



Preparation and Characterization of a Porous Material from Algerian Desert Sand

Ghania Mecheri^{1*}, Said Hafsi¹, Noureddine Gherraf²

¹Laboratory of Applied Chemistry and Materials Technology Larbi ben M'Hidi university, Oum El Bouaghi, 04000, Algeria

²Laboratory of Natural Resources and Management of Sensitive Environments, Larbi ben M'Hidi university, Oum El Bouaghi, 04000, Algeria

ABSTRACT

The objective of the present work was 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 was prepared according to the mechanism of co-operative self-assembly. The method was consisted of a polymerizing 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 led to the final material which was characterized by XRF, XRD, MEB-EDX, FTIR, and BET techniques.

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

Corresponding author: Ghania Mecheri

e-mail ngherraf@yahoo.com

Received: 26 October 2017

Accepted: 28 January 2018

INTRODUCTION

Nowadays, porous materials play a very important role in our daily life (Zdravkov et al. 2007). These materials are practically encountered in all fields: such as treatment of industrial and household effluents, ceramics, heterogeneous catalysis, pharmaceutical applications, and so on (Gonzalez et al. 1988, Iskander et al. 2010; Bagshaw et al. 2001; Sayari et al. 2005). Porous materials can be obtained from a large number of raw materials, such as carbon-rich materials, synthetic zeolites, and geo-materials (Wang et al. 2005; Kandah et al. 2006; Mekatel et al. 2015; Peng et al. 2018; Ling et al. 2018; Bentaleb. 2017; Sdiri et al. 2014). In this study, we were interested in a geo-material namely the sand of the great Algerian desert for the preparation of porous materials. Sampling of sand was 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

1.1. Material

The sand used for the preparation of porous material was taken from the region of El-Oued. Its chemical composition was determined by X-ray fluorescence spectrophotometry (model: ZSX Primus II-Rigaku). The results obtained are summarized in Table 1, and it has been shown that the preponderant

mineralogical composition of the used sand is silica. The comparison of the sand diffractogram was 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 which confirmed an α -SiO₂ type silica with a hexagonal unit cell of parameters: space group of P3221 (154);

Z = 3; a = b = 4.91340; c = 5.40530Å. Sodium carbonate (Na₂CO₃), cetrimonium bromide (CTAB) and hydrochloric acid (HCl) were obtained from Fisher, Sigma-Aldrich and Merck; respectively.

Table 1. Sand composition

Compound	CO ₂	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl
Mass (%)	10.7	0.162	0.545	2.54	78.2	0.119	0.0672	0.0114
Compound	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	Rb ₂ O	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 was sodium silicate, and the structuring agent was cetrimonium bromide (CTAB). The latter was an ionic surfactant, widely used for structuring mesoporous materials (Tadros. 2005; Wang et al. 2015).

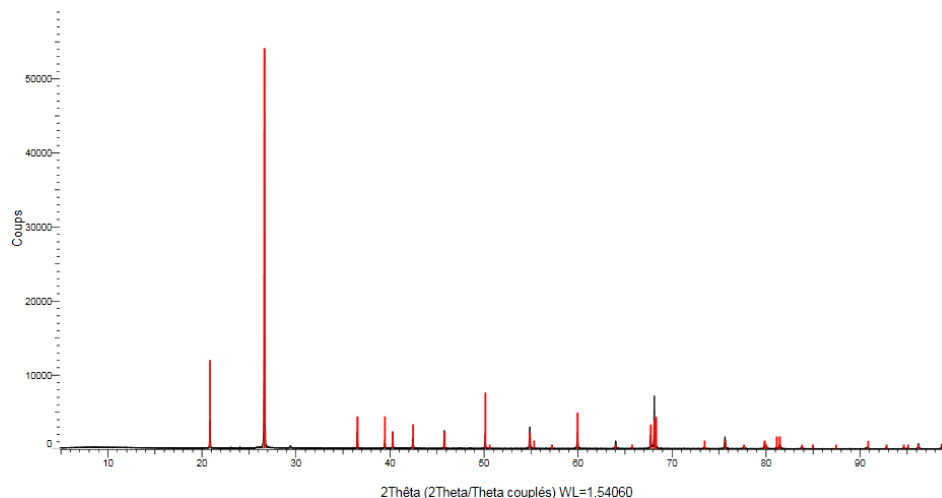


Figure 1. XRD analysis of the sand

1.1. Preparation of porous material

The sand was 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 $\frac{\text{Na}_2\text{CO}_3}{\text{sand}} = 1.8$). After

cooling, a solid was obtained. A mass of 0.5 g of this solid was introduced into a beaker, made up with 30 ml of distilled water at 20°C, and then homogenized. The solution was filtered to remove insoluble products. 40 ml of a 0.16 M concentration surfactant solution (CTAB) were added to the filtrate. The mixture was stirred vigorously for 7 hours. The pH was set at 7 with a solution of HCl (2M). At this pH value, the gel was 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 AgNO₃ test. The material thus obtained was calcined at a temperature of 650°C for 5 hours.

This step destroyed the surfactant, and thus created a high porosity of the final material (Benamor, 2011).

RESULTS AND DISCUSSION

1.2. 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 showed that the grains were mostly rounded to sub-rounded for a magnification of 500X. For a high magnification, the existence of small fragments (Figure 2) which appeared in a white color, was observed. The EDX analysis of these fragments (Figure 3) showed that they were formed mainly of silicon (% by mass = 37.46, atomic % = 25.19) and oxygen (% by mass = 54.84, atomic % = 64.73). The calculations showed that the atomic ratio $\frac{\text{O}}{\text{Si}} = 2.57$ and the mass ratio $\frac{\text{O}}{\text{Si}} = 1.46$. These

results corresponded to a structure close to SiO₂. The observation with different magnifications of the prepared material showed the existence of a porous structure at the surface (Figure 4). The analysis by EDX (Figure 5) showed that it was formed mainly of silicon (% by mass = 29.10, atomic % = 19.79) and oxygen (% by mass = 51.74, atomic % = 61.78). From these results, the atomic ratio $\frac{\text{O}}{\text{Si}} = 1.78$ and the mass

ratio $\frac{\text{O}}{\text{Si}} = 3.12$, were found. This suggested that there was the possibility of formation of a product rich in oxygen

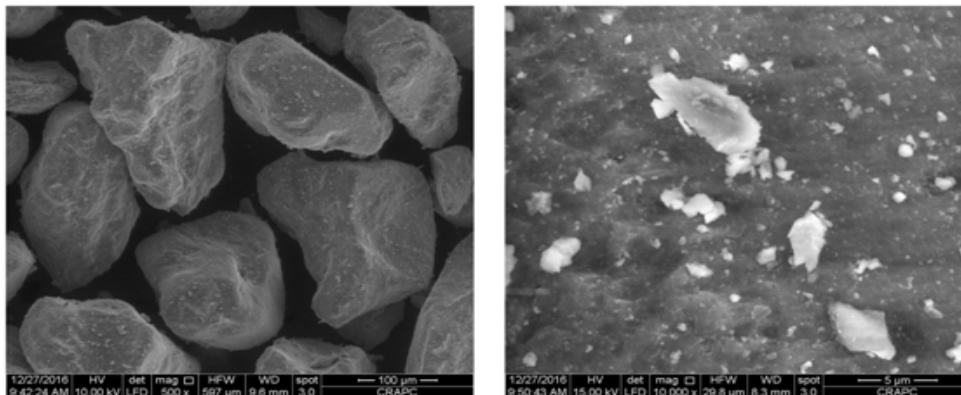


Figure 2. SEM images of the sand

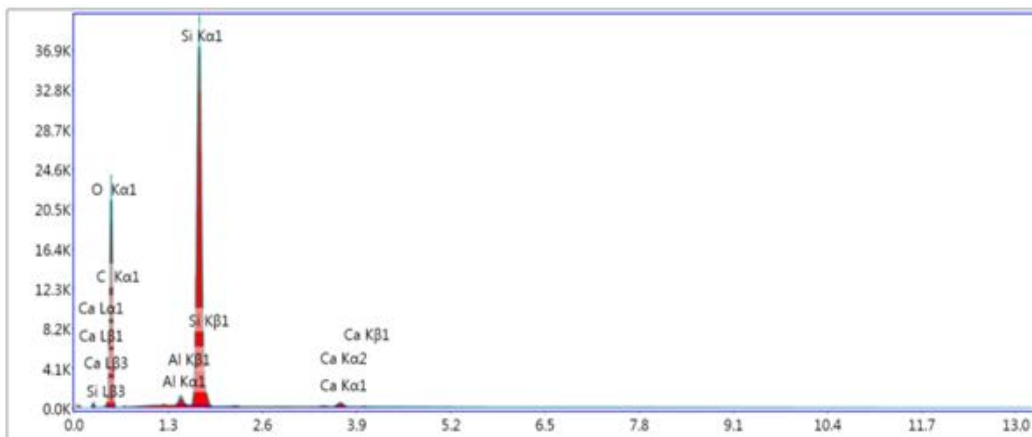


Figure 3. EDX analysis of the fragments

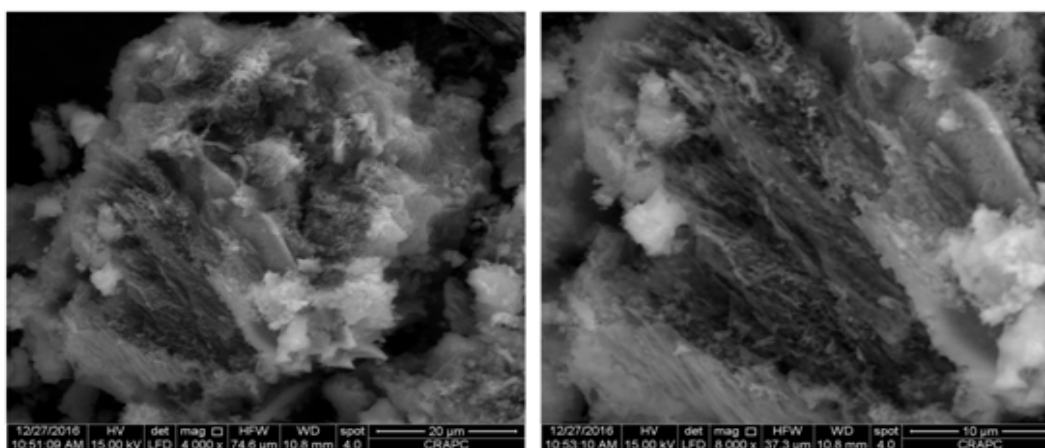


Figure 4. SEM images of the prepared material

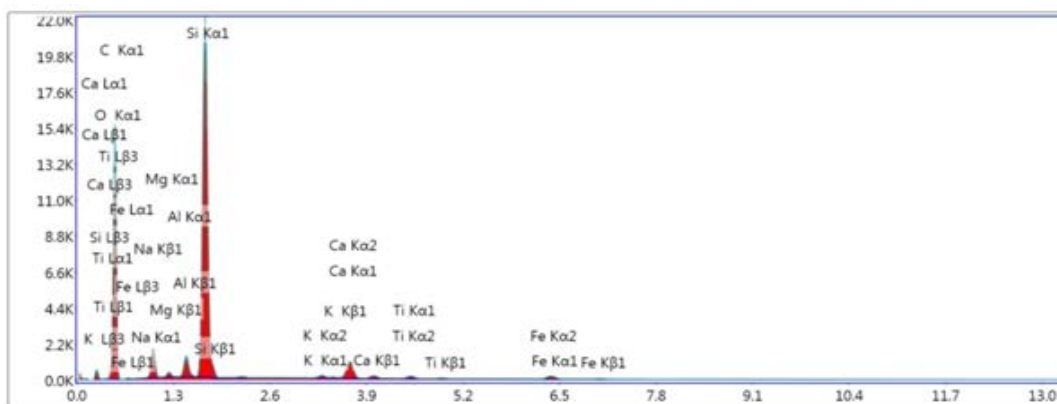


Figure 5. EDX analysis of the prepared material

1.1. 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} was due to the deformation vibrations of Si-O-Si. The bands located at 778 cm^{-1} and 796 cm^{-1} were attributed to the SiO₂ species present in the form of quartz (Ramasamy and Suresh, 2009). The strong band

centered at 1064 cm^{-1} was due to the asymmetric elongations Si-O-Si (Gremlich and Bing, 2001). For the prepared material, the asymmetric and symmetric elongation vibrations Si-O-Si were 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 $2850\text{-}2960\text{ cm}^{-1}$ (Long et al. 2015)

on the spectrum of the prepared material, confirmed that the surfactant has been removed after the calcining at high temperature. The absorption band at 3406 cm⁻¹ was attributed to the elongation vibration of silanol groups O-H formed on the surface of the prepared silicic material (Alfaro *et al.* 2014; Singh *et al.* 2009).

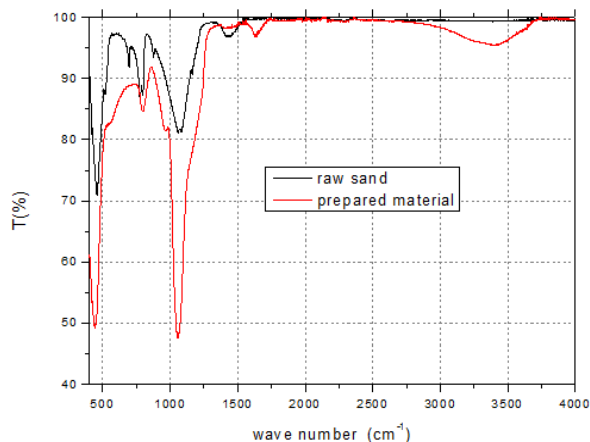


Figure 6. IR spectra of sand and prepared material

1.1. 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) (Brunnaur *et al.* 1938) was used. Its linear form was written as follows:

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

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

In which, P is the equilibrium adsorbate partial pressure, P₀ 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 gave good results, especially in the field; 0.05 < Pr < 0.35. The specific surface area of the sample was given by the following equation:

$$S_p = \frac{V_m N_A \sigma}{V_M m} \tag{2}$$

Where :

S_p : specific surface area (m²/g), V_m : volume of gas required to cover the monolayer (cm³), V_M : molar volume (22414 cm³/mole; NCTP), N_A : Number of Avogadro (6.022x10²³ molecules/mole), σ : Area occupied by a molecule of gas (N₂; 16.20x10⁻²⁰m²) and m is the mass of the sample (g).

The measurements were recorded on the Micromeritics ASAP 2020. The adsorption gas used was nitrogen, and the measurements were made at 77K and P₀ = 753.676mmHg. The measured volume was 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 showed that the prepared material had a specific surface area much greater than that of sand.

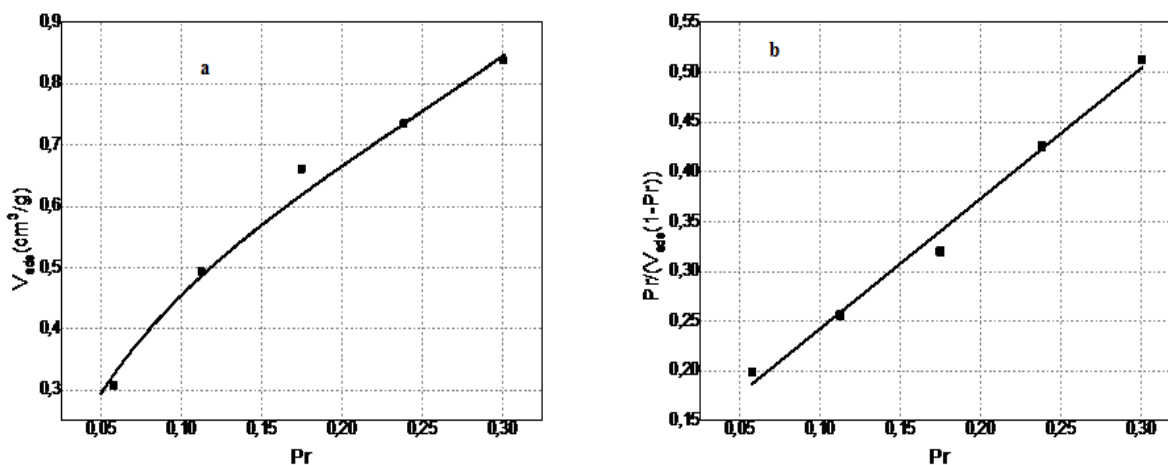


Figure 7. N₂ adsorption isotherm at 77K on sand (a: standard form, b: linearized form according to BET)

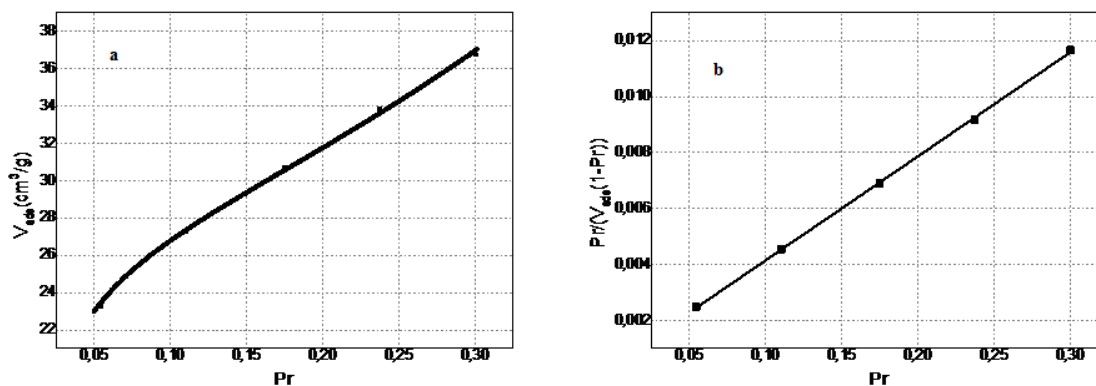


Figure 8. N₂ adsorption isotherm at 77K on the prepared material (a: standard form, b: linearized form according to BET)

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 concerned the valorization of Algerian desert sand for the production of a porous material with a large specific surface area. The method was comprised of 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 obtained gel;
6. Destruction of the surfactant by calcining the gel at 650°C, and obtaining the final material.

Surface measurements by the BET method showed that the specific surface area of the prepared material greatly exceeded that of sand. These results have opened 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).

REFERENCES

1. Alfaro, P., Palavicini, A., Wang, C., (2014) Hydrogen, oxygen and hydroxyl on porous silicon surface: A joint density-functional perturbation theory and infrared spectroscopy approach, *Thin Solid Films*, 571(1):206-211.
2. Bagshaw, S. A., (2001) The effect of dilute electrolytes on the formation of non-ionically templated [Si]-MSU-X mesoporous silica molecular sieves, *Journal of materials chemistry*, 11: 831-840
3. Benamor, T., (2011) Synthèse et caractérisation de silices mésoporeuses hydrophobes à porosité contrôlée, Doctorate thesis, University of Haute Alsace, France.
4. Bentaleb, K., (2017) Enhanced adsorption of 2, 4-dichlorophenol from aqueous solution using modified low cost Algerian geomaterial, *Journal of the Taiwan Institute of Chemical Engineers*, 80: 578-588.
5. Brunnaur, S., Emmett, P.H., Teller, E., (1938) Adsorption of gases in multimolecular layers, *Contribution from the Bureau of chemistry and soils and george Washington university*, 60:309-319.
6. Gonzalez, C.J.R., Shneider, M., Nawata, K., Kusano, H., (1988) Porous silicate beads by gelation, *Journal of non-crystalline solids*, 100: 274-277.
7. Gremlich, H.U., Bing, Y. (2001) *Infrared and Raman Spectroscopy of Biological Materials*, Eds., Marcel Dekker, Inc.,
8. Iskander, M., Sadek, S., Louis, G., (2010) Geotechnical properties of silica gels, Springer-Verlag Berlin Heidelberg, modeling with transparent soils, SSGG, , chapter 6: 85-115.
9. Kandah, M.I., Shawabkeh, R., Al-Zboon, M.A., (2006) Synthesis and characterization of activated carbon from asphalt, *Applied surface science*, 253:821- 826.
10. Ling, R., Chen, W., Hou, J., (2018) Preparation of modified MFI (ZSM-5 and silicalite-1) zeolites for potassium extraction from seawater, *Particuology*, , 36, 190-192.
11. Long, G., Ji, Y., Pan, H., Sun, Z., Li, Y., Qin, G., (2015) Characterization of thermal denaturation structure and morphology of soy glycinin by FTIR and SEM, *International journal of food properties*, 18(4):763-774.
12. Mekatel, E., Amokrane, S., Aid, A., Nibou, D., Trari, M., (2015) Adsorption of methyl orange on nanoparticles of a synthetic zeolite NaA/CuO, *Comptes Rendus Chimie*, 18(3): 336-344.
13. Peng, C., Liu Z. (2018) Preparation of nanosized SSZ-13 zeolite with enhanced hydrothermal stability by a two-stage synthetic method, *Microporous and Mesoporous Materials*, 255: 192-199.
14. Ramasamy, V., Suresh, G., (2009) Mineral characterization and crystalline nature of quartz in Ponnaiyar river sediments, Tamilnadu, India, *American-Eurasian Journal of Scientific Research*, 4(2):103-107.
15. Sayari, A., Hamoudi, S., Yang, Y., (2005) Applications of pore-expanded mesoporous silica. 1. Removal of heavy metal cations and organic

- pollutants from wastewater, *Chemistry of materials*, 17 (1): 212-216.
16. Sdiri, A., Higashi T., Bouaziz, S., Benzina, M., (2014) Synthesis and characterization of silica gel from siliceous sands of southern Tunisia, *Arabian journal of chemistry*, 7: 486-493.
 17. Singh, K., Bala, I., Kumar, V., (2009) Structural, optical and bioactive properties of calcium borosilicate glasses, *Ceramics International*, 35:3401-3406.
 18. Tadros, T.F. (2005) *Applied surfactants, principles and applications*, Eds., Wiley-VCH: Verlag GmbH & Co. KGaA, Weinheim.
 19. Wang, J., Huang, S., Hu, K., Zhou, K., Sun, H. (2015) Effect of cetyltrimethylammonium bromide on morphology and porous structure of mesoporous hydroxyapatite, *Transactions of nonferrous metals of society of China*, 25(2): 483-489.
 20. Wang, L.K., Yung- Tse, H., Nazih K, S., (2005) *Physico-chemical treatment processes*, Handbook of environmental engineering, Humana Press, 3:573-576.
 21. Zdravkov, D.B., Cermak, J.J., Sefara, M., Janku J., (2007) Pore classification in the characterization of porous materials: A perspective, *Central European journal of chemistry*, 5(2): 385-395.