

A FABRICATION OF A LOW-COST ZEOLITE BASED CERAMIC MEMBRANE VIA PHASE INVERSION AND SINTERING TECHNIQUE

(Fabrikasi Membran Seramik Kos Rendah Berasaskan Zeolit Melalui Kaedah Penyongsangan Fasa dan Sinteran)

Mohd Ridhwan Adam¹, Mohd Hafiz Dzarfan Othman^{1*}, Mohd Hafiz Puteh², Mohammad Arif Budiman Pauzan¹, Mukhlis A Rahman¹, Juhana Jaafar¹

¹Advanced Membrane Technology Research Centre (AMTEC), Faculty of Chemical and Energy Engineering

²Faculty of Civil Engineering

Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor, Malaysia.

*Corresponding author: hafiz@petroleum.utm.my

Received: 26 August 2016; Accepted: 8 January 2017

Abstract

The usage of ceramic membranes is gaining enormous attention due to their higher selectivity, permeation rate, and chemical and thermal stability as compared to the polymeric membrane. Owing to the fact of these superior properties, the search of a low-cost ceramic membrane is still in demand. To date, the fabrication of ceramic membrane using natural zeolite as the membrane ceramic loading has not yet been explored. Thus, this study aims the development of natural zeolite (Clinoptilolite) as the ceramic source in the fabrication of low-cost hollow fibre ceramic membrane (HFCM) via phase inversion and sintering techniques. Several fabrication parameters were also studied namely air gap distance, bore fluid flow rate and sintering temperature throughout this research. The best ceramic membrane was fabricated using 5 cm air – gap distance, 13 mL min⁻¹ of bore fluid flow rate and 1000 °C of sintering temperature. The acceptable strength and morphological behaviour of finger-like and sponge-like voids were found to be an advantageous characteristic of the fabricated membrane. The cheap and yet abundant raw ceramic material as well as low sintering temperature are eventually reduced the cost of membrane production.

Keywords: natural zeolite, ceramic membrane, phase inversion, sintering

Abstrak

Penggunaan membran seramik semakin mendapat perhatian ramai berasaskan sifat pemilihan yang tinggi, kadar keserapan, dan daya ketahanan yang tinggi terhadap suhu dan bahan kimia berbanding dengan membran polimer. Berdasarkan fakta tentang sifat-sifat yang hebat ini, maka pencarian terhadap membran seramik kos rendah masih lagi menjadi permintaan. Sehingga kini, fabrikasi membran seramik menggunakan zeolit semulajadi sebagai bahan seramik masih belum dikaji. Justeru itu, kajian ini memfokuskan kepada pembangunan zeolit semulajadi (Clinoptilolite) sebagai bahan sumber seramik dalam fabrikasi membran seramik gentian berongga (HFCM) berkos rendah melalui kaedah penyongsangan fasa dan sinteran. Beberapa parameter fabrikasi telah dikaji iaitu jarak ruang udara, kadar aliran cecair penebuk dan suhu sinteran. Membran seramik terbaik telah diperolehi menggunakan jarak ruang udara sebanyak 5 cm, kadar aliran cecair penebuk iaitu 13 mL min⁻¹ dan 1000 °C bagi suhu sinteran. Nilai kekuatan dan sifat morfologi yang memuaskan bagi struktur span dan jejari dikenal pasti menjadi ciri - ciri kelebihan bagi membran yang difabrikasi. Harga yang murah dan sumber asli bahan seramik yang banyak serta suhu sinteran yang rendah justeru mengurangkan kos penghasilan membran ini.

Kata kunci: zeolit semulajadi, membran seramik, penyongsangan fasa, sinteran

Introduction

In recent years, the development in hollow fibre membrane contactors has gained an enormous attention for the elimination of various volatile contaminants including ammonia [1]. A membrane contactor is a system that attains gas/liquid and liquid/liquid mass transfer without the dispersal of one phase within another. Usually, most of the hollow fibres used are commonly has microporous and hydrophobic properties. In the case of the gas/liquid separation, the penetration of aqueous solution into gas-filled pores is avoided since the hydrophobic properties of the membrane hindered the penetration of this high surface tension materials. Hence, the volatile compound will volatilize from the feed, diffuse through the gas-filled membrane pores, and then be removed by a sweep gas, sucked up by a vacuum or reacted with a stripping solution [2].

Hollow fibre membrane contactors have shown to be useful for eradicating low-concentration solutes from wastewater and they may verify to be a smart substitute for the present work. Hollow fibre membrane contactors, usually in a shell and tube configuration, offer many benefits over traditional contact operations. Membrane contactors provide a large and stable interfacial area. Two fluids flowing across the hollow fibre allow mass transfer to occur between the fluids. The hydrophobic microporous membrane provides the transfer area and restricts the permeation of water. The transfer takes place at the pore opening, inside the pore, or at the pore exit.

Currently, most of the commercially available and commonly used hollow fibre membranes are made from polymeric materials such as polyethylene, polypropylene, polyimide, etc., For instance, for gases in water, polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) are normally used as hydrophobic polymers [3,4]. Most of these polymeric hollow fibres are vulnerable to chemical and thermal stresses, resulting in morphological changes and membrane swelling. These changes have weakening effects towards the membrane performance [5,6,7]. Therefore, polymeric membranes are limitedly applicable in mild operating conditions, namely low temperature and low acidity or alkalinity.

As a solution into this matter, a new approach has been developed in the invention of hollow fibre ceramic membranes (HFCM). Owing to the fact of their better thermal stability chemical resistance, ceramic membranes are superior over polymeric membranes in harsher environment. Numbers of studies have shown the achievement in the preparation of hollow fibre membranes of the ceramic materials such as aluminium oxide (Al_2O_3), $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ (SCYb), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF), $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_{3-\alpha}$ (LSCF), etc. [8,9]. However, the production of a low cost ceramic membrane is still searching. Thus, zeolite is known to have a potential in producing a cheaper but effective HFCM.

Natural zeolites are abundant raw materials across the globe, and have been shown to possess interesting ceramic properties especially through high temperature ($\sim 1150^\circ\text{C}$) phase transformations [10]. Natural zeolites are the principal inorganic cation exchangers that possesses high selectivity, ion exchange capacity and compatibility towards the natural environment. Currently, various different types of this mineral have been discovered. The most abundant natural zeolite that occurs in relatively large minerable sedimentary deposits in satisfactorily high purity in many parts across the globe is known as clinoptilolite [11].

The ion-exchange features of the zeolite minerals were first discovered in 1858 [12]. Clinoptilolite is also known to be as one of the ion exchanger with a high affinity for ammonium ion. Clinoptilolite possesses significant macroporosity since it shows a classical alumina silicate like structure. In nature, the cations present on clinoptilolite are sodium, potassium and calcium. The selectivity order of natural zeolite among cations shows that ammonium ion is one of the highest selected cations toward zeolite. Therefore, it is strongly believed that natural zeolite has an ability in the removal of ammonia from the solution concerning adsorption and ion exchange feature.

This work aims the development of low cost ceramic membrane in liquid-liquid membrane contactor system. It is known that most of the ceramic-typed membranes are made of metal oxides, which are normally hydrophilic in nature. This is due to the presence of hydroxyl (OH^-) groups on the surface. This property avoids them to be applicable in some applications which necessitate only hydrophobic membranes, such as non-polar solvent extraction, membrane contactor, vapour permeation and water ozonation [13]. However, the hydrophobicity properties of ceramic membranes can be enhanced by surface modification. More than a few types of surface

modifying agents can be used such as fluoroalkylsilanes (FAS), polydimethylsiloxane (PDMS), alcohol, chloroalkylsilanes, etc. [14]. Thus, the fabrication of zeolite-based HFCM for the liquid-liquid membrane contactor system is highly aimed to be realized. As a consequence, the removal of ammonia in wastewater via ceramic membrane contactor system can be done.

Materials and Methods

Raw materials

The fine zeolite powder was prepared by grinding and sieving the zeolite stone purchased from Indonesia prior to the experiment. Polyethersulfone (PESf, Radel A300, Ameco Performance, USA), Arlcel P135 gel (CRODA), and N-methyl-pyrrolidone (NMP, QRëC™) were used as polymer binder, dispersant and solvent, respectively. The suspension composition (ceramic powder weight ratio of 35 wt.%) and the hollow fibre ceramic membrane (HFCM) fabrication parameters namely air – gap distance and bore fluid flow rate are listed in Table 1 and Table 2, respectively.

Table 1. The composition of zeolite based hollow fibre ceramic membrane

Composition	Zeolite (g)	Arlcel P135 (g)	PESf (g)	NMP (g)
35 wt.%	35	1	5	59

Table 2. Zeolite based hollow fibre ceramic membrane spinning parameters used

Fibre	Bore Fluid Flow Rate (mL/Min)	Air Gap (Cm)
1	10	3
2	10	5
3	10	7
4	7	5
5	10	5
6	13	5

Preparation of spinning suspension

The low-cost zeolite based hollow fibre ceramic membrane was prepared by immersion-induced phase inversion and sintering technique. Firstly, Arlcel P135 was dissolved in NMP solvent at vigorous stirring. After a homogeneous solution was formed, the pre-dried zeolite powder (the weight ratio specified in Table 1) was slowly added and projected into the ball milling process using NQM-2 planetary ball mill. After 48 hours of milling, PESf of desired weight was added into the dope and further milled for another 48 hours. The resulting suspension was degassed for 30 minutes at room temperature to eliminate the air bubbles.

Fabrication of zeolite based hollow fibre ceramic membrane

After the degassing process, the spinning suspension was inserted into a syringe pump and extruded through a tube-in-orifice spinneret with internal diameter of 0.5 mm and external diameter of 2.8 mm. Tap water was used as the internal coagulant or also known as bore fluid solution. The fibre membrane precursor passed through a certain air-gap distance were immersed in a water coagulant (external coagulant) bath for 24 hours (Figure 1) to let the phase inversion process to be completed. Afterwards, the membrane precursors were dried at room temperature. Finally, the hollow fibre ceramic membrane precursors were calcined in air for 4 hours at various sintering temperatures in the range of 950 - 1050 °C by using a tubular furnace (XL - 1700). About 5 – 8 of membrane precursors were placed into the alumina boat and subjected into the furnace for stipulated time. The temperature was increased from room temperature to 600 °C at a rate of 2 °C min⁻¹ and held for 2 hours, then to target temperature at a rate of 5 °C

min⁻¹ and held for 4 hours. The temperature was later cooled down at a rate of 5 °C min⁻¹ to room temperature. In this process, the polymer binder was burned off leaving only ceramic material in the HFCM.

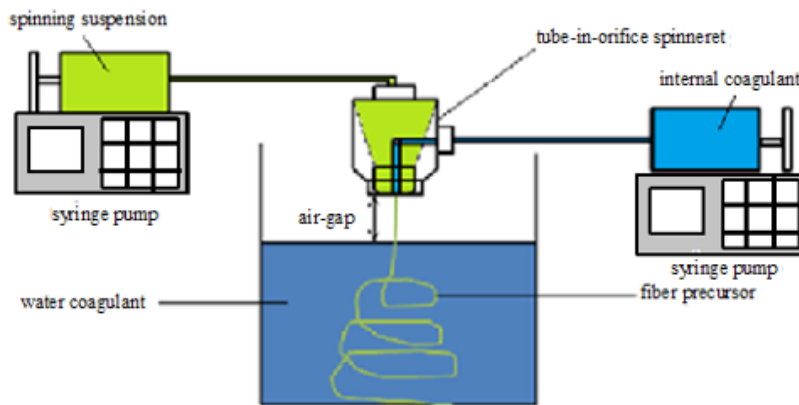


Figure 1. The schematic diagram of the phase inversion process set up for the fabrication of hollow fibre ceramic membrane

Characterization

The viscosity of the spinning suspension was measured instantly prior to the spinning process using viscometer (BROOK FIELD) at shear rate range between 1 s⁻¹ and 100 s⁻¹ at room temperature. The morphologies of the HFCM for all parameters studied were analyzed using scanning electron microscopy (SEM, Hitachi Model TM 3000) at different magnifications. Prior to the SEM analysis, the samples were gold coated under vacuum for 3 minutes. The morphological behavior as well as the wall thickness were examined through this analysis. In addition, the three-point bending tests were done in order to measure the mechanical strength of the zeolite HFCM using INSTRON 3342. The HFCMs about 5 cm in length were tested in three – point bending instrument and at least a triple set of test were done for each parameter studied. The mechanical strength (σ_F) was calculated using Equation (1) as follow [15];

$$\sigma_F = \frac{8FLD_o}{\pi(D_o^4 - D_i^4)} \quad (1)$$

where F is the maximum load at which the fracture occurred while L, D_o, and D_i are the length of span (43 mm), the outer diameter, and the inner diameter of the hollow fibres, respectively.

Results and Discussion

Rheology of ceramic suspension

In this study, the presence of ceramic (35 wt.%) loading has affected the viscosity of the suspension. The viscosity of the ceramic suspension at shear rate of 1 – 100 s⁻¹ is shown in Figure 2. The rheological profile of this ceramic suspension containing Zeolite/NMP/Arlacel/PESf is found to conform the non-Newtonian behavior that has been previously reported by Kingsbury and Li [16]. The viscosity of Zeolite/NMP/Arlacel/PESf suspension was determined at a shear rate of 30 s⁻¹. The viscosity of this suspension was found to be 1.0308 Pa.s. From the SEM analysis, all HFCMs spun at this ceramic loading show the formation of the finger-like voids. According to Kingsbury and Li, the formation of finger-like structure is mainly dominated by the viscosity of the ceramic suspension [16]. A finger-like formation occurred when less viscous fluid (non-solvent) comes into contact with high viscous fluid (ceramic suspension) [17]. In addition, they have investigated that the critical viscosity value for their ceramic is 12.1 Pa.s at the shear rate of 30 s⁻¹. This value has been established as the threshold value for the formation of finger-like void in the membrane morphology. In other words, if the viscosity value obtained was beyond above this critical viscosity value, the formation of finger-like void is unfavorably to occur. In this study, the viscosity of the 35 wt.% ceramic loading suspension is far lesser than the critical viscosity value. Thus, the

formation of finger-like void is most likely to attain. This theory is positively supported by the SEM analysis results which shown the presence of finger-like structure in most of the fabricated HFCMs.

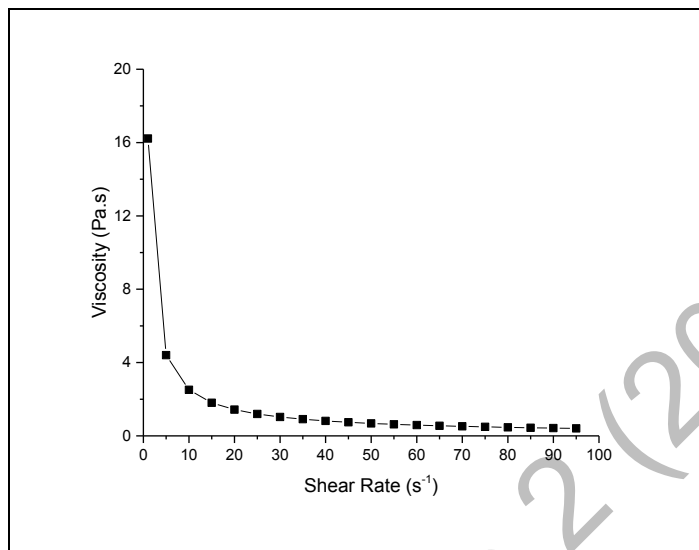


Figure 2. The rheological profile of ceramic suspension containing Zeolite/NMP/Arlacel/PESf with 35 wt. % of zeolite content

Effect of air-gap distance

The effect of air-gap distance on the structural behavior of zeolite based HFCM was studied at three different air-gap distances at a constant bore fluid flow rate of 10 mL min⁻¹. The obtained HFCM precursors were first sintered at 1000 °C prior to the morphological analysis through SEM. The SEM images of these HFCMs were depicted in Figure 3.

From Figure 3, it can be clearly seen that all three HFCMs showed the formation of finger-like void and sponge-like structures in all membranes. The finger-like void is significantly observed and obtained as the air-gap distance increased. The voids were elongated from the inner part towards the outer of the fibre as the air-gap distance enhanced. The best finger-like void was obtained by the air-gap of 5 cm (Figure 3b) since it gives the higher value in mechanical strength (Figure 4). In addition, the elongation of finger-like structure was not significantly enhanced as the air-gap increased from 5 to 7 cm. Furthermore, the formation of finger-like void were in good agreement with the viscosity analysis findings. According to Kingsbury and Li, the presence of water moisture in the air has encouraged a minor combination between non-solvent and solvent and thus amplified the viscosity at the outer surface. This phenomenon thus stifled the formation of outer finger-like void and preferred the formation of inner finger-like structure. In addition, 5 cm was selected as the best air-gap distance due to its mechanical strength (Figure 4). The lower value of mechanical strength possessed by air-gap 7 cm (Figure 3c) is due to the significant distortion suffered by the inner structure of the membrane. Similar phenomenon has been reported in Li et al. study [18].

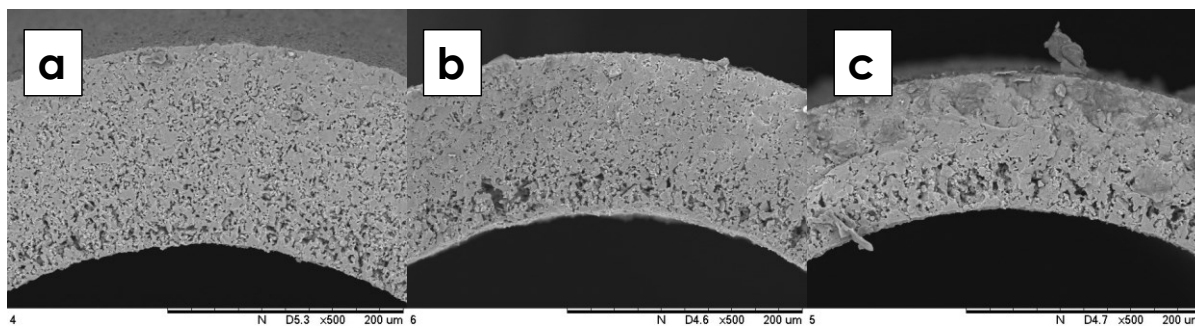


Figure 3. Cross-sectional SEM images of the zeolite based HFCMs spun at different air-gap distance: (a) fibre 1, 3 cm; (b) fibre 2, 5 cm; and (c) fibre 3, 7 cm, at a fixed bore fluid flow rate of 10 mL min^{-1} and 35 wt.% of ceramic loading, respectively

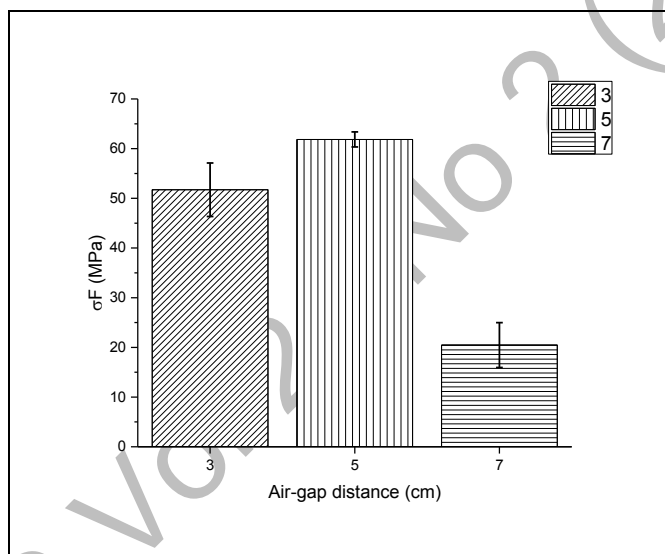


Figure 4. Flexural strength of the zeolite based HFCMs spun at different air-gap distance: (a) fibre 1, 3 cm; (b) fibre 2, 5 cm; and (c) fibre 3, 7 cm, respectively

Effect of bore fluid flow rate

The morphological behavior of zeolite based HFCM spun at different bore fluid flow rate were depicted in Figure 5. The studied bore fluid flow rate in this study namely 7 mL min^{-1} , 10 mL min^{-1} , and 13 mL min^{-1} , at a static air-gap distance of 5 cm and ceramic loading of 35 wt.% of zeolite. From the figure, it can be seen that the alteration of bore fluid flow rate has significantly change the morphologies of the HFCMs produced. The low flow rates (7 mL min^{-1} and 10 mL min^{-1}) is found to distort the bore shape formation of the fibre. However, the regular formation of the outer contours of the fibre was obtained by all fibres spun at different bore fluid flow rate without any distortion. The deformation of inner shape of the fibre can be clearly seen when the fibres spun at low bore fluid flow rates (7 mL min^{-1} and 10 mL min^{-1}), while a completely circular shape was obtained by the bore fluid of 13 mL min^{-1} .

The shrinkage of the HFCM was always obtained in the phase inversion process. This is due to the rate of solvent (NMP) diffusion from the suspension is always faster than the rate of diffusion of water into the suspension [19]. The shrinkage of the fibre was also attributed to the inward radial force which eventually resulted in the deformation of the inner shape of the fibre. There are two main reasons attributed into this phenomenon namely hydrodynamic

force and solidification rate. A low bore fluid flow rate (7 mL min^{-1} and 10 mL min^{-1}) could not generate a sufficient hydrodynamic force(outward) against the ceramic suspension which is thus resulting in the distortion of the bore shape.

The low bore fluid flow rates also produced a slow solidification rate. The slow solidification rate attributed to the incomplete solidification of polymer in the inner surface of the fibre which in turn is not durable enough to resist the inward radial force and thus distorted the formation of the circular contour of the fibre. The flow rate of 13 mL min^{-1} is found to be the best bore fluid flow rate in order to produce the perfect circular shape of the inner contour of the zeolite based HFCM.

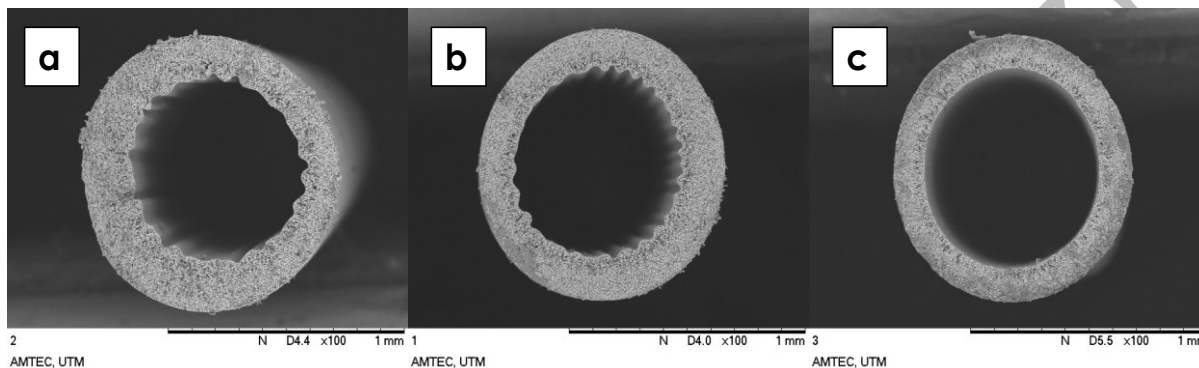


Figure 5. SEM images of the zeolite based HFCMs spun at different bore fluid flow rate: (a) fibre 4, 7 mL min^{-1} ; (b) fibre 5, 10 mL min^{-1} ; and (c) fibre 6, 13 mL min^{-1} , at a fixed 35 wt.% of ceramic loading and air-gap distance of 5 cm, respectively

Effect of sintering temperature on zeolite based HFCM properties: Sintering shrinkage

The zeolite based HFCM precursors were subjected into air calcination in order to remove the polymer binder and only ceramic would remain in the fibre. The sintering profile of the zeolite based HFCM is depicted in Figure 6. At first stage of the calcination, all polymer binders were eliminated at 600°C . The grain growth of the ceramic particles is occurred at targeted sintering temperature ($950^\circ\text{C} - 1100^\circ\text{C}$). Figure 7 shows the cross-sectional images of the zeolite based HFCMs before and after calcination at varying sintering temperatures. From the images, it can be clearly seen that the fibre has shrunk when sintered as compared to the fibre precursor. The shrinkage of the fibre is further incremented as the temperature increased.

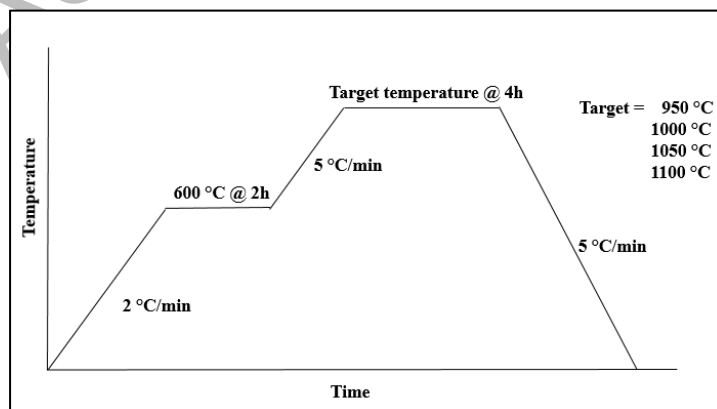


Figure 6. Sintering profile of the zeolite based HFCM

The radial shrinkage of the zeolite based HFCMs increased from 22% to 37% as the sintering temperature increased from 950 °C to 1100 °C. The increment in the shrinkage value suggesting the formation of sintering neck caused by the diffusion of the particles in the fibre [18]. Further enhance in sintering temperature has led to the destruction of the fibre due to the melting of the ceramic.

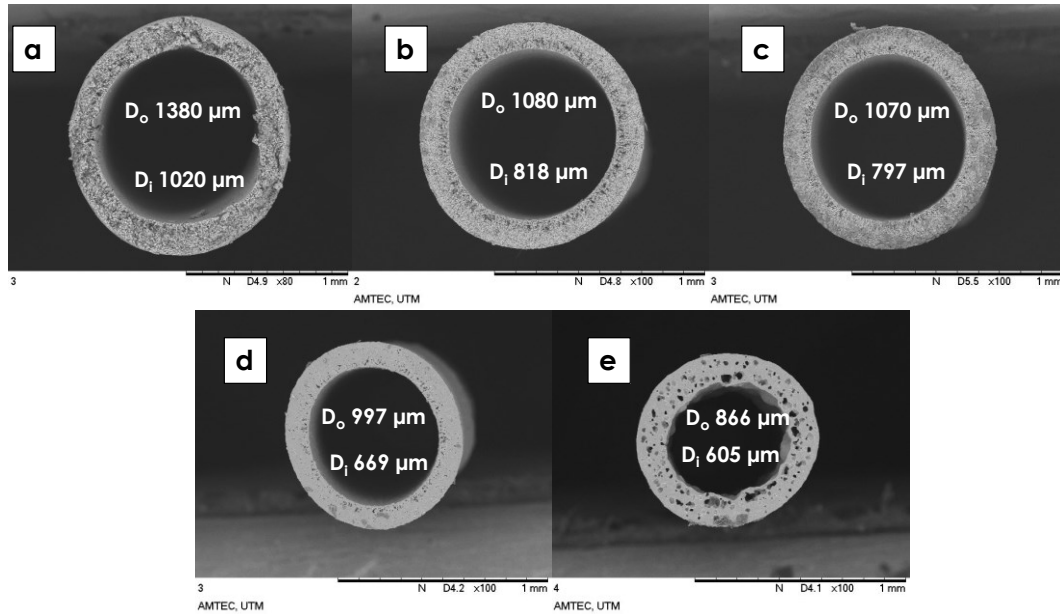


Figure 7. Cross-sectional SEM images of the zeolite based HFCMs (fibre 6) before (a) and after calcination at different sintering temperatures: (b) 950 °C; (c) 1000 °C; (d) 1050 °C; and (e) 1100 °C, fabricated at a fixed air-gap distance of 5 cm, bore fluid flow rate of 13 mLmin⁻¹, and ceramic loading of 35 wt.% of zeolite, respectively.

SEM microstructure of zeolite based HFCM

Figure 8 depicts the microstructure of the cross-sectional zeolite based HFCMs before and after the sintering process has taken place at different temperature. The images of these membranes were taken at the magnification of 500 x in order to see the porous microstructure of the membranes.

From the images, it can be clearly seen that the sintering temperature had significantly affect the microstructure porosity of the inner and outer parts of the membranes. Before the sintering process has done, the particles of the ceramic altogether with the binder were freely distributed throughout the membrane and loosely packed in the membrane. As the sintering process has taken place, the polymer has been eliminated and left only the ceramic in the membrane. During this process, the grain growth of the particles occurred and the membrane is shrunk and densified. The formation of finger-like void is also significantly enhanced as the sintering temperature increased from 950 °C to 1000 °C. Similarly, Wang et al. [20] reported the densification of β -sialon ceramics at a temperature of 1650 °C, for the highest mechanical strength for the ceramic.

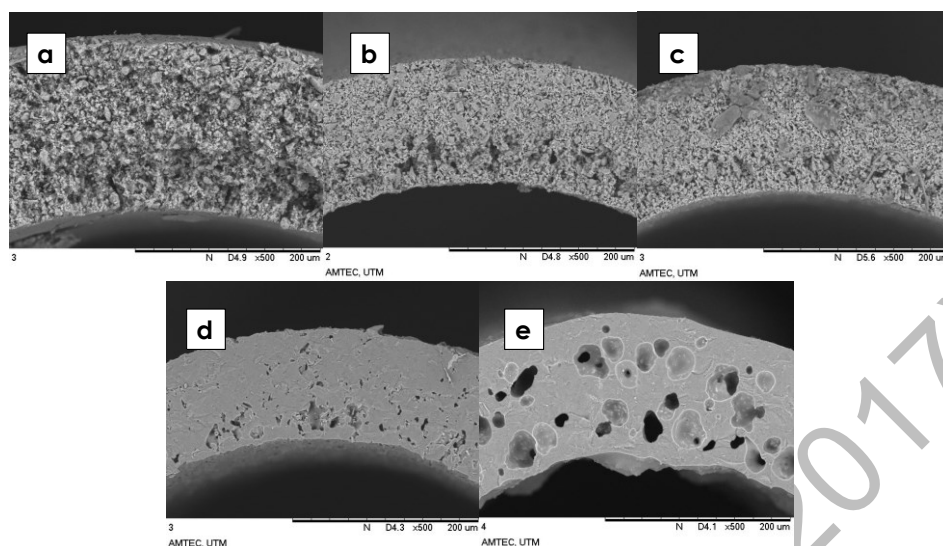


Figure 8. Cross-sectional SEM images (magnification 500x) of the zeolite based HFCMs (fibre 6) before (a) and after calcination at different sintering temperatures: (b) 950 °C; (c) 1000 °C; (d) 1050 °C; and (e) 1100 °C, respectively

As the temperature further increased to 1050 °C, the ceramic particle became densified both in inner and outer parts of the membrane. The destruction in finger-like voids and the formation of macro voids were significantly increased. At 1100 °C, the membrane became completely dense and compacted accompanied with the presence of macro voids all over the structure. At this stage, the ceramic material is approaching its melting point. The formation of macro voids could be attributed by the space left by the particles when it starts to closely packed to one another. The closed-up images of the particles is shown in Figure 9 where the images were taken at 3000 x magnification. Therefore, the best sintering temperature for the fabrication of zeolite based HFCM is 1000 °C. Although the most densified membrane could give the highest mechanical strength, but it is unfavorably desired since it will eventually give a lower permeation and flux.

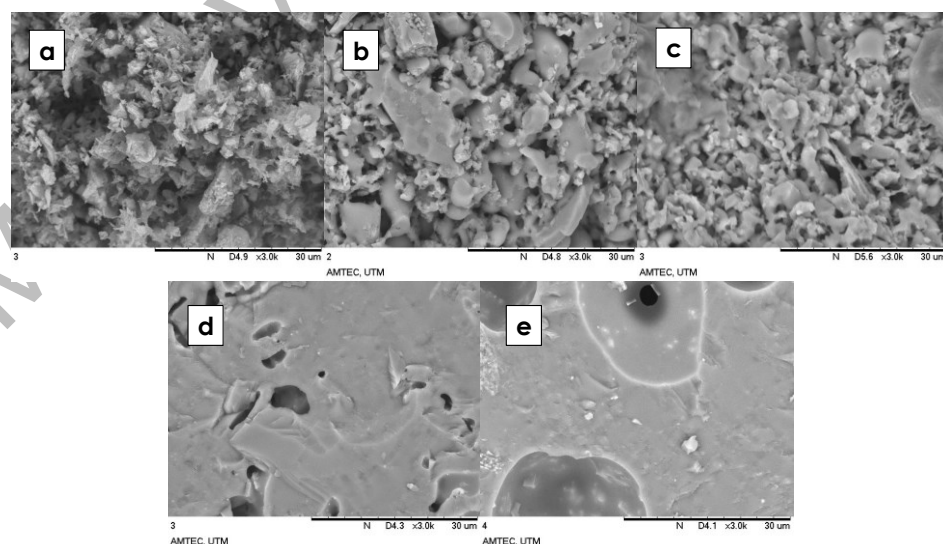


Figure 9. SEM images (magnification 3000x) of the cross-sectional zeolite based HFCMs (fibre 6) before (a) and after calcination at different sintering temperatures: (b) 950 °C; (c) 1000 °C; (d) 1050 °C; and (e) 1100 °C

Conclusion

A low-cost zeolite based hollow fibre ceramic membrane was successfully fabricated using phase inversion and sintering techniques. The best fabrication parameters were 5 cm air-gap distance, 13 mLmin⁻¹ of bore fluid flow rate and sintering temperature of 1000 °C. The acceptable strength and morphological behavior of finger-like and sponge-like voids were found to be an advantageous characteristic of the fabricated membrane. Its pleasant structure with a separation layer from either inner and outer surface may be beneficial for applications in separation and filtration of volatile compounds such as ammonia in liquid-liquid membrane contactor system.

Acknowledgement

This research is fully supported by HICoE grant, R.J090301.7846.4J194. The authors fully acknowledged Ministry of Higher Education (MOHE) and Universiti Teknologi Malaysia (UTM) for the approved fund which makes this important research viable and effective.

References

1. Ozturk, I., Altinbas, M., Koyuncu, I., Arikan, O. and Yangin, C. G. (2003). Advanced physico-chemical treatment experiences on young municipal landfill leachates. *Waste Management*, 23: 441 – 446.
2. Gabelman, A. and Hwang, S. (1999). Hollow fiber membrane contactors, *Journal of Membrane Science*, 159: 61 – 67.
3. Keshavarz, P., Ayatollahi, S. and Fathikalajahi, J. (2008). Mathematical modelling of gas-liquid membrane contactors using random distribution of fibres. *Journal of Membrane Science*, 325: 98 – 108.
4. Tan, X., Tan, S. P., Teo, W. K. and Li, K. (2006). Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water. *Journal of Membrane Science*, 271: 59 – 68.
5. Barbe, A. M., Hogan, P. A. and Johnson, R. A. (2000). Surface morphology changes during initial usage of hydrophobic, microporous polypropylene membranes. *Journal of Membrane Science*, 172: 149 – 156.
6. Wang, R., Li, D. F., Zhou, C., Liu, M. and Liang, D. T. (2004). Impact of DEA solutions with and without CO₂ loading on porous polypropylene membranes intended for use as contactors. *Journal of Membrane Science*, 229: 147 – 157.
7. Dindore, V. Y., Brilman, D. W. F., Feron, P. H. M. and Versteeg, G. F. (2004). CO₂ absorption at elevated pressures using a hollow fiber membrane contactor. *Journal of Membrane Science*, 235: 99 – 109.
8. Liu, S., Tan, X., Li, K. and Hughes, R. (2001). Preparation and characterisation of SrCe_{0.95}Yb_{0.05}O_{2.975} hollow fibre membranes. *Journal of Membrane Science*, 193: 249 – 260.
9. Liu, S., Li, K. and Hughes, R. (2003). Preparation of porous aluminium oxide (Al₂O₃) hollow fibre membranes by a combined phase-inversion and sintering method. *Ceramic International*, 29: 875 – 881.
10. Velez, M. H., Herrera, O. R., Martin, A. A., Rodriguez, A. J. and Malherbe, R. R. (1995). New materials obtained from high temperature phase transformation of natural zeolites. *Journal of Material Science Letter*, 14: 1653 – 1656.
11. Mumpton, F. A. (1978). Natural zeolites: A new industrial mineral commodity, in: L.B. Sand, F.A. Mumpton (Eds.), *Natural Zeolites, Occurrence, Properties, Use*. Pergamon Press, New York: pp. 285 – 302.
12. Li, J. L. and Chen, B. H. (2005). Review of CO₂ absorption using chemical solvents in hollow fibre membrane contactors. *Separation and Purification Technology*, 41: 109 – 122.
13. Alami Younssi, S., Iraqi, A., Rafiq, M., Persin, M., Larbot, A. and Sarrazin, J. (2003). γ alumina membranes grafting by organosilanes and its application to the separation of solvent mixtures by pervaporation. *Separation and Purification Technology*, 32: 175 – 179.
14. Krajewski, S. R., Kujawski, W., Dijoux, F., Picard, C. and Larbot, A. (2004). Grafting of ZrO₂ powder and ZrO₂ membrane by fluoroalkylsilanes. *Colloids and Surface A*, 243: 43 – 47.
15. Othman, M. H. D., Wu, Z., Droushiotis, N., Doraswami, U., Kelsall, G. and Li, K. (2010). Single-step fabrication and characterisations of electrolyte / anode dual – layer hollow fibres for microtubular solid oxide fuel cells. *Journal of Membrane Science*, 351: 196 – 204.
16. Kingsbury, B. F. K. and Li, K. (2009). A morphological study of ceramic hollow fibre membranes. *Journal of Membrane Science*, 328: 134 – 140.
17. Nitman, J., Daccord, G. and Stanley, H. E. (1985). Fractal growth of viscous fingers: Quantitative characterization of a fluid instability phenomenon. *Nature*, 314: 141 – 144.

18. Li, L., Chen, M., Dong, Y., Dong, X., Cerneaux, S., Hampshire, S., Cao, J., Zhu, L., Zhu, Z. and Liu, J. (2016). A low-cost alumina-mullite composite hollow fiber ceramic membrane fabricated via phase-inversion and sintering method. *Journal of the European Ceramic Society*, 36: 2057 – 2066.
19. Bonyadi, S., Chung, T. S. and Krantz W. B. (2007). Investigation of corrugation phenomenon in the inner contour of hollow fibre during the non-solvent induced phase-separation process. *J. Membrane Sci*, 299: 200 – 210.
20. Wang, J. W., Li, L., Zhang, J. W., Xu, X. and Chen, C. S. (2016). β -Sialon ceramic hollow fiber membranes with high strength and low thermal conductivity for membrane distillation. *Journal of the European Ceramic Society*, 36: 59 – 65.

MJAS Vol 21 No 2 (2017)