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Effects of Thermal and Acidic Treatments on The Characteristics of Algerian Bentonite

MOHAMED LAHMEK† and ABDUL AZIZ RAMADAN*
Depatrtment of Chemistry, Faculty of Science, Aleppo University, Aleppo, Syria
Fax: (963)(21)2670600
E-mail: dramadan@scs-net.org; aaramadan@alepuniv.shern.net

The natural and treated Algerian bentonite were studied using different methods such as chemical analysis, thermal analysis, X-ray diffraction, infrared absorption and nitrogen adsorption, to determine their constituents and to characterize the effect of treatment on their superficial structures and textural properties. Results show that the natural bentonite is composed essentially of montmorillonite, quartz and a small quantity of albite. The natural material was thermally treated at 650 and 1100°C, then refluxed with 6 N HCl (B650 and B1100). The B650 sample is composed of quartz, albite, spinel and a small quantity of keatite. The B1100 sample is composed of cristobalite, spinel and a small quantity of quartz. The surface areas (S_{BET}) and the total pore volumes are decreased with raising the temperature of thermal treatment ($S_{B600} = 160$ m^2/g, $S_{B650} = 112$ m^2/g, $S_{B750} = 50$ m^2/g, $S_{B850} = 24$ m^2/g, $S_{B950} = 17$m^2/g, $S_{B1000} = 13$ m^2/g and $SB_{1100} = 12$ m^2/g).

Key Words : **Bentonite, Thermal treatment, Acid refluxing, Pore volume distribution.**

INTRODUCTION

Clay minerals belong to the phyllosilicates. The principal building elements of the clay minerals are two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminum- or magnesium-oxygen-hydroxyl octahedra. In most clay minerals, such sheets of tetrahedra and of octahedra are superimposed in different fashions[1].

Bentonite is a rock name and not a mineral name, although it is often used as such in chemical literature. Montmorillonite is the principal clay mineral of bentonite rock, which originates from volcanic ash. The structure of the minerals of montmorillonite group is derived from that of the prototypes of pyrophyllite and talc by substitution of certain atoms for other atoms[2].

Bentonite clays are used in many industrial products and processes. Clays are the essential part of paper, drilling fluids, a certain lubricating grease[3] and they are used for clearing wine, bleaching of edible oils, regenerating motors oils and

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†Dept. de chimie, Ecole Normale Superieure, Vieux-Kouba, N.P.: 92, Alger, 16308, Algeria.

in treatment of wastewater for removing heavy metals and other pollutants[4–8]. Bentonite is widely distributed in the world, as for example, in Syria and in northwest of Algeria[3, 4, 9–12]. Some studies on the clays available in Algeria for chemical analysis of constituents, removal of dyes from wastewater and textile industry wastewater were reported[6, 9, 13].

EXPERIMENTAL

The textural properties of the different treatment products were determined from the adsorption of nitrogen at 77 K using a Gemini Micromeritics III 2375 surface area analyzer. Prior to all measurements, the samples were degassed at 100°C under a reduced pressure of 10^{-4} torr. The differential thermal analysis (DTA) of the natural bentonite was obtained using Netzsch DTA model 404Ep Philips X-ray diffractometer type PW 1710 fitted with $Cu\text{-}K_\alpha = 1.5418$ E was used for X-ray analysis. IR spectra were determined by Perkin-Elmer spectrum apparatus. All the used solvents and chemicals were of extra pure grade. The samples under investigation were procured from Roussel Quarry, near Maghnia town (northwest Algeria).

Preparation of samples : Samples were crushed with a hammer to obtain small pieces, purified of gravels and dried at 105°C for 36 h. After that the samples were ground in a jar mill, then sieved in order to have granules in the diameter range 125–150 μm. Suitable amounts of these samples were thermally treated at different degrees from 250–1100°C with 50°C step for 3 h using porcelain crucibles, then sieved. Thus 18 samples were obtained. Each sample was refluxed with 6 N HCl for 48 h to remove all soluble oxides and then washed with bidistilled water until the excess Cl^- ions were no longer detected by the $AgNO_3$ test, then dried at 110°C for 24 h and sieved in the same diameter range.

RESULTS AND DISCUSSION

The chemical compositions of the natural Algerian bentonite, B650 and B1100 were studied. It was found that the samples contained the following compounds: SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, H_2O, Na_2O and TiO_2 (Table-1).

TABLE-1
CHEMICAL COMPOSITION OF NATURAL BENTONITE AND TREATED (B650 and B1100) ALGERIAN BENTONITE

Compound	Natural bentonite (%)	B650 (%)	B1100 (%)
SiO_2	56.10	66.20	77.60
Al_2O_3	19.60	21.80	15.00
Total Fe as Fe_2O_3	2.40	0.81	0.31
MgO	5.20	6.10	5.60
CaO	1.50	0.72	0.20
Na_2O	2.90	3.20	0.80
TiO_2	0.25	0.28	0.31
H_2O	11.60	0.68	–
Total	99.55	99.78	99.82

Differential thermal analysis (DTA): Fig. 1 shows the DTA trace of the natural Algerian bentonite. It exhibited four endothermic peaks. The first appears at 145°C, corresponding to the loss of water of hydration. The second,occurring at about 670°C, is related to the loss of hydroxyl or water molecules adsorbed between interlayers. The two endothermic peaks, appearing at 820 and 895°C, may be attributed to the removal of the hydroxyl groups[14].

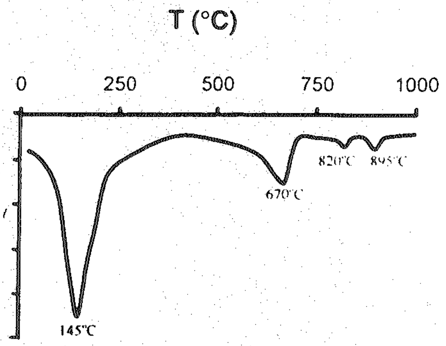

Fig. 1. Differential thermal analysis curve for natural bentonite

X-Ray diffraction (XRD): It is clear from the X-ray diffraction[15, 16] of the natural bentonites that it is composed essentially of montmorillonite, quartz (SiO_2) and small quantity of disordered albite ($NaAlSi_3O_8$). The B_{650} sample is composed of quartz (SiO_2), albite, spinel ($MgAl_2O_4$) and small quantities of keatite (SiO_2). The B_{1100} sample is composed essentially of cristobalite (SiO_2), spinel and small quantity of quartz (Fig. 2).

Infrared spectrometry: Examination of the infrared spectra of natural bentonite, B650 and B1100 samples (Fig. 3), leads to the following peaks[14, 17–19].

Natural samples

- 3628.2 cm^{-1}: corresponding to the stretching vibration of hydroxyl groups of the octahedral layer, which characterize of the montmorillonite phase.
- 3418.4 cm^{-1}: corresponding to the valence vibrations of hydroxyl groups of structural water and also to the vibration of OH bond of hydration water.
- 1636.1 cm^{-1}: corresponding to the vibration of hydroxyls of water molecules adsorbed between interlayers.
- 1039 cm^{-1}: corresponding to tetrahedral sheet of montmorillonite. For montmorillonites this band which ought to appear at 1100 cm^{-1} was shifted to low frequency because trivalent Al^{3+} ions were substituted by silicon in the tetrahedral structure; this band is too large for phyllosilicates than for free silica.
- 540.1 cm^{-1}: corresponding to vibrations of Si-O-Al in the montmorillonites.

B650 sample

- 3419.7 cm^{-1}: corresponding to vibration of hydroxyl groups of structural water.

- 1088.1, 796.1 and 489.6 cm^{-1}: corresponding to a stretching mode involving displacements primarily associated with the oxygen atoms, a stretching mode of similar type for the Si atoms and Si-O bending mode.

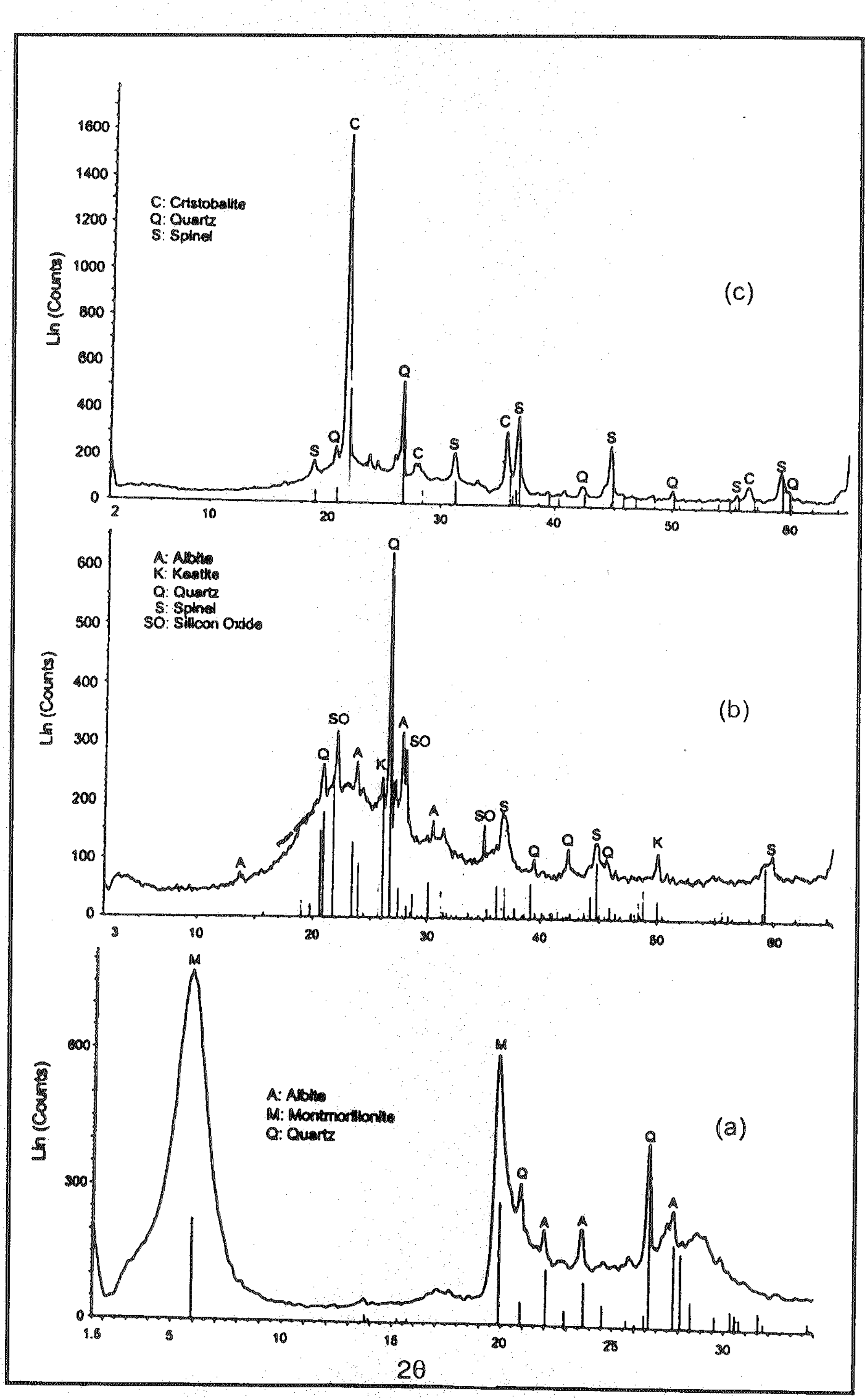

Fig. 2. X-ray diffractograms of natural bentonite (a), B_{650} (b), B_{1100} (c) samples

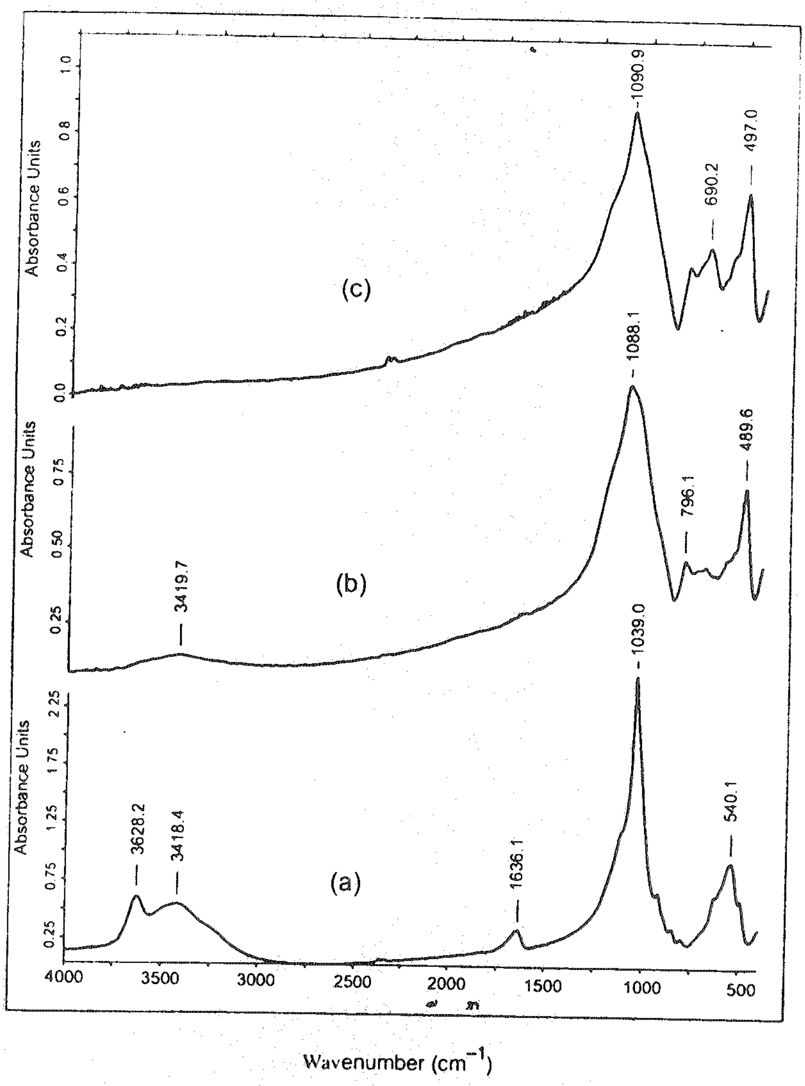

Fig. 3. Infrared spectra of natural bentonite (a), B_{650} (b), B_{1100}(c) samples

B1100 sample

- 1090.9 and 497.0 cm^{-1}: corresponding to a stretching mode involving displacements primarily associated with the oxygen atoms.
- 690 cm^{-1}: corresponding probably to the presence of spinel ($MgAl_2O_4$).

Surface properties

The textural properties, *i.e.*, the specific surface areas, the total pore volumes and mean pore radius, of natural and treated bentonites (at different temperatures from 600–1100°C, then refluxing with 6 N HCl) from the adsorption of nitrogen at 77 K were determined. The adsorption was carried out until near saturation (P/P *ca.* 0.95), then desorption was followed until the hysteresis loop was closed (Fig. 4). Representative adsorption-desorption isotherms of nitrogen for B_{650} and B1100 are shown in Fig. 5. The isotherms are between II and IV types of Sing20 and BDDT[21] classifications, which indicate the presence of mesoporous structure.

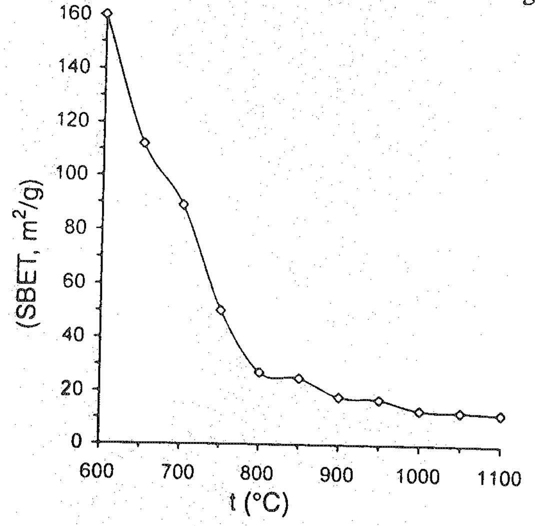

Fig. 4. Surface area (S_{BET}) of treated Algerian bentonite at different temperatures

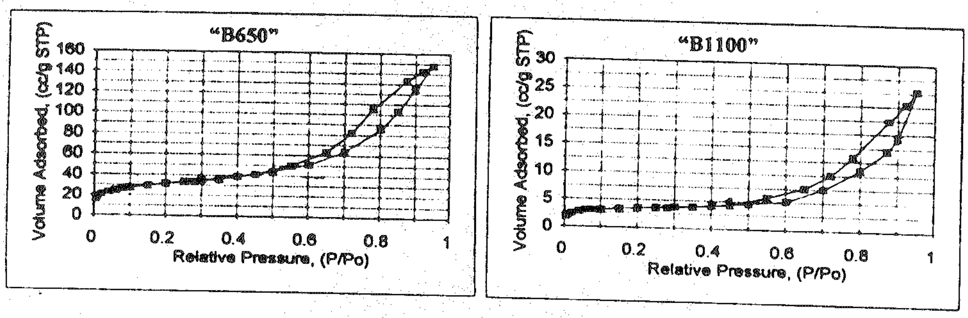

Fig. 5. Adsorption-desorption isotherms of nitrogen at 77 K on B_{650} and B_{1100} samples.

Application of the linear BET equation to the data of nitrogen adsorption obtained was found to be in the range of relative pressures (0.02–0.25). The data also allows the determination of pore size distribution (Fig. 6). The total pore volumes (V_p, mL/g) were taken from the adsorbed volumes at $P/Po = 0.95$ in the liquid form and the mean pore radius was calculated using the following equation:

$$r\,(\text{Å}) = 2 \times 10^4\, V_p/S_{BET}$$

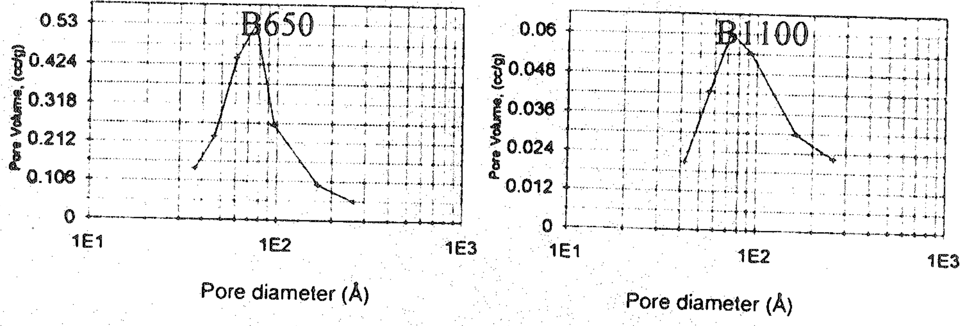

Fig. 6. Pore volume distribution of B_{650} and B_{1100} samples

The following table shows the surface properties of the investigated samples:

Sample	Surface area (m^2/g) BET method	V_p (mL/g)	$\bar{r}$ (Å)
B650	112	0.2285	40.6
B1100	12	0.0391	64.7

It is clear from the observed data that the S_{BET} and V_p values are decreased sharply with increasing the heat treatment, whereas the values are increased.

Conclusion

In the present work, the effects of thermal and chemical treatments on changing the structure of the Algerian bentonite are established. The surface area and the total pore volume of the bentonite thermally treated at 650°C and then refluxed with 6 N HCl is found to be higher than that at 1100°C. The isotherms indicate that the prepared samples are mesoporous materials.

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