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Effect of Thermal Treatment on Textural Properties of Natural Montmorillonite

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This paper presents the effect of heating time over natural Jordan Diatomite. The sample was selected for this study from the Azraq area, which is approximately 110 km northeast of Amman. Natural diatomite was heated in a programmable furnace starting at room temperature and upto T = 150 °C with a heating rate of 10 °C/min without any further purification or acid treatment. The heating process was at various holding times (*i.e.* 6, 12, 18 and 24 h duration, respectively). Samples for each individual holding period was then characterized for determining specific surface area, pore size and pore volume as well as XRD patterns. Results indicated that the surface areas increased after 2 h of heating hold time, while a slight increase in the pore size and pore volume appeared after 24 h. The increased surface area had not changed after 5 h of holding heating time. Furthermore, the presence of peaks intensity strongly depends on the heat holding time; the longer holding heat time the higher the peak intensity (T = 150 °C) became.

Keywords: Diatomite, Heating effect, Surface area, X-ray diffraction.

INTRODUCTION

In principle, diatomite consists of amorphous hydrated silica ($SiO_2 \cdot nH_2O$) and small quantities of bounded water, where n = 3.5-8.0. In addition, small amounts of inorganic components-alumina and lesser amounts of iron, alkaline earth, alkali metals and other minor constituents are present [1]. Diatomite has world-wide applications [2-6] like water treatments, filtration, fillers and adsorbents. It was reported that diatomite can be used also as an adsorbent because it has the effective capability to remove basic dye from aqueous solution [7,8]. Based on multiple applications of diatomite in industry, several physico-chemical investigations were performed to understand the properties of diatomite collected from various locations across the World [9].

One of these resources is natural Jordan diatomite. The structure and morphology of natural Jordan diatomite were, investigated by scanning electron microscopy (SEM) [10] [10] and for the prediction of catalytically active sites, the conversion of methylbutynol was applied [11]. However, until present their characterization methods like X-ray fluorescence (XRF) are limited. Khoury [12] reported that Jordan is a rich source with natural clays. Further investigations have been performed as comparing their properties with the Russian type, including the behaviour towards the catalytic activity [13]. In general, Knözinger and Daniell [14] have investigated the effect of adding silica to alumina on the structure of samples by FTIR spectroscopy.

In the present paper, physico-chemical methods have been applied to determine the effect of various holding heating time on natural Jordan diatomite. The XRD technique was used to illustrate the effect of heating time on the crystalline patterns of the investigated diatomite.

EXPERIMENTAL

The selected sample in the recent investigation was collected from Azraq area, which is about 110 km far from Amman. The major chemical composition of diatomite was using XRF [15]. The chemical mass percentage indicated that the sample consists of mainly SiO_2/Al_2O_3 and additional traces of ferric oxide (5.8 % wt.), calcium oxides (7.2 % wt.) and magnesium oxide (1.2 % wt.). The phase composition also indicated traces of kaolinite, illite and quartz [16].

Characterization: Natural Jordan diatomite samples were heated in a programmable furnace starting at room temperature and up to T = 150 °C with a heating rate of 10 °C/min.

The heat-holding period was apportioned into four periods (*i.e.* 6, 12, 18 and 24 h duration).

For studying the effect of the heat at several holding times, series of measurements for isotherm adsorption were conducted as a function of the equilibrium gas pressure at constant temperature. Both adsorption and desorption isotherms of N_2 were performed on the natural clay sample (4 g) at T = 150 °C.

The isotherms characteristic samples were subjected to the Brunauer-Emmet-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods for determining the specific surface area and the total pore distribution in turn using Micromeritics Gemini 2375 and Gemini V). Prior to the experiments the samples were outgassed at 150 °C in vacuum. For increased accuracy of the results, samples of fraction < 2 μm were used and X-ray data collected in a continuous scan mode 3-90° (2θ). Two solid particles of fraction (untreated and heated to 150 °C) were applied to identify clay mineral associations. The XRD used was type Philips X'Pert with a cobalt tube anode diffractometer (λ = 0.1867 nm, ran at 30 KV).

RESULTS AND DISCUSSION

Influence of thermal treatment on surface area: Influence of thermal treatment on surface area, presents the physical characterization of diatomite after several heating periods. It is evident that all parameters shown in Fig. 1 rise with the increase of heating time. The highest specific area (BET), pore size and pore volume were obtained after a heating duration of 6 h at T = 150 °C (Fig. 1).

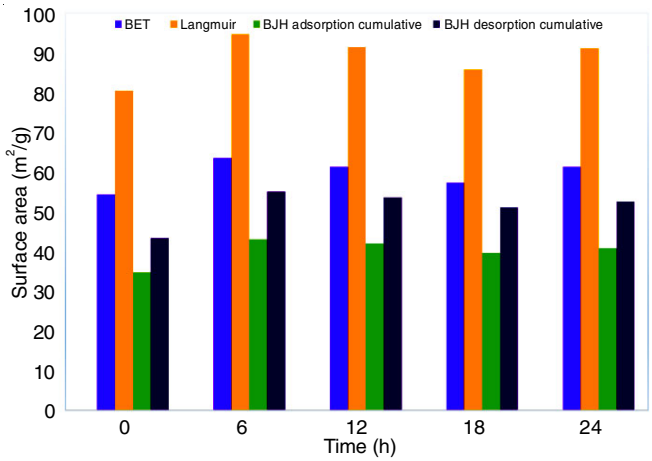

Fig. 1. Physical characterization of diatomite, after several heating periods

Furthermore, low-temperature N_2 adsorption isotherm was of type IV in the classification of IUPAC (Fig. 2).

In Table-1, physical properties like surface area, pore size and pore volume, were in accordance with the effect of heating time on diatomite sample at various heating times. The expression 'zero holding time' was given in all tables to highlight that the diatomite sample was measured without further heating. The subsequent results were recorded as follows; 63.2 $m^2 g^{-1}$, 46.65 $cm^2 g^{-1}$, 0.074 $cm^3 g^{-1}$, respectively. After an 18 h heating period,

TABLE-1
PHYSICAL CHARACTERIZATION OF DIATOMITE AFTER VARIOUS HEAT HOLDING TIMES

Time (h)	Specific surfaced area ($cm^2 g^{-1}$)	Langmuir isotherm	BJH adsorption cumulative	BJH desorption cumulative
0	54.22	80.43	34.60	43.21
6	63.42	94.56	43.00	54.95
12	51.20	91.41	41.88	53.55
18	57.22	85.71	39.60	50.95
24	61.18	90.99	40.77	52.45

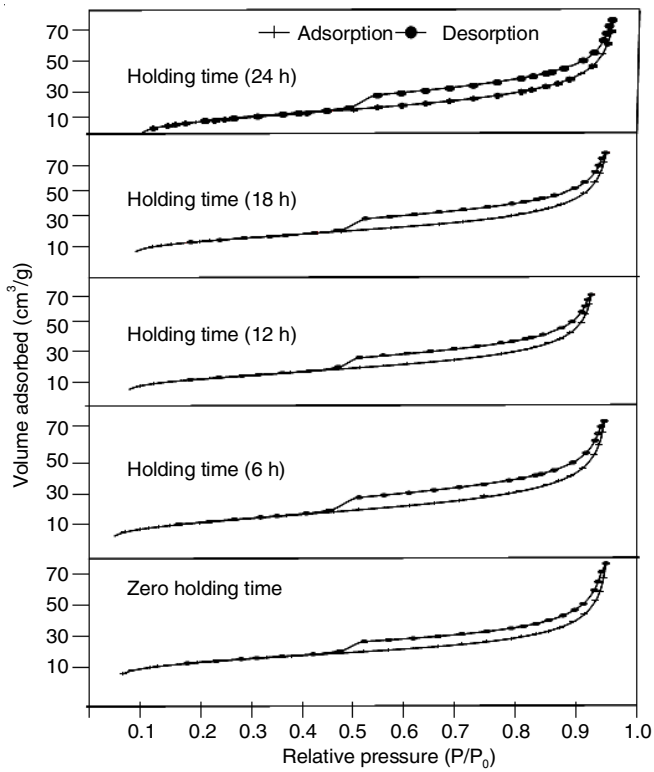

Fig. 2. Low-temperature N_2 sorption isotherms for different holding time

a small decrease was observed in the values then raised again up after a heating holding period of 24 h.

Effect of heating, time on pore size and pore volume of diatomite: Table-2 illustrates the effect of heating, holding time on natural diatomite porosity. In general, the depicted results in Table-2 show that no remarkable change took place for the pore width after 24 h of heating time. Observed only a slight loss width in the pore size when compared to its innate shape, after 24 h with a value of 0.21 cm^3/g. After 6 h of heating hold period, increased loss in the pore width of sample (Table-2).

TABLE-2
EFFECT OF HEATING TIME ON THE ADSOPRTION AVERAGE OF PORE WIDTH, BJH AND DESORPTION AVEARGES DIAMETER ADSORPTION

Time (h)	Pore size average (Å)	BJH adsorption average diameter (Å)	BJH desorption average diameter (Å)
0	47.5394	94.9550	79.354
6	46.6491	83.7920	69.244
12	47.0532	83.3880	68.921
18	47.5782	84.2220	69.245
24	47.3289	86.4070	70.994

Additionally, increasing the length of the heating time at 150 ºC gave an increase in the values obtained for pore volume, BJH adsorption and desorption of cumulative volume as shown in Table-3.

Fig. 3 illustrates a more summarised profile in relation to the effect of holding heating, time on natural diatomite behaviour. The highest was the heating holding time, the higher is the surface areas. In addition, diatomite from the Ankara region of Turkey was investigated for the effect of heating on the surface area and on its porosity. The study was performed on three diatomite forms; as received, under different temperature calcinations and after

TABLE-3
EFFECT OF HEATING TIME ON THE ADSOPRTION AVERAGE PORE VOLUME, BJH ADSORPTION AND DESORPTION AVERAGE

Time (h)	Pore volume average (Å)	BJH adsorption cumulative volume of pores (cm^3/g)	BJH desorption cumulative volume of pores (cm^3/g)
0	0.0664	0.0821	0.0857
6	0.0739	0.0900	0.0951
12	0.0719	0.0873	0.0922
18	0.0680	0.0833	0.0822
24	0.0723	0.0063	0.0931

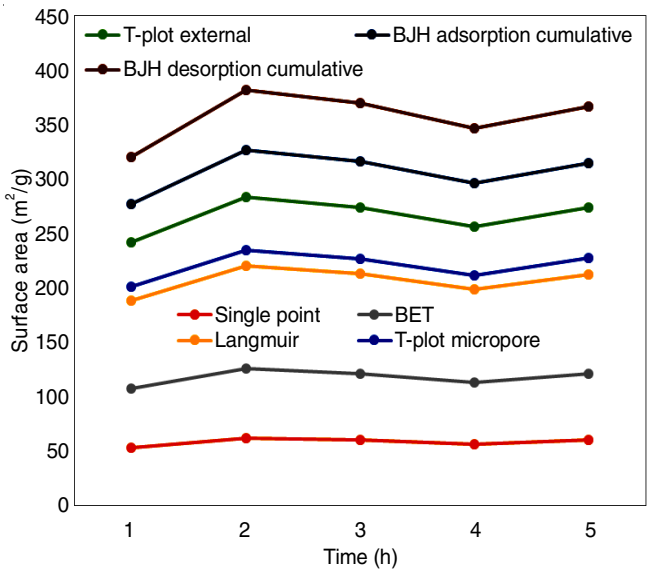

Fig. 3. Effect of heating time on different parameters

treatment with hydrochloric acid. The results showed that surface area drastically reduced when purified with hot acid. This reduction ranged from 204 to 136 $m^2 g^{-1}$. Moreover, no considerable change in the surface areas for samples treated with hot hydrochloric acid and followed by calcination were observed at different temperatures between 700 and 1150 °C [17].

Furthermore, correlation of results with another type of diatomite from an Egyptian study was considered [18]. The effect of acid treatment on different forms of highly and purified Egyptian diatomite was performed [19]. The conclusion of the above study stated that the structure of diatomite changes depended on the treated temperatures. Thermochemical treatment improved sample properties and specific surface area after treatment. It was rated between 120 and 150 $m^2 g^{-1}$.

X-ray diffraction analysis: Fig. 4 shows the powder X-ray diffraction patterns of natural diatomite before and after heating at constant temperature 150 °C at various holding times (0, 6, 12, 18 and 24 h). It was utilized the XRD technique to measure heat holding time effect on size, shape and internal stress of small crystalline regions for natural diatomite calcite (C), montmorillonite (M) and quartz (Q).

From Fig. 4, the mineral main peaks were shown for montmorillite [M] at 2θ = 12, 19, 20, 32, 68°, calcite [C] at 2θ = 27, 50, 60° and quartz [Q] at 2θ = 24°. Also, from Fig. 4, it can be seen that all samples have the same peak positions with a typically sharp and symmetric basal reflection, which indicates an order crystalline structure.

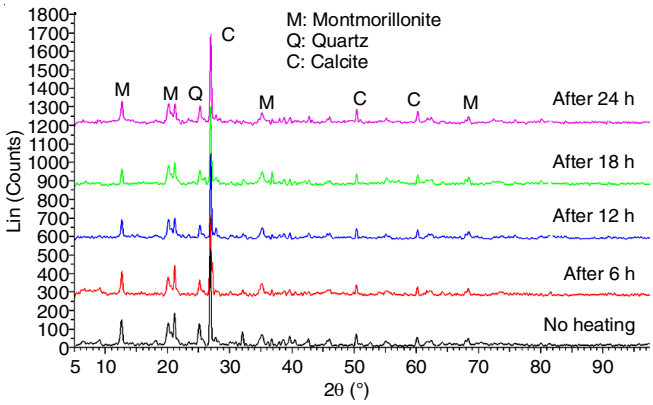

Fig. 4. Comparative diagram of XRD patterns for natural diatomite samples heated at temperature T = 150 °C at different holdings time

Other investigations [19] were performed on prepared silica nanoparticles. It has been found that from the XRD spectra no sharp peaks resulting the absence of ordering crystalline structure.

In addition, investigations on local diatomite showed peak that is related to montmorillonite [M] at d-spacing 2θ = 12.0° and the heating, holding time for 24 h did not affect the crystalline region of natural sample at 150 °C.

Balek and Murat [20] investigated the effect of higher heat temperature (T = 600 °C) on clay with different crystallinity. The higher temperature caused dehydroxylation reaction to form metakaolin as an effect of broad noisy peaks at 2θ = 15-30°. Kustrowski *et al.* [21] also found when using X-ray on samples of derived hydrotaclites at a higher calcination temperature 600 °C that the formation of mixed oxide phases occurred. The observed XRD patterns of the samples reflections occurred at 2θ 43º and 63° corresponding to a magnesium oxide like phase. Another investigation [22] was performed utilizing XRD on precipitated silica by neutralization of sodium silicate solution (water glass) with a sulfuric acid solution. The investigation concluded with an improvement of amorphous peak located at 2θ = 37°. Moreover, results show that the presence of peaks intensity strongly depends on the heat holding time; the longer holding heat time the higher is the peak intensity. Subsequently, a better improvement in the crystallinity resulted with a longer heat holding period for 24 h at the low temperature (T = 150 °C).

Conclusion

The XRD investigations have indicated that the diatomite was affected by the temperature of T = 150 °C for different period time of 24 h. The longer the heating period time, the higher was the intensity peak. In addition, the surface area enhanced by increasing the heat-holding period after 2 h. A constant surface area behaviour was observed after clearly 5 h at the low temperature (T = 150 °C).

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