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Preparation and characterization of a porous material from an Algerian desert sand

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Abstract

The objective of the present work is to prepare and characterize a porous material using quite particular and localized dunar sand (erg) of the desert near the El-Oued (south-east of Algeria). The porous material is prepared according to the mechanism of co-operative self-assembly. The method consists of polymerizing a silicic precursor (sodium silicate obtained by alkali fusion of sand with the sodium carbonate) around micelles of surfactant in an acid aqueous solution according to the sol-gel process. The elimination of the surfactant by calcining at high temperature leads to the final material which was characterized by XRF, XRD, MEB-EDX, FTIR and BET techniques.

Keywords: characterization, sand, porous material, silica gel, surfactant

Introduction

Nowadays, porous materials play a very important role in our daily life [1]. These materials are practically encountered in all fields: such as treatment of industrial and household effluents, ceramics, heterogeneous catalysis, pharmaceutical applications, and so on [2- 5]. Porous materials can be obtained from a large number of raw materials, such as carbon-rich materials, synthetic zeolites and geomaterials [6 -14]. In this study, we are interested in a geomaterial namely the sand of the great Algerian desert for the preparation of porous materials. Sampling of sand is carried out near El-Oued, a city located in the south-east of Algeria and north of the great eastern Erg. This dunar sand can reach a height up to 200 m. The sands of El-Oued are siliceous, very fine and hard.

Material and methods

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Material

The sand used for the preparation of porous material was taken from the region of El-Oued. Its chemical composition is determined by X-ray fluorescence spectrophotometry (model: ZSX Primus II-Rigaku). The results obtained are summarized in Table 1 and show that the preponderant mineralogical composition of the used sand is silica. The comparison of the sand diffractogram recorded on a diffractometer (D8 Advance Bruker) in the range of 2θ: 5 to 100° (Figure 1) with the diffractograms of reference compounds stored in the PDF (Powder Diffraction File) database confirms an α-SiO_2 type silica with a hexagonal unit cell of parameters: space group P3221 (154); Z = 3; a = b = 4.91340; c = 5.40530Å. Sodium carbonate (Na_2CO_3), cetrimonium bromide (CTAB) and hydrochloric acid (HCl) were obtained from Fisher, Sigma-Aldrich and Merck respectively.

Table 1. Sand composition

Compound	**CO_2**	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**
Mass (%)	10.7	0.162	0.545	2.54	78.2	0.119	0.0672	0.0114
Compound	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**Rb_2O**	**SrO**	**ZrO_2**
Mass (%)	0.577	6.43	0.105	0.0118	0.453	0.0017	0.0091	0.013

In this work, the inorganic precursor used for the preparation of the porous material is sodium silicate and the structuring agent is cetrimonium bromide (CTAB). The latter is an ionic surfactant, widely used for structuring mesoporous materials [15, 16].

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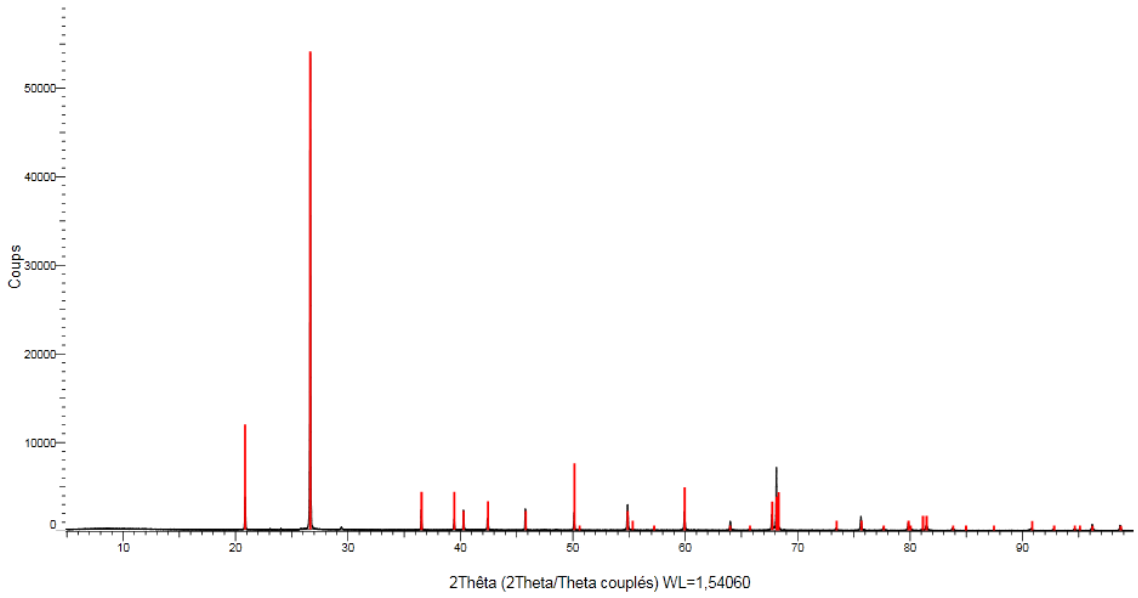

Figure 1. XRD analysis of the sand

Preparation of porous material

The sand is washed several times with distilled water, dried at 105 °C for 24 hours, and sieved with a 125 µm mesh size sifter to obtain a homogeneous sample. The sodium silicate was obtained by dry process from the alkali melting of a sand mixture of 125 µm and sodium carbonate in a platinum crucible at 1200°C for 2 hours (mass ratio $\frac{Na_2CO_3}{sand} = 1.8$). After cooling, a solid is obtained. A mass of 0.5 g of this solid is introduced into a beaker, made up with 30 ml of distilled water at 20°C, and then homogenized. The solution is filtered to remove insoluble products. 40 ml of a 0.16 M concentration surfactant solution (CTAB) are added to the filtrate. The mixture is stirred vigorously for 7 hours. The pH is set at 7 with a solution of HCl (2M). At this pH value, the gel is formed instantly. The gel obtained was washed several times with distilled water and then centrifuged for 5 min. The elimination of chloride ions was confirmed by the $AgNO_3$ test. The material thus obtained was calcined at a temperature of 650°C for 5 hours. This step destroys the surfactant and thus creates a high porosity of the final material [17].

Results and Discussion
Observation under MEB-EDX

The analysis was carried out on a Quanta 250 FEI type scanning electron microscope associated with AMTEK's Octane Pro X-ray Dispersive Energy Microanalysis. Several acquisitions of high resolution images with different magnifications were made. The observation of the sand shows that the grains are mostly rounded to sub-rounded for an magnification of 500X. For a high magnification, one observes the existence of small fragments (Figure 2) which appear in a white color. The EDX analysis of these fragments (Figure 3) shows that they are formed mainly of silicon (% by mass = 37.46, atomic % = 25.19) and oxygen (% by mass = 54.84, atomic % = 64.73). Calculations show that the atomic ratio $\frac{O}{Si} = 2.57$ and the mass

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ratio $\frac{O}{Si} = 1.46$. These results correspond to a structure close to SiO_2. The observation with different magnifications of the prepared material shows the existence of a porous structure at the surface (Figure 4). Analysis by EDX (Figure 5) shows that it is formed mainly of silicon (% by mass = 29.10, atomic % = 19.79) and oxygen (% by mass = 51.74, atomic % = 61.78). From these results, we find that the atomic ratio $\frac{O}{Si} = 1.78$ and the mass ratio $\frac{O}{Si} = 3.12$. This suggests that there is the possibility of formation of a product rich in oxygen.

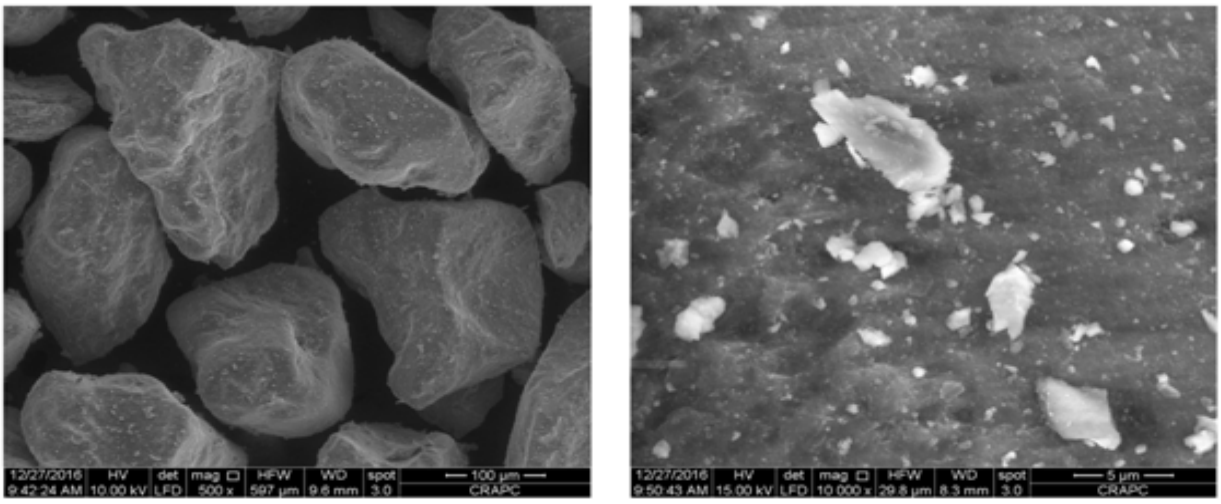

Figure 2. SEM images of the sand

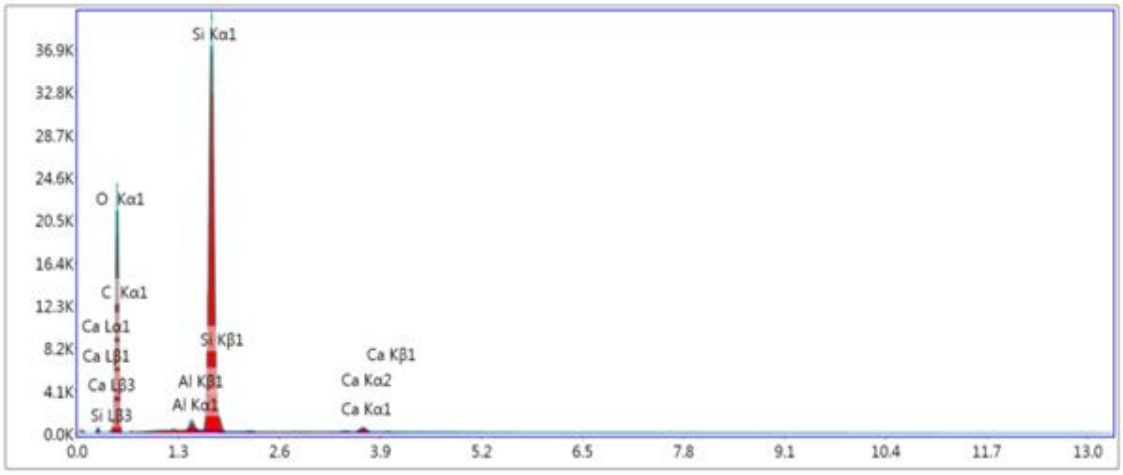

Figure 3. EDX analysis of the fragments

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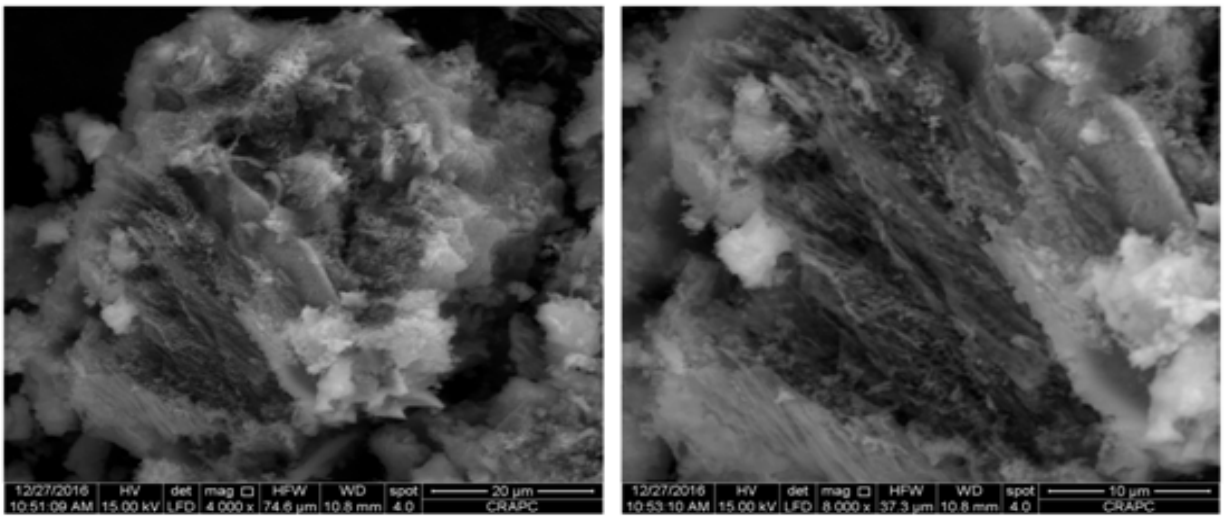

Figure 4. SEM images of the prepared material

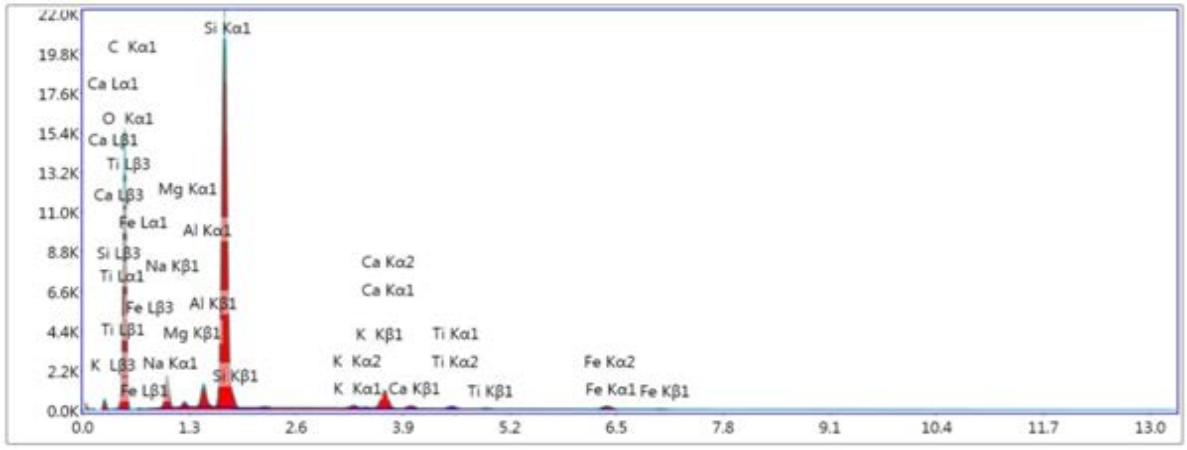

Figure 5. EDX analysis of the prepared material

FTIR analysis

The IR spectra of the sand and the final material (Figure 6) were recorded on VERTEX 70, BRUKER. On the sand spectrum, the band located at 456 cm^{-1} is due to deformation vibrations Si-O-Si. The bands located at 778 cm^{-1} and 796 cm^{-1} are attributed to the SiO_2 species present in the form of quartz [18]. The strong band centered at 1064 cm^{-1} is due to asymmetric elongations Si-O-Si [19]. For the prepared material, the asymmetric and symmetric elongation vibrations Si-O-Si are clearly observed at 1057 cm^{-1} and 798 cm^{-1} respectively, as well as the elongation band Si-OH at 966 cm^{-1}. In addition, the absence of the symmetric and asymmetric elongation bands C-H located between 2850-2960 cm^{-1} [20] on the spectrum of the prepared material, helps to confirm that the surfactant has been removed after the calcining at high temperature. The absorption band at 3406 cm^{-1} is attributed to the elongation vibration of silanol groups O-H formed on the surface of the prepared silicic material [21, 22].

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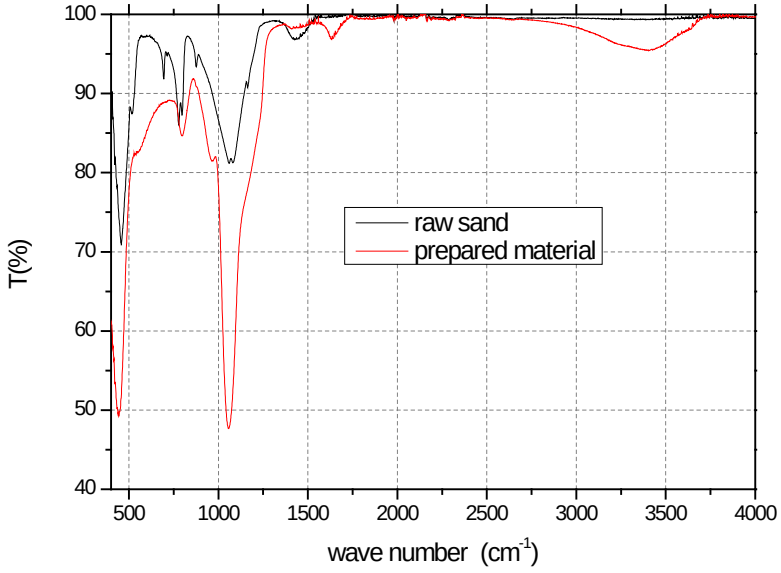

Figure 6. IR spectra of sand and prepared material

Determination of specific surface area according to BET

Among the methods for measuring the specific surface area of a material, the gas adsorption determination described by the Brunauer, Emmett and Teller isotherm (BET method) [23]. Its linear form is written as follows:

$$\frac{Pr}{V_{ads}(1-Pr)} = \frac{C-1}{CV_m}Pr + \frac{1}{CV_m} \qquad (1)$$

$$\text{with } Pr = \frac{P}{P_0}$$

In which P is the equilibrium adsorbate partial pressure, P_0 is the saturated vapor pressure of the adsorbate at the experiment temperature, V_{ads} is the adsorbed gas volume per gram of adsorbent, V_m is the volume corresponding to a monolayer of adsorbed molecules, and C is the BET constant which is characteristic of the interaction between the adsorbate and the adsorbent. This method gives good results, especially in the field; 0.05<Pr <0.35. The specific surface area of the sample is given by the following equation:

$$S_p = \frac{V_m N_A \sigma}{V_M m} \qquad (2)$$

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Where :

S_p : specific surface area (m^2/g), V_m : volume of gas required to cover the monolayer (cm^3), V_M : molar volume (22414 cm^3/mole ; NCTP), N_A : Number of Avogadro ($6.022x10^{23}$ molecules/mole), σ : Area occupied by a molecule of gas (N_2 ; $16.20x10^{-20}m^2$) and m is the mass of the sample (g).

The measurements were recorded on the Micromeritics ASAP 2020. The adsorption gas used is nitrogen and the measurements are made at 77K and P_0 = 753.676mmHg. The measured volume is brought back to the normal conditions of pressure and temperature. The parameters relating to the BET isotherm for the sand and the prepared material calculated from the curves of Figure 7 and Figure 8 are collected in Table 2. The results obtained show that the prepared material has a specific surface area much greater than that of sand.

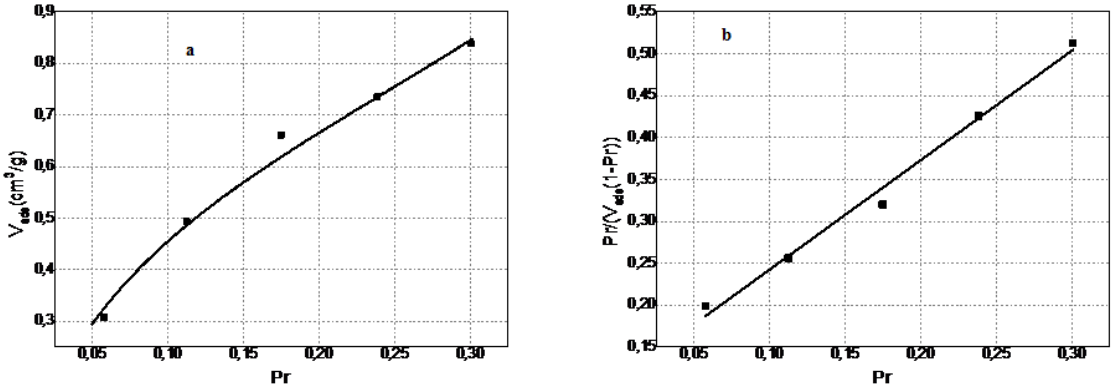

Figure 7. N_2 adsorption isotherm at 77K on sand (a: standard form, b: linearized form according to BET)

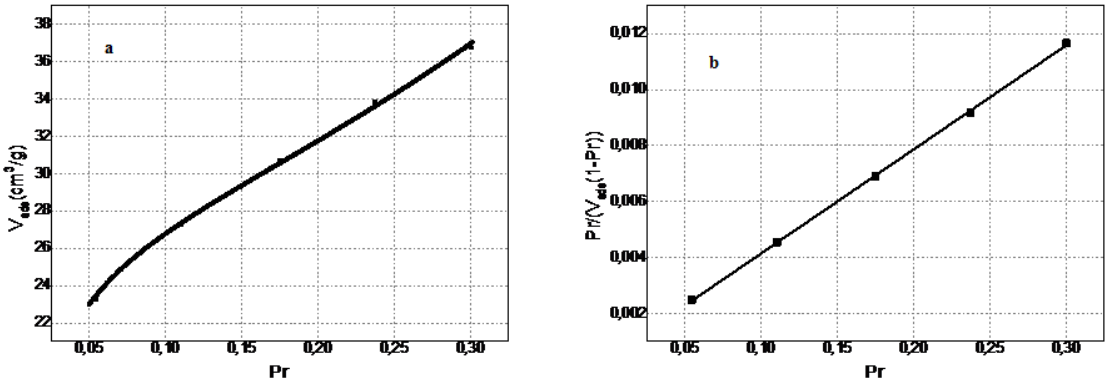

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Figure 8. N_2 adsorption isotherm at 77K on the prepared material (a: standard form, b: linearized form according to BET)

Table 2. The parameters of the BET isotherm

parameters	**V_m (cm^3/g)**	**C**	**S_P (m^2/g)**	**R^2**
sand	0.70	12.69	3.04	0.9904
prepared material	26.57	87.92	115.64	0.9997

Conclusion

The present work concerns the valorization of Algerian desert sand for the production of a porous material with a large specific surface area. The method comprises the following steps:

1. Washing, drying and sieving the sand at 125 μm;

2. Preparation of sodium silicate from the alkali melting of sand with sodium carbonate at 1200°C;

3. Addition of a surfactant (structuring agent);

4. Addition of a solution of hydrochloric acid;

5. Washing and drying the gel obtained;

6. Destruction of the surfactant by calcining the gel at 650°C and obtaining the final material.

Surface measurements by the BET method show that the specific surface area of the prepared material greatly exceeds that of sand. These results open new perspectives for the valorization of desert sand in the manufacture of porous materials with wide field of applications (adsorption, heterogeneous catalysis ... and so on).

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