

Preparation of Silica Gel Obtained From Early Cretaceous Sidi Aich Sands (Central Tunisia)

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Abstract

The study describes the chemical–mineralogical characterization of Barremian sand deposits. These Sidi Aich sands were collected in central Tunisia. The collected raw silica sand from the Jebel Meloussi (central Tunisia) was characterised by different techniques, such as X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM). X-ray diffraction showed a predominance of quartz and potassic feldspars and lower amounts of kaolinite and calcite. The obtained silica gels had pore diameters over 20 Å and specific surface areas up to 183 m²/g, close to those reported for commercial silica gel materials. The N₂ adsorption isotherms have shown that new materials synthesised from Tunisian silica sands are mesoporous materials with high chemi-physical adsorption capabilities.

1 Introduction

The exploitation of deposits and more particularly the silica sands has become an important activity for the industrial development (manufacture of glass, pigments and silica gels) considering the increased consumption of these substances in the industry. While their uses are subject to specific criteria according to well-defined standards.

World production of silica sand for the needs of the industry is about 140 Mt / year: United States (24%), the Netherlands (20%) and France (5%). The price of silica sand varies according to its characteristics (such as particle size and purity). The silica sands cost 35 dollars/tones, while the price of extra-silica sands can reach 40 dollars/kg.

Global reserves of silica sands are important and represent more than a century of consumption at the current rate of production. In Tunisia, there are large deposits of silica sands. These materials have an economic significant interest. Indeed, the consumption of silica sands in Tunisia has not ceased to increase given the large quantity of silica sands imported from various countries such as: Belgium, France, Germany, Italy, Spain, USA, Mexico ...

In 2015, imports of silica sand were estimated about 11.5 Million USD, (INS, 2016). These imports weigh for the country's trade balance and the deadlines for completion of the various projects. In order to make up for this deficiency in silica sands, several prospecting works have been carried out previously to search for potential resources in these materials [1–5].

Silica gel is an amorphous material with a high adsorption capacity [6]. This material is used as a moisture adsorbent or in the purification of effluents [7–9]. This material has several advantages:

- Easy to regenerate (Silica gel when it becomes saturated can be regenerated by heating at 100 - 120 °C until it returns to its original state);
- Non-toxic, environmentally benign and chemically inert with a high melting point (it is very similar to silica sand and quartz and can therefore be transferred safely by any means of transport).

Recent studies have investigated the versatility of this amorphous material in applications including fillers [10], coatings [11], electronics [12] optics [13], and pharmaceuticals [14]

This work is aimed to promote local georesources (silica sands) for the preparation of silica gel.

2 Experimental Details

2.1 Geological setting

In this study, the natural sand (M) material was collected from the Barremien deposits (Sidi Aich Formation) outcropping of Jebel Melloussi (central Tunisia) (Fig. 1). The Sidi Aich Formation was deposited in a regressive context in a field of passive margin [15, 16] Central Tunisia is characterised by E–W and NW–SE oriented faults [17].

2.2 Methods

The mineralogical composition of the raw samples (silica sand) and the silica was carried out by X-ray diffraction (XRD) using a Panalytical X'Pert PRO X-ray diffractometer (CuK α , $\lambda = 0.154056$ nm) [18]. The collected data ($10\text{--}80^\circ$ 2θ range, scan rate of 0.02° (2θ)) were processed by Panalytical X'Pert Highscore software. The chemical composition of these silica sands was estimated, on powdered samples, by X-ray fluorescence (XRF) using a PanalyticalAxios Dispersive X-ray Fluorescence Spectrometer. The distribution of grain sizes was found by dry sieving using the AFNOR series (the French normalisation system). Scanning electronic microscopy (SEM) was used to investigate the morphology of the products (Hitachi, SU 70). Specific surface area (SSA) and the porosity were measured by the Brunauer, Emmett and Teller method (BET) using a FlowPrep060 system, via nitrogen adsorption and desorption at 77 K. Sieved fractions under 150 microns in size were degassed for 72 hours at 70 °C under high vacuum [19].

2.3 Silica gel preparation

The fabrication of silica gel was carried out in three steps:

- 1) the synthesis of sodium silicates
- 2) their dissolution, and
- 3) the formation of silica gels (GM).

An intermediate compound of amorphous sodium silicate was produced by heating a mixture of sodium carbonate and silica sand at 1060 °C, with molar ratios of $\text{SiO}_2/\text{Na}_2\text{O} = 1.5$ [20,21]. 10 g of this product was then dissolved in 500 ml of distilled water at 160 °C, while being stirred for 10 min, to obtain the hydrated sodium silicate [20,22]. The final product (silica gel) was extracted after the drop wise addition of a 2M solution of hydrochloric acid at pH 3, followed by washing with distilled water to eliminate

chloride ions [21,23]. This was then dried for 24 h / 60 °C in a drying oven. The stages are depicted in Fig. 2.

We report here the preparation of silica gels at various pH values of 3, 6 and 10 from silicates, which were denoted as GM3, GM6 and GM10, respectively (Table 1).

3 Results And Discussions

3.1 Characterisation of studied sands

The XRD of the raw sample shows the presence of quartz (91%) associated to feldspars (7%) (Fig. 3). Minor proportions of kaolinite and calcite were also detected. The dominance of quartz suggests that the depositional basins were associated with a passive margin [16]. Table 2 also gives the chemical composition of the tested silica sand sample by X-ray fluorescence. This analysis showed a dominance of SiO₂ (84.30%) and Al₂O₃ (7.45%).

The particle size distribution of "M" quartz sand (Sidi Aich Formation) presents a mean size approximating 150 µm (Fig. 4).

3.2 Characterisation of the silica gel

The XRD patterns of the silica gels are shown in Fig. 5. The obtained material (silica gel) has virtually identical mineralogical compositions irrespective of the pH during synthesis. All are characterised by a large amorphous hump centred at around $2\theta = 23^\circ$, indicating their accentuated amorphous nature.

The SEM images of silica gel are reported in Fig. 6. The silica gels all exhibit similar structures, consisting of large aggregations of particles between 1.14-5.45 µm. The variation in size is caused by the aggregation of the silica gel particles, and contributes greatly to their inter-particle porosity. This mirrors the results found by Brahmi et al. (2014) [22] for a similar size of silica gel, prepared from Algerian siliceous sands.

The BET specific surface area (SSA) of the silica gels prepared from the Tunisian silica sands (M) are shown in Table 1. The SSA of the silica gels prepared at pH 3, 6 and 10 were 183, 86 and 39 m²/g, respectively. This demonstrates that the silica gel synthesised at pH 3 (GM3) clearly had a higher SSA compared to that produced at pH 6 (GM6) and pH 10 (GM10). The SSA value of this silica gel prepared at pH 3 is very close to that of a commercial silica gel (GI, Industrial Gel), which is 253 m²/g. These values are also in excellent agreement with previous literature results. Nitrogen adsorption-desorption isotherms of our silica gels are shown in Fig. 7, possessing a type II adsorption isotherm. They have pore volumes ranging from 0.10 to 0.42 cm³/g (see Table 1), and have pore diameters between 68 to 118 Å. The largest values are for GM3, indicating that this is a mesoporous material, with pore diameters > 20 Å [24].

The silica gel synthesised at pH 3 (GM3) shows an isotherm with a type H2 hysteresis loop, which indicates the presence of spherical pores [22,25]. This sample has a broad H2 type loop, in which the

desorption branch is at a much steeper angle than the adsorption branch. With synthesis at a neutral pH of 6), desorption begins slowly, which may be due to their being interconnected pores of varying shapes/forms [22]. The adsorption–desorption isotherm of this silica gel (GM6) is wider at relative pressures (P/P_0) = 0.6. For synthesis in an alkaline medium at pH = 10 the isotherms do not have a plateau when the relative pressure (P/P_0) approaches 1. This is a hysteresis loop shape typical for aggregates, and it was observed that the silica gel's BET SSA decreased when synthesis was carried out in a neutral or alkaline medium, this effect increasing with pH. This is in good agreement with previously reported results [22,25].

4 Conclusion

In this work, it has been studied the used to a local natural Tunisian quartz sand for the preparation of silica gels. It was concluded that the quartz sands consisted mostly of silica and feldspars. The silica gel could reach specific surface areas up to 183 m²/g. These characteristics display a very porous texture and consequently, a great potential of adsorption for this new material.

Declarations

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Author Contribution The authors equally contributed for the preparation of the manuscript

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Availability of Data and Material The data and material are available within the manuscript.

Compliance with ethical standards

This is the new work and submitted to any journal first time. The manuscript is praped as the ethical standard.

Conflict of interest: The authors declare that they have no conflict of interest.

Consent to Participate Yes

Consent for Publication Yes

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Tables

Table 1 Synthesis conditions and physical properties of prepared silica gels. G: Silica Gel, M: Melloussi, I: Industrial, pH = 3, 6 or 10

Sample	pH	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)
GM3	3	183	0.42	103
GM6	6	86	0.19	68
GM10	10	39	0.10	118
GI		253	0.28	45

Table 2 Mineralogical and chemical quantification of studied silica sand samples (M: Melloussi). LOI = loss on ignition

	M
Quartz	91
Feldspars	7
Calcite	1
Kaolinite	1
SiO ₂	84.30
K ₂ O	5.76
Al ₂ O ₃	7.45
Fe ₂ O ₃	0.71
Cr ₂ O ₃	0.05
TiO ₂	0.72
MnO	-
CaO	0.26
LOI	0.80

Figures

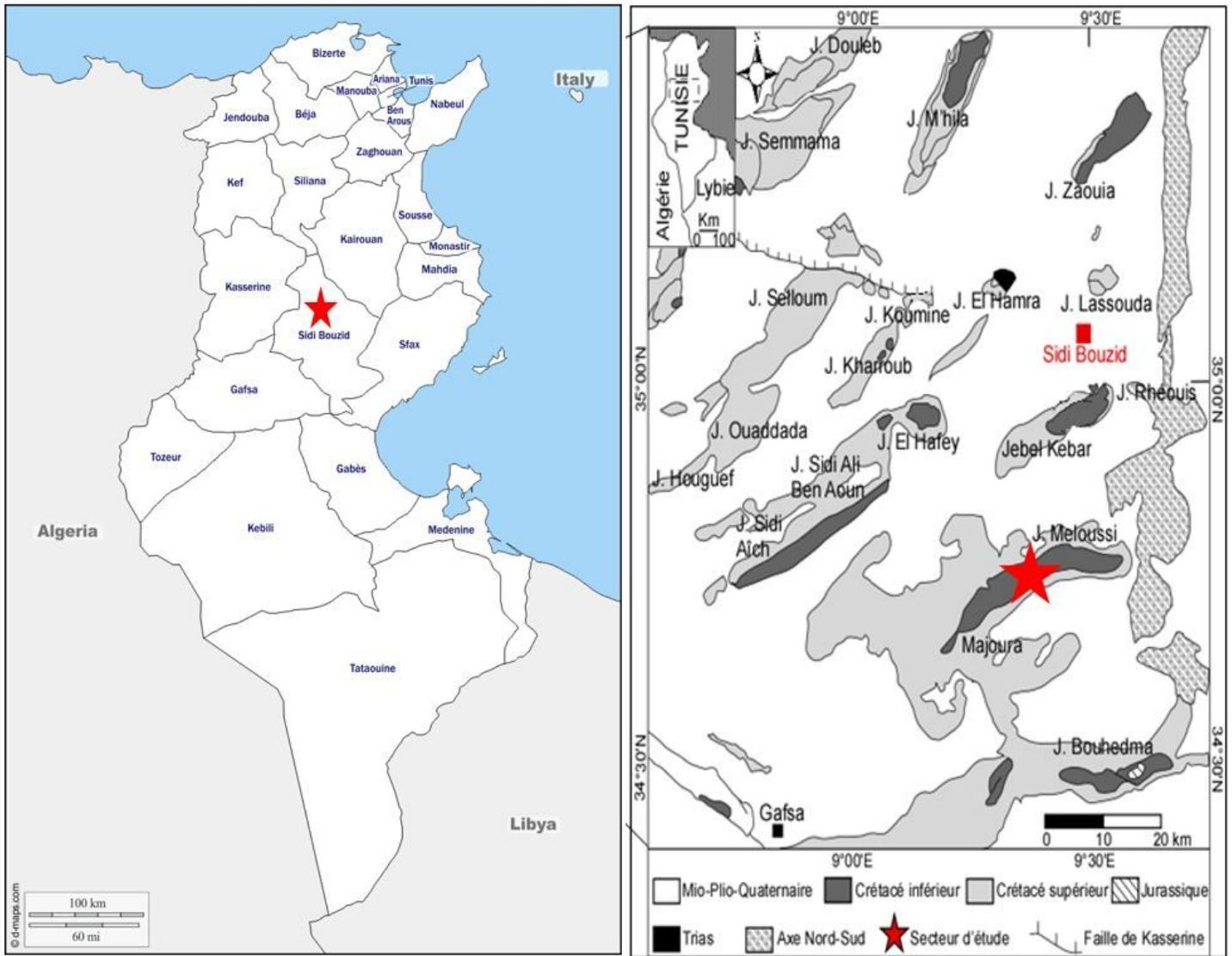


Figure 1

Location of Study Area Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

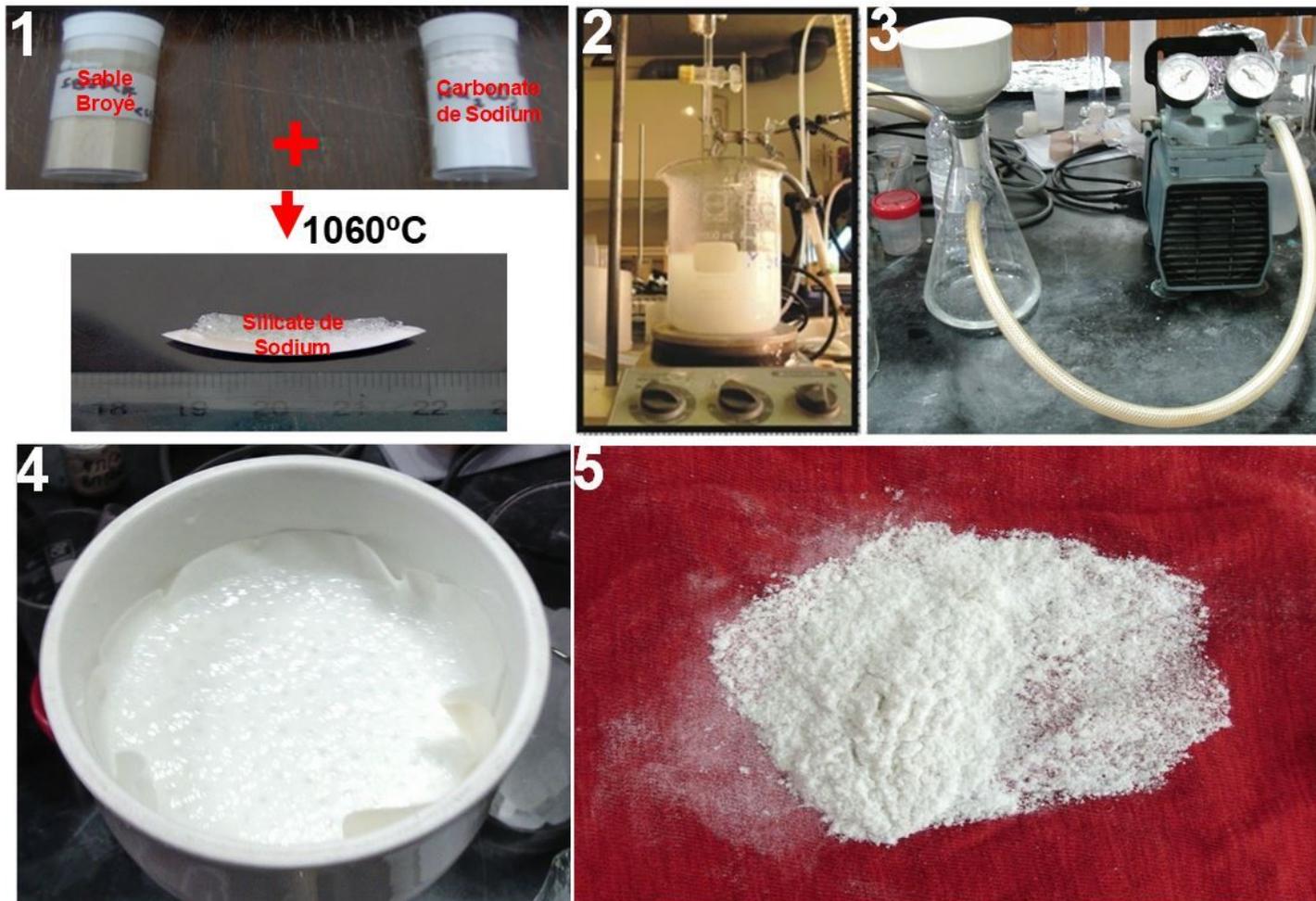


Figure 2

The stages of manufacturing a silica gel

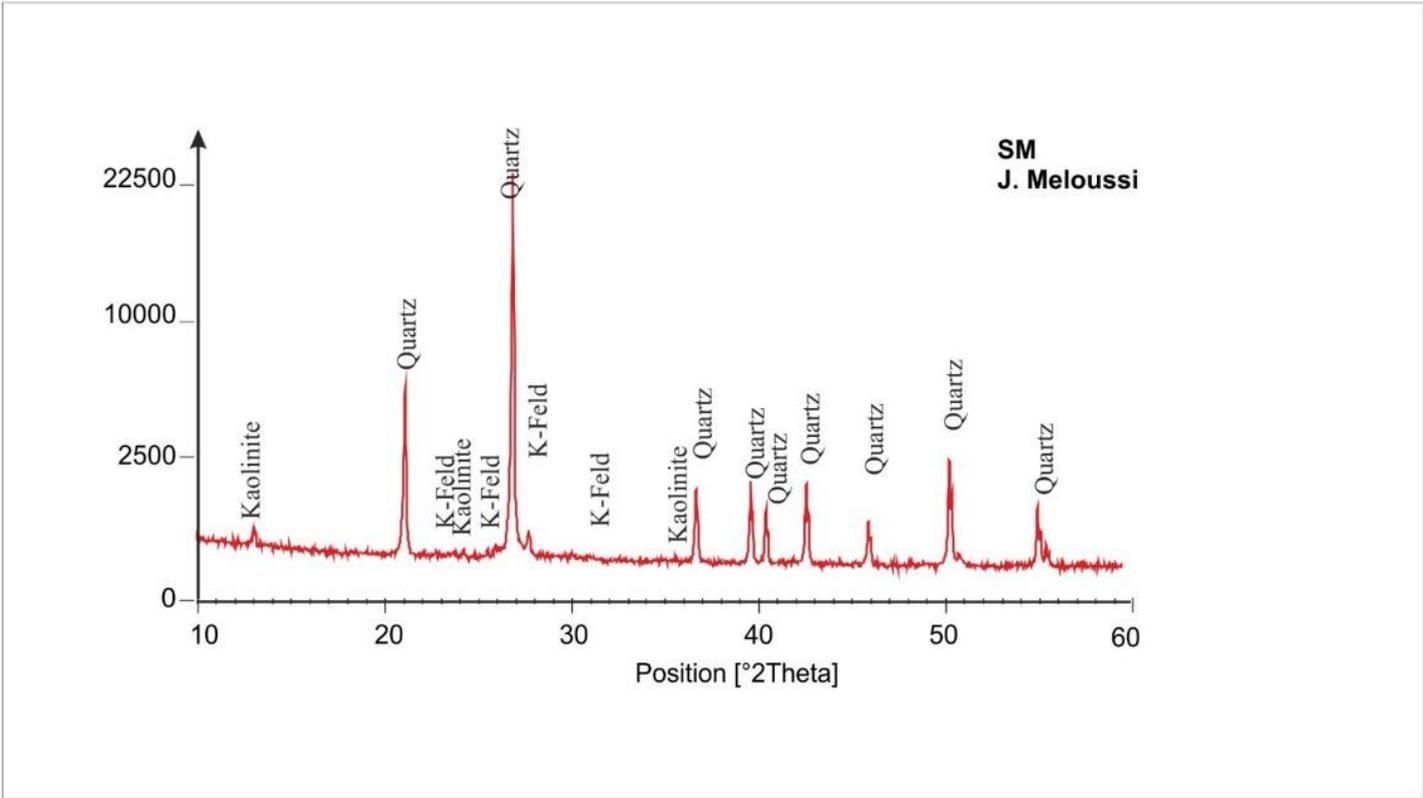


Figure 3

Mineralogical analysis of quartz sand sample

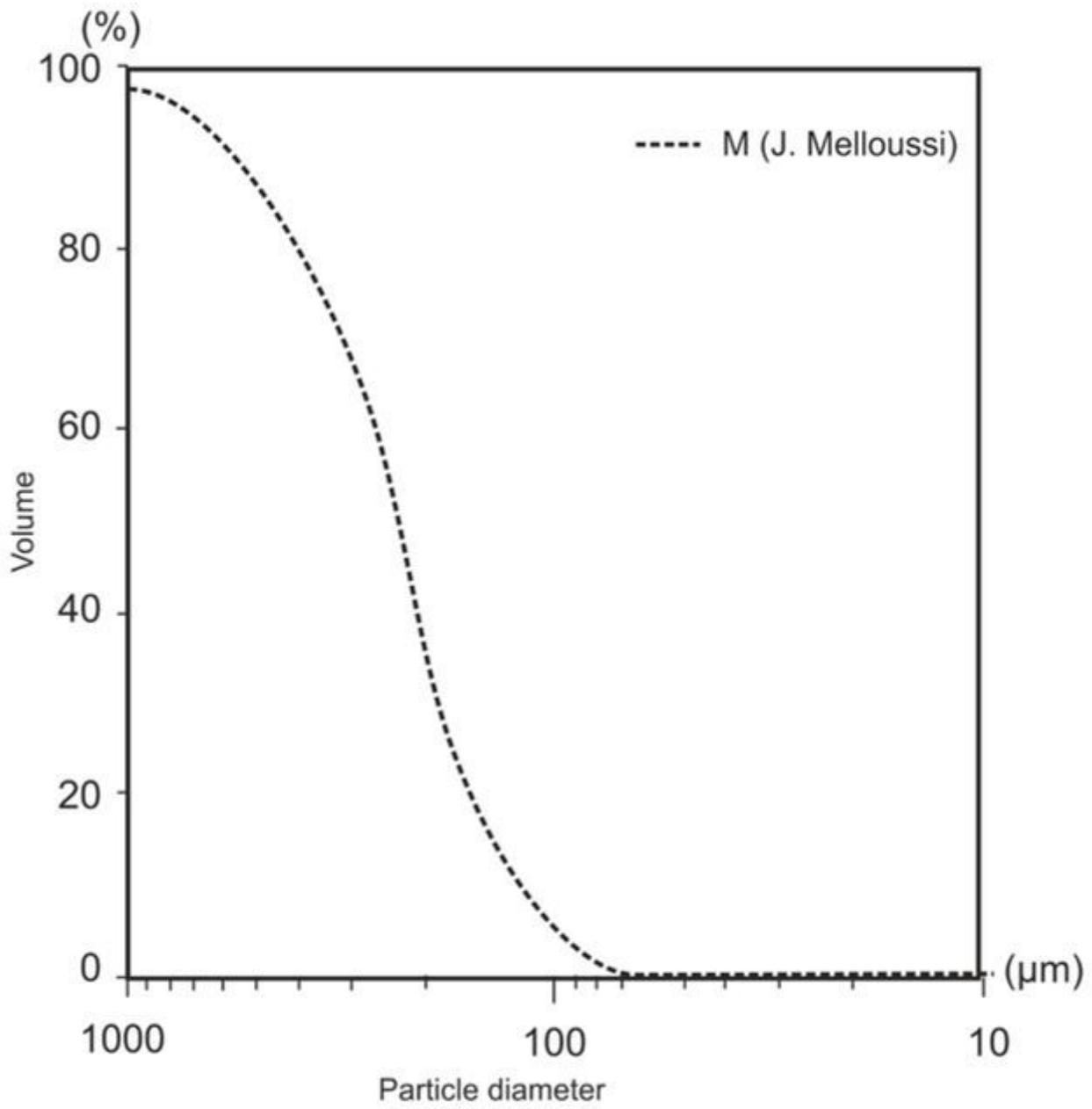


Figure 4

Granular distribution of the quartz sand

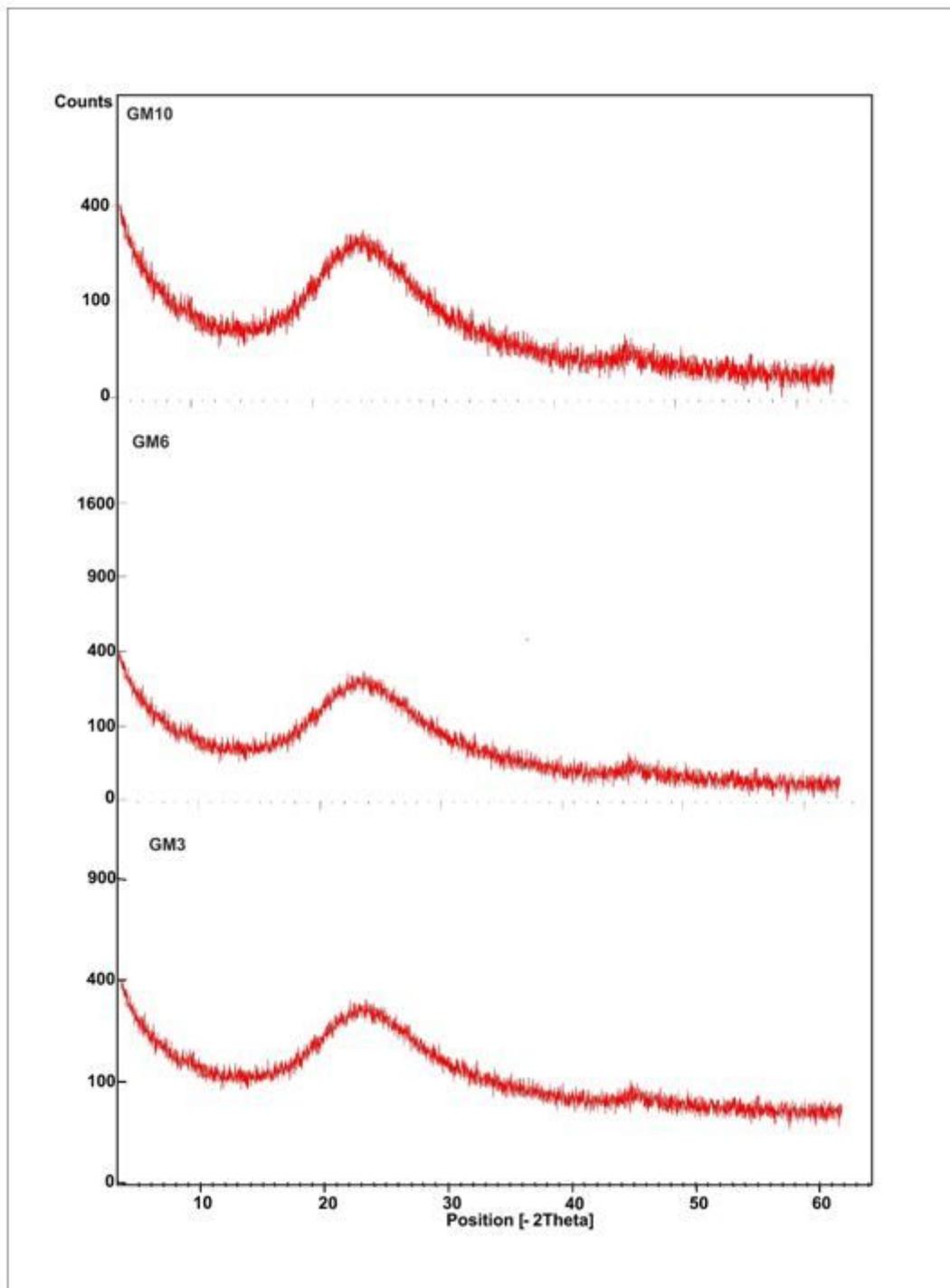


Figure 5

Mineralogical analysis of silica gel at different pH (3, 6 and 10)

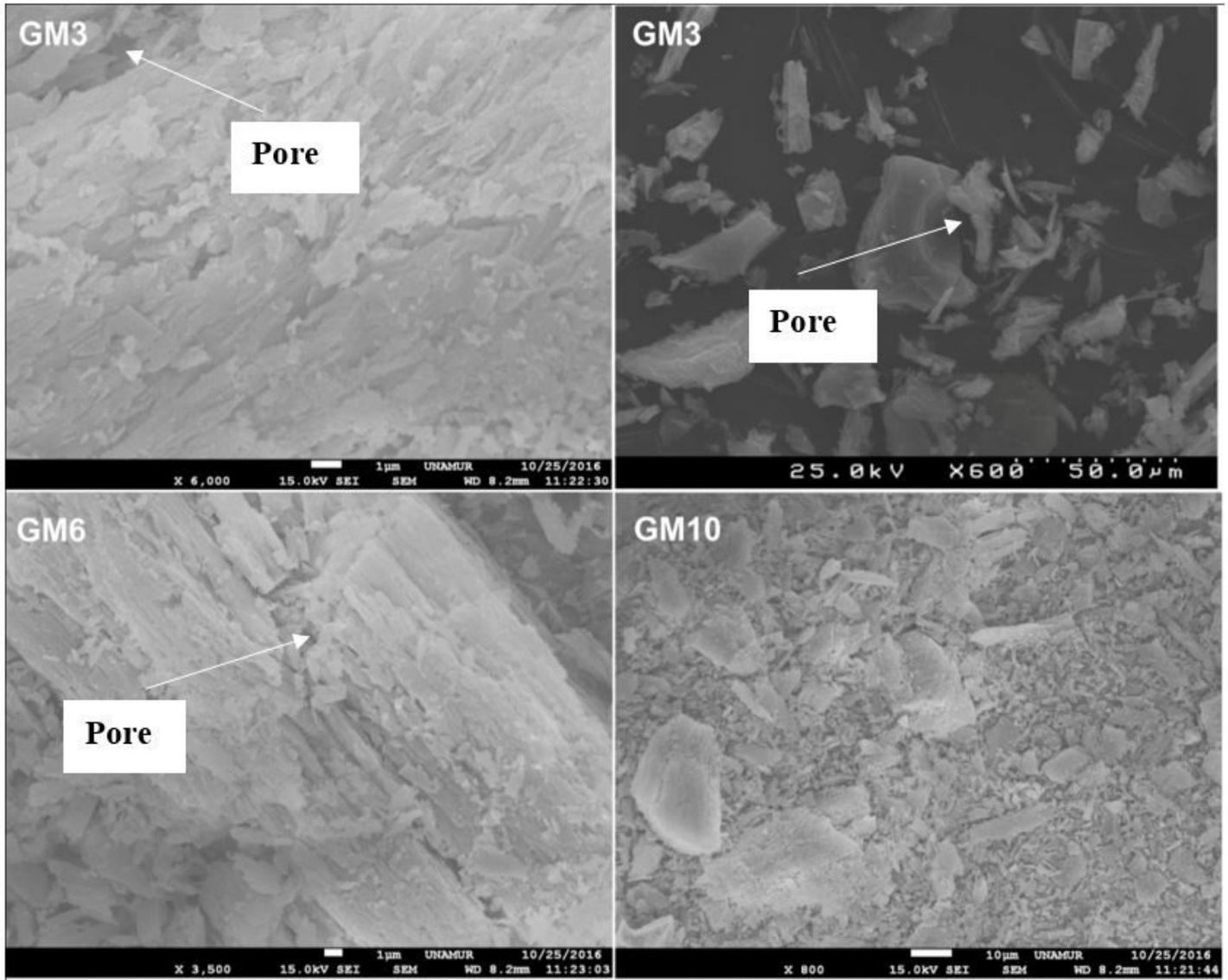


Figure 6

Scanning electron microscopy micrographs of silica gels

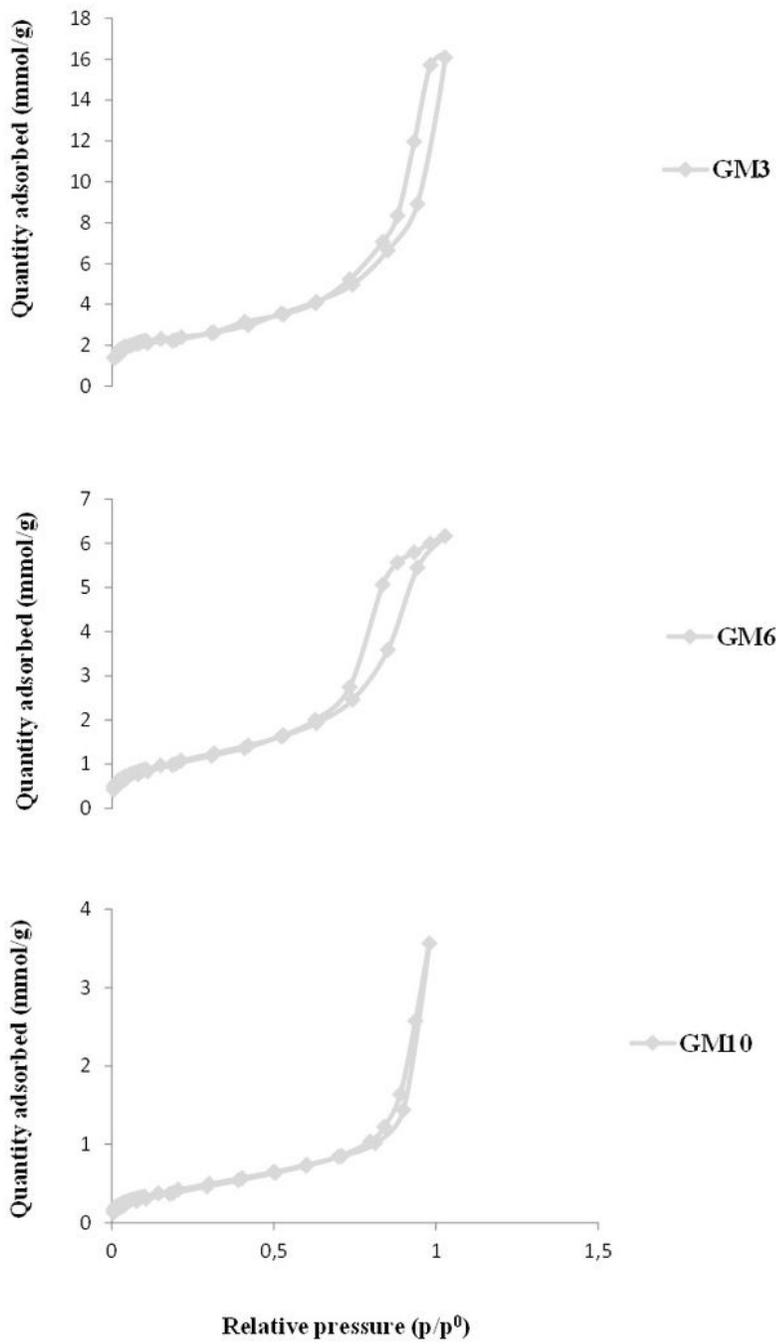


Figure 7

Adsorption isotherms for silica gels at different pH (3, 6 and 10)