Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1058726

57 (2016) 13388–13393
June

Taylor & Francis
Taylor & Francis Group

Preparation of macroporous membrane using natural Kaolin and Tunisian lignite as a pore-forming agent

I. Hedfi[a,*], N. Hamdi[a], M.A. Rodriguez[b], E. Srasra[a]

[a]*Centre National des Recherchesen Science des Matériaux, BorjCedria Techno-Park, B.P. 95-2050, HammamLif, Tunis, Tunisia, Tel. +34603527304; emails: imen_hedfi@yahoo.fr (I. Hedfi), nouryhamdi@gmail.com (N. Hamdi), srasra.ezzedine@gmail.com (E. Srasra)*
[b]*Instituto de Cerámica y Vidrio, CSIC, C/Kelsen 2849, Madrid, Spain, email: mar@icv.csic.es*

Received 28 January 2015; Accepted 1 June 2015

ABSTRACT

The objective of this study was to prepare low-cost macroporous ceramic membranes using natural kaolin and natural lignite, as porogen agent, both from Tunisia. The characteristics of this membrane have been defined to be used in filtration processes and as a support for multilayer ceramic membranes. This study includes the characterization of the raw materials in order to define optimal processing parameters to obtain the membranes. A study of the effect of lignite content has been carried out. Porosity, density and mechanical strength were the considered parameters to be optimized. A lignite percentage of 20% and a sintering temperature of 1,050˚C were chosen. Obtained membranes show good porosity above 43% but with a slightly low mechanical strength that does not exceed 20 MPa. These membranes can be considered as efficient regarding the results shown in the gas permeation tests.

Keywords: Kaolin; Membrane; Processing; Permeability

1. Introduction

Ceramic membranes have been widely studied for energy and environmental applications due to its unique advantages especially such as high thermal, chemical and mechanical stability, environmentally friendly, and low energy-consumption [1]. However, because ceramic membranes have higher cost than polymeric counterparts, their applications have been limited in some traditional industries such as food, beverage, and pharmaceutical. Also, limited types of membrane materials (such as Al_2O_3, ZrO_2, TiO_2, and their composite oxides) hinder their further applications [2–4]. With increased needs of massive liquid effluent treatment and low-cost catalysis-separation supports, it is of great importance to develop low-cost ceramic membranes.

A significant effort has been provided in membrane technology field in order to find new low-cost ceramic materials [5–7].

Porous ceramic materials have been used in numerous applications, including filters and membranes [8,9], fuel cell electrodes [10,11], catalyst supports for bio-materials [12], piezoelectric materials [13,14], and thermally or acoustically insulating bulk materials [15].

Several processing routes to produce porous ceramics have been reported [16,17]. In order to produce

*Corresponding author.

high porosity level, porogen agents have shown potential results. The principle is that organic particles are burnt out during heating to the firing temperature, leaving voids in the ceramic body. The morphology of these voids will depend on the selected pore-forming agent, and thus can be controlled through suitable incorporation content and particle size distribution [18]. Numerous porogen agents have been investigated, including starch [19–25], graphite [26–30], lycopodium [31–33], sucrose [34,35], among others [36–38].

In this study, the objective is to prepare macroporous membranes using a Tunisian kaolin with lignite as a porosity agent in order to decrease the cost of preparation and to improve the competitiveness of the low-cost ceramic membranes.

2. Experimental procedure

2.1. Raw material

The raw materials used in this study are kaolin and lignite.

The kaolin is extracted from the region of Tabarka located on the northwest of Tunisia. In order to determine the composition of the clay, its thermal behavior, and its morphology, a characterization was carried out [39]. The main characteristics are shown in Table 1, including the values of the specific surface, the temperature transformation gap, and the particle size. It has also been necessary to determine the curve of pressure vs. density of the clay in order to define the best pressing pressure to obtain the membranes.

This curve describes the evolution of the density as a function of pressure. It was plotted using a universal testing machine with a cell of 50,000 N (Instron, UK).

The lignite was extracted from a deposit located in the region of Nabeul, Tunisia. In order to determine its mineralogical composition, X-ray diffraction was carried out with a Pan analytical Xpert High Score Plus diffractometer (UK) equipped with a Cu anticathode.

In order to know the thermal behavior of the lignite sample and more information about its composition, a thermogravimetry has been performed between 100 and 550˚C.

To be able to estimate the pore size and to know the particle size distribution, the lignite was analyzed by laser scattering in aqueous suspension (Mastersizer S, Malvern. England).

2.2. Membranes

After the characterization of the raw material, the second step was the preparation of flat supports. Different compositions of kaolin and lignite were studied. The shape forming of the flat support was carried out by pressing the composition at the chosen pressure using an electro-mechanical pressing machine with displacement control (Tonindustrie GmbH, Germany).

The third step was the characterization of the porosity using a mercury porosimeter mod. Auto pore II 9215 (Micromeritics, USA). The density has been calculated geometrically.

Finally, the mechanical strength has been measured through compressive tests using a universal testing machine (Instron, UK) with a cell of 5,000 N.

To characterize the morphology, a study by scanning electron microscopy S4700 (Hitachi, Japan) was carried out.

The permeability of the porous samples obtained was tested using N2 as permeate with a system described elsewhere [40].

3. Results and discussion

Results of kaolin characterization are shown in the Table 1. It has a relatively small particle size and a high specific surface higher than the specific surface expected from the particle size, this is due to the agglomeration of clay particles. The most important phases found were kaolin and quartz. From TGA-DTA study (not shown in this work), the main thermal transformations takes place between 800 and 1,100˚C.

In order to complete the characterization and to define the optimal pressing pressure, it was necessary to determine the curve of the density as a function of the pressing pressure of the clay powder,

Observing this curve (Fig. 1), it has been concluded that the best pressure for pressing this clay is between 19 and 26 MPa. Because it is the region of the intersection between the two virtual linear tangents of the curve that defines the compressible region of the clay

Table 1
Main characteristics of the kaolin

Main phases	Particle size (μm)	Specific surface (m^2/g)	Transformation zone (DTA-TGA) (˚C)
Kaolin and Quartz	3	18	880–1,100

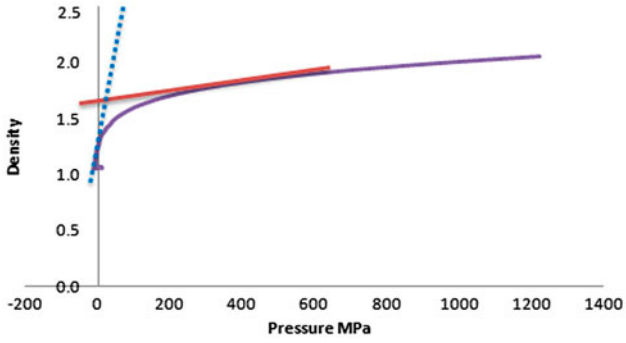

Fig. 1. Density vs. pressure curve.

in order to get a resistant material that keep its porosity. In this study, the selected pressure has been 23 MPa.

The X-ray diffraction pattern of the raw lignite is shown in Fig. 2. Two diffraction peaks' characteristics of the quartz to 3.34 and 2.26 Å show the impurity of the sample. A wide diffraction peak corresponding to an amorphous phase defining lignite can be also observed which is in agreement with Flogeac [41].

Through the evolution of the loss of mass (Fig. 3), two steps can be described as follows: a weight loss between 25 and 100°C, corresponding to 14% of loss due to water evaporation and a linear variation between 200 and 450°C, until a value of about 73% corresponding to the loss of the major organic part of the sample. A 13% of inorganic impurities remain after thermal treatment.

Hence, it can be concluded that the natural lignite is composed of 14% water, 73% organic, and 13% inorganic material (quartz mainly).

The control of the particle size is an important factor for the homogeneity of the pore diameters on

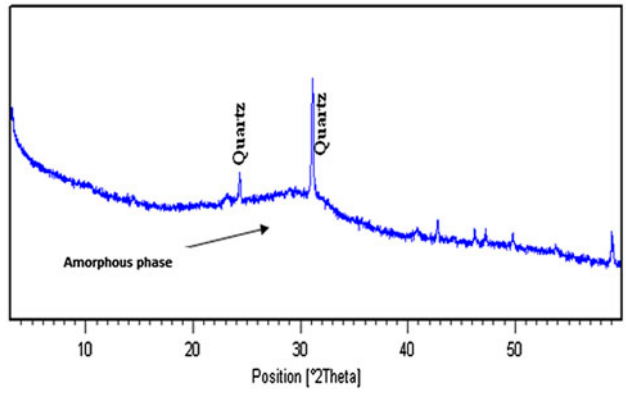

Fig. 2. X-ray diffraction of the lignite, describing the patterns corresponding to the main phases.

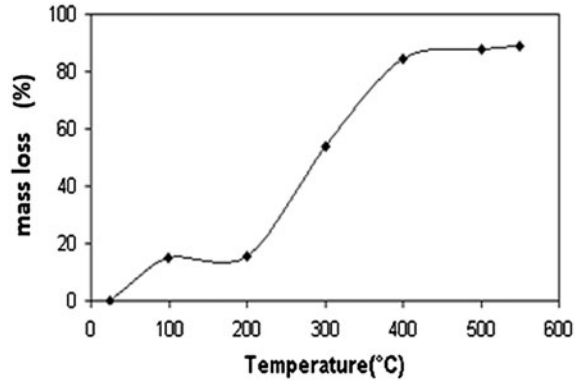

Fig. 3. Evolution of mass loss of lignite with the temperature.

the membrane. The particle size of the lignite has to be, theoretically, between one-sixth and one-third of the particle size of the clay sample in order to generate similar pore size as originally generated by the kaolin.

The particle size distribution curve (Fig. 4) shows a distribution with a single population with a maximum around 1 μm which means that the sample has the adequate particle size.

3.1. Membrane preparation

In order to study the effect of the percentage of pore-forming agent on the membrane characteristics, five mixtures have been prepared with a different percentage of lignite (Table 2). Using the results obtained from the analysis of the pressure curve and those of the thermal behavior of the clay, the applied pressure was 23 MPa and the sintering temperature was 950°C for 2 h with a heating rate of 5°C/min. The membranes were shaped as disks of 2.5 cm in diameter and 4 mm thicknesses.

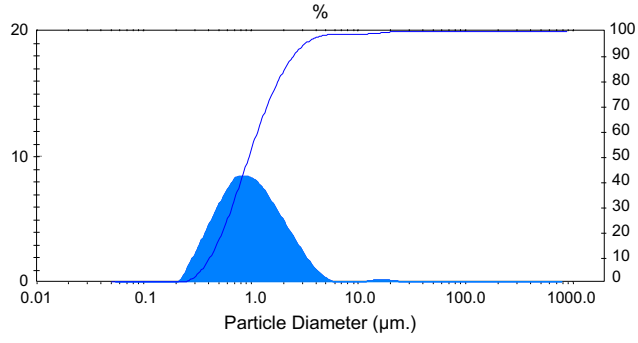

Fig. 4. Lignite particle size distribution.

Table 2
Mixtures composition

Mixture	Lignite content (wt.%)	Kaolin (wt.%)
M0	0	100
M1	5	95
M2	10	90
M3	15	85
M4	20	80

Table 3
Properties of membranes sintered at 950˚C for 2 h

Mixture	Density (g/cm^3)	Porosity (vol.%)	Compressive strength (MPa)
M0	1.8	30	57
M1	1.7	38	30
M2	1.6	42	18
M3	1.5	43	13
M4	1.4	46	8

The characteristics of the obtained membranes are described in Table 3.

It can be noted that the porosity increases with the percentage of lignite to reach up to 46% with 20% of lignite addition. On the other hand, the mechanical strength has an opposite behavior and it decreases with the percentage of lignite up to 8 MPa with 20% of lignite.

These results were expected, and the loss of the organic material at higher temperatures than 570˚C is the origin of the porosity. The higher porosity that follows the increase of the percentage of lignite makes the membrane less resistant mechanically.

These results suggest a compromise to obtain macroporous support with high porosity but also with a good mechanical strength. It was so necessary to increase the sintering temperature to get a higher mechanical strength.

Observing the dilatometry of the kaolin, it has been decided to increase the sintering temperatures up to 1,050 and 1,100˚C using 20% of lignite addition. The results of membranes prepared under these conditions are shown in Table 4.

It can be noted that porosity decreases with the temperature which is due to the transformation of the clay and the formation of the glassy phase. Nevertheless, and due to the pore coalescence, the pore diameter increase significantly. On the other hand, the mechanical strength has been improved with the temperature because of the transformation of the kaolin and the presence of glassy phase at high temperature.

Table 4
Evolution of membrane's properties with temperature

Temperature (˚C)	Density	Pore diameter (μm)	Porosity	Compressive strength (MPa)
1,050	1.33	0.5	43	20
1,100	1.41	10	21	24

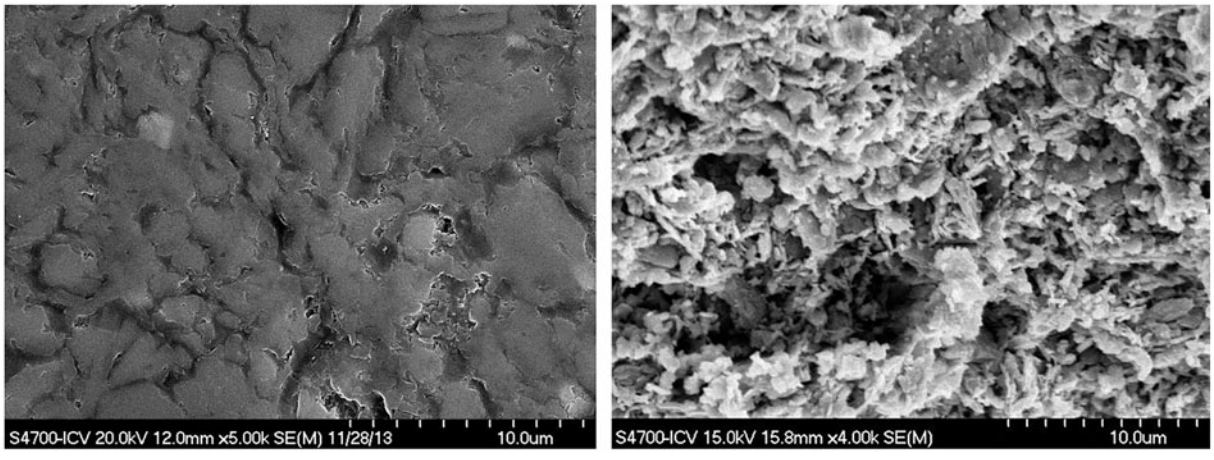

Fig. 5. Image SEM of the membrane 20% 1,100˚C (a) and 20% 1,050˚C (b).

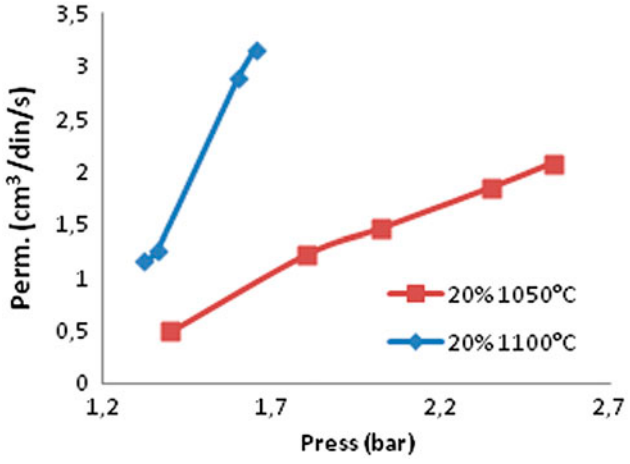

Fig. 6. Flow evolution with the pressure for samples heated at 1,050 and 1,100˚C.

Observing the pore size, a big difference can be noted between the two temperatures, which could have a direct effect on the permeability. This difference of pore size and volume is also confirmed by the microstructures observed by scanning electron microscopy shown in Fig. 5.

It can be concluded that the increase of the heating temperature closes the porosity and also induces the pore coalescence which engage a bigger pore size.

Results of permeation evaluation are shown in Fig. 6. A near linear evolution of the flow vs. pressure can be noted with both of the sintering temperature. The permeability was around 3 $cm^3/din/s$ under a pressure of 1.6 bar for the membrane sintered at 1,100˚C and a value of permeability of around 2 $cm^3/din/s$ under a higher pressure (2.5 bar) for the membrane sintered at 1,050˚C; these values of permeability are different from the expected results observing the porosity because they are directly related to the bigger pore size generated by the a higher sintering temperature. This result confirms that the pore size is more important for the permeability than the total pore volume. The effect of the use of lignite can be clearly observed comparing the results obtained for these membranes with those obtained previously with a membrane made only from kaolin [39]. In this case, the permeability is much higher than the permeability of samples without lignite; this is due to the lower volume of porosity and the smaller pore size.

The selection of the optimal sintering temperature needs to be related to the processing, because the big pore size can lead to the use of intermediary layers, increasing the complexity of the process. So the choice is to use the membrane sintered at 1,050˚C.

4. Conclusions

The study of the possibility of preparing low-cost ceramic membrane from regional kaolin and lignite leads to prepare porous membranes with a good porosity that reach 43% (vol.) and a good mechanical strength of about 20 MPa using 20% of lignite additions and a sintering temperature of 1,050˚C. The evaluation of the performance of the membranes has been made through gas permeation tests. The obtained values show an increase of permeability with the increase of the sintering temperature. These results suggest that membranes could also be tested to evaluate their performance for liquid permeation.

The mechanical strength is still insufficient if the membrane is designated for an industrial use which suggests the introduction of some additives in order to improve the mechanical strength without impacting the porosity.

Acknowledgments

This work was supported by the MINECO (Spain) project MAT2013-48426-C2-1-R.

References

[1] Y. Dong, J.-E. Zhou, B. Lin, Y. Wang, S. Wang, L. Miao, Y. Lang, X. Liu, G. Meng, Reaction-sintered porous mineral-based mullite ceramic membrane supports made from recycled materials, J. Hazard. Mater. 172 (2009) 180–186.
[2] J.Z. Hamada, C. Ha, M.D. Kennedy, G.L. Amy, Application of ceramic membranes for seawater reverse osmosis (SWRO) pre-treatment, Desalin. Water Treat. 51 (2013) 25–27.
[3] S. Khemakhem, A. Larbot, R. Ben Amar, New ceramic microfiltration membranes from Tunisian natural materials: Application for the cuttlefish effluents treatment, Ceram. Int. 35 (2009) 55–56.
[4] P. Pandey, R. Chauhan, Membranes for gas separation, Prog. Polym. Sci. 26 (2001) 853–893.
[5] S. Chemlal, M. Sghyar, M. Rafiq, A. Larbot, L. Cot, Elaboration de membranes de spinelles de cobalt $CoAl_2O_4$ et de spinelle de manganèse $MnAl_2O_4$ pour l'ultrafiltration, Ann. Chim. Sci. Mater. 25 (2000) 57.
[6] Y. Li, X. Zhang, J. Wang, Preparation for ZSM-5 membranes by a two-stage varying temperature synthesis, Sep. Purif. Technol. 25 (2001) 459–466.
[7] J.M. Benito, M.J. Sánchez, P. Pena, M.A. Rodríguez, Development of a new high porosity ceramic membrane for the treatment of bilge water, Desalination 214 (2007) 91–101.
[8] K. Suresh, G. Pugazhenthi, Development of ceramic membranes from low-cost clays for the separation of oil–water emulsion, Desalin. Water Treat. 52 (2014) 1–13.
[9] J. She, T.Ohji, Z.Y. Deng, Thermal shock behavior of porous silicon carbide ceramics, J. Am. Ceram. Soc. 85 (2002) 2125–2127.

[10] S.F. Corbin, J. Lee, X. Qiao, Influence of green formulation and pyrolyzable particulates on the porous microstructure and sintering characteristics of tape cast ceramics, J. Am. Ceram. Soc. 84 (2001) 41–47.
[11] J.J. Haslam, A.Q. Pham, B.W. Chung, J.F. DiCarlo, R.S. Glass, Effects of the use of pore formers on performance of an anode supported solid oxide fuel cell, J. Am. Ceram. Soc. 88 (2005) 513–518.
[12] A.R. Walpole, Z. Xia, C.W. Wilson, J.T. Triffitt, P.R. Wilshaw, A novel nano-porous alumina biomaterial with potential for loading with bioactive materials, J. Biomed. Mater. Res. Part A 90 (2009) 46–54.
[13] T. Zeng, X. Dong, S.T. Chen, H. Yang, Processing and piezoelectric properties of porous PZT ceramics, Ceram. Int. 33 (2007) 395–399.
[14] H.L. Zhang, J.F. Li, B.P. Zhang, Microstructure and electrical properties of porous PZT ceramics derived from different pore-forming agents, Acta Mater. 55 (2007) 171–181.
[15] E. Gregorová, W. Pabst, Porous ceramics prepared using poppy seed as a pore-forming agent, Ceram. Int. 33 (2007) 1385–1388.
[16] P. Colombo, Conventional and novel processing methods for cellular ceramics, Philos. Trans. R. Soc. A 364 (2006) 109–124.
[17] A.R. Studart, U.T. Gonzenbach, E. Tervoort, L.J. Gauckler, Processing routes to macroporous ceramics: A review, J. Am. Ceram. Soc. 89 (2006) 1771–1789.
[18] Rui M. Novais, M.P. Seabra, J.A. Labrincha, Ceramic tiles with controlled porosity and low thermal conductivity by using pore-forming agents, Ceram. Int. 40 (2014) 11637–11648.
[19] E. Gregorová, Z. Zivcová, W. Pabst, Porosity and pore space characteristics of starch-processed porous ceramics, J. Mater. Sci. 41 (2006) 6119–6122.
[20] Z. Zivcová, E. Gregorová, W. Pabst, Starch as a pore-forming and body-forming agent in ceramic technology, Starch 61 (2009) 495–502.
[21] Z. Zivcová, E. Gregorová, W. Pabst, Low- and high-temperature processes and mechanisms in the preparation of porous ceramics via starch consolidation casting, Starch 62 (2010) 3–10.
[22] L.B. Garrido, M.P. Albano, L.M. Genova, K.P. Plucknett, Influence of starch type on characteristics of porous 3Y-ZrO_2 prepared from a direct consolidation casting method, Mater. Res. 14 (2011) 39–45.
[23] F. Chen, L. Ma, L. Zhang, Pore structure control of starch processed silicon nitride porous ceramics with near-zero shrinkage, Mater. Lett. 65 (2011) 1410–1412.
[24] Z. Zivcová, J. Locs, M. Keuper, I. Sedlárova, M. Chmelicková, Micro-structural comparison of porous oxide ceramics from the system Al_2–ZrO_2 prepared with starch as a pore-forming agent, J. Eur. Ceram. Soc. 32 (2012) 2163–2172.
[25] R.M. Khattab, M.M.S. Wahsh, N.M. Khalil, Preparation and characterization of porous alumina ceramics through starch consolidation casting technique, Ceram. Int. 38 (2012) 4723–4728.
[26] M. Boaro, J.M. Vohs, J. Gorte, Synthesis of highly porous yttria-stabilized zirconia by tape-casting methods, J. Am. Ceram. Soc. 86 (2003) 395–400.
[27] S. Ding, S. Zhu, Y.P. Zeng, D. Jiang, Gas permeability of mullite-bonded porous silicon carbide ceramics, J. Mater. Sci. 42 (2007) 7171–7175.
[28] S. Ding, S. Zhu, Y.P. Zeng, D. Jiang, Fabrication of mullite-bonded porous silicon carbide ceramics by insitu reaction bonding, J. Eur. Ceram. Soc. 27 (2007) 2095–2102.
[29] A. Sanson, P. Pinasco, E. Roncari, Influence of pore formers on slurry composition and microstructure of tape cast supporting anodes for SOFCs, J. Eur. Ceram. Soc. 28 (2008) 1221–1226.
[30] S. Sarikaya, F. Dogan, Effect of various pore formers on themicro-structural development of tape-cast porous ceramics, Ceram. Int. 39 (2013) 403–413.
[31] Z. Zivcová, E. Gregorová, W. Pabst, Porous alumina ceramics produced with lycopodiums pores as pore-forming agents, J. Mater. Sci. 42 (2007) 8760–8764.
[32] Z. Zivcová, E. Gregorová, W. Pabst, Alumina ceramics prepared with new pore-forming agents, Process. Appl. Ceram. 2 (2008) 1–8.
[33] R. Seržane, J. Locs, L. Berzina-Cimdina, R. Sadretdinovs, Development of porous ceramics by lycopodium using uniaxial pressing and sintering, Process. Appl. Ceram. 4 (2010) 231–235.
[34] C. Wang, T. Kasuga, M. Nogami, Macroporous calcium phosphate glass–ceramic prepared by two-step pressing technique and using sucrose as a pore former, J. Mater. Sci. Mater. Med. 16 (2005) 739–744.
[35] A.M. Ray, H. Gautier, J.M. Bouler, P. Weiss, C. Merle, A new technological procedure using sucrose as porogen compound manu-facture porous biphasic calcium phosphate ceramics of appropriate micro-and macrostructure, Ceram. Int. 36 (2010) 93–93.
[36] M.H.P. Silva, A.F. Lemos, I.R. Gibson, J.M. Ferreira, J.D. Santos. Porous glass reinforced hydroxyapatite materials produced with different organic additives, J. Non-Cryst. Solids 304 (2002) 286–292.
[37] J. Bai, X. Yang, Y. Shi, S. Xu, J. Yang, Fabrication of directional SiC porous ceramics using Fe_2O_3 as pore-forming agent, Mater. Lett. 78 (2012) 192–194.
[38] B.A. Horri, C. Selomuya, H. Wang, Characteristics of Ni/YSZ ceramic anode prepared using carbon microspheres as a pore former, Int. J. Hydrogen Energy 37 (2012) 15311–15319.
[39] I. Hedfi, N. Hamdi, E. Srasra, M.A. Rodriguez, The preparation of micro-porous membrane from a Tunisian kaolin, Appl. Clay Sci. 101 (2014) 574–578.
[40] A. Conesa, A. Fernandez-Roura, J.A. Pitarch, I. Vicente-Mingarro, M.A. Rodriguez, Separation of binary gas mixtures by means of sol-gel modified ceramic membranes. Prediction of membrane performance. J. Membr. Sci. 155 (1999) 123–131.
[41] J. Feng, Y. Fan, H. Qi, N. Xu, Co-sintering synthesis of tubular bilayerα-alumina membrane, J. Membr. Sci. 288 (2007) 20–27.