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Analytical study of the variation of physico-chemical and structural properties of a Kieselgühr during its decarbonation

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Abstract. The physico-chemical properties and the structure/texture of a Kieselgühr, of Algerian origin, have been investigated in this study by using several analytical techniques (atomic absorption spectroscopy, IR, XRD, gas adsorption, porosimetry and microscopies). The results show that the natural product is contaminated heavily by calcium carbonate. Nevertheless, it presents an interesting porosity. After decarbonation by HCl acid and thermal (1 000 °C) treatments, we obtained the Kieselgühr with pure silica phase and well developed porosity. The treated product could be very interesting for filtration and clarification applications.

Key words. Kieselgühr analysis — treatment — texture — structure — surface.

Introduction

The Kieselgührs are composed of siliceous carapaces of diatomeous fossils deposited since thousands of centuries. They have relatively insoluble and non-compressible structures with high porosity [1], and are frequently used in the industry as filters, clarifiers and reinforcement agents [2], chromatographic and catalytic supports [3,4]. However, the product is never pure in its original form and it contains various mineral impurities, generally related to its origin. These impurities, according to their nature and concentration, can cause inconveniences in industrial applications. Therefore, it is necessary to modify the raw material before its utilisation. Reagents and treatment conditions have been much studied: such as inorganic bases and acids attacks [5], ammonium salts and acid carbonates [6], chlorides [7] and thermal treatments [8].

The natural Kieselgührs of Algerian origin are polluted by their high level of calcium carbonates (Tab. I). If the level of $CaCO_3$ is greater than 10%, the food products (such as beer, fruit juices or wine) filtered by filters made from Kieselgührs will have bad taste. They also will have basic pH according to the formation of basic complexes during the dissolution of $CaCO_3$ [9]. Considering the easy dissolution of calcium carbonates by chlorhydric acid, we have used this simple and economic process in preparing materials which might be used as clarification filters. In this respect, it is interesting, on one hand, to determine the physico-chemical, structural and textural properties of this product, which has not yet been systematically studied before. On the other hand it is interesting to examine what are the modifications in the structure and in the texture of diatomite after elimination of these calcium carbonates, and also to understand how these modifications lead to a variation of the physico-chemical properties of the raw material until obtaining an alluvium clarification filter type [10].

Experimental part

HCl and thermal treatment

The basic raw material used in this study is provided from Sig deposit (west of Algeria). After grinding and sifting, the particle size fraction between 40 – 60 µm was collected. This product, called «KANT», was treated with 1N HCl in concentration, at reflux during 6 hours (5 g in 100 cm^3 of HCl). Then the HCl was eliminated by a continuous washing with distilled water in a Soxhlet extractor during 24 hours. The residual chloride ions were checked by $AgNO_3$ titration .

After that operation, the sample was thermally treated from ambient temperature to 1 000 °C in an oven using a heating speed of 5 °C/mn. The obtained Kieselgührs are named «KAT».

Characterization techniques

The physico-chemical, structural and textural properties of these two types of Kieselgührs have been characterized by the following experimental techniques:

Table I. Chemical composition of the Kieselgühr samples.

Chemical composition (%)	*KANT*	*KAT*
SiO_2	67.32	92.77
$CaCO_3$	19.11	0.55
Al_2O_3	1.91	0.52
Fe_2O_3	1.63	0.65
MgO	1.32	0.37
K_2O	0.75	0.27
Na_2O	1.12	0.21
TiO_2	0.17	0.11
H_2O	5.63	4.52

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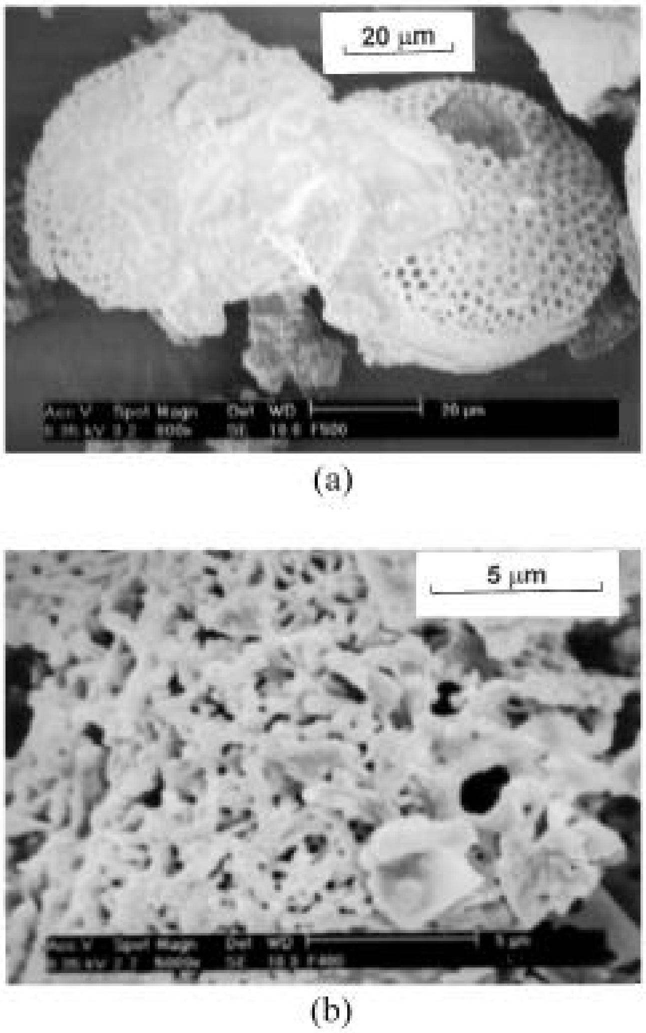


Fig. 1. Mineral impurities (central area in the image) on the surface of the sample KANT observed by SEM a) and an enlarged image of these impuries b).

(1) The analysis method for silicates [11-13] has been adopted to characterize the chemical composition of the Kieselgührs by atomic absorption spectroscopy. A Pye Unicam SP 9A spectrophotometer was used.

(2) Specific surface areas have been determined by N_2 adsorption at 77 K according to BET method [14], using a volumetric apparatus of Micrometrics (Accusorb 2100E type). Before N_2 adsorption, the samples were heated to 140 °C under vacuum (10^{-6} mmHg) kept by a primary and a secondary pump for 12 hours in order to eliminate the physisorbed molecules.

(3) Total porous volume (V_t) and the total porosity (P_t) have been obtained by Hg and He densimetry [15]. The mercury and helium auto-pycnometers of type Micromeritics Series II 9220 and 1320 were used.

(4) The scanning electronic microscopy (SEM) pictures have been realized with a Phillips XL 30 instrument and the atomic force microscopy (AFM) has been performed on a Nanoscope II [16] (Digital Ins.).

Table II. Physico-chemical characteristics of the samples KANT and KAT.

Characteristics	*KANT*	*KAT*
Colour	yellowish white	snow white
pH	7.9	5.9
S, (m^2/g)	22	4
$d_{app.}$, (g/cm^3)	0.6120	0.3685
D_{real}, (g/cm^3)	2.1461	2.3251
V_p, (cm^3/g) (*)	1.168	2.284
D_p, nm (Hg porosimetry)	100 – 2000	1000 – 10000
D_p, nm (SEM)	200 – 2000	1000 – 2000
P_t, (%) (**)	71.48	84.15

(*) $V_p = \frac{1}{d_{app.}} - \frac{1}{d_{real}}$ (**) $P_t = \frac{d_{real} - d_{app.}}{d_{real}}$, (%).

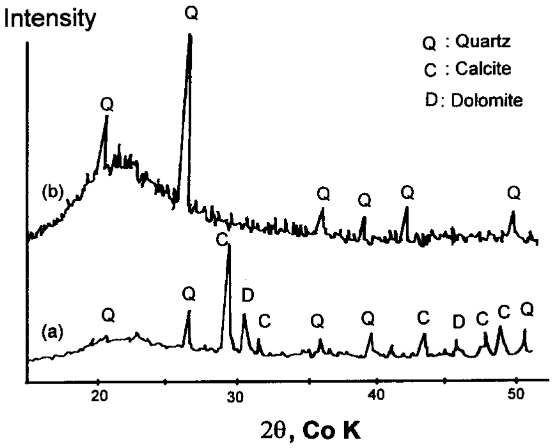


Fig. 2. X-rays diffraction spectra of the two samples of Kieselghür: KANT a) and KAT b).

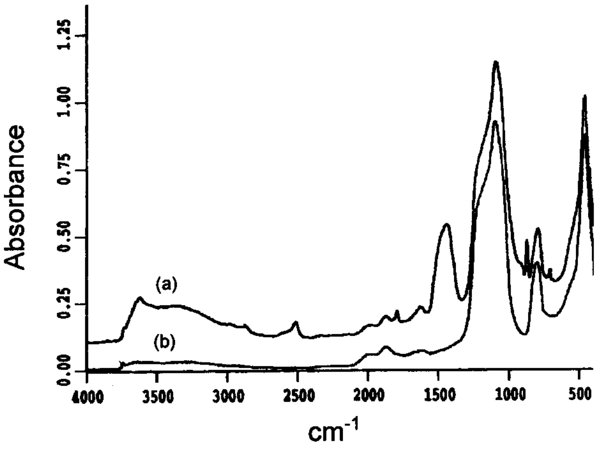
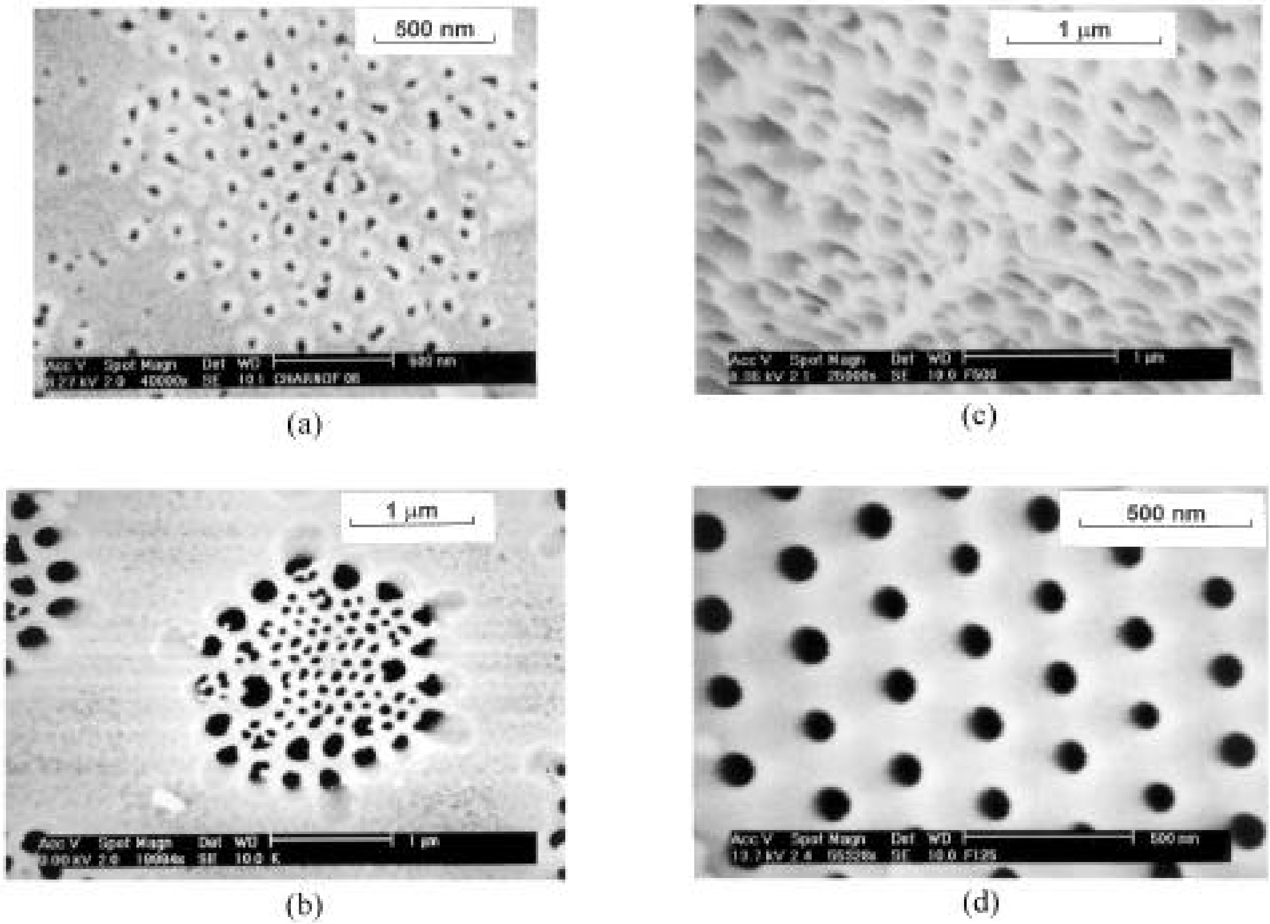
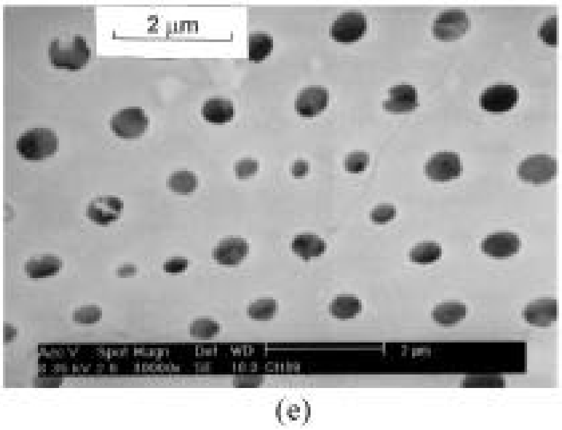


Fig. 3. IR spectra of the sample KANT a) and KAT b).

(5) The pore diameters have been determined by Hg porosimetry with a Carlo Erba 200 and a Micromeritics Series II 9220 apparatus, and by SEM and AFM microscopies.


(a) (c)

(b) (d)


(e)

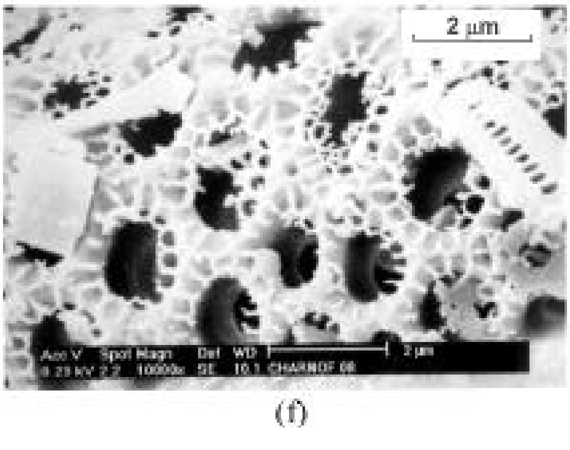

(f)

Fig. 4. SEM images of the raw Kieselgühr KANT showing the different pore nature of the material: a) membrane with irregular pore arrangement over a macro pore; b) membrane with more regular pore pattern over a macro pore; c) irregular macro pore form and arrangement; d) regular macro pore form and arrangement; e) regular macro pore form but irregular pore arrangement and f) macro pore with porous membranes destroyed.

(6) Fourier Transform Infrared (FTIR) analysis has been carried out on Perkin Elmer spectrophotometer (pellet thickness: 0.2 mm, 2% of Kieselgühr in KBr).

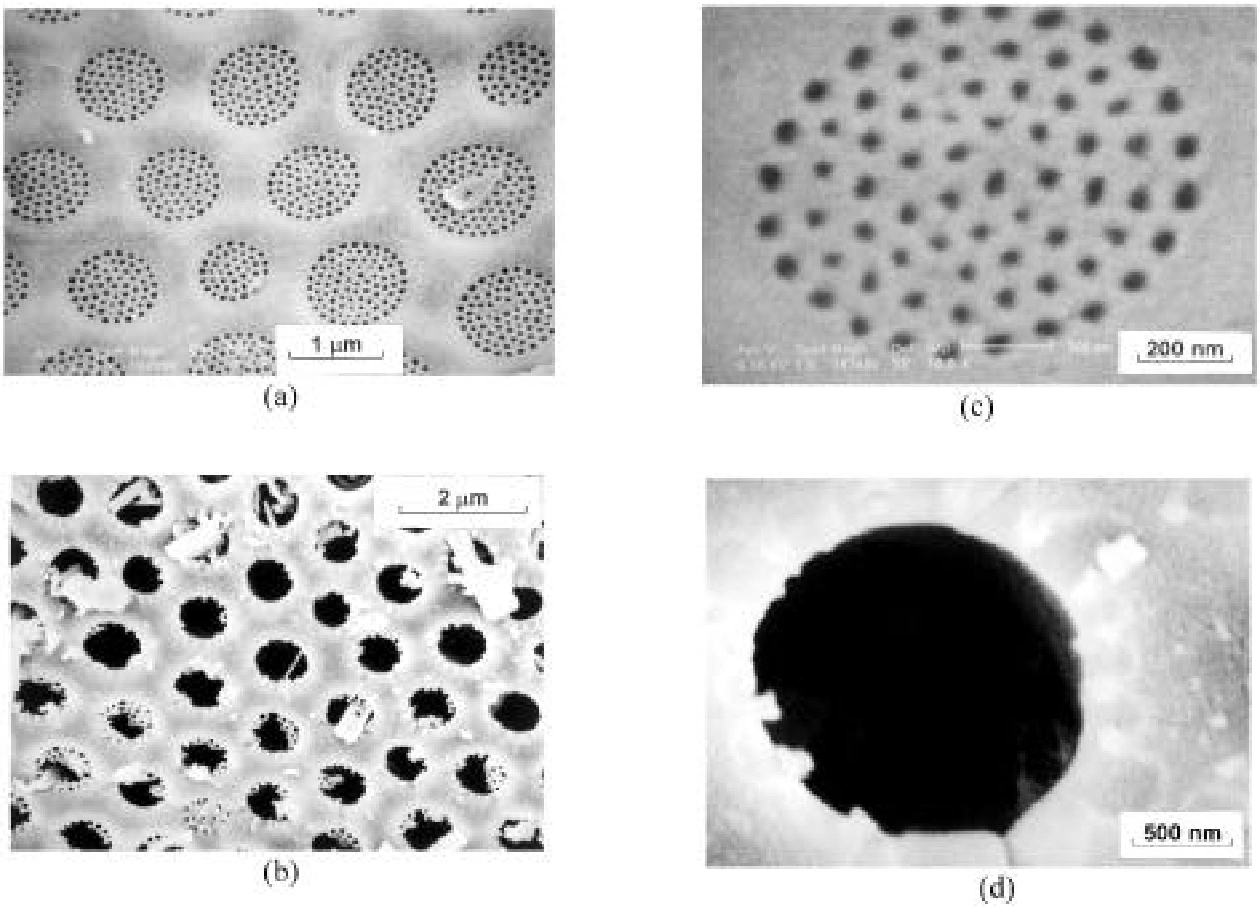
(7) Crystalline phases have been analyzed by a Siemens X-rays diffractometer, using Cobalt anticathode (λ = 1.789 Å) with a 40 kV – 30 mA current alimentation.

(8) Suspensions of the Kieselgühr particles (2 g) in distilled water (100 cm^3) were prepared for testing the acidity of the solid samples. A pH-meter of Tacussel type [17] was used.

Results and discussion

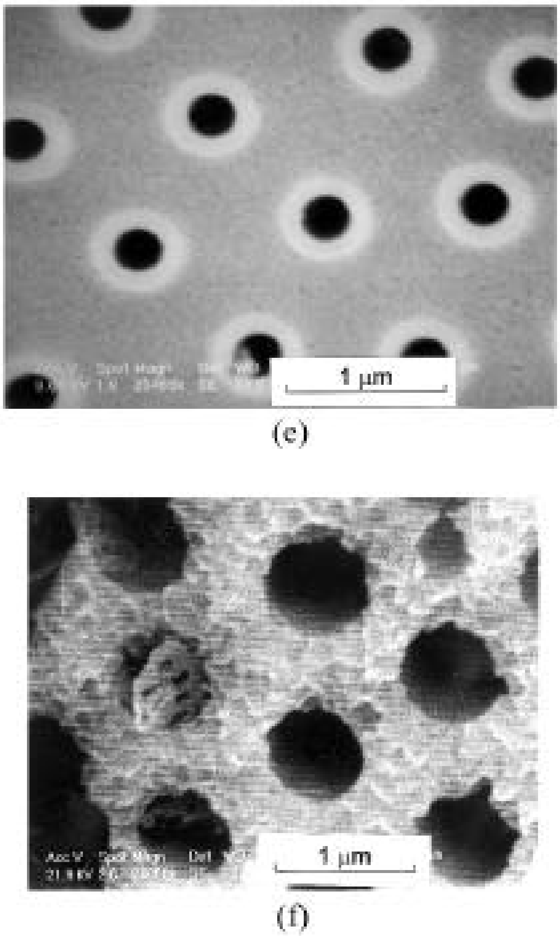
Chemical composition analysis

Table I shows that the natural product is essentially composed of silica with $CaCO_3$ as the main impurity (19%) which contaminates the surface of the raw material. Furthermore, the impurities can mask a part of the porous



(a) (c)

(b) (d)



(e)

(f)

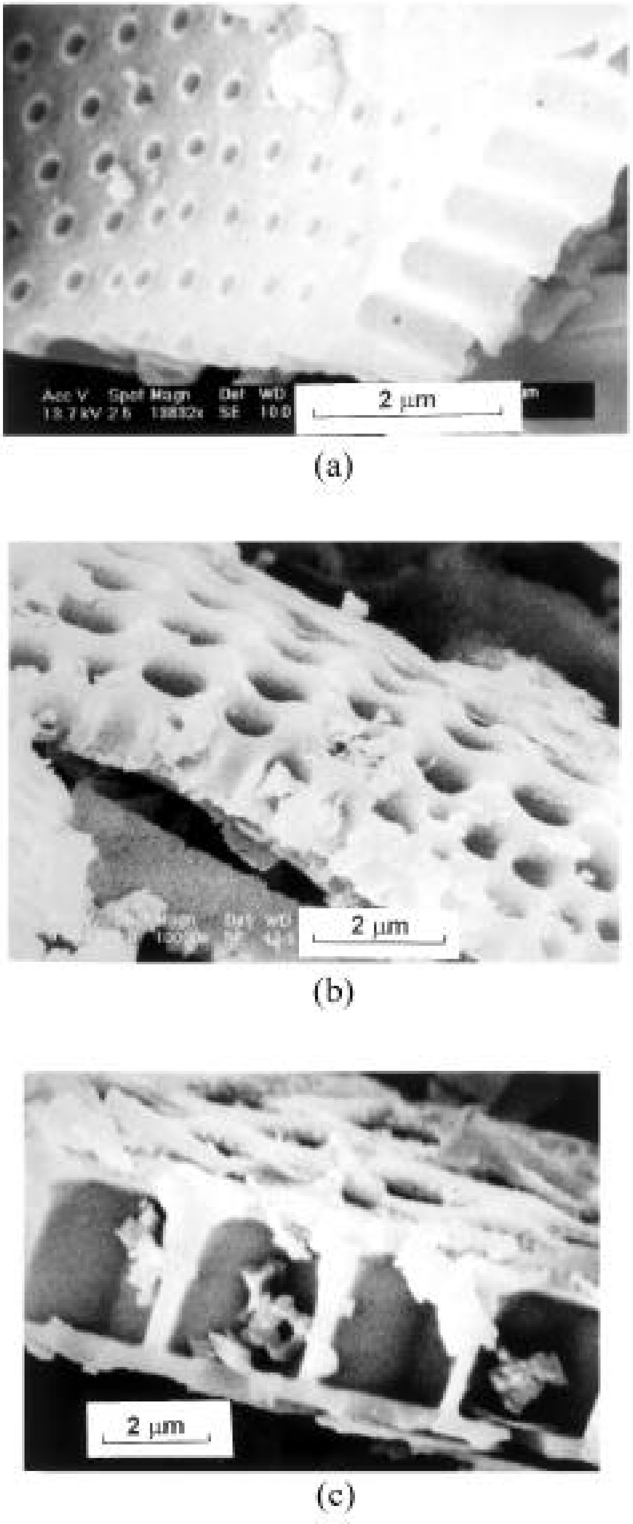
Fig. 5. SEM images of the Kieselgühr before a, c, e) and after b, d, f) the HCl and heat treatment showing the pore structure evolution. After the treatments, most porous membranes have been broken a, b). This is shown more clearly in c, d). The solid surface becomes also rougher e, f).

matrix, and the permeability of the product will be affected, as we can see clearly on SEM pictures a) and b) of the figure 1.

After chemical (HCl) and thermal treatments of the natural product, we can observe notable variations of its chemical composition. The impurities have been efficiently cleaned off from the raw material. The $CaCO_3$ content has been greatly decreased and the amount of the other impurities such as Fe_2O_3, Al_2O_3 and MgO are also diminished.

Physico-chemical analysis

The physico-chemical properties of the KANT and KAT are presented in table II. From these results we can distinguish fundamental differences of the two samples. Indeed, we first note a change in color of the natural product, which moves from a yellowish white to a snowy white, due to the transformation of the iron oxide in an uncolored iron silicate complex by the temperature effect [18].



(a)

(b)

(c)

Fig. 6. SEM images of the sample KANT in section showing the sheet form of the Kieselgühr and the macro pores with two orifices opened on the two basal surfaces: a) difference of pore diameters observed on the basal surface and in section; b) cylindrical pores across the sheet; c) thick cylindrical macro pores with small orifices.

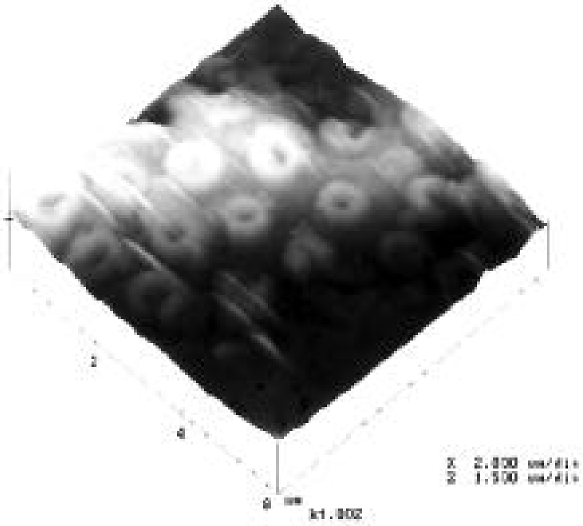


Fig. 7. Pore structure of the sample KAT observed by AFM.

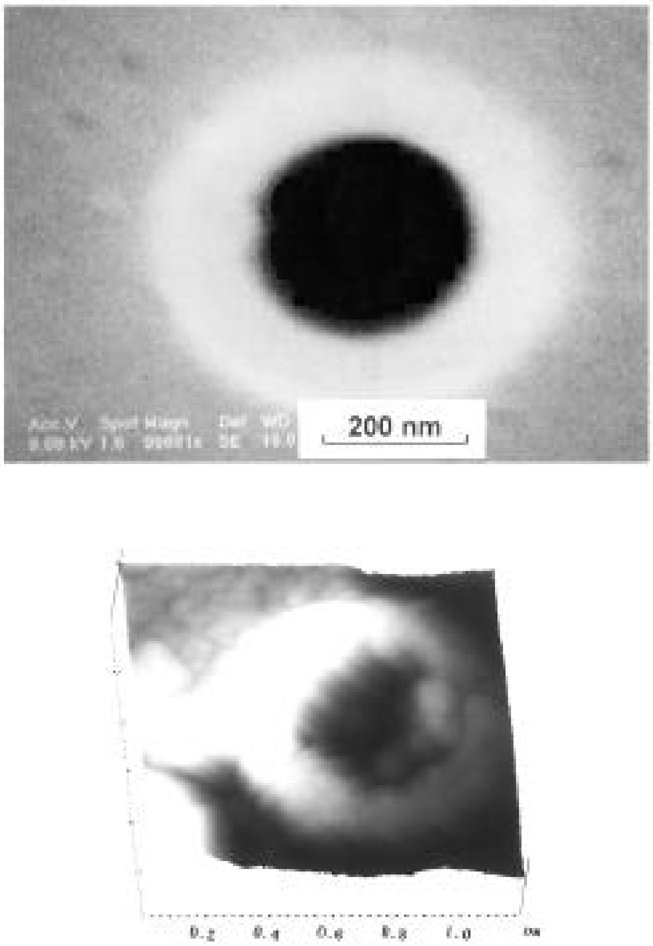


Fig. 8. SEM a) and AFM b) images of a pore.

The basic pH of the natural product, due to the presence of calcium carbonate, becomes acid after the treatments. A remarkable decrease of the specific surface area is observed: it goes from 22 to 4 m^2/g. This change is due to the enlargement of the pores. Effectively, the pore diameters as determined by Hg porosimetry and SEM increase considerably after the purification. The porous volume has also doubled because of the opening of the thin pores to give larger orifices (pictures b) and d) of Fig. 5). However total porosity Pt changes weakly: this is due to the structure of these products, composed of SiO_2 skeleton with a great emptiness [19], as confirmed by the SEM images.

X-rays diffractometry analysis

Phase analysis by X-rays (Fig. 2) showed that the non-treated natural diatomeous earth (from Sig) contains three crystalline phases: SiO_2 (quartz form), $CaCO_3$ (calcite and dolomite form) and amorphous SiO_2. However, clay phases have not been found in this product even at trace concentration, contrary to many other diatomeous earth from other origins [20]. We can estimate that the crystallization ratio of this product is high. After carbonization of the natural sample, we observe considerable variation in the phases composition. The X-rays signals corresponding to the two crystalline forms of $CaCO_3$ (calcite and dolomite) have completely disappeared on the KAT diffractogram. The quality reflection became stronger because of the new conditions created after dissolution of calcium carbonates. We also note that after decarbonation, one part of crystalline SiO_2 becomes amorphous.

Infrared spectroscopic analysis

In order to further study the effect of decarbonization on chemical properties of KANT, Fourier transform IR spectroscopy has been used to analyse the two compounds. Their spectra are compared in figure 3. Effectively, CO_2 deformation bands at 713.2 cm^{-1} , 876.5 cm^{-1}, 2 515.2 cm^{-1} and specially at 1 456 cm^{-1} [21], are absent on KAT spectrum where the existing absorption bands correspond only to the vibration bands of SiO_2, 463 cm^{-1}, 803.2 cm^{-1}, 1 102.2 cm^{-1} and 1 873 cm^{-1}. The large band situated at 3 620 cm^{-1} is due to the physisorbed water.

SEM and AFM observation

SEM has been used to study the different forms of porosity and the structure modification of the KANT product of the structure due to the decarbonation. Images a-f) of figure 4 and a), c) and e) of figure 5 show different original porous structures with several diameters, from 80 nm to 2 µm. We can note that the pores are predominantly in circular form. The fragments of the Kieselgühr are in slice form with two faces opened (Fig. 6) and we can also see the cylindric nature of the pores.

After decarbonation (double effects of HCl and temperature), the porous membranes, constituted by rather thin pores, are broken down and larger pores appear (Fig. 5, images b) and d)). On image *f* of the same figure, we can observe also another and new pore distribution.

We have also observed a KAT sample by AFM (Fig. 7). The image shows that the surface is constituted by a high density of well-ordered opened pores. The enlargement of one third-dimension pore as shown by image b) of figure 8, reveals pores with «cupping» form, this morphology can not be easily observed by SEM as compared in figure 8a.

Conclusion

The physico-chemical, textural and structural properties of a Kieselgühr before and after decarbonation have been examined by several techniques. The natural product is seriously contamined by high ratio of $CaCO_3$ which leads to its inferior quality. However, the material presents interesting pore structure and high porosity. After decarbonation by HCl and calcination at 1 000 °C, the treated Kieselgühr has a high purity in amorphous silica and quartz and a high porosity exceeding 80% of the volume, thus providing a good permeability for liquid. Therefore, the treated Kieselgühr can be used as a clarification filter of good quality.

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