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RESEARCH ARTICLE

Effect of sintering temperature on physical properties of bauxite-based hollow fiber membrane

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Abstract

With abundant Malaysian bauxite minerals as the selected materials, hollow fiber ceramic membrane was fabricated for efficient production of high quality water from oil field oily wastewater. Effect of sintering temperature between 1250°C and 1450°C on membrane porosity, size of membrane pore, hydrophilicity, mechanical strength and water permeation were examined and the results were analyzed to determine the most suitable hollow fiber membrane for the application. Based on obtained findings, the most suitable sintering temperature was 1350°C. The acceptable strength and morphological behavior of finger-like and sponge-like voids were found to be advantageous characteristics for the fabricated bauxite hollow fiber membrane. Its pleasant structure with good outer and inner layers of separation might be beneficial for the oily wastewater purification applications.

Keywords**:** Natural bauxite, ceramic membrane, oilfield oily wastewater treatment

INTRODUCTION

Bauxite ($Al(OH)_3$) is a naturally occurring heterogeneous material. Compared to other minerals, the content of alumina in bauxite is generally high with approximately 60-80% (Dong *et al*, 2008; Li *et al* 2016: Cao *et al*, 2014), so it can be considered as a potential ceramic material in the membrane fabrication technology. Recently, ceramic hollow fiber membrane has showed some considerations in the purification of the oily-wastewater application as stated by Abadi *et al* (2011) because of its advantageous characteristics including raw bauxite which offers high porosity (Cao *et al*, 2014), low average in membrane pore size (Lü *et al*, 2014), good mechanical strength and high resistance towards corrosion. In addition, bauxite is also superhydrophilic which can counter the fouling problems. Zhu *et al*. (2016) prepared porous mullite ceramic membrane using coarse bauxite and fine kaolin powders via in-situ synthesis. The result showed low cost mullite ceramic membranes with good mechanical strength and high porosity. Li *et al*. (2016) successfully used the Chinese bauxite as the starting material for the fabrication of low cost hollow fiber ceramic membrane using the phase-inversion and sintering techniques. Results showed that the structure was consisted of finger-like thick layer and a sponge-like thin layer separation. When comparing to pure alumina ceramic membrane which usually too expensive and too hard to handle (Dong *et al*, 2006), the bauxite hollow fiber membrane can achieve excellent physical properties at much lower sintering temperature, which is between 1200℃ and 1350℃ (Li *et al*, 2016; Zhu et al, 2016; Cao *et al*, 2014: Liu *et al*, 2003) . Nonetheless, the study on bauxite hollow fiber membrane in the suitablity of the membrane for the oily wastewater treatment is still new and limited.

In this research, in order to improve the membrane technology in the oily wastewater treatment, the ceramic hollow fiber membrane was fabricated using raw bauxite from Malaysia. The physical properties of the membrane were characterized and discussed. In order to get the optimum bauxite hollow fiber membrane, several sintering temperatures (1250, 1300, 1350, 1400 and 1450 °C) were selected in this study and the experimental results were analyzed via membrane morphology, mechanical strength and pure water permeability.

EXPERIMENTAL

Materials

Available commercial raw bauxite, which composed of non-specific weight percentage of Al_2O_3 and SiO_2, was obtained from Aras Kuasa Sdn Bhd in Kuantan, Pahang, in which it was dried in oven and grinded into the micron size powder form. This raw bauxite powder form was used as the starting material of the bauxite hollow fiber membranes. Other than that, N-methyl-2-pyrrolidone (NMP) (HPLC grade, Rathbone) and Polyethersulfone (PESf) (Radel A-300, Ameco Perfomance) were used as solvent and binder, respectively. Polyethyleneglycol 30-dipolyhydroxystearate (Alacel P135, Uniqema) was used as dispersant.

Preparation of ceramic suspensions

The ceramic preparation and fabricatrion technique is based on Hubadillah *et al*'s (2017) and Wei *et al*'s (2008) experimental procedures to get the most suitable results. The suspension compositions were based on the ratio of ceramic material and polymer binder (Bauxite:PESf). The value of the ratio was fixed to 8:1. The suspension composition is shown in Table 1.

Bauxite powder and PESf were first dried overnight in 60 ºC oven to remove the remaining moisture content. Dope suspension preparation started by first mixing Alacel P135 with NMP solution by normal stirring in alumina jar. The bauxite powder was slowly added into the alumina jar after the solution became homogeneous. Then, the alumina jar was subjected to the ball milling process (Model: NQM-2, Magna) with 3 pieces of 10 mm and 2 pieces of 20 mm agate mill balls. The ball milling process was ran for 48 hours at a constant rate of 182 RPM to ensure the ceramic materials and solvents were well-mixed. Then, the milling process was continued for another 48 hours with addition of calcutated PESf. Lastly, the prepared suspension was degassed for 1 hour at room temperature to eliminate air bubbles.

Table 1 The composition of bauxite based hollow fiber ceramic membrane.

Composition (wt.%)	Bauxite (g)	Arlacel P135 (g)	PESf (g)	NMP (g)
50	50	1	6.250	42.750

Fabrication of bauxite based hollow fiber ceramic membrane

After degassing, the dope suspension was transferred into the extrusion syringe (Model: Cole Parmer and Harvard Equipment) and extruded through a tube connected to spinneret with 0.5 mm internal diameter and 2.8 mm external diameter. The spinning process was conducted according to the spinning parameters listed in Table 2. The suspension solution was spun simultaneously with the internal coagulant, which was tap water through the spinneret by using syringe pumps to constantly control the extrusion rate of suspension and the flow rate of tap water.

The precusor was passed through the air-gap distance prior to the immersion in a water coagulant bath for 24 hours to complete the process of phase inversion. The completed membranes was left to dry overnight at room temperature. In this study, the precursor was sintered at different sintering temperatures which were in between 1250°C to 1450°C in tubular furnace (Model: XL-1700, Magna). The process were initiated as stated by Mohtor *et al* (2017) with the membrane sintered from room temperature to 600°C with the rate of 2°C/min and the sintering process was held for 2 hours, then the temperature was increased to targeted temperature and held for another 3 hours. Lastly, the temperature was reduced from targeted temperature to room temperature at the rate of 5°C/min. The bauxite hollow fiber membrane was completed when the sintering process finished.

Table 2 Bauxite-based hollow fiber ceramic membrane spinning parameters used.

Bore Fluid Rate (mL/min)	Air Gap (cm)	Suspension Rate (mL/min)
10	5	9

X-ray fluorescence spectrometry

X-ray fluorescence spectrometry (XRF: Axios-Advanced, PANalytical Corporation, Netherlands) was used to examine the chemical composition of the bauxite powder. Chemical composition of raw bauxite was shown in weight percentage (wt.%).

X-ray diffraction analysis

X-ray diffraction (XRD: X'pert Pro α1, Philips, Amsterdam, The Netherlands) was conducted in ambient conditions with Cukα radiation (λ=1.5406Å) to measure crystallinity of bauxite powder and bauxite hollow fiber membrane. All diffraction patterns of the samples were recorded from 10 to 80° 2Θ with step size 0.026 and step time 50s, operated at 40 kV and 30 mA with fixed 1/4° anti-scatter slit.

Contact angle measurement

The hydrophilicity of membrane was determined by contact angle measurement that carried out by contact angle goniometer (Model: OCA 15EC, Dataphysics). Deionized water was used as contact droplets with dosing volume of 0.5 μL and dispensed on the membrane surface. The average of 10 independent measurements was taken at different surface spots for each membrane in order to minimize experimental error of taken measurements.

Morphological studies

Structures of the cross sectional and surfaces of bauxite hollow fiber membrane were observed using a scanning electron microscopy (SEM: TM3000, Hitachi) operating at 30 kV in various magnifications. Prior to the SEM testing, the bauxite hollow fiber membranes were cut gently to get the smooth cross-section then the membranes were put on the metal holder before being sputter-coated with gold under vacuum for 3 minutes (Wei *et al,* 2008; Paiman *et al,* 2015).

Mechanical strength

Mechanical resistance of bauxite hollow fiber membranes was examined by three-point bending strength method. The method was carried out using an Instron Micro Tester 5848 with a load cell of 2 2 kN (Instron calibration laboratory, United Kingdom). Each bauxite hollow fiber membrane with an average length of ~25 mm was placed on a span of 5 cm and loaded at a crosshead speed of 0.25 mm/min until fractured. The step was repeated for three times for each sample. The mechanical strength, of each single membrane was calculated using the following equation:

$$\sigma_F = \frac{8FLD}{\pi(D^4 - d^4)} \tag{1}$$

where F is, the force measured at the fracture point of the membrane, L is the span (5 cm), D and d are the outer and inner diameters of the membrane, respectively.

Measurement of water flux through bauxite hollow fiber membrane

A cross flow filtration system was used for water flux and PW separation. The flux (J) measurement was carried out under 2 bar pressure and determined by calculating the permeable volume in unit time as defined in following equation:

$$J = \frac{V}{A\ x\ t} \tag{2}$$

where V (L) is the volume of permeated water, A (m2) is the valid area of the membrane and t (s) is the permeation time.

RESULTS AND DISCUSSION

Analysis of bauxite powder using XRF and XRD

Table 3 and Fig. 1 show XRF and XRD analyses of bauxite used in this study, respectively. Based on Table 3, the composition of the raw bauxite was identified. The results confirmed that the most common oxide found in the raw bauxite was aluminium oxide, similar to Li *et al*.'s (2016) findings. But, the results showed a major difference in the percentage of Fe_2O_3. The previous study tested raw bauxite from China, while this experiment used raw bauxite from Malaysia. This could be concluded that the chemical composition of bauxite are varied and dependant on their origin.

Based on Fig. 1(A), the major crystalline phases were corundum (PDF#46-1212) and mullite (PDF#15-0776). As explained by Li *et al*. (2016), formation of mullite began from the decomposition of kaolinite which produced diaspore and cristabolite, and as the decomposition continued with both materials, corundum was produced. The reaction within the corundum was contributed in the mullite formation. Mullite is a good ceramic material due to its excellent mechanical and thermal stability also good chemical resistance (Abbasi *et al,* 2010). Fig. 1(B) showed the result of previous study when compared to the results obtained in this experiement in Fig. 1(A), it shown that there are some differences because of the large presence of iron oxide, also other impurities like vanadium oxide.

Table 3 Chemical composition (wt. %) of raw bauxite.

	Chemical Composition (wt.%)					
	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	P_2O_5	MnO
Raw Bauxite	58.60	22.80	11.20	7.21	0.12	0.10
Cao *et al.* (2014)	63.53	7.08	10.41	2.97	0.22	0.11

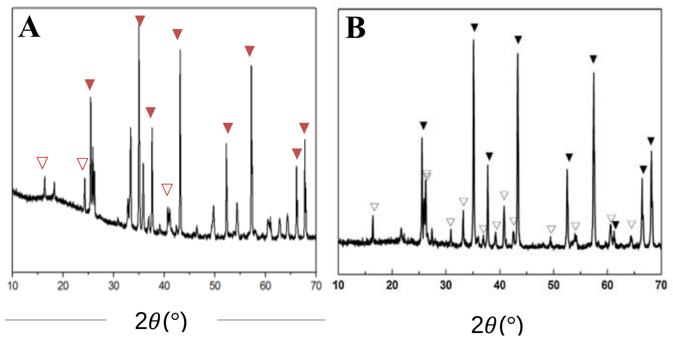

Fig. 1 XRD pattern of raw bauxite (A) sintered at 1400℃ and (B) Li *et al*. (2016) sintered at 1600°C.

Contact angle analysis on different sintering temperatures

To get more accurate results, an average value for the contact angle of each membrane was obtained using four measurements. During the experiments, accurate results were difficult to obtain since the water drop would diffuse too fast. Because of that, the way of calculating the result has been changed by calculating the time taken for the contact angle to reach 0°(Hubadillah *et al,* 2017).

From Table 4, the time taken for the water contact angle to reach 0° was increased when the sintering temperature rose from 1250°C to 1450°C. These results proved that the bauxite hollow fiber membrane has great hydrophilic properties. Even though the length of the time taken was increased along with the sintering temperature, the membrane remained in its hydrophilic nature. According to Mohtor *et al*. (2017), hydrophilicity is the most crucial value for application of oily-wastewater separation since the hydrophilic surface is very selective and only allow the water to pass through while rejecting the oil. In addition, hydrophilic surface might prevent the membrane surface from fouling.

Besides that, contact angle also relied on the pore size of the membrane (Hubadillah *et al,* 2017). If the pore size is too big, the water could not retain on the membrane surface, thus it might affect the contact angle reading.

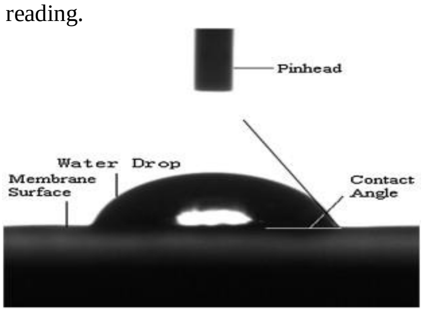

Fig. 2 Schematic diagram of the device for the water contact angle tests.

Table 4 Water Contact Angle Results.

Bauxite Content (wt.%)	Sintering Temperature (°C)	Time Taken for Contact Angle to 0° (s)
50	1250	1.47
	1300	2.35
	1350	4.13
	1400	6.78
	1450	9.07

Sintering temperature effect on morphology studies

Fig. 3 showed the surface and cross-sectional of bauxite hollow fiber membrane at various sintering temperatures varying from 1250°C to 1400°C. It should be noted here that ceramic suspension with sintering temperature higher than 1450°C has been investigated. Unfortunately, the result showed that the bauxite hollow fiber membrane started to melt when the temperatre went beyond 1450°C and the membrane could no longer be used in the experiment.

By increasing sintering temperature, the sponge-like voids layer became denser whereas no significant changes were observed for finger-like voids. As could be seen, bauxite hollow fiber membrane sintered at 1350°C showed the most porous structure for both cross section and surface. When the sintering temperature was increased to 1400°C, pore sizes of the sponge-like voids in bauxite hollow fiber membrane cross section were reduced slightly and isolated pores started to grow on the surface of bauxite hollow fiber membrane.

When the SEM images were related to Table 4, it proves that increasing sintering temperature would affect the contact angle measurement by decreasing the pore size of membrane due to membrane densification.

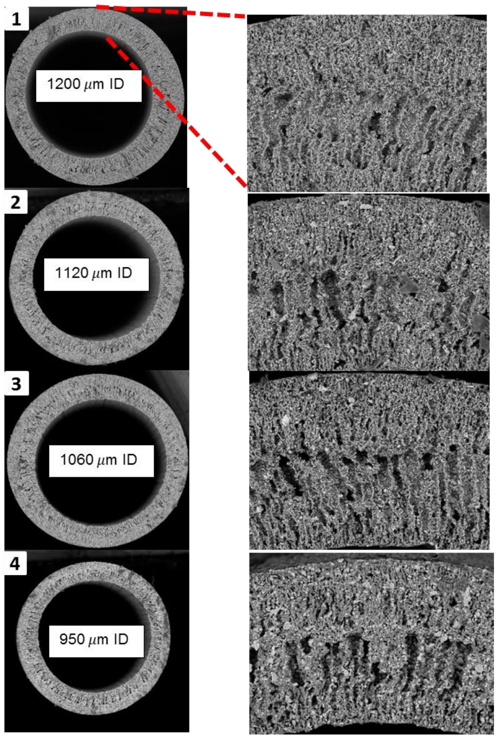

Fig. 3 Cross-sectional SEM images of fiber membrane after sintered at different sintering temperatures: (1) 1250 ◦C,(2) 1300 ◦C,(3) 1350◦C and (4) 1400◦C, fabricated at a fixed bore fluid flow rate of 10 mL min−1, air-gap of 5 cm and solid loading of 50 wt. %.

Sintering temperature effect on mechanical strength and water permeation

The bauxite hollow fiber membrane mechanical resistance was tested using 50 wt.% bauxite content at various sintering temperatures (1250-1450°C) and the obtained results were shown in Fig. 4. The membrane mechanical resistance was gradually increased along the sintering temperature from 1250°C to 1450°C. The changes could be justified by the necks growth that occurred between the particles of ceramic, creating bonds within the particles which built up the durability of the ceramic membrane (Mohtor *et al*, 2017). Thus, higher temperature could contribute in creating bonds within the particles, which lead to the good mechanical strength of the membrane. Similar trend was also observed in Liu *et al*.'s (2003) study for alumina hollow fiber membranes when they used similar sintering temperature ranging from 1300°C to 1600°C in their experiment. As explained in their study, the mechanical strength of the membrane was affected greatly by the sintering temperature because of the crucial needs in sufficient bond and chain within the particles of ceramic, so they concluded that the temperature for the sintering should be chosen within ¾ of the melting point of the ceramic material. According to the results achieved in this experiment, it showed that the suggested temperature for the bauxite membrane was 1350°C due to its sufficient mechanical strength for the membrane testing.

As for the pure water permeation, the results showed two patterns of decrement. From 1250°C to 1350°C, the pattern seemed to gradually decreased. However, when the temperature started to reach 1400°C and 1450°C, the results showed a drastic reduction of water permeation. These results could be explained by the densification of bauxite hollow fiber membranes pores as shown in Fig. 3. When the temperature applied on sintering started to reach 1400°C, there was a sudden change on the pores of the membranes. The composition of the bauxite hollow fiber membrane could not withstand a temperature higher than 1400°C since it then, melted and the pores between them closed. In conclusion, higher temperature could lead to the reduction of the permeation performance that might be resulted from densified membrane pores.

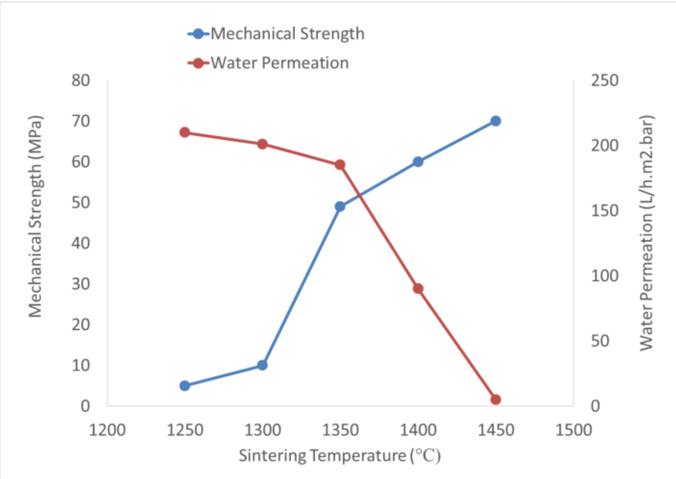

Fig. 4 The mechanical strength and water permeability of bauxite membrane with different sintering temperatures.

CONCLUSION

Bauxite hollow fiber membrane was successfully fabricated using Malaysia raw bauxite by phase-inversion method and sintering technique. Based on our findings, the optimum temperature was at 1350°C. The acceptable strength and morphological behavior of finger-like and sponge-like voids were found to be advantageous characteristics of the fabricated membrane. Its pleasant structure with good outer and inner layers of separation might be beneficial for the oily wastewater purification applications in separation and filtration of dissolved oil compounds.

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