

Elaboration and Characterization of Natural Diatomite in Aktyubinsk/Kazakhstan

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Abstract: This study investigated the structure, mineralogical specifics and chemical composition, of a natural and modified diatomite ore, which obtained from the Aktyubinsk /Kazakhstan deposits by using SEM, XRF, XRD, FTIR, TGA and SDTA. Three modified forms of diatomite's were prepared by calcinations at 900°C and/or calcinations and acidification by 0.5 N HCl (D, D-HCl, D-900 and D-900-HCl). The iron(Fe₂O₃) and silica (SiO₂) contents in natural raw diatomite were about 3.9 % and SiO₂ 80.23 % respectively. Whereas, the modified diatomite which treated with 0.5 N HCl followed calcination at 900° C revealed 0.92% and 84.75% of Fe₂O₃ and SiO₂ respectively. This proved that the elimination of the impurities which may be found as clay minerals, especially mica and kaolinite. The SEM micrographs investigation of acid activation and/or acid activation followed by calcinations showed the original geometry of the pores to be preserved, but there is collapse in the skeleton structure.

Key Words: Diatomite, Characterization, XRD, XRF, SEM, DTA, Kazakhstan.

1. INTRODUCTION

Diatomite is comprised of the sedimentary remains of diatoms, a class of unicellular algae found in both fresh and sea water. It is their microscopic skeletons, composed primarily of amorphous opaline silica. These skeletons take a variety of forms spheres, disks, wheels, needles, ladders – but all are characterized by a porous, lace-like structure [1].

Diatomites (or kieselguhrs) are mineral deposits of diatomaceous algae, those commercially exploited being restricted to a relatively modern age, starting from the Miocene. Older deposits have suffered tectonic processes, bringing about modifications of the texture and crystalline phase of the mineral. Amorphous silica, a constituent of the diatom frustulae, is the main component of diatomite, although variable quantities of other materials (metal oxides, clays, salts (mainly carbonates) and organic matter) may also be present. Chemical precipitation and atmospheric contact, together with the prevailing environmental conditions, are determinant factors in the nature and importance of the impurity content of a deposit.

Diatomite used for the manufacture of cements, clay diet, and bricks [2]. It is known that more promising and economically effective is use of these valuable mineral resources for manufacture of adsorbents, filter powders, fillers, and catalysts [3-8]. As a siliceous rock made up largely from diatoms, diatomite has a unique combination of physical and chemical properties, making it applicable for the removal of heavy metals and organic pollutants, and as a filtration medium in a number of industrial uses [9-11]. For its high permeability, high porosity and chemical inertness, many studies

[10-14] have recently been attempted to take diatomite as a cheap absorbent for dyes removal. Most efforts were focused on the research of adsorption properties of diatomite. However, an application of diatomite on the wastewater treatment depends mightily on its origin and a few more efforts should be attempted to enhance its adsorption capability.

2. EXPERIMENTAL

The raw diatomites obtained from (Aktyubinsk/Kazakhstan) under investigation were subjected to treatment under various conditions. The first sample is the natural sample (D). The second one (D-110-HCl) is treated by 0.5 N HCl, then washed by distilled water and finally dried in drying oven at 110 °C for 5 hours. The third one is calcined diatomite at 900°C (D-900) using muffle furnace. While the fourth one, is natural diatomite milled carefully and treated with by 0.5 N HCl, washed by distilled water, dried and then, calcined at 900°C (D-900-HCl). All the four samples dried at 110 °C for 5 hours in drying oven followed by milled in a ball mill machine and sieved below 80 micron. The four final treated products were subjected to comprehensive physicochemical studies.

2.1. X-Ray Diffraction Analysis

X-ray diffraction is one of the most successful tools which are used precisely in the identification of the crystalline phases. The phase's compositions of the materials were characterized by X-ray powder diffraction technique [14, 15] (A DRON-3M diffractometer using cobalt target =1.791 Å and a nickel filter at 30KV and 20mA). The selected scanning speed was 1°/min. and the sample was used to fill the aluminium mould of the diffractometer with an average thickness of about 1.0 mm. The phases were identified by correlation with the corresponding standard X-ray cards

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(ASTM) data. Powder XRD analysis (Fig. 1) showed that on treatment with HCl, disappeared of the kaolin and mica peaks. And on calcination some of the opaline silica converted to cristobalite phase. Shrinks, hardens, reduction in the fine structure of individual particles as well as formation of agglomerates or clusters of particles through fusion may take place. All of these parameters may be contributing to decrease the surface area and hence increased the due to the nature of agglomerate packing. It was observed that the calcination turned off the white natural diatomite into pink. This may be attributed to the oxidation of iron [1, 16].

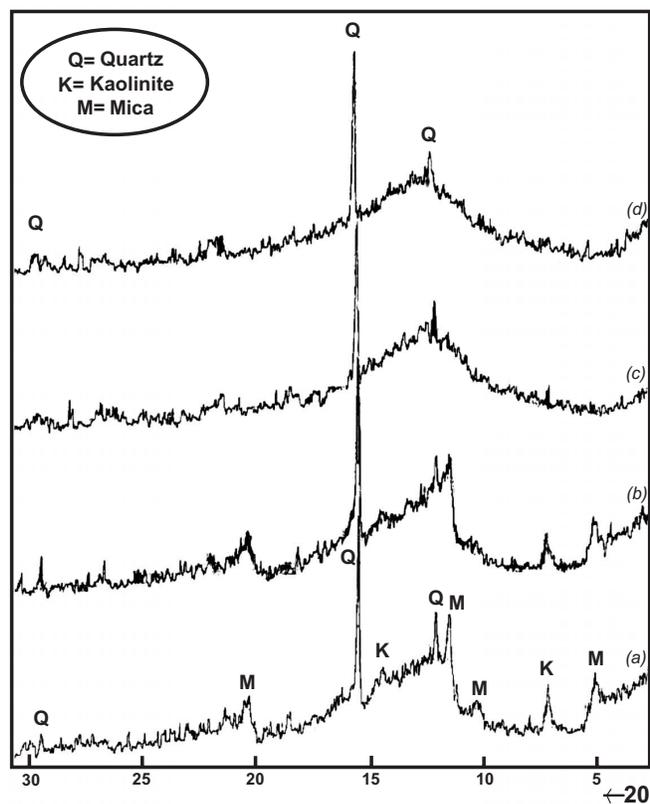


Fig. (1). XRD patterns of the diatomite samples (a): [D], (b): [D-HCl], (c): [D-900], (d): [D-900-HCl].

2.2. X-Ray Fluorescence Analysis

The elemental composition analysis of natural raw diatomite and their modified forms expressed as weight percentages of metal oxides are given in Table 1. The main components of the natural raw diatomite are oxides of: Si, Al

and Fe, while the main components of the other samples activated with acid are oxides of Si and Al. The data reveal, the acid treatment reduces or eliminates all other oxides relative to SiO₂ [17].

2.3. Scanning Electron Microscope (SEM)

The morphology and microstructure of the materials were studied by using scanning electron microscopy (SEM) technique. SEM micrographs were performed in a JNCA 8N8RGY/OXFORD(UK INSTRUMENTS) scanning electron microscope. The materials were introduced onto a conductive carbon tape and coated with gold to prevent charging. The powdered samples were dispersed in ethyl alcohol and then left to settle on a disc. After drying, each is coated with thin film of carbon using a vacuum evaporator with cathodic rays, to prevent or minimize the accumulation of the electric charges of the incident electron beam on the sample surface.

A super probe 733 JOEL(JAPAN) to EDX unit, with accelerating voltage up to 25 KV, magnification 10 X up to 40,000 X, and resolution for W (3.5 nm) was used.

The morphology of starting materials (Fig. 2) showed the dominant granulated species [18]. The micrograph of the diatomite calcined at 900 °C revealed the detail of diatomite still showed a sign of its original diatomite structure, but the concave and convex surfaces were almost all gone and smoother surfaces were formed instead. The SEM micrographs of both acid activation and/or acid activation and followed by calcinations at 900 °C showed the original geometry of the pores to be preserved, but there are some sort of collapse in the skeleton structures.

2.4. TGA and SDTA

TGA and SDTA profiles of the four samples are displayed in Fig. (3a and b). Some chemical and mineralogical behaviors of those can be inferred from each other; in spite of they revealed different thermal trends.

In general, except those calcined at 900 °C there are broad endothermic peaks between 25° and 100°C ± 10 are related to the mechanically trapped and/or physically adsorbed water. Their intensities depend on the particle size and surface area of the samples [7]. There are also second endothermic step, appears between 100 and 350° ± 20. This is due to structural water loss, and is mainly related with the nature of the opaline phase. It is typical of Opal-A, the main component of diatomite, highly disordered, nearly amorphous, natural hydrous silica. Between those last two steps, one or more additional losses are sometimes detected. There

Table 1. The Chemical Compositions of Diatomite Materials Determined by XRF

Diatomite Materials	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	ClO ₂	K ₂ O	CaO	TiO ₂	FeO	Total
D_110	0.93	1.26	10.38	80.23	0.19	1.40	1.42	0.48	0.62	3.09	100.00
D_110_HCl	0.16	1.05	10.39	84.55	0.15	0.78	1.18	0.24	0.57	0.93	100.00
D_900	1.20	1.09	11.00	83.40	0.00	0.00	1.29	0.75	0.75	2.52	100.00
D_900_HCl	0.48	1.11	10.26	84.75	0.11	0.20	1.26	0.30	0.61	0.92	100.00

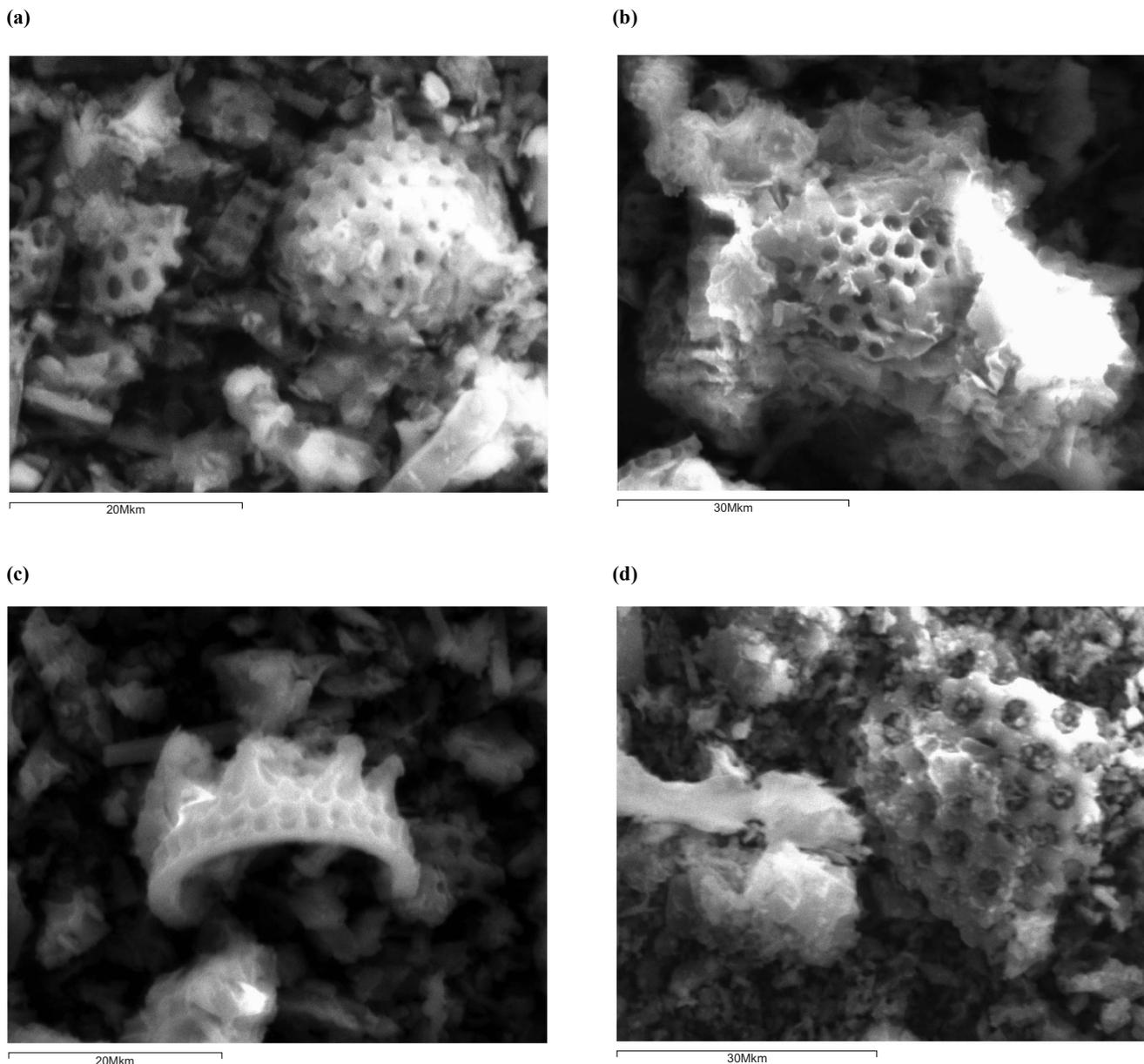


Fig. (2). The SEM for the diatomite samples (a): [D_110], (b): [D_110_HCl], (c): [D_900], (d): [D_900_HCl].

is a temperature loss at 350° indicated the evolution/decomposition of organic matters as usual components of diatomite.

2.5. FTIR

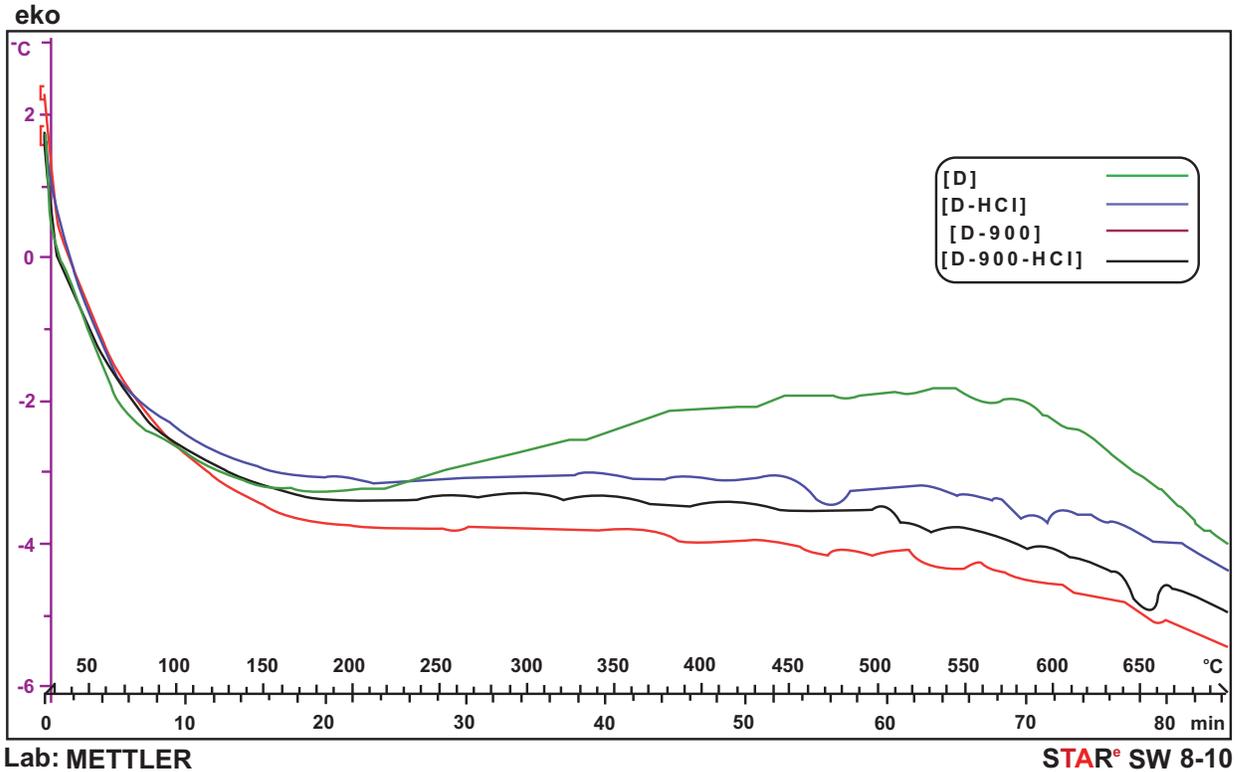
The analysis of FTIR spectra results are shown in Fig. (4). These resulted agreed with the corresponding XRD data. The peaks found at 3698 and 3621 cm^{-1} bands of natural raw diatomite are attributed to OH vibration mode of hydroxyl groups of kaolinite which were eliminated after calcinations [9]. The broad band centered on 3432–36 cm^{-1} was attributed to OH vibration mode of the physically adsorbed H_2O [10]. The peaks related to Si–OH and/or Al–OH are found at 917 cm^{-1} and Si–O–Al and are related to the Al octahedral sheet found at 533 cm^{-1} are disappeared on calcination. This

means that the clay mineral structure was destructed with calcinations. The bands were found around 793–798 cm^{-1} are related to the free silica and/or quartz and are found in all starting diatomite materials and did not affected by acid and/or thermal treatment. The absorption bands of diatomite in the region of stretching of vibration of Si–O are quite difficult to solve because the trapped by Si–O bands of clay minerals. However, based on our curve-fitting, the Si–O–T (T = Si or Al) stretch vibrations were assigned at around 1060 cm^{-1} and 1090 cm^{-1} . This band was reduced after acid leaching and calcinations.

3. CONCLUSION

- ✓ Natural raw diatomite collected from the main resource in (Aktyubinsk /Kazakhstan) contains quite high amount

a:



b:

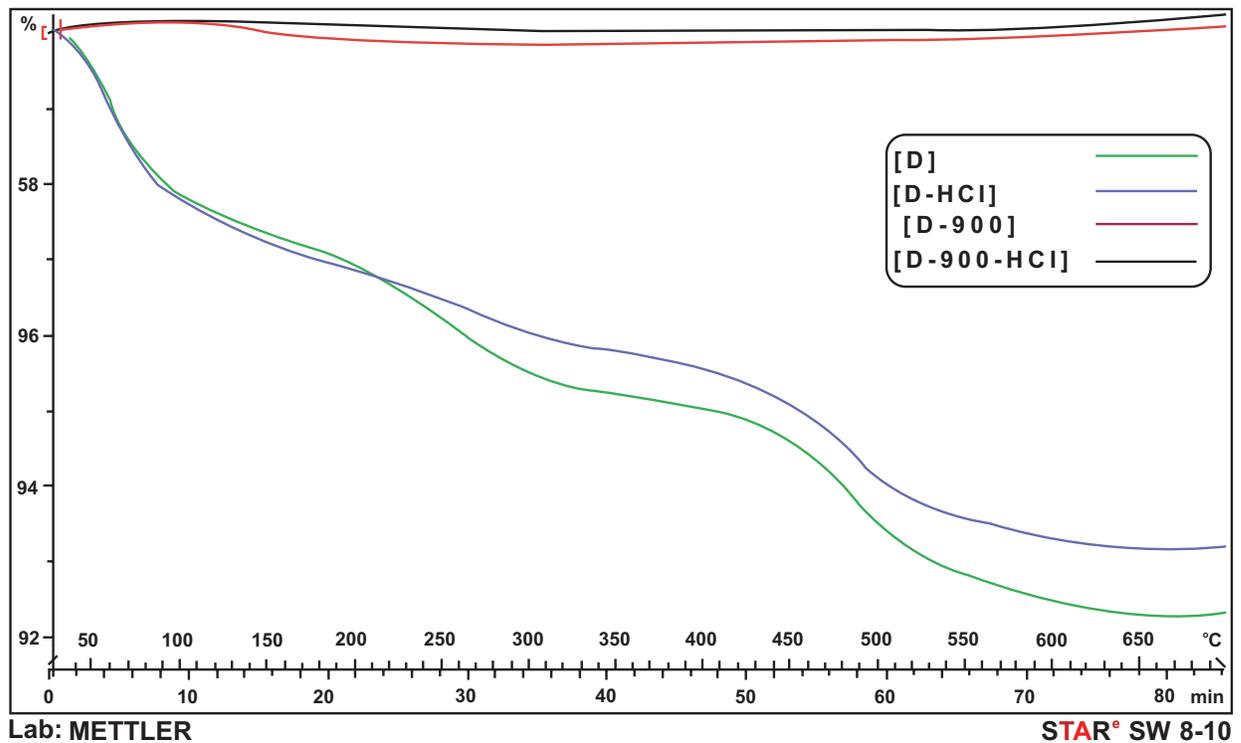


Fig. (3). a: TGA of the diatomite samples (a): [D], (b):[D-HCl], (c): [D-900], (d): [D-900-HCl]. (3). b: SDTA of the diatomite samples (a): [D], (b): [D-HCl], (c): [D-900], (d): [D-900-HCl].

of iron impurity (about 3.9 wt% expressed as Fe₂O₃) and some clay minerals especially mica and kaolinite.

- ✓ Acid leaching can remove iron impurity and some of clay minerals from the natural raw diatomite and this cause

the increase of silica content. The thermal treatment at 900 °C is not affected on the content of silica.

- ✓ The morphological structure examination by SEM revealed that, the thermal treatment at 900°C causes that,

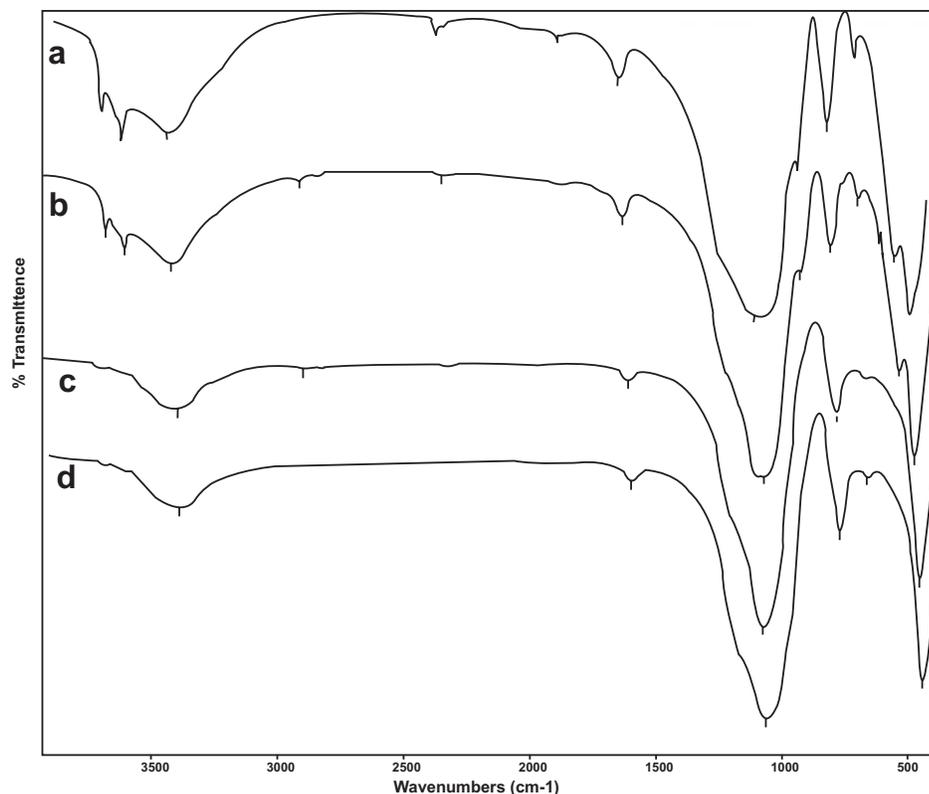


Fig. (4). The FTIR for the diatomite samples (a): [D_110], (b): [D_110_HCl], (c): [D_900], (d): [D_900_HCl].

the concave and convex surfaces were almost all gone, and smoother surfaces were formed instead.

- ✓ Thermo-gravimetric methods (*TGA and SDTA*) proved to be an efficient and rapid method for mineral diagnosis. From the thermal behavior of curves, we can conclude the carbonate and silica contents in the diatomite samples.

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Received: September 19, 2008

Revised: December 26, 2008

Accepted: March 13, 2009

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