



ORIGINAL ARTICLE

Synthesis and characterization of silica gel from siliceous sands of southern Tunisia



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Abstract The present work aimed to achieve valorization of Albian sands for the preparation of sodium silicates that are commonly used as a precursor to prepare silica gel. A siliceous sand sample was mixed with sodium carbonate and heated at a high temperature (1060 °C) to prepare sodium silicates. The sodium silicates were dissolved in distilled water to obtain high quality sodium silicate solution. Hydrochloric acid was then slowly added to the hydrated sodium silicates to obtain silica gel. The collected raw siliceous sands, as well as the prepared silica gels, were characterized by different techniques, such as X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal analysis (DSC). XRF confirmed that the detrital sand deposits of southern Tunisia contain high amounts of silica, with content ranging from 88.8% to 97.5%. The internal porosity varied between 17% and 22%, and the specific surface area was less than 5 m²/g. After the treatment described above, it was observed that the porosity of the obtained silica gel reached 57% and the specific surface area exceeded 340 m²/g. Nitrogen adsorption isotherms showed that the prepared silica gels are microporous and mesoporous materials with high adsorption capacities. These results suggest that the obtained silica gels are promising materials for numerous environmental applications.

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1. Introduction

In southern Tunisia, the Dahar plateau extends from Tataouine in the north to the Tripolitan border in the south and is bordered to the east by the Jeffara coastal plain. The stratigraphic succession covers all Mesozoic periods and provides very important reserves of siliceous sands (Busson, 1967; Ben Ismail et al., 1989; Benton et al., 2000). These deposits, which are exposed along Dahar cliffs, are excavated for use in building. However, investments in these natural resources remain below the expected levels because of the lack of detailed studies

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encouraging developers to focus on the exploitation of silica sands.

For this reason, Tunisia is pursuing policies aimed at expanding the use of local materials, such as carbonates, clay and silica sands. Many works have been undertaken to deepen knowledge of facies, thickness variation and the physical and chemical characteristics of Albian sands of southern Tunisia (Bouaziz et al., 1989; Louhaichi, 1991; Bouaziz, 1995). High purity siliceous materials are used for glass making (Louhaichi, 1991) and, more recently, for various environmental applications (Besbes, 1999; Jesionowski, 2002; Marzouk et al., 2004).

Silica gels, which are known for their high specific surface area and their good gas adsorption capacities, could be produced from sodium silicate solutions by hydrothermal methods using sol-gel processes (Bouaziz et al., 1993; Marzouk et al., 2004).

This work aimed (1) to characterize a local material (silica sands), (2) to prepare a local adsorbent that would partially substitute for imported zeolite and active carbon and (3) to seek possible environmental uses for local silica sands.

2. Materials and experimental methods

2.1. Materials

For the purpose of this study, six sand samples were collected from the Albian continental formation outcropping in Douiret (S1), Oum diab (S2, S3), Ouni (S4) and Dehibat (S5, S6) in

Tataouine district (southern Tunisia) (Fig. 1). The continental deposits of the Oum diab formation consist of 15 m thick sand layers alternating with shale. At the “bled Oum diab” location, outcropping beds contain up to 20 m of loose sands. Special attention was devoted to this location due to the promising physicochemical characteristics of the deposits.

2.2. Physical and chemical characterization

Prior to analyses, samples were dried for 24 h at 105 °C under vacuum conditions. Grain size distribution was carried out by dry sieving. The chemical composition of the studied samples was determined using X-ray fluorescence with an ARL® 9800 XP spectrometer (Thermo electron corp., Germany). Differential scanning calorimetry (DSC) was performed with a Perkin Elmer thermal analysis system (PerkinElmer Inc., Germany). About 5 mg of < 63 µm-sized samples were heated from room temperature to 600 °C at a heating rate of 10 °C/min under air atmosphere. The total pore volume and percentage of porosity were determined by pycnometry. X-ray diffraction patterns were obtained by an X-ray diffractometer (“PANalytical X’ Pert High Score Plus”, The Netherlands) equipped with a dual goniometer of Cuα ($\lambda = 1.5406 \mu\text{m}$) using an acceleration voltage of 40 kV. The diffraction angle was scanned from 5° to 70° 2θ, at a range of 2°/min. SEM images were obtained using a Philips XL-30 electron microscope (Philips Electronics corp., The Netherlands).

The specific surface area and pore size distribution were determined with a SORPTOMATIC 1990 (CE instrument,

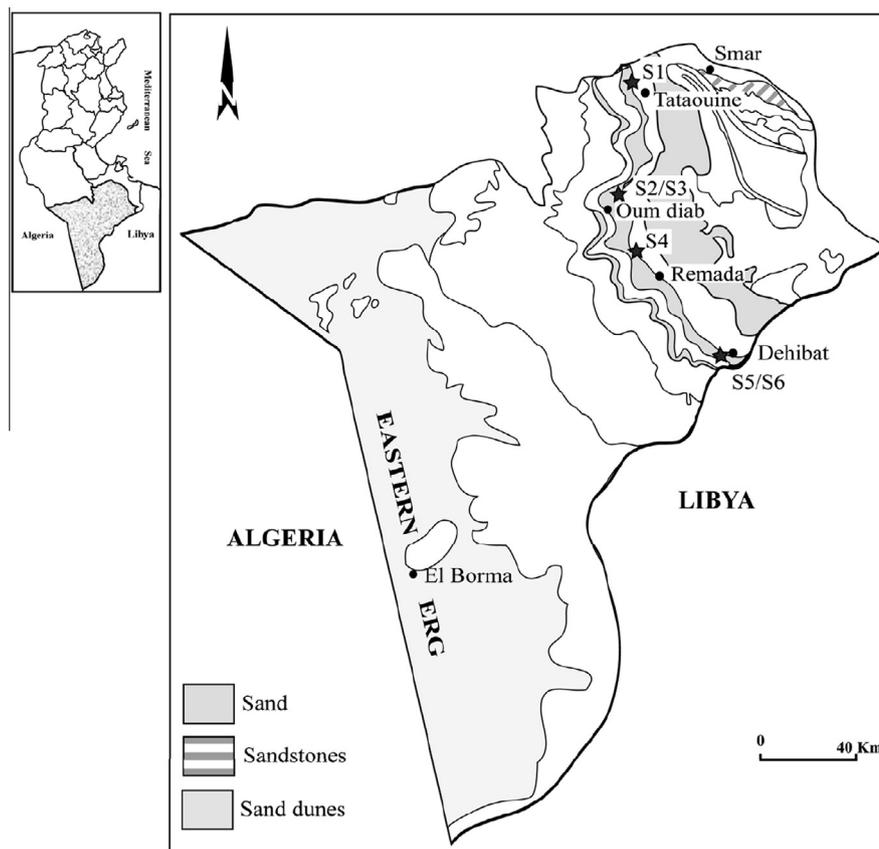


Figure 1 Outcrops of the continental deposits of southern Tunisia (modified after Bouaziz et al., 1989) and locations of the collected sand samples (stars).

Table 1 Physicochemical properties of the collected sand samples.

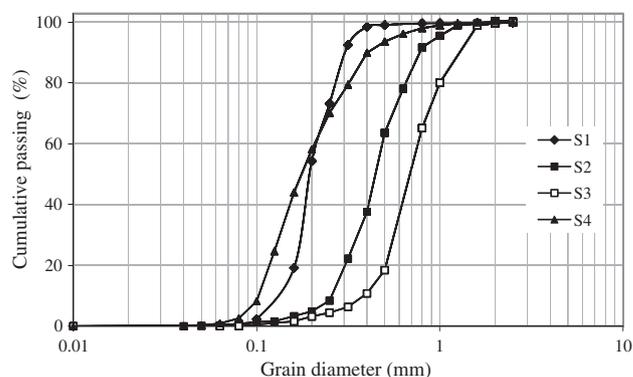
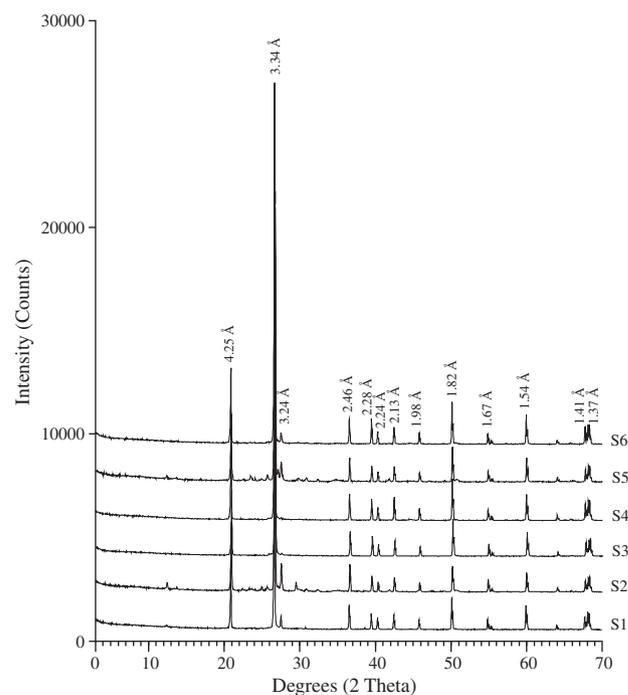
Sample	Locality	Chemical composition (wt%)						Physical properties					
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	LOI	ρ_{abs} (g/cm ³)	ρ_{app} (g/cm ³)	Porosity (%)	Pore volume (cm ³ /g)	S _{BET} (m ² /g)	
S1	Douiret	94.44	2.32	2.23	0.32	0.12	0.37	2.49	2.11	15.26	0.07	5.0	
S2	Oum diab	88.80	5.88	2.01	2.68	0.20	1.27	2.40	1.98	17.21	0.09	4.5	
S3		97.43	1.36	0.67	0.06	0.11	0.18	2.70	2.08	22.96	0.11	1.2	
S4	Oumi	95.96	1.25	2.33	0.07	0.08	0.12	2.50	1.98	21.24	0.11	–	
S5	Dehibat	91.27	4.29	2.15	1.37	0.18	0.51	2.63	2.19	16.81	0.08	3.0	
S6		96.45	2.08	0.63	0.35	0.13	0.17	2.65	2.00	24.53	0.12	1.5	

LOI, loss on ignition.

Germany) using the adsorption–desorption isotherms of nitrogen.

2.3. Synthesis of silica gels

The preparation of silica gel from the selected siliceous sand (S3) began with: (1) the preparation of metasilicate sol and (2) the destabilization of metasilicate sol with dropwise addition of 2 M hydrochloric acid under continuous stirring (Bouaziz et al., 1993; Besbes, 1999; Marzouk et al., 2004). Silicates were prepared by heating a mixture of sands and sodium carbonate of a known molar ratio SiO₂/Na₂O. The resulting vitreous compound was dissolved in hot water to prepare hydrated sodium silicate. The last step consisted of preparing silica gel particles. These experiments were carried out by dropwise addition of 2 M hydrochloric acid to diluted sodium silicate under continuous stirring until polymerization. The obtained silica gels were washed several times with distilled water

**Figure 2** Granular curves of the representative sand samples.**Figure 3** XRD patterns of the collected sand samples.

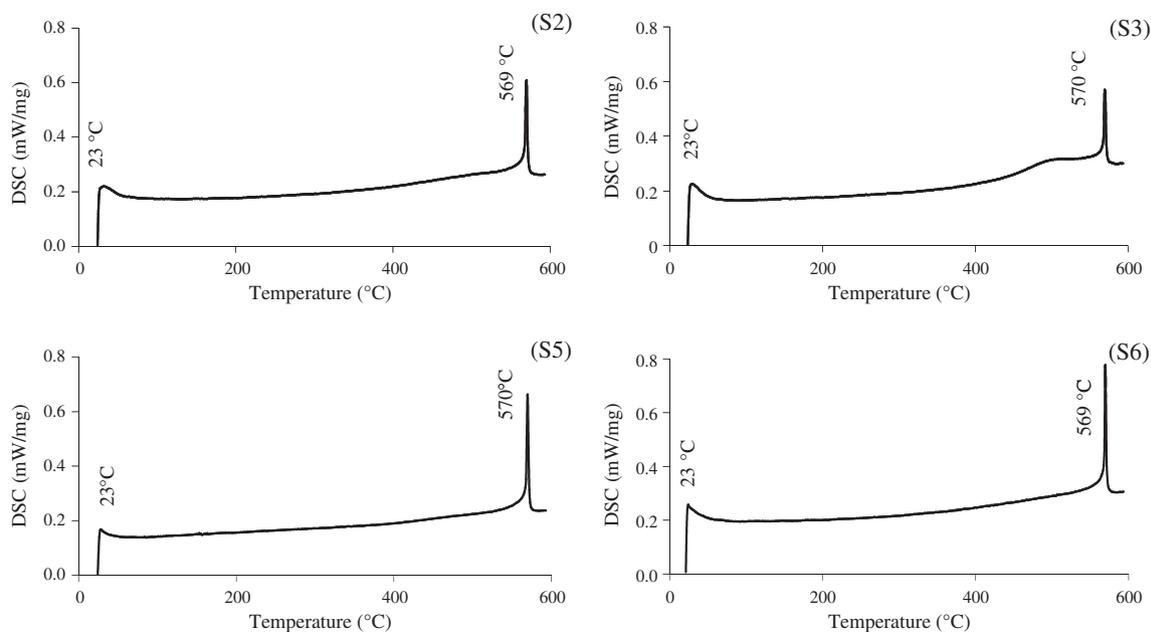


Figure 4 Thermal curves of representative sands.

to remove chloride anions, dried at 105 °C for 24 h and stored in desiccators for further analysis. Eight gel samples (G1–G8) were prepared at different pH and molar ratios.

2.4. BET adsorption isotherms

The degassed silica gel powder was kept inside a glass tube; nitrogen was used as an adsorbate at 77 K to form a monolayer on the sample (Benzina, 1990; Benzina and Bellagi, 1990). At each step, a certain volume (V) of nitrogen was adsorbed by the walls of the pores, and the corresponding change in partial pressure (p/p_0) was recorded. The lower portion of the adsorption isotherm was used for the measurement of specific surface areas, whereas the entire adsorption-desorption isotherm was used for pore analyses (Jesionowski, 2002).

Physical gas adsorption is often the technique of choice for examining the pore characteristics of materials (Benzina, 1990; Benzina and Bellagi, 1990). The technique determines the amount of gas adsorbed on silica gel; this is a direct indication of the porous properties, and, therefore, the overall structure, of the material. The isotherm obtained from these adsorption measurements provides information about the surface area, pore volume and pore size distribution (Gregg and Sing, 1982; Groen et al., 2003). Silica gel samples were degassed at 150 °C for 180 min before measurements.

3. Results and discussions

3.1. Characterization of sands

3.1.1. Chemical composition

Chemical compositions of silica sands by X-ray fluorescence are shown in Table 1. The amount of SiO_2 ranged from 88.80% to 97.40%. Silica content plays an important role in

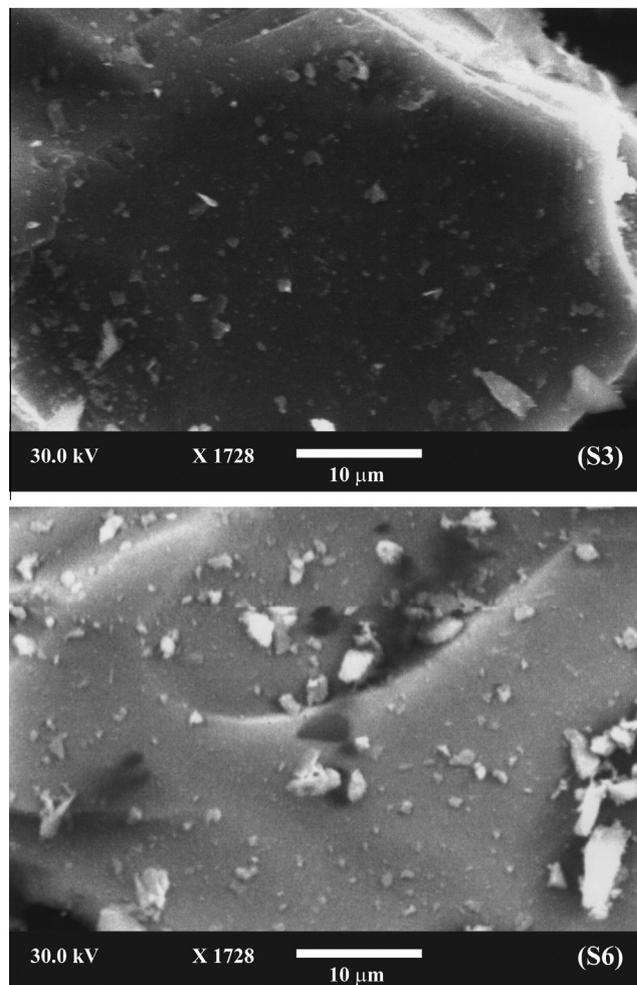


Figure 5 SEM photograph of representative sands.

the production of pure sodium silicates from sands. Al_2O_3 and Fe_2O_3 reached 5.88% and 2.33%, respectively, together with small amounts of K and Mg oxides. Loss on ignition (LOI) varied between 0.12% and 1.27%. Based on chemical analyses, only the pure sand sample (S3) was selected for the preparation of high quality sodium silicates.

3.1.2. Grain size distribution and porosity measurements

The particle size distributions of the studied sand samples showed that these samples are fine to very fine. The S3 sample (collected in the Oum diab location) was coarser than the other samples (Fig. 2). All curves showed redressed sigmoid shapes indicating little variation in their granulometry (Bederina et al., 2005). In addition, a sorting index (SO) (defined as $\text{SO} = \sqrt{q_3/q_1}$) confirmed well-sorted sands, where q_1 and q_3 represent the grain-size corresponding to cumulative contents of 75% and 25%, respectively.

The physical properties of the studied sands are given in Table 1. Results show that the porosity varies from 15% to 24%, and apparent density was between 1.98 and 2.19 g/cm^3 , whereas absolute density ranged between 2.49 and 2.65 g/cm^3 . These values may indicate that the studied material has a low specific surface area, as was confirmed by the pore volume of less than 0.123 cm^3/g .

3.1.3. X-ray diffraction (XRD)

XRD patterns of studied sands are shown in Fig. 3. Those patterns indicate the characteristic peak of quartz prevailing at 3.34 Å. The other peaks appearing at 4.25, 3.24, 2.46, 2.28, 2.24, 2.13, 1.98, 1.82, 1.67 and 1.54 Å are also characteristics of quartz and confirm the siliceous nature of the Albian sands of southern Tunisia. Detailed mineralogy was identified by the characteristic reflections according to Moore and Reynolds (1989).

Table 2 Physical properties of prepared silica gels.

Sample	pH	Molar ratio = n $\text{SiO}_2/\text{Na}_2\text{O}$	ρ_{abs} (g/cm^3)	ρ_{app} (g/cm^3)	Porosity (%)	Pore volume (cm^3/g)	V_m : monolayer volume (cm^3/g)	S_{BET} (m^2/g)
G1	6	2.5	1.11	0.75	33.00	0.44	79.86	340
G2	3	2.5	1.72	1.03	40.25	0.39	142.40	668
G3	6	2.5	1.51	0.81	46.21	0.57	109.98	464
G4	9	2.5	1.51	0.89	41.34	0.47	86.82	371
G5	3	3.5	2.20	1.30	40.90	0.31	163.30	702
G6	6	1.5	2.08	1.08	49.20	0.46	125.85	590
G7	9	1.5	1.44	0.70	51.40	0.73	133.79	602
G8	6	3.5	1.77	0.76	57.06	0.75	87.98	374

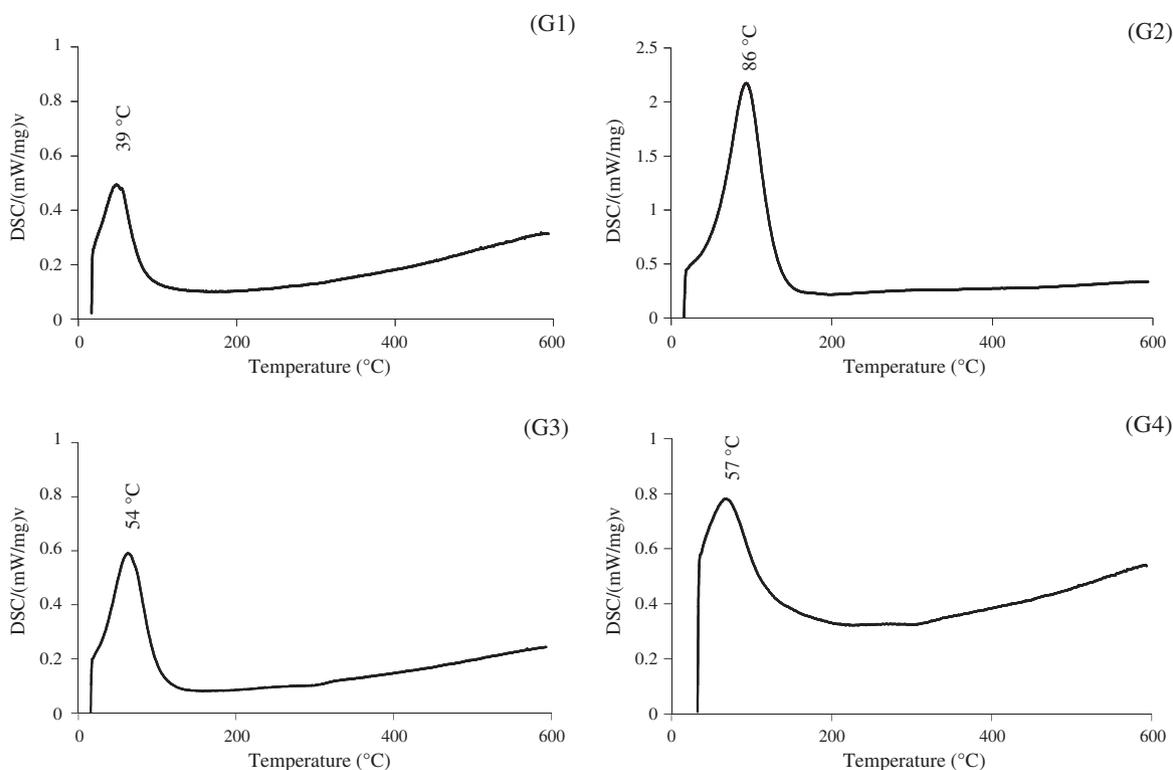


Figure 6 Thermal curves of representative silica gels.

3.1.4. Differential scanning calorimetry (DSC)

According to the thermal analysis data (Fig. 4), each curve presented two peaks. The first peak (at 23 °C) corresponded to the energy provided to remove physically bound water, while the second one was ascribed to the transformation from $\text{SiO}_2\alpha$ to $\text{SiO}_2\beta$ near 570 °C. Some thermal curves also showed an additional endothermic hump at 500 °C, which was attributable to the dehydroxylation of clay minerals (Chakchouk and Samet, 2006; Sdiri et al., 2010).

3.1.5. Scanning electron micrograph (SEM)

It can be seen from the SEM images that Albian sands exhibit smooth grains, confirming the textural data (surface area and porosity) (Fig. 5). It was obvious that the absence of micropores and mesopores in the studied siliceous sands of southern Tunisia provide such a texture. Therefore, it was expected that this material would show low specific surface area and internal porosity.

3.2. Characterization of the prepared silica gels

3.2.1. Physical properties

Physical properties of the prepared silica gels are shown in Table 2. Porosity measurements by the pycnometric method show that the obtained silica gels are characterized by high porosity, varying between 33% and 57.06% for G1 and G8, respectively. Both absolute and apparent densities are lower than 1.3 g/cm^3 , showing that the prepared silica gels are classified as lightweight materials (Table 2). This property may be beneficial for the use of the prepared gel in many environmental and industrial applications.

3.2.2. Differential scanning calorimetry (DSC)

Thermal curves, measured from ambient to 600 °C, are shown in Fig. 6. The DSC curves showed endothermic peaks at 39, 86, 54 and 57 °C for G1, G2, G3 and G4, respectively. These reactions were due to the removal of physically bound water. This was further confirmed by enthalpy values ranging between 7.2 and 11.75 J/g. The water molecules bound to the G2 sample evaporated at a higher temperature of 86 °C. The G2 sample had the highest specific surface area among the studied samples (G1, G2, G3 and G4); this likely explains its higher water adsorption capacity. Therefore, the strongly bound water molecules were not easily removed from the surface. Between 100 and 600 °C, the thermal curves did not show significant variation.

3.2.3. Scanning electron micrograph

Various SEM images of the obtained silica gels showed their porous structure (Fig. 7). In general, similarity in SEM morphologies accounts for the uniformity of the silica source (sands) that produced silica gels with comparable particle sizes (Tsai, 2004; Kima et al., 2005). The observation of pore sizes using SEM confirmed that the obtained silica gels are mesoporous, microporous materials.

3.2.4. BET adsorption isotherms

Fig. 8 shows the nitrogen adsorption isotherms of the representative silica gels. It can be seen that this material has both microporous and mesoporous structures. These physical properties depend on pH and molar ratio ($\text{SiO}_2/\text{Na}_2\text{O}$), as described in the literature (Bouaziz et al., 1993; Besbes, 1999;

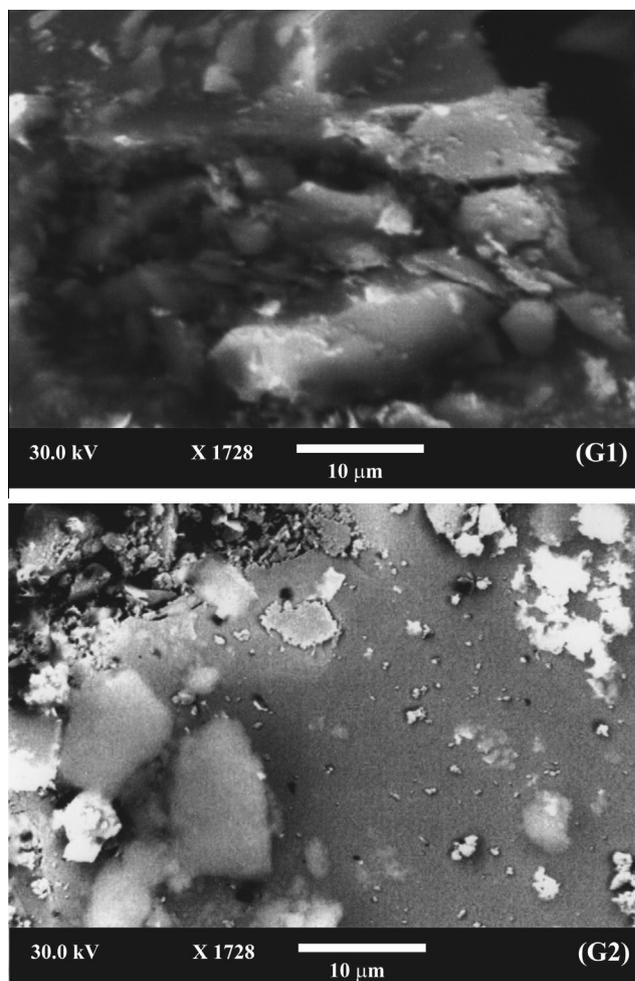


Figure 7 SEM photographs of representative silica gels.

Kwon and Park, 2004). G2 and G5 silica gel powders are microporous in structure, while G1 and G4 are mesoporous (Fig. 8). Adsorption on G2 and G5 resulted in type I isotherms in the BET classification. This is indicative of microporosity, along with very limited mesoporosity (Groen et al., 2003). In contrast, G1 and G4 gave type IV isotherms, indicating mesoporous materials. In these cases, capillary condensation occurs during adsorption via “cylindrical meniscus”, while capillary evaporation during desorption occurs via “hemispherical meniscus”, separating the vapor and capillary-condensed phases. This results in hysteresis loops (Fig. 8a and c) and confirms the mesoporous structure of the prepared silica gels (Groen et al., 2003).

Table 2 shows the parameters derived from BET nitrogen gas adsorption isotherms. It can be seen from these results that specific surface area was directly related to the type of isotherm, and consequently to the pore structure. Moreover, adsorption-desorption properties of the prepared silica gels are likely to be influenced by some network effects, such as the tensile strength effect (Groen et al., 2003; Dutta et al., 2005). Specific surface area (S_{BET}) of the prepared silica gels ranged between 340 and 702 m^2/g and provided high adsorptive capacity. This observation was further confirmed by the high volume of adsorbed nitrogen (Table 2). It was clearly observed that the specific surface area was higher for a pH of 3,

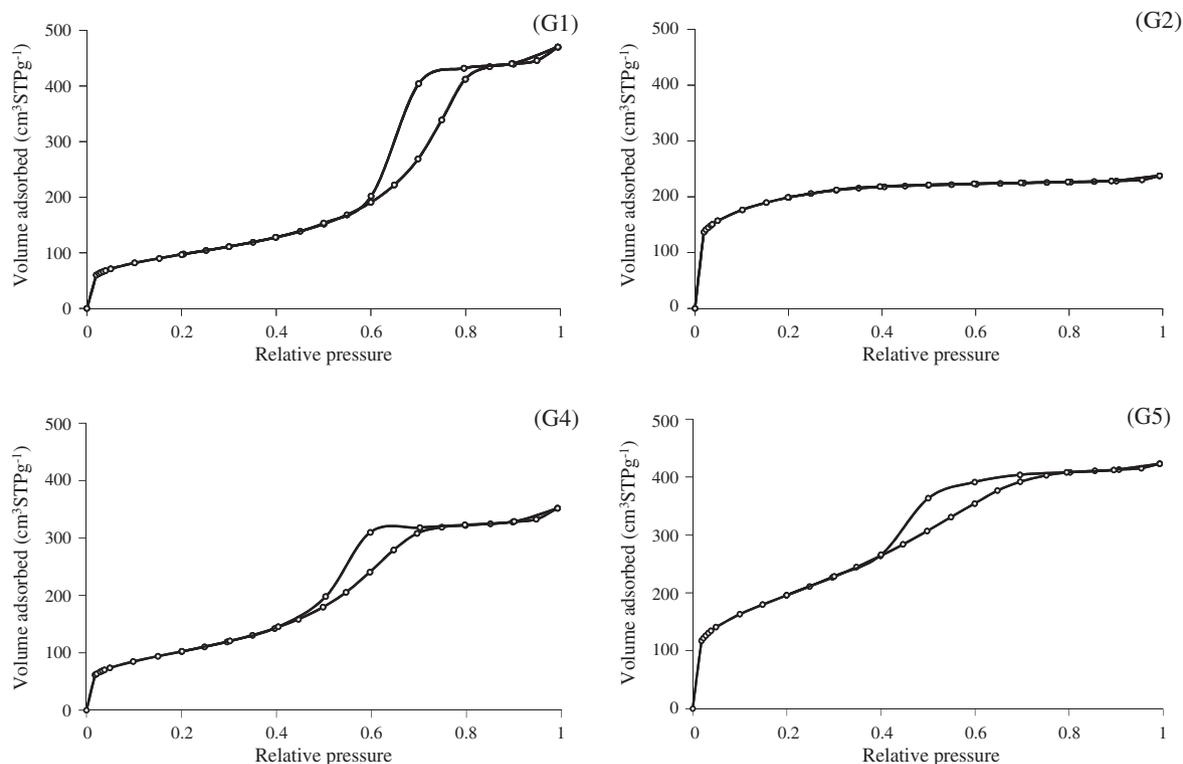


Figure 8 Nitrogen adsorption isotherms at 77 K for representative silica gels.

proving the higher monolayer volume of adsorbed nitrogen. The effect of pH was shown to be an influencing factor on the structure of the silica gel obtained. However, the effect of the molar ratio ($\text{SiO}_2/\text{Na}_2\text{O}$) was likely to follow a random distribution.

4. Conclusions

This work was undertaken in order to exploit the potential local sands for the preparation of silica gel. It was concluded that the studied sands consisted of more than 89% silica. In addition to its current use as a building material, the continental deposit of southern Tunisia would provide an additional resource for manufacturing high quality glassware. Furthermore, the Albian sands at the Oum diab site were found to be suitable for the preparation of high quality sodium silicate, used as a precursor in the preparation of silica gel. The specific surface area of the prepared silica gels exceeded $340 \text{ m}^2/\text{g}$, and the monolayer volume was higher than $79 \text{ cm}^3/\text{g}$. The microporous and mesoporous natures of these products constitute promising characteristics for their use as adsorbents in environmental projects, such as heavy metal removal from wastewater and the adsorption of volatile organic compounds. The use of silica gels prepared from Tunisian sands as an adsorbent needs further examination.

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