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Characterization between crude diatomite and diatomite Treated chemically

L.A. Benzelmat*, R. Cherraka, M. Hadjel, A. Ketteb, N.Goual

Larboatoire des Sciences, Technologie et Génie des Procédés - LSTGP.
Université des sciences et de la Technologie d'Oran Mohamed Boudiaf – USTO MB.
Ecole Nationale Polytechnique (ENP) - Alger, Laboratoire de Recherche des Sciences de l'Eau (LRS-EA U).

*Corresponding author: benzelmat.lamia@gmail.com ; Tel.: +213 00 00 00;

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ABSTRACT/RESUME

Abstract:*diatomite of SIG also called Kieselguhr, is a white substance of fossil organic origin formed by microscopic skeletons of diatoms which are unicellular algae found in aqueous systems, it has very specific properties such as a porosity greater than 72% and a high adsorption capacity, its main component is amorphous silica, This mineral material is not pure in its natural state and is full of impurities that occupy the pores, that is why the objective of this work is to modify this diatomite before use, in order to improve the quality of the pores and valorized this material, Our diatomite sample was crushed, sieved and the fraction of 500 µm was collected then it underwent a chemical treatment to the 5M nitric acid at 60% for 2 hours at reflux. The raw and treated diatomite were characterized by the following methods X-ray fluorescence, scanning electron microscope, particle sizes, infrared IR, X-ray diffraction, for a subsequent comparison between the raw and the treated diatomite. The results of the crude diatomite show that it contains certain components such as silica, iron, alumina and the calcium carbonates which occupy the pores, whereas for the treated diatomite there is a total disappearance of the impurities, namely the Calcium carbonates thatdoes not reach 1%, and a predominance of silica that exceeded 79%. This treatment made it possible to modify the surface characteristics to improve the performance of the porous structure.*

I. Introduction

In Algeria there is a diatomite reserve also called Kieselguhr estimated at several million tonnes located in the SIG region. A diatomite is a sedimentary accumulation of silice ous skeletons of microscopic aquatic plants known as diatoms [1].
Diatomite is an environmentally friendly and a very inexpensive material, it is used in the industry as a filter, filler, adsorbent, abrasive material and surface cleaning material [2, 3]. Catalyst [4]. As demonstrated by Rui Shan and all by developing solutions using diatomite as catalytic support for the production ofbiodiesel [5]. And this the diatomite owes to its great specific surface, to the sizes of these pores. [6, 7], with low thermal conductivity and low density [8, 9]. Its main component is amorphous silica [10], however the diatomite is not pure in its natural state and is full of impurities such as metal oxides, minerals (mainly carbonates), clays, salts and organic matter, on its surface [11, 12] which occupy the pores, limiting the use of the latter and which can cause inconvenience in industrial applications [13];
It is for this that it is necessary to modify the surface characteristics of this mineral. There are different methods such as a chemical or thermal treatment which makes it possible to modify the surface characteristics, among them the acidic chemical treatment which can increase the surface and size of the pores, due to the removal of impurities responsible for pore blockage [14, 15] such as carbonate groups, which are photo catalytic

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reaction inhibitors employing hydroxyl ions. In fact, hydroxyl ions are trapped by carbonates and lead to less reactive radicals [16].
Let us not forget that the performance of a catalyst is directly related to the specific surface. Extensive studies have been conducted to evaluate the effect of acid treatment on texture and / or porous structure [17, 18] Having demonstrated that the reactivity of diatomite is related to the presence of reactive sites on its surface such as hydroxyl groups which are themselves reactive sites. In addition to hydroxyl groups, acidic sites such as iron or aluminum oxides are also considered important sites on the surface of diatomite [19]. There are several works that have treated acid diatomite among its works there are those with chloridic acid HCl [20, 21] and sulfuric acid [22], we have opted for a nitricacid treatment under reflux, the materials obtained has been characterize, this work will put forward a comparison between diatomite Crude and diatomite treat with 5M nitric acid to determine if an acid treatment is beneficial or not.

II. Materials and methods

II.1. Experimental Procedures

A simple method was used to purify our diatomite samples, it is an experimental device for heating to boiling while avoiding the loss of reagent vaporization. using a soxhlet extractor, the details of the practice are described in the following sections.

II.2.materials

The crude diatomite (DT) sample was brought back from the ENOF of SIG (a national non-ferrous mining company) and nitric acid was obtained from Sigma Aldrich.

II.3.Sample Preparation

The crude diatomite was crushed, sieved and the 500 µm fraction was collected. The DT was treated with nitric acid HNO_3 at 5M, 20g per 100 ml of acid, for 2 hours under reflux, the neutralized with NaOH until a pH of about 6.5 to 7 was reached. Thenit was filtered and dried at 378°K, in the autoclave for 24 hours, the material obtaine dis named DTN.

II.4.Characterization of Crude Diatomite and Treated Diatomit

impurities can hide pores, making it difficult to penetrate the surface. That's why a nitric acid treatment was undertaken and our raw and treated diatomite are labeled DT and DTN were characterized by X-ray fluorescence "RigakuZsu Primus II", X-ray spectroscopy spectra and particle sizes, performed in laboratory (Lafarge) laboratory analysis in Oran with a device of the "Quanta 250 FEI" type, submitted at ambient temperament conditions). Infrared spectroscopy was performed by a spectroscopy laboratory "Perkin-Elmer" (University of Oran) and to study the morphology of our diatomite, SEM-Leo scanning electron scanne microscope type 440i was used in the LSTGP laboratory. From USTO MB University.

III. Results and discussion

III.1. FRX / EDX

The percentage of the different elements obtained by X-ray fluorescence which identify the chemical components of crude diatomite and diatomite treated with nitric acid labeled DT and DTN are expressed in the form of oxides and are reported in Table 1. Chemical analysis of the crude diatomite shows the predominance of silica (47.52%), as well as the presence of calcium oxide and aluminum oxide of the order of 22.44% and 2.85%, while iron oxide, magnesium oxide, sodium oxide and sulfur trioxide are very low, while acid-treated diatomite analysis showed a change in chemical composition by increasing the silica content reaching 79.92%, a slight increase in iron, aluminum oxide and sodium, which should be considered reactive sites on the surface of the diatomite [19]. At the same time, a significant decrease in calcium, magnesium oxide and sulfur trioxide is determined as the main impurity [11, 12],
The increase in the SiO_2 ratio can be attributed to the fact that the silica is relatively resistant to acid attack while the Mg salts are more soluble under acidic conditions [23].
Calcium is mainly in the form of carbonate, which decomposes easily in acidic medium. Thus, the CaO content has clearly decreased after the addition of the acid, and finally the increase in sodium is due to the neutralization of the treated diatomite which was made by soda.

The FRX also indicates that the concentration of 5 M in HNO_3 is sufficient to completely eliminate calcite as already observed in the study of T. Benkacem and which highlights the comparison between an Algerian diatomite treat with nitric acid and a Thai diatomite treated with sulfuric acid [24].

Table 1: composition FRX of Crude Diatomite and treated diatomite

	SiO_2	CaO	MgO	SO_3	Fe_2O_3	Al_2O_3	Na_2O
DT	47,52	22,44	1,21	0,14	1,22	2,85	0,09
DTN	79,92	0,98	0,15	0,11	2,55	4,97	0,12

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Table 2: Composition EDX of Crude Diatomite and Treated Diatomitis

	Calcite	Dolomite	Quartz	Illite	Kaolinite	Topaz
DT Brute	38,93	4,83	19,02	6,69	10,4	0,73
DTN	14,26	0,14	10,51	17,82	16,27	0,07

The results of the FRX and EDX, shows that a large part of the diatomite is composed of several clay minerals [21, 25, 26, 27]. As shown in Table 2, the chemical treatment show the elimination of mineral clay, which is considered to be impurity.

The removal of carbonates change the density and specific surface are as well as the porosity of diatomite.

The color of the treated diatomite has changed from snow white to brown. This can be attributed to the migration of iron ions to the surface; as well as the conversion of various iron-containing minerals to Fe_2O_3 [28]. And as Mellah indicated in his search [29].

Figure 1 shows the size of the particles of the crude diatomite which vary between 1 µm to 40 µm and from 100 .µm to 160 µm, while figure 2 shows the size of the particles of the DTN which vary between 8 µm and 10 µm the chemical treatment to unify the poresize.

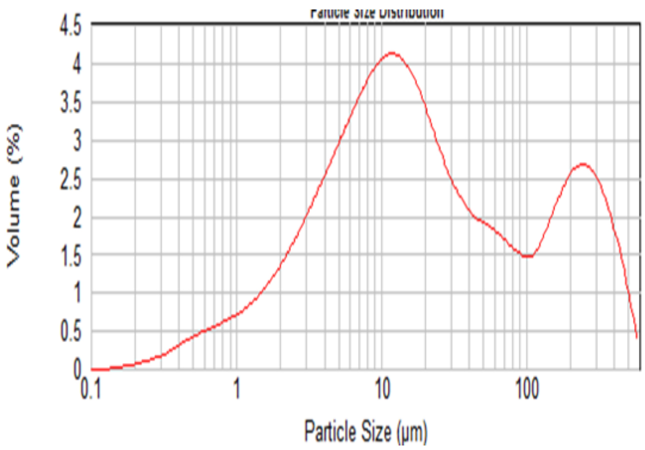

figure1: *particle sizes of DT*

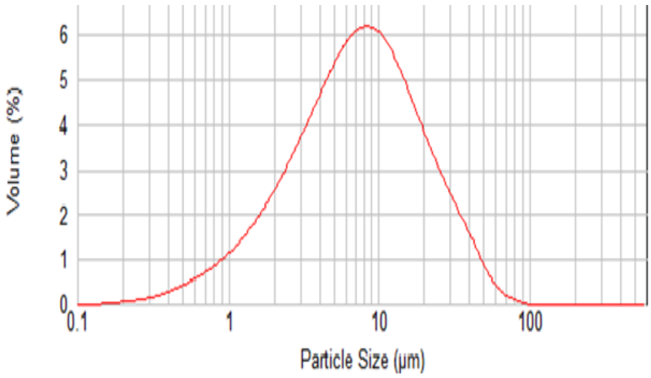

figure2: *particle sizes of DTN*

Table3: pore volume of raw diatomite and treated diatomite

element	Vp (%)
DT	6.620
DTN	4.560

After acid treatment a decrease in pore volume of 6,620 cm^3/g to 4,560 cm^3/g is observed. This change is because to the enlargement to the pores after the chemical activation [11, 30,31].

III.2. Characterization of the DRX

The X-ray diffraction spectrum figure 3 and 4 confirms the EDAX analysis, from which the crude diatomite is composed of silica in the form of quartz and amorphous silica, calcite and dolomite. The amorphous band maybe due to the formation of SiO_2 glass. The peaksat 2 ϴ = 20 °, 27 °, 30 °, 40 ° are the characteristic peaks of crude diatomite [32,33]. The spectrum of the treated diatomite shows the disappearance of the carbonate peak which confirms the X-ray fluorescence analysis.

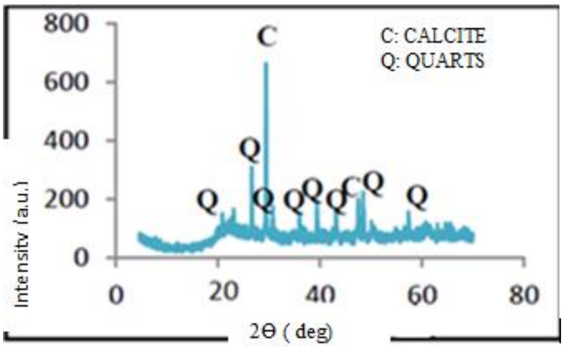

Figure 3: *X-ray diffraction of the raw diatomite*

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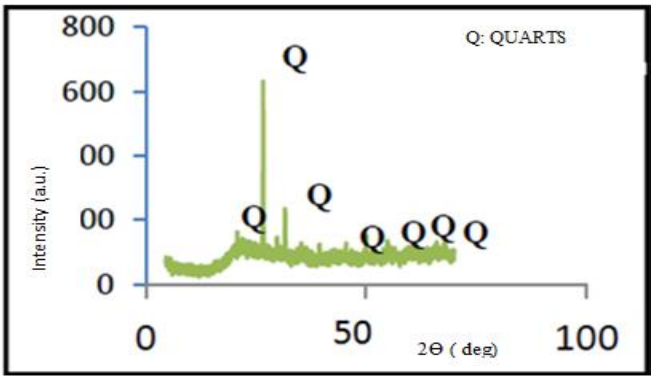

***Figure 4**: X-ray diffraction of treated diatomite*

III.3.Characterization of SEM

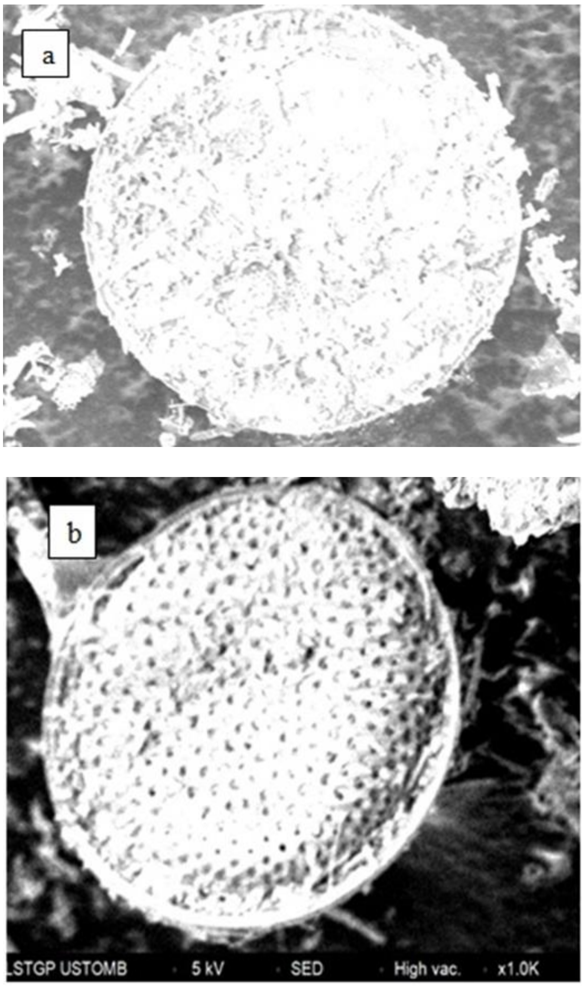

***figure.5:** SEM images before chemical treatment: (a) Irregular porosity diatomite, (b)*

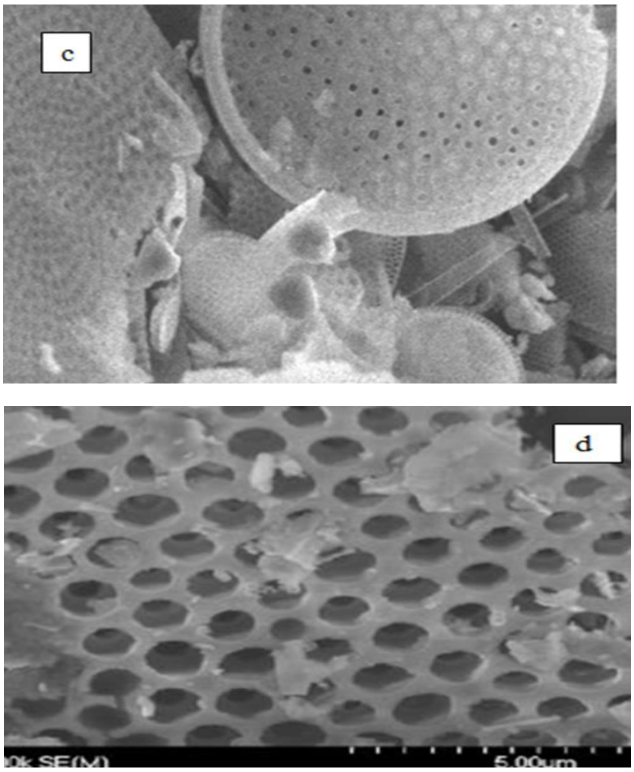

***figure.6:** SEM images after chemical treatment: (c), (d)*

The morphology of diatomite is observed using scanning electron microscopy (SEM). Figure.5 (a) and (b) at 30 µm show the gross diatomite covered with small visible impurities indicating the presence of CaO particles while Figure 6 (c) and (d) clearly shows that the pores were released.

Which means the absence of impurities, and we have observed that acid treatment has preserved the morphology of diatomite other wise the dominant form of our diatomite is circular with a view to the penal form and rings, as show in Figure 5 : (a) and (b).

III.3. Spectroscopy (IR)

To obtain information on the function algroups present on the surface of DT and DTN, will use IR spectroscopy.

The IR spectra obtained for the crude diatomite and the treated diatomite are represented by the figure: 7 and the figure: 8 respectively**,** the two spectra show us major adsorption bands of 712, 795 and 874 cm^{-1}, which can be attributed to Si-O vibrations [24],

the peakat 1062 cm^{-1}corresponds to the asymmetric stretching of the siloxane group (Si-O- Si)vibrations of the meso-porous diatomite structure. [34, 35], The peakat 457 cm^{-1}.

Is attributed to the Si-O-Si bending vibration or to the Si-O-Al bond (bound to the octahedral sheet) [36, 37], for the spectrum of DT the reis the band at

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1279 cm^{-1}which is due to asymmetrics tretching of the CO_3^{-2} group [38].

While the IR spectrum of the diatomite treated DTN shown in Figure: 8 observing the disappearance of the CO_3^{-2} binding which confirms the X-ray fluores cenceand the XRD, the band at 1636 cm^{-1} is attributed to the H-stretch-OH, water [27, 38, 39].

And finally the broad band at 3445cm^{-1} is given to -OH stretching and flexing vibrations of adsorbed water molecules [40].

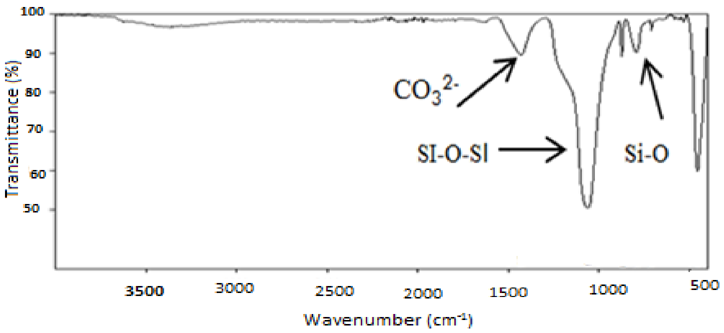

Figure 7: *IR spectrum of DT*

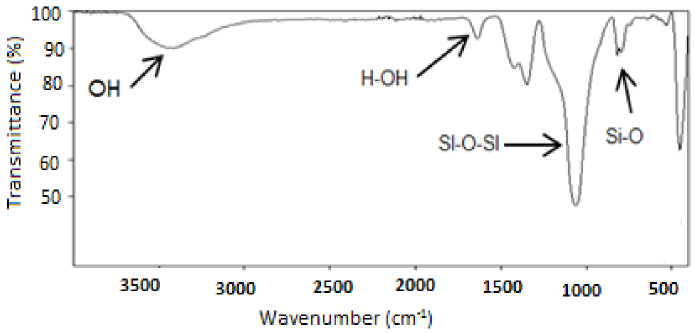

Figure 8: *IR spectrum of DTN*

IV. Conclusion

In order to improve the performance of the diatomite one has been interested to study the influence of the acid treatment on the latter, knowing that the treatment of the diatomite has the nitric acid has advantages proportional one is the elimination of Impurities such as calcium carbonate found on its surface that will limit the use, and the other which is the improvement of the properties of its specific surface that is due to the presence of reactive sites on the surfaces such as hydroxyl groups , iron and aluminum oxide According to the results of the X-ray fluorescence, IR and SEM analysis, the treatment of diatomite is successful. Thus let us not forget the accretion of the silica ratio which indicates that the diatomite can be used as alternative and inexpensive source of silica.

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