J. Applied Membrane Science & Technology, Vol. 25, No. 3, December 2021, 1–15

Clay Ceramic Support Membrane Optimization Using Factorial Design Approach

M. Ait Baih, N. Saffaj*, A. Bakka, R. Mamouni, N. El baraka,
H. Zidouh & N. El Qacimi

Laboratoire Biotechnologie, Matériaux et Environnement, Université Ibn Zohr,
Faculté des Sciences, BP 8106 - Cité Dakhla, Agadir, Morocco

Submitted: 6/1/2021. Revised edition: 30/4/2021. Accepted: 18/7/2021. Available online: 15/11/2021

ABSTRACT

In the present study, the effect of Sintering temperature, Particle size and Heating rate of the ceramic support membrane Elaboration based on dry clay were evaluated using full factorial design and investigated by porosity and mechanical strength measures. The flat supports have been prepared from 5 g of the material with a two fraction 2 and 30 µm, the extrusion was performed using the uniaxial pressing in applicant a pressure of 12 tones, the supports sintered between 900° C and 1200°C with a different heating rate (1°C/min and 10°C/min). By using full factorial design 2^3, it was found that the sintering temperature is the main controlling factors of the physical properties of dry ceramic support membrane, and its increase had a positive effect on Mechanical strength and negative effect on porosity. The interactions between the factors were relatively less important, and they had different (antagonistic/synergetic) influence on the properties. The optimal factors to elaborate the support membrane include a particle size of 2 µm, sintering temperature of 950°C, Heating rate of 1°C predicting the porosity of 40, 8% and Mechanical strength of 12 MPa.

Keywords: Ceramic, membrane, clay, factorial design

1.0 INTRODUCTION

Due to their widely application in industrial field, the membrane process had a great interest in recent years. Filtration whatever, microfiltration, ultrafiltration and nanofiltration, is generally referred to by its everlasting service also its disposal capacity of suspended solids and microorganisms [1].

By their high thermal and chemical potential, ceramics membranes have several key performance advantages over its organic counterpart such as thermal and chemical resistances and better mechanical strength under high pressure [2].

However, high cost of ceramic inorganic membrane has probably restricted their widespread use for different commercial application. The new ceramic composite membrane, that were produced based on abundant natural material such as clay, showed significant advantages from an economic point of view [2-4].

Ceramic filters are generally constituted of a thick support (10 mm) and mono or multiple thin membrane (from 10 µm to 40 µm for each one). Therefore, replacing the more expensive starting materials, by cheaper raw materials used as support (which constitute about 99% of the filter mass) is significantly important. A significant support has been taken in the last years in membrane technology field in order to find out new porous ceramic materials at low cost such as clay [4-6].

* Corresponding to: N. Saffaj (email: saffaj@gmail.com)
DOI: https://doi.org/10.11113/amst.v25n3.208

However, the technologies properties of dry ceramic support membranes are influenced by some factors such as chemicals mineralogical, particle size, processing operations such as shaping, drying and sintering temperature [6-8].

Experimentally, many trials are required for evaluating, the effect of these factors and their mutual interaction on ceramic properties. The Response surface methodology (RSM) is generally used for the reduction of the number of experiments and the determination of a response value for any chosen natural variables belonging to the investigated experiments domains [9-10]. The full factorial design has also proven to be useful method for such studies. Many reports work related to this statistical tool have evaluated the effects of the mixture of raw materials on technological properties of ceramic materials [11-12]. the effects of manufacturing conditions using full factorials design to elaborate the membrane ceramics is not enough investigated.

The aim of the work was to investigate the properties of the elaboration of ceramic dry support membrane from Moroccan Sahara Clay and evaluate the effects of particle size, sintering temperature and heating rate on porosity and mechanical strength using full factorial design.

2.0 MATERIALS AND METHODS

2.1 Materials

The raw material used in this study is the clay coming from the south of Morocco (SAHARA). The natural clay was crushed and sieved to an average size of 45 µm to prepare the ceramic support membrane.

2.2 Experimental Procedures

The main steps of processing to elaborate the ceramic support are reported in Figure 1. The sample was placed in a stainless steel mould, pressed at 12 Ton using a hydraulic press (uniaxial pressing). The elaborated flat disk 2 mm thick and a diameter of 4cm were dry and heat-treated in a programmable furnace. The thermic treating program ended at a temperature ranging from 900°C to 1200°C with a plateaus at 250°C for the elimination of physical adsorbed water and 550°C for carbonate decomposition (Figure 2).

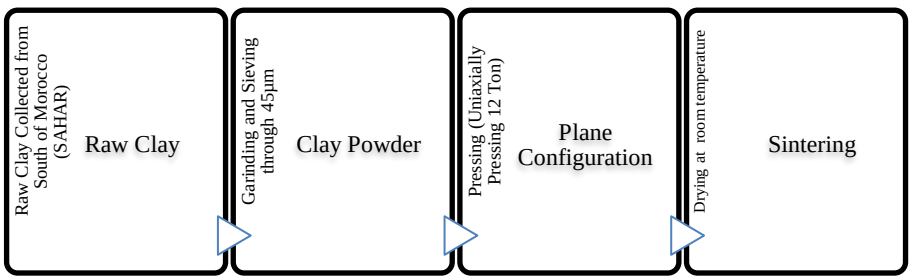

Figure 1 Diagram showing the process used for porous ceramic support membrane elaboration

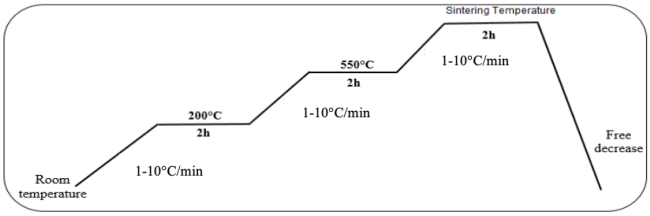

Figure 2 Program of thermal treatment

2.3 Methods of Characterization

Different techniques were used to investigate the properties of clay and developed support membrane. The chemicals composition of powder clay was analyzed using X-Ray dispersive fluorescence (SRS200). The particle sizing accusizer model 770 (Particle sizing system Santa Barbara) was used to determine the particle size distribution. The structure was determined by X-Ray diffraction (XRD) using a Siemens 500 diffractometer operating with CuKα radiation=1.5481Å at 40 KV in the range between 3 and 90°. The porosity was determined by a mercury intrusion porosimetry method (Micrometrics, Model Autopore 9220) for sintered specimens support at different temperature. The thermal evolutions of the clay powder were performed with simultaneous DTA-TGA 2960 instruments under the air with a heating rate of 10 ◦C/min from room temperature to 1000 ◦C. The objective of thermal analysis is to identify temperature regimes where predominant losses (and hence transformations) occur in the membrane. Thereby, an understanding could be developed for analyzing the effect of various temperature regimes on the porous structure, pore diameter and mechanical strength of the membrane.

The Mechanical strength (MS) of sintered specimens was measured in a bending load of three-point method according to ASTM C674-88 standard using Equation (1):

$$MS = \frac{3PL}{2bd^2}$$

Where P (N) is the maximum load at rupture, L (mm) is the distance between the two supports, b (mm) and d (mm) are the width and the thickness of the sample, respectively.

The test was performed to control the resistance of the material sintered at different temperatures. The mechanical resistance of the ceramic material was evaluated on specimens with the following dimensions: length 4 cm, thickness 2 mm and width 10 mm. Specimens were elaborated using the formulation and the thermal program adopted previously for supports elaboration. Each value given on the curve is the arithmetic average of at least 10 determinations. The margin of error calculated in this case for each measure is 3%.

2.4 Methodology of the Factorial Design

The study of full factorial design consists of exploring all possible combination of factors considered in the experiments [13]. Note that the design XK means that this experiment concerns a system with K factors with X levels.

Usually, two values of X's (called levels) are used. The use of only two levels implies that the effects are monotonic on the response variable, but not necessarily linear [13-14]. For each factor, the two levels are denoted using the "rating yates" notation by -1 for the low level of each factor and by +1 the high level of each factor. Thus, the number of experiments carried out by full factorial design with 2 levels is given by $n=2^K$, where K is the number of factors to be considered.

The advantage of full factorial designs is the ability to estimate not only the main effects of factors, but also all their interactions, i.e. two by two, three by three, up to the interaction involving all K factors. However, when the number of factors increases, the use of such design leads to a prohibitive number of experiments simulations.

The elaboration of dry ceramic membranes depends on some factors. There are chemicals mineralogical, particle size, processing operation (drying and sintering) and so forth. Only one factor is varied by time and the others are fixed when any factor is optimized; subsequently, the best value obtained by this procedure is fixed and other factors will be varied by the time; thus, using the unvaried procedure to optimize all variables is time consuming.

The interaction among all factors are neglected in invariable procedure, so the best conditions could be achieved [14]. Full factorial design of experiments was performed by practicing with different levels of factor's all probable combinations [15]. The results of the experiments design were analyzed using statistical software to evaluate the effect as well as the statistical parameters, the statistical plots (Pareto, normal probability of the standardized effects, main effects and interactions plots). 23 full factorial design having 8 experiments for membrane ceramic elaboration was studied and a matrix was established according to their high and low levels, represented by +1 and -1 respectively. The coded value of variables with the response (Porosity and Mechanical Strength) were illustrated in Table 3. The interactions between the independent factors were determined with analysis of variance (ANOVA) and the main effect of the ceramic membrane elaboration was identified based on the P value with 95% of confidence level.

The following codified equation was used to explain the 2^3 factorial designs.

$$Y = b_0 + \sum_{i=1}^{K} b_i X_i + \sum_{i,j=1}^{K} b_{ij} X_i X_j + \sum_{i,j,K=1}^{K} b_{ij} X_i X_j X_m + \cdots, (1)$$

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \ (2)$$

Where X_1, X_2 and X_3 are the coded variable corresponding to particle size (Ps), sintering temperature (St) and Heating rate (Hr) respectively with K the number of factors.
Where:

$$X_1 = \frac{PS - PS_0}{\Delta PS}\ ; X_2 = \frac{St - St_0}{\Delta St}\ ; X_3 = \frac{Hr - Hr_0}{\Delta Hr}$$

With Ps_0, St_0 and Hr_0 are the value at the centers of the experiments range. ΔPs, ΔSt, ΔHr are the variations steps of natural variables, respectively. Details of this model are given elsewhere [16]. The value of the coefficients b_i and b_{ij} were determined by least squares regression. For this purpose, eight experiments; i.e. 2^K experiments (K is the number of natural variable (3) were planned.

The planned experiments and the corresponding measured property (Porosity (Y_1) and Mechanical Strength (Y_2) are reported in Table 3.

3.0 RESULTS AND DISCUSSION

3.1 Physico-Chemical Properties of Clay Powder

The chemical composition of the clay is given in Table 1, it reveals that the clay powder is essentially formed of large amount of silica with alumina and calcium oxide. Sulphate, Iron, Magnesium oxides presents a lower proportion.

The particle size distribution date of the clay ranges from 1 to 30 µm (Table 2). More than 80% of the particles present a diameter less than 8 µm.

Table 1 Chemicals Composition of the clay

Oxides	**SiO_2**	**Al_2O_3**	**SO_4**	**Fe_2O_3**	**MgO**	**K_2O**	**CaO**	**Lo.I**
Wt.(%)	42.00	10.55	5.73	4.02	2.24	1.16	10.00	24.30

Table 2 Particle size distribution of the clay

Particle size (µm) (Average)	**30**	**7**	**2**
Percentage (%)	10	20	70

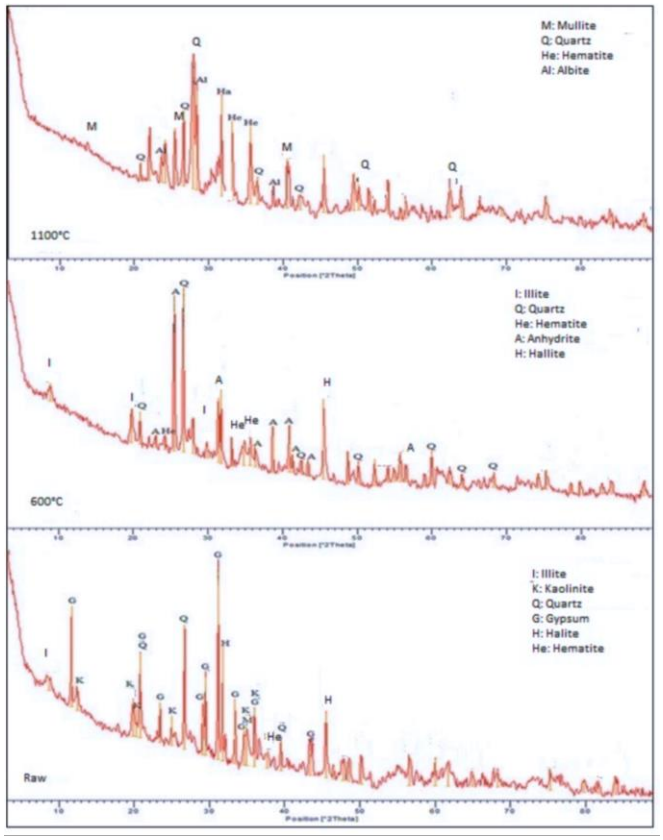

Figure 3 XRD patterns of raw and sintered clay of 2µm fraction

Figure 3 presents the XRD patterns of raw and sintered clay, it shows that kaolinite (K), illite (I), quartz (Q), Gypsum (G), Halite (H) and Hematite (He) are the main minerals present in the raw clay and lowercase for gypsum, halite and hematite.

After calcination of the sample at 600°C, all the peaks in the diffractogram due to kaolinite disappear, this is due to the transformation of kaolinite to amorphous metakaolinite [4, 5, 17].

On the contrary, the peaks of quartz and illite do not change. New peak appears of Anhydrite (A) due of deshydratation of gypsum (G).

At a temperature of 1100°C, peaks of illite (I) disappear also, whereas peaks of mullite (M) appear due to the

transformation of metakaolinite. The peaks of quartz remain without change in the diffractogram which confirms the thermal stability of this phase [17-18].

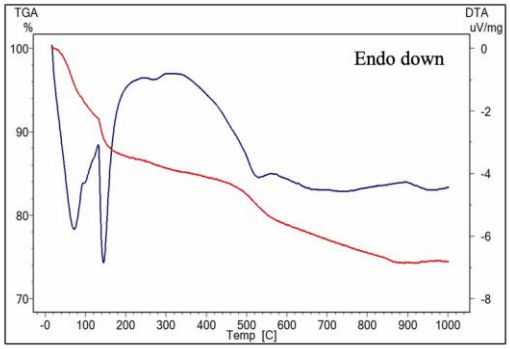

Figure 4 TGA-DTA of the clay

Figure 4 presents TGA and DTA of the clay when subjected to thermogravimetric analysis by heating the dry clay in an α-alumina crucible from room temperature to 1000 °C at a heating rate of 10 °C/min.

The weight loss is of the sample is observed to 24.5%, which can be explained to the elimination of physisorbed water around 100°C, deshydroxylation of the clay due of the transformation of kaolinite into metakaolinite [4-5].

During the DTA treatment, we observed two endothermic peaks at 100 °C and 520 °C, which can be explained by the elimination of the physisorbed water and the transformation of kaolinite into metakaolinite due to the deshydroxylation of clay respectively [4-5].

In the high temperature, structural reorganization processes of the ceramic materials occur as suggested by the presence of an exothermic phenomena located between 900°C and 950°C due to the structural reorganization of metastable metakaolinite transitional phase to mullite (M) [17-18].

3.1 Characterization of Ceramic Membrane Support

The evolution of porosity of the membrane supports as a function of sintering temperature is shown in Figure 5. The results show a decrease in the porosity as a function of sintering temperature for the membrane and reach a pick at 950 °C for the both particle size. The temperature at which the porous percentage reached 40,8% and 40% for the particle size of 2 and 30 µm respectively.

The first part of the curves corresponds to an opening of the pores with temperature, whereas the last part is caused by the beginning of the material densification and decrease of porosity.

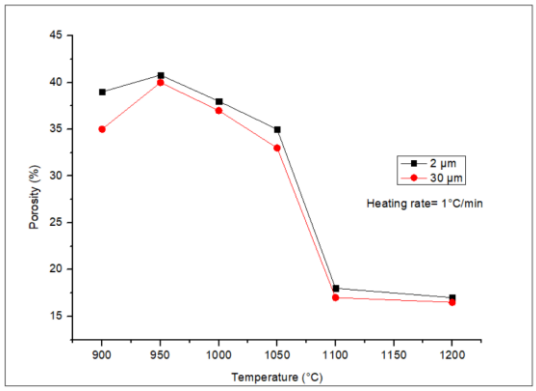

Figure 5 The porosity versus sintering temperature during constant heating rate

The mechanical strength and the porosity are strongly related to temperature changes, mainly the final sintering temperature. The Mechanical strength reported in Figure 6 increases with increasing sintering temperature [4]. The Mechanical strength, also known as modulus of rupture (σ), reflects good strength of the elaborated support. Indeed, the ceramic consolidates by densification and becomes more rigid.

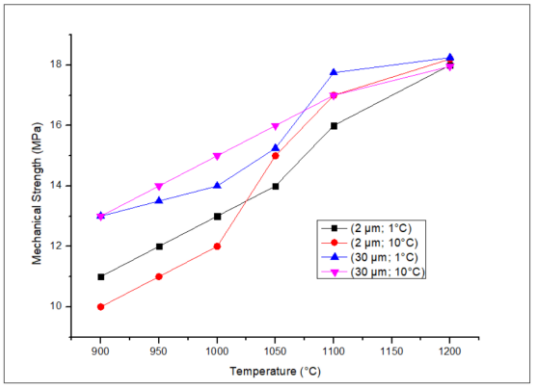

Figure 6 Mechanical strength versus sintering temperature

The sintering temperature between 900°C and 1050°C, The Mechanical strength depends strongly on the particle size and a little less of Heating rate. This is can be explained by the fine particles are more prone to agglomeration, so the green density is often lower than for coarser particle. Beyond 1100°C, the Mechanical strength depend strongly of Sintering temperature, otherwise the particle size and heating rate had little influence. The grain boundaries expand due to the absorption of small grains by the largest. This gives great rigidity to the ceramic and ensures to it good mechanical strength [6].

3.1 Effects of the Processing Factors on the Physical Properties of Support Membrane

The measured value of the technological properties (Mechanical Strength and Porosity) of the sintered test specimens as a function of particle size and sintering parameters (Heating rate, sintering temperature) are given in Table 3.

A regression equation was obtained for each ceramic dry support membrane using factorial design at a 5% level of significance. Analysis of ANOVA and plots of observed values versus predicted one were used to confirm the validity and precision of model.

Table 3 Experiment design matrix and measured values of the considered responses (Y_1: Porosity; Y_2: Mechanical Strength (MPa)

Run	Coded Values			Experimental Values			Experimental Response		Predicted Response	
	A	B	C	Particle size (µm) (A)	T°C (B)	Heating rate (°C/min) (C)	Y_1 (%) Porosity	Y_2 (MPa) Mechanical Strength	Y_1 (%) Porosity	Y_2 (MPa) Mechanical Strength
1	1	-1	1	30	900	10	35.2	13	35,175	13,000
2	1	1	1	30	1200	10	16	17.96	15,875	18,105
3	1	1	-1	30	1200	1	16.5	18.25	16,625	18,105
4	-1	-1	-1	2	900	1	39	11	38,975	10,500
5	1	-1	-1	30	900	1	35	13	35,025	13,000
6	-1	-1	1	2	900	10	39.1	10	39,125	10,500
7	-1	1	1	2	1200	10	16	18.20	16,125	18,100
8	-1	1	-1	2	1200	1	17	18	16,875	18,100

The results equations of Porosity (%) (Y_1) and Mechanical strength (MPa) (Y_2) are reported after:

$$Y_1 = 26.72 - 1.050\,A - 10.35\,B - 0.1500\,C + 0.9250\,A.B - 0.2250\,B.C \quad (3)$$

$$Y_2 = 14.93 + 0.6263\,A + 3.176\,B - 0.624\,A.B \quad (4)$$

Based on the experimental data, regression models were fitted for Y_1 and Y_2, as shown in Equations (3) and (4), respectively. The adequacy of the initial model was tested vis parity plot for observed versus predicted values, as demonstrated in Figure 7. As seen in Figure 7, the high value of the correlation coefficient (R^2 =0,99) demonstrates good correlation between the observed and the predicted responses by initial models.

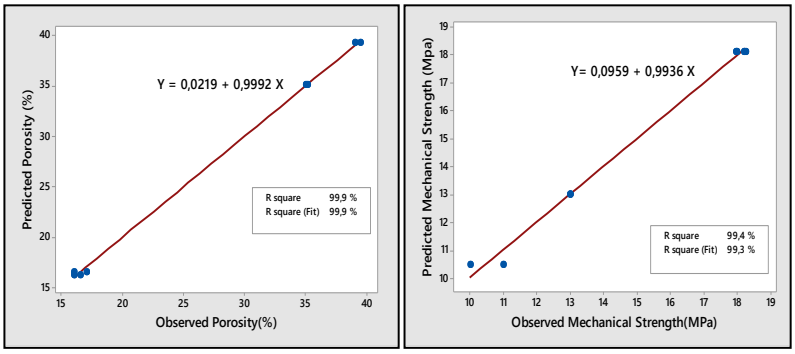

Figure 7 Parity Plot of predicted versus observed responses for Porosity and Mechanical Strength

Analysis of variance (ANOVA) was employed to investigate the adequacy and significance of the model. The effect of a factor is defined as the change in response produced by a change in the level of the factor. This is frequently called the main effect because it refers to the primary factors of interest in the experiments. The ANOVA results showed that the equation adequately represented the actual relationship between each response and the significant variables. The F-value implies that the models are significant and value of Prob>F less than 0,05 indicate that the models terms are significant. Especially larger F-value with the associated P value (smaller than 0,05, confidence intervals) means that the experimental system can be modelled effectively with less error.

According to the ANOVA results (Table 4 and 5), the values of F_{cal} (5373,72 and 206,29 for Porosity (Y_1) and mechanical strength (Y_2) respectively were higher and P values were lower than 0,05 which shows the significance and suitability of full factorial model. Moreover, the normal probability of the residuals almost indicated no departures from the normality (Figure 8).

As shown in the Table 6, High coefficient of determination (R^2: 0,999 and 0,993 for Y_1 and Y_2 respectively) and adjusted coefficient of determination (R^2adj: 0,999 and 0,988 for Y_1 and Y_2 respectively) indicate the good agreement of experimental response values with model predicted values. The predicted R-squared (R^2 pred: 0,998 and 0,974 for Y_1 and Y_2 respectively) was also in reasonable agreement with adjusted R-squared and showed a good prediction of model.

Table 4 Analysis of Variance (ANOVA) for response surface for the prediction of Porosity

Source	**Sum of Square (SS)**	**Df**	**Mean Squares (MSS)**	**F Value**	**P-Value Probability (P)>F**
Model	873,230	5	174,646	5373,72	0,000
Particle Size (µm) - A	8,820	1	8,820	271,38	0,004
Sintering Temperature (°C) - B	856,980	1	856,980	26368,62	0,000
Heating rate (°C/min)- C	0,180	1	0,180	5,54	0,143
$A * B$	6,845	1	6,845	210,62	0,005
$B * C$	0,405	1	0,405	12,46	0,072
Error	0,065	2	0,033		
Total	873,295	7			

Table 5 Analysis of Variance (ANOVA) for response surface for the prediction of Mechanical Strength

Source	**Sum of Square (SS)**	**Df**	**Mean Squares (MSS)**	**F Value**	**P-Value Probability (P)>F**
Model	86,9585	3	28,9862	206,29	0,000
Particle Size (µm) -A	3,1375	1	3,1375	22,33	0,009
Sintering Temperature (°C) - B	80,7085	1	80,7085	574,39	0,000
$A * B$	3,1125	1	3,1125	22,15	0,009
Error	0,5621	4	0,1405		
Total	87,5206	7			

Table 6 Values of correlation coefficient (R^2) related to the adopted models

Response	**R^2 Coefficient of Determination**	**R^2 Adjusted**	**R^2 Predicted**
Y_1: Porosity (%)	0,999	0,999	0,998
Y_2: Mechanical Strength (MPa)	0,993	0,988	0,974

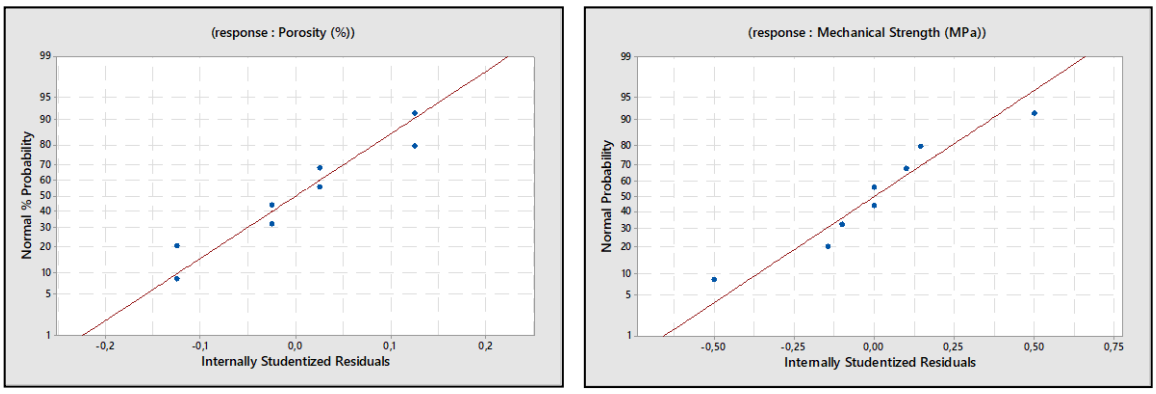

Figure 8 Normal Probability of the Residuals of Porosity and Mechanical strength

Factors that influence the porosity (%) and Mechanical strength (MPa) were evaluated by using factorials plots: main effect, interaction effects, Pareto and normal probability plots [19].

Taking into consideration the value of linear coefficient shown in the above equations, the weight effect of the considered parameters followed the order: B>A>C for the porosity and Mechanical Strength

The main effect which are helpful in visualizing which factors most affects the response of each parameters represent deviations of the average between high and low levels of each one of them as shown in Figure 9.

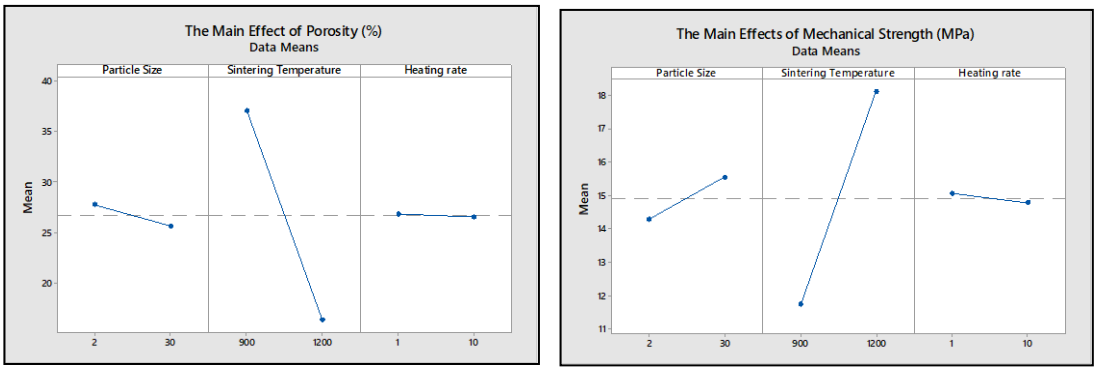

Figure 9 Main Effects for Porosity and Mechanical Strength

Each level of factor effects the response differently; if the slop is close zero, then the magnitude of the main effects will be small. As The results show, for both responses, the sintering temperature appears to have a great effect on the response as indicated by steeply slope due the great surface followed by particle size and heating rate.

The increase of the temperature decreases the porosity and increase the Mechanical Strength. Such effects are related to the strong influence of temperature on the melt formation and consequently on the sintering process. However, the Heating rate had a little influence on the technological properties of ceramic support membrane.

The interaction effect of each parameters is shown in Figure 10. If the interactions between the lines are not parallel, the interactions among control factors is strong and vice versa. The figures show the interaction between sintering temperature and particle size for the two response is significant. These phenomena can be explained that the powder with the small particle size (high surface area) is easily sintered and became a single, large solid body. Otherwise, the main disadvantage of the large specific area is tendency to agglomerate and form uncontrolled lumps and clusters [6, 10, 11, 22, 23].

Agglomerates contain nearly random-size pores, and the largest of these pores can seriously interfere with sintering, as well as causing others problems like warping and cracking of the membrane support [6, 10, 11, 22, 23, 27].

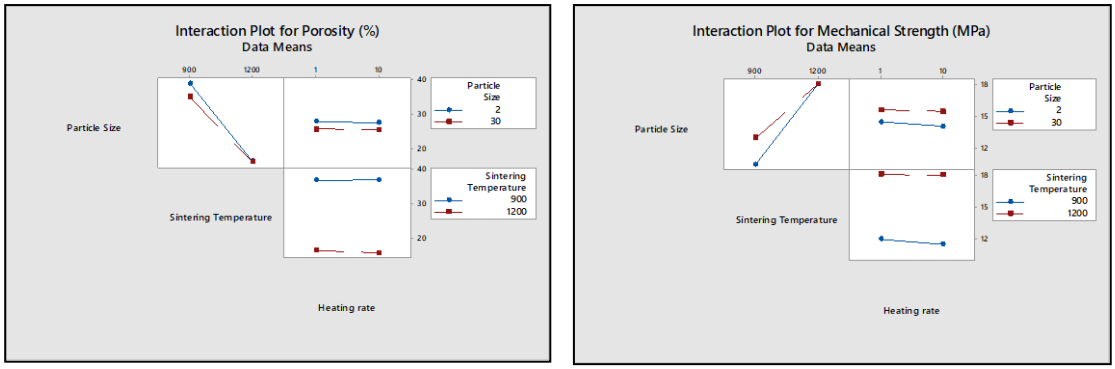

Figure 10 Interaction Effects for Porosity and Mechanical Strength

A Normal probability plot of the standardized effects is used and presented in Figure 11. One point on the plot is assigned to each effect. According to the normal probability plots, the points which are close to a line fitted to the middle group of points represent those estimated factors that do not demonstrate any significant effect on the response variables. Points far away from the line likely represent the authentic factor effects [20-21].

For the Porosity the main factor (Temperature and Particle size) and their interaction (temperature*Particle size) are far away from the straight line and are therefore considered to be significant. The temperature and particle size exist on the left of the line which proves that they have a negative effect whereas the interactions (Temperature*Particle size) exists on the right of the straight line which mean the interaction between the two-factor acted antagonistically and varied independently.

For Mechanical strength, the temperature and particle size have a positive effect and their interaction (temperature*Particle size) exists on the left side of the straight line which mean the interaction acted antagonistically. the Heat rate factor doesn't significant [22-24].

The relative importance of the main effects and their interactions was also observed on the Pareto Chart as shown in Figure 12. The value that exceed the reference line are considered significant values and those which do not are considered insignificant [13, 26]. According to this figure, for Porosity and Mechanical strength, the temperature, particle size and their interaction are significant [22, 25, 27].

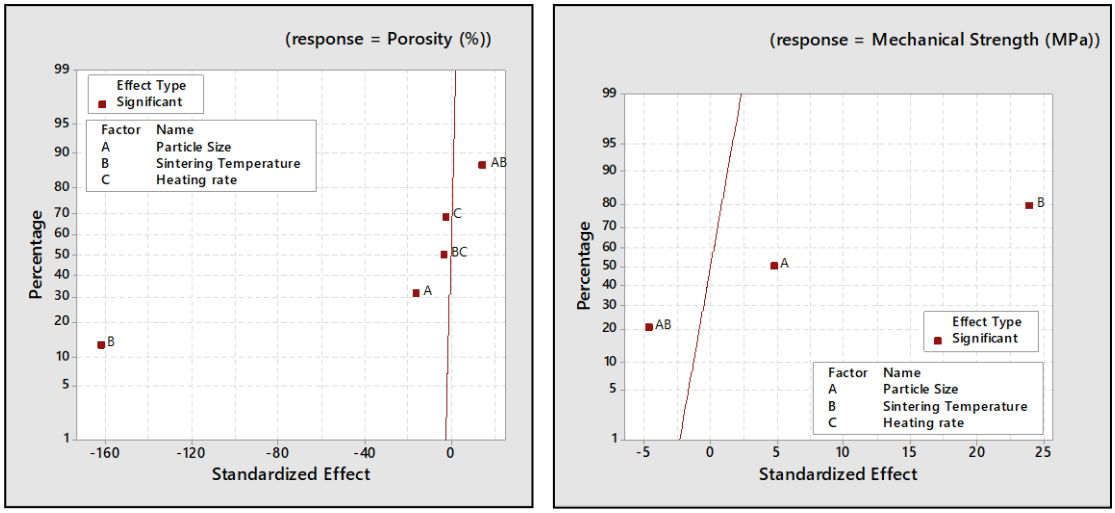

Figure 11 Normal Plot of the Standardized effects for Porosity and Mechanical Strength

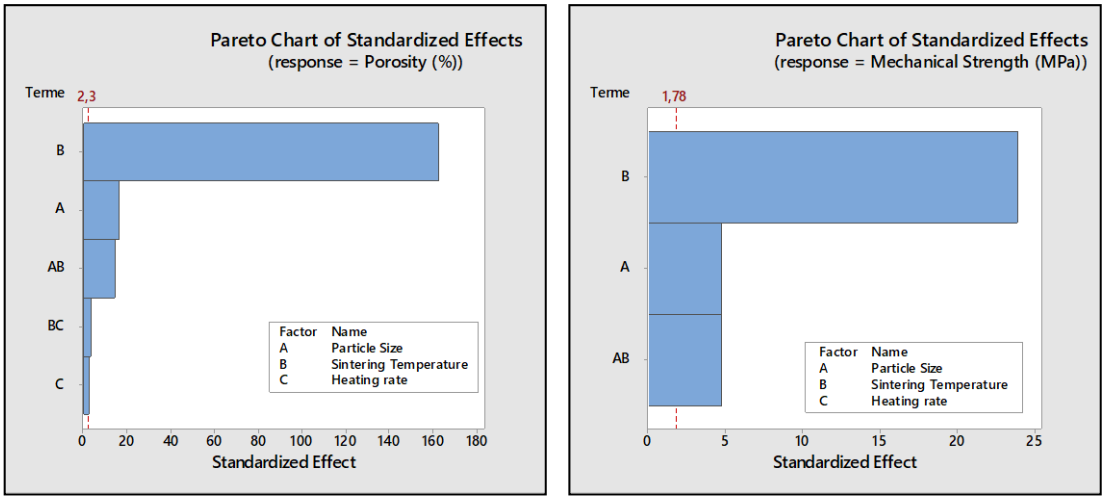

Figure 12 Pareto Chart of Individual Factors effects of Porosity and Mechanical Strength

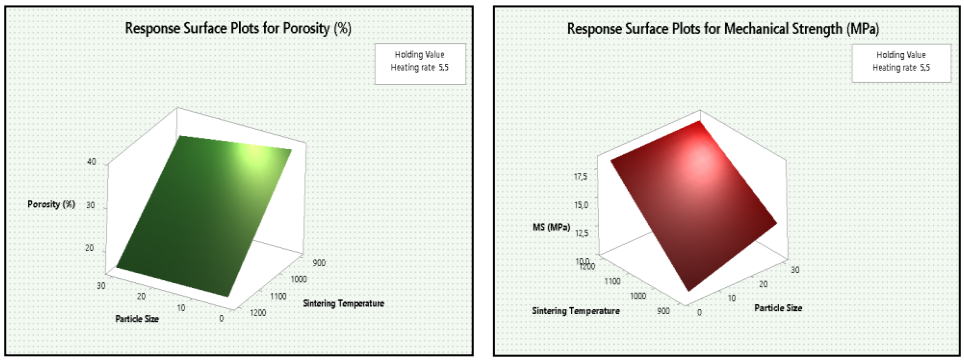

Figure 13 Response Surface Plots for Porosity and Mechanical Strength

Figure 13 shows the calculated response surfaces for each technological property (Porosity and Mechanical Strength) for the sintered test specimens. These 3D surface correspond to graphical representation

of Equation (1) and (2), and very helpful in determining the response value for the sintered parameters investigated. The surface response allowed the simultaneous assessment for the both variable (Particle size and sintering temperature) and also the determination the region with the best performances of the technological properties. It can be seen that at a higher sintering temperature, the mechanical strength was higher and the porosity obtained was lower. However, the Particle size has a little influence in Mechanical strength and the porosity when the temperature is around 900 °C, but when the temperature reaches 1200 °C, the influence of particle size becomes insignificant.

Our final objective is to obtain a higher porosity for a low hydrodynamic resistance and a high Mechanical resistance to work a high pressure. After all the above results, the elaboration of ceramic support membrane from a Moroccan clay at optimal factors including particle size of 2 µm, sintering temperature of 950°C, Heating rate of 1°C predicts the porosity of 40,8% and Mechanical strength of 12MPa.

4.0 CONCLUSION

The use of experimental design with a full factorial design is an effective tool to evaluate the effects the firing cycle (Temperature, Heating rate) and particles size parameters on the technological properties of clay used in ceramic support membrane.

The calculated regression models for each technological property were found to be statically significant and presented low variability.

The investigation has demonstrated that the sintering temperature is the main controlling factor of the technological properties of ceramic membrane support. The increase of sintering temperature had a positive effect on the mechanical strength but reduce the porosity due the densification of the materials. The particle size has also a significant influence of the support porosity, this is can be explained that the powder with the small particle size is easily sintered and became a single, large solid body. The elaboration of ceramic support membrane from a Moroccan clay at optimal factors including particle size of 2 µm, sintering temperature of 950°C, Heating rate of 1°C predicts the porosity of 40,8% and Mechanical strength of 12MPa.

REFERENCES

[1] M. K. Purkait, R. Singh. 2018. *Membrane Technology in Separation Science*. Taylor and Francis Group. LLC. London: NewYork.

[2] C. Das, S. Bose. 2017. *Advanced Ceramic Membrane and Application*. Taylor and Francis Group, LLC, London, NewYork.

[3] Y. C. Dong, S. F. Chen, X. B. Zhang, J. K. Yang, X. Q. Liu, G. Y. Meng. 2006. Fabrication and Characterization of Low Cost Tubular Mineral-based Ceramic Membranes For Microfiltration from Natural Zeolite. *J. Membr. Sci.* 281. 592-599. https://doi.org/10.1016/j.memsci.2006.04.029

[4] N. El Qacimi, N. El Baraka, N. Saffaj, R. Mamouni, A. Laknifli, S. Alami Younssi, A. Faouzi, H. Zidouh. 2019. Preparation and Characterization of Flat Membrane Support Based on Sahara Moroccan Clay: Application to the Filtration of Textile Effluents. *Desal. Water*

Treat. 143. 111-117. https://doi.org/10.5004/dwt.2019.23516.

[5] N. Saffaj, M. Persin, S. A. Younssi, A. Albizane, M. Cretin, A. Larbot. 2006. Elaboration and Characterization of Microfiltration and Ultrafiltration Membranes Deposited on Raw Support Prepared from Natural Moroccan Clay: Application to Filtration of Solution Containing Dyes and Salts. *App. Clay Sci.* 31: 110-119. https://doi.org/10.1016/j.clay.2005.07.002.

[6] D. J. Shanefield. 1995. *Organic Additives and Ceramic Processing with Application in Powder Metallurgy, Ink and Paint*. Kluwer Academic Publishers, Boston/Dordrecht/ London

[7] G. M. do Nascimento. 2016. Clays, Clay Minerals and Ceramic Materials Based on Clay Minerals, ExLi4EvA.

[8] A. A. Taleb, N. E. Baraka, N. Saffaj, A. Laknifli, R. Mamouni, A. Fatni, A. E. Hammadi, N. E. Qacimi. 2018. New Tubular Ceramic Membranes from Natural Moroccan Clay for Microfiltration Application. *E3S Web Conf*. 37: 01011. https://doi.org/10.1051/e3sconf/20183701011.

[9] A. Khalfaoui, M. Hajjaji, S. Kacim, A. Baçaoui. 2006. Evaluation of the Simultaneous Effects of Firing Cycle Parameters on Technological Properties and Ceramic Suitability of a Raw Clay Using the Response Surface Methodology. *J. Am. Ceram. Soc.* 89: 1563-1567. https://doi.org/10.1111/j.1551-2916.2006.00955.x.

[10] S. L. Correia, D. Hotza, A. M. Segadaes. 2004. Simultaneous Optimization of Linear Firing Shrinkage and Water Absorption of Triaxial Ceramic Bodies Using Experiments Design. *Ceramics International*. 30: 917-922. https://doi.org/10.1016/j.ceramint.2003.10.013.

[11] G. T. Saleiro, A. Z. Destefani, J. N. F. Holanda. 2012. Use of Factorial Design in the Study of the Influence of Firing Cycle Parameters on the Technological Properties of Brazilian Kaolinitic Material. *Adv. in Ceram. Sci. Eng.* 1: 11-18.

[12] L. Hamdi, L. B. Toumi, Z. Salem, K. Allia. 2016. Full Factorial Experimental Design Applied to Methylene Blue Adsorption onto Alfa Stems. *Desal. Wat. Treat.* 57: 6098-6105. https://doi.org/10.1080/19443994.2015.1029003.

[13] R. G. Easterling. 2015. *Fundamentals of Statistical Experimental Design and Analysis*. John Wiley & Sons. Ltd. New Mexico.

[14] J. Goupy, L. Creighton. 2006. *Introduction to the Experimental Design*. Dunod. Paris.

[15] J. R. Smith, C. Larson. 2019. Statistical Approaches in Surface Finishing. Part 3. Design of Experiments. *Transactions of the IMF*. 97: 289-294. https://doi.org/10.1080/00202967.2019.1673530.

[16] D. Njoya, M. Hajjaji, D. Njopwouo. 2012. Effects of Some Processing Factors on Technical Properties of a Clay-based Ceramic Material. *Appl. Clay Sci.* 65-66. 106-113. https://doi.org/10.1016/j.clay.2012.05.013.

[17] G. Kakali, T. Perraki, S. Tsivilis, E. Badogiannis. 2001. Thermal Treatment Of Kaolin: The Effect of Mineralogy on the Pozzolanic Activity. *Appl. Clay Sci*. 20: 73-80. https://doi.org/10.1016/S0169-1317(01)00040-0.

[18] A. Lahsini, J. Bentama, A. Addaou, M. Rafiq. 1998. Physicochemical Characterization and Study of the Sintering of a Clay Intended for the Development of Tangential Filtration Membranes. *J. Chim. Phys.* 95: 1001-1019. https://doi.org/10.1051/jcp:1998227.

[19] M. Loutou, W. Misrar, M. Koudad, M. Mansori, L.Grase, C. Favotto, Y. Taha, R. Hakkou. 2019. Phosphate Mine Tailing Recycling in Membrane Filter Manufacturing: Microstructure and Filtration Suitability. *Minerals*. 9(5): 318. https://doi.org/10.3390/min9050318.

[20] M. Loutou, M. Hajjaji, M. Mansori, C. Favotto, R. Hakkou. 2016. Heated Blends of Clay and Phosphate Sludge: Micostructure and Physical Properties. *J. Asi. Ceram. Soc.* 4: 11-18. https://doi.org/10.1016/j.jascer.2015.10.003.

[21] J. Yu, H. Wang, J. Hou, J. Zhang, G. Qiao, Z. Jin. 2008. Investigation of Flexural Strength and Porosity of Porous Si3N4 Ceramics through Orthogonal Experimental Design. *J. Ceram. Proc. Res*. 9(6): 624-629. http://www.jcpr.or.kr/journal/archive/view/598.

[22] S. L. Correia, D. Hotza, A. M. Segadaes. 2005. Optimising Mechanical Strength and Bulk Density of Dry Ceramic Bodies Through Mixture Design. *Bol. Soc. Esp. Ceram.* 44(1): 53-58. http://boletines.secv.es/upload/20070116122020.44[1]53-58.pdf.

[23] D. Njoya, M. Hajjaji. 2015. Quantification of the Effects of Manufacturing Factors on Ceramic Properties Using Full Factorial Design. *J. Asi. Ceram. Soc.* 3: 32-37. https://doi.org/10.1016/j.jascer.2014.10.002.

[24] W. Misrar, M. Loutou, L.Saadi, M. Mansori, M. Waqif, C. Favotto. 2017. Cordierite Containing Ceramic Membranes from Smectetic Clay Using Natural Organic Wastes as Pore-Forming Agents. *J. Asi. Ceram. Soc.* 5: 199-208. https://doi.org/10.1016/j.jascer.2017.04.007.

[25] J. D. de Oliveira Henriques, M. W. Pedrassani, W. Klitzke, A. B. Mariano, J. V. C. Vargas, R. B. Vieira. 2017. Thermal Treatment of Clay-Bbd Ceramic Membranes for Microfiltration of Acutodesmus obliquus. *Appl. Clay Sci.* 150: 217-224. https://doi.org/10.1016/j.clay.2017.09.017.

[26] M. Loutou, M. Hajjaji, M. Mansori, C. Favotto, R. Hakkou. 2016. Heated Blends of Phosphate Waste: Microstructure Characterization, Effects of Processing Factors and Use as a Phosphorus Source for Alfalfa Growth. *J. Environ. Manage*. 177: 169-176. https://doi.org/10.1016/j.jenvman.2016.04.030.

[27] M. N. Rahaman. 2007. *Sintering of Ceramics.* Taylor and Francis Group, LLC, London, NewYork.