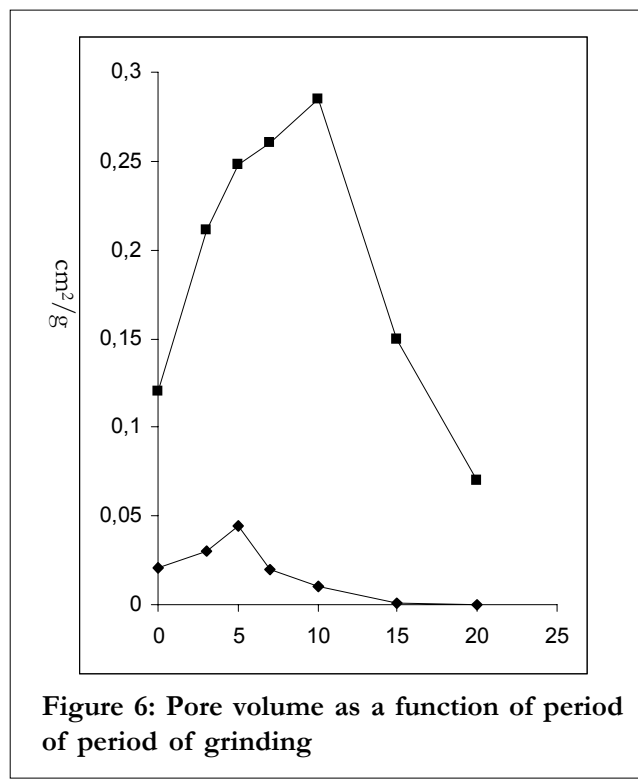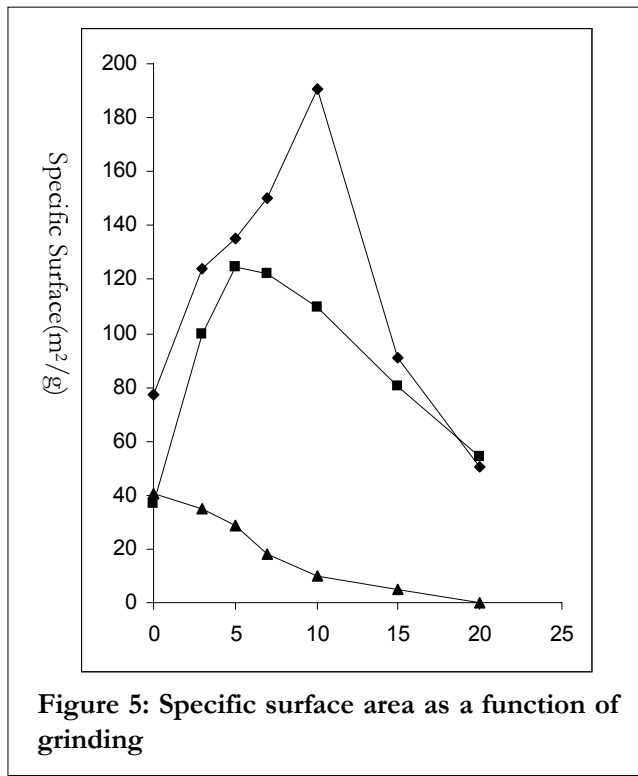

Figure 3: Nitrogen adsorption-desorption isotherms of untreated material (G0) and different grinded samples

Figure 4: *t*-plots of the nitrogen adsorption isotherms of untreated and grinded samples

Figure 5: Specific surface area as a function of grinding

Figure 6: Pore volume as a function of period of period of grinding

t-plotes treated at a period below 15 mn, suggest the presence of micropore volume, after 20 mn of treatment, the linear section passes through the origin, and microporosity seems to be absent. TABLE 3 lists the textural parameters for untreated and treated clay. The specific surface area and porous volume increase from 77.38m²/g and 0.12cm³/g (non-treated montmorillonite) to 190 m²/g and 0.28 cm³/g after 10 mn of grinding .

A maximum of the external surface area and the S_{ext} (124.5 m²/g) is reached after 5 mn of grinding. The variation of the specific surface area micropore volume with time of grinding is given in figure 6 and 7.

The observation of the evolution of the specific surface area shows two stages of evolution; during the first time of treatment (1-10 mn), we noticed an increase of S_{BET} section, which is approximately proportional to the grinding, after that, the surface area
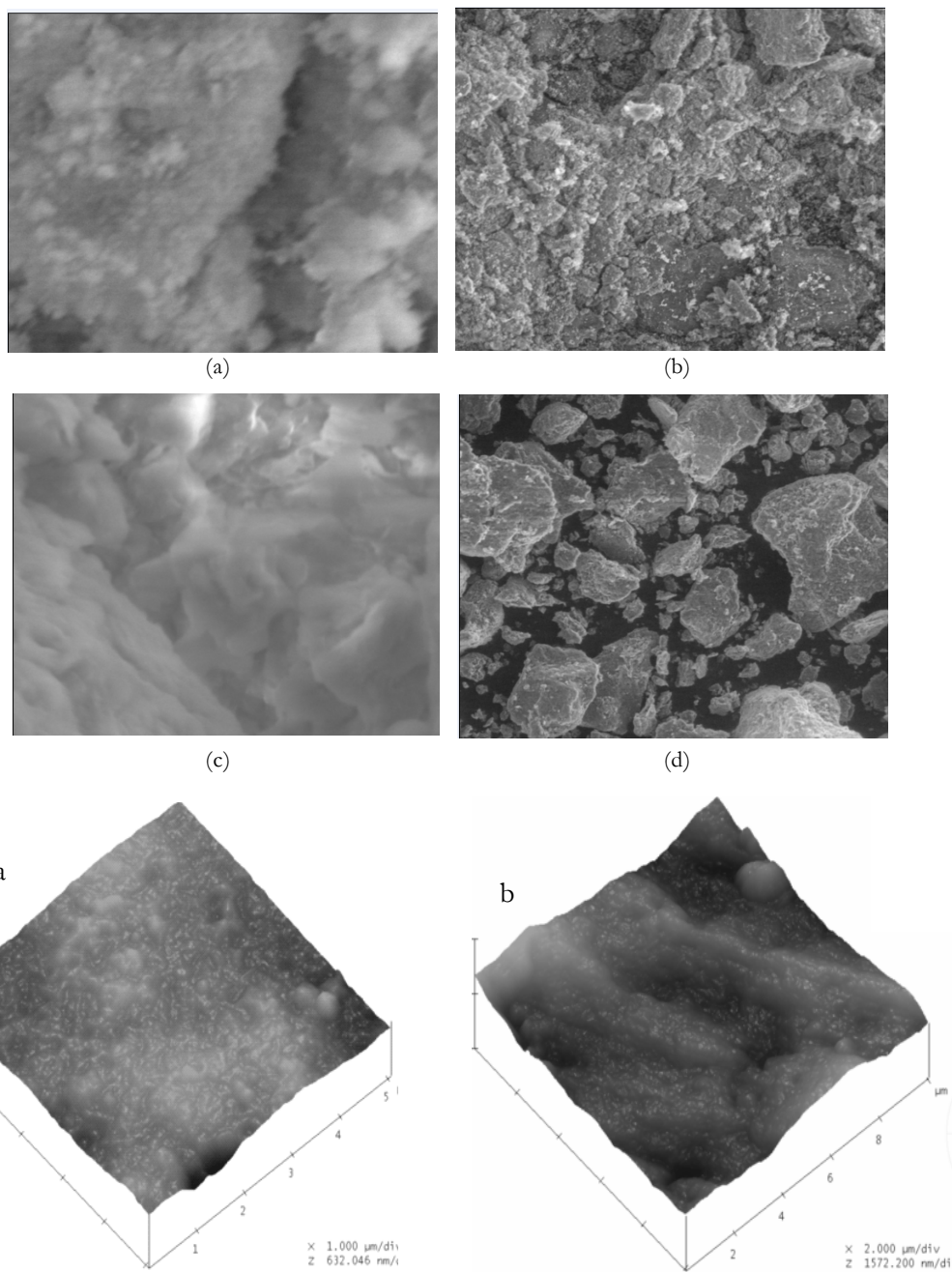
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Figure 7: AFM image of (a) untreated sample (b) G20

decreased.

All these results prove that in the first minute of grinding, clay particles show a fragmentation in their dimension and an increase of the pore of interparticles. These results explain that obtained by[1-2]. They have reported that the mechanochemical adsorption of phenol by solid solid reaction increase during the first 7 mn of grinding and after that it decreased.

Another approach was also taken to provide additional information on the changes of montmorillonite surface structure induced by the fine dry grinding process. This was to evaluate and compare the surface fractal dimension D of the examined montmorillonites through the nitrogen isotherms. Usually, the surface fractal dimension is between 2 and 3. A surface of D=2 is regular and smooth. A

TABLE 2: Surface area and pore volume calculated by the BET method and *t*-plot

Sample	SBET m²/g	Vᵃpor Cm³/g	Sᵇext m²/g	Sᶜµpor M²/g	Vᵈµpor cm³/g	Fractal dimension
G0	77.38	0.1206	36.9	40.48	0.02083	3
G3	123.82	0.211	100	35	0.03552	2.77
G5	135	0.2481	124.5	28.7	0.04429	2.74
G7	150	0.2644	122.4	17.76	0.021448	2.76
G10	190	0285	109.4	10	0.01	2.71
G15	90.7	0.15	80.2	5	0.001	2.70
G20	50.49	0.07	54.14	0	0	2.56

ᵃTotal pore volume   ᵇExternal Specific Surface   ᶜSpecific micropore surface area   ᵉmicropore volume

higher D value suggests a greater "wiggle" and thus a more space-filling surface. At a D value close to 3, the surface is extremely irregular. Therefore, the D value can be considered an operative measure of the surface roughness[15]. As demonstrated in TABLE 2, the D value for untreated sample is 3, which correspond to a sample with important roughness, that is generated to the existence of pore size distribution and the coexistence of micropores and mesopores in its pore structure. After grinding, D values shows a decrease with grinding, the decrease of D values after treatment is in agreement with the decrease of micropore volume, it attains 2 for G20, which corresponds to a smooth surface and the absence of micropore volume.

The morphology of starting and treated sample for 20 mn were observed by SEM and AFM images, Figures 7c,d represent the SEM images of the starting sample, we can see the lamellar structure of montmorillonite. After 20 mn of grinding, the particle size decreased and became more compacter, that is due to the agglomeration. The figure of G20 shows irregularity shaped flaky and plate-like particles, whose surface at high magnification appears with sharp edges and with few sub-micrometric particles and agglomerates.

It's interesting to note that the outline between particles and agglomerates is less clear than the untreated clay. We can not see a crystalline structure, that supposes that the grinding process favours the creation of a new amorphous structure.

The same observation is reported in AFM images it can be seen the mean size of particles decreases for G20 compared to untreated sample, thus the grinding creates sub-micrometric particles.

CONCLUSION

The effect of fine dry grinding on the physico-chemical structure, textural and morphology of expanded clay used for the preparation of organo-clay have been studied. It is concluded that:

For a period of treatment under 7 mn, the grinding process has for effect the amelioration of adsorption properties. Below this period of treatment, the grinding did not significantly alter the chemical structure of montmorilonite, therefore, we assume that the most effective period for the preparation of an organo-clay by solid-solid reaction is a period below 7 mn. However for a period above 10 mn, some physic-chemical changes occurred, namely, the disruption of the clay layers, the disturbance of the crystal structure, the decrease of micropore volume and adsorption properties, the destruction of some bonding and the appearance of a prototropic effect.

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