Jurnal
Teknologi

Full Paper

THE FEASIBILITY OF KAOLIN AS MAIN MATERIAL FOR LOW COST POROUS CERAMIC HOLLOW FIBRE MEMBRANE PREPARED USING COMBINED PHASE INVERSION AND SINTERING TECHNIQUE

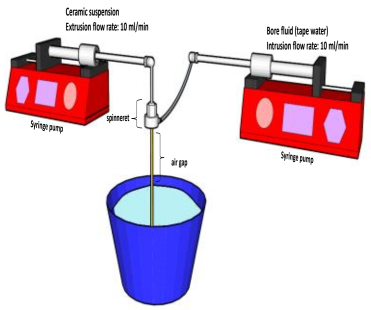
Article history
Received
20 August 2016
Received in revised form
24 September 2016
Accepted
1 December 2016

Siti Khadijah Hubadillah, Mohd Hafiz Dzarfan Othman*, A. F. Ismail, Mukhlis A. Rahman, Juhana Jaafar

Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author
hafiz@petroleum.utm.my

Graphical abstract



Abstract

Ceramic hollow fibre membrane (CHFM) demonstrated superior characteristics and performance in any separation application. The only problem associated with this kind of technology is the high cost. In order to effectively fabricate and produce low cost porous CHFM, a series of CHFMs made of kaolin were fabricated via combined phase inversion and sintering technique. The CHFMs from kaolin named as kaolin hollow fibre membranes (KHFMs) were studied at different kaolin contents of 35 wt.%, 37.5 wt.% and 40 wt.% sintered at 1200°C. The result indicated that by varying kaolin contents, different morphologies were obtained due to changes in the viscosity of ceramic suspension containing kaolin. The optimum kaolin content for KHFM was identified. It was found that KHFM prepared at 37.5 wt% has a mechanical strength and pure water flux of A and B respectively.

Keywords: Kaolin, Ceramic hollow fibre membranes (CHFM), Phase inversion, Sintering, Low cost membrane

1.0 INTRODUCTION

Nowadays, low cost porous ceramic membrane from kaolin presents a new insight into various separation/purification applications such as oily wastewater treatment [1], support for gas separation [2, 3] and catalytic substrates. According to Hedfi *et al.* [4], kaolin is a preferred raw material for porous ceramics due to its crystal order, chemical composition and mineralogical qualities. Moreover, Mittal *et al.* [5] stated that kaolin provides low plasticity and high refractory properties to the membrane. A study conducted by Vasanth *et al.* [6] revealed that ceramic membrane fabricated from 50% kaolin, 25% quartz, 22% calcium carbonate and 3% titanium oxide provides a steady state flux and a rejection of 87% for oily wastewater separation. It is interesting to mention that Dong *et al.* [7] found that defect formation mechanism during the removal of the template due to thermal expansion was mismatched between alumina support and zeolite membrane. Therefore, Mohammadi and Pak [8] decided to use kaolin as a ceramic support for zeolite NaA membranes in order to have high consistency. However, separation factor of the membrane was very low according to the pore diameter increases by increasing calcination temperature, and also due to the slip casting technique and electrophoretic deposition. According to Li [9], slip casting is a traditional method but the casting time is very long and the wall thickness is difficult to control and is usually thick.

Another method that is frequently used for ceramic membrane fabrication is the pressing method. This method is commonly used for preparation of flat sheet or disc shape ceramic membrane. Using this method, the ceramic particle is mixed with some solvent, turned into slurry and consolidated into a dense layer by an applied force. A special press machine is used to apply more than 100 MPa, owing to the expensive fabrication technique. Moreover, the pressing method produces a small surface area membrane and symmetric structure. The diameter of the membrane is usually a few centimetres, the thickness is often around 0.5 mm and it is dense after the sintering process [10]. Therefore, a feasible fabrication technique to produce low cost ceramic membrane from kaolin is desired. Another significant development in fabricating ceramic membrane from kaolin has been achieved in our previous work, where a more advanced and simple phase inversion technique is employed [2, 3, 11, 12]. By using this technique followed by a sintering process, the desired low cost ceramic membrane from kaolin with asymmetric structure has been developed in a single step. In our previous work, low cost ceramic membrane from kaolin has been successfully prepared by investigating the effect of kaolin particle size, kaolin content and non-solvent coagulant bath. The best ceramic membrane as a support for gas separation application has been produced by small kaolin particles, with kaolin content up to 54.0 g and distilled water as a non-solvent coagulant bath. However, membranes in flat sheet or disc configuration produce small surface areas. Moreover, we found that flat sheet ceramic membrane from kaolin is difficult to handle during operation [2]. As reported by Baker, hollow fibre membrane has an advantage of formation compact modules with a high surface area. A review has been made by listing the advantages of membranes in hollow fibre configuration [13].

Concerning the significance of the hollow fibre configuration for ceramic membrane, the objective of this work, is, therefore, to study the feasibility of kaolin as a ceramic material for low cost porous ceramic hollow fibre membrane prepared using combined phase inversion/sintering technique. By varying the ceramic content, i.e. kaolin in this study, from 35 wt.% to 40 wt.% to manipulate the spinning suspension viscosity, the kaolin hollow fibre membrane (KHFM) morphology can be varied greatly. The macrostructure of these hollow fibres was studied using scanning electron microscopy (SEM) and the performance was characterized using a water permeation test and three-point bending test.

2.0 METHODOLOGY

The KHFMs were prepared using phase inversion-based extrusion and sintering technique as shown in Figure 1. Prior to the fabrication technique, ceramic suspension was prepared according to Table 1. Kaolin powder (<1μm, RM60/kg) was purchased from BG Oil Chem Sdn Bhd, Malaysia and PESf (Radel A300, Ameco Performance, USA) was dried to ensure that no moisture was trapped. Arlacel P135 gel (CRODA) was melted in an oven overnight at 60 °C to completely remove all moisture. Then, Arlacel P135 was dissolved in NMP by stirring, before kaolin powder was added. The dispersion was then milled in a NQM-2 planetary ball mill for 48 h to ensure that the kaolin powder, NMP and Arlacel P135 were mixed well. The milling was continued for another 48 h after the addition of PESf as a binder. The prepared spinning suspension was degassed for 10 min using a vacuum pump to remove any air bubbles in the suspension. Immediately after degassing, the prepared suspension was transferred into stainless steel syringes. The ceramic dope was extruded through the spinneret at a constant flow rate of 10 mL min^{-1} at 25 °C, while the bore fluid (distilled water) was delivered by a syringe pump (PHD 2000, Harvard Apparatus). The precursor hollow fibres were then immersed in water overnight to ensure the completion of the phase inversion, followed by a thorough washing with water. The precursor fibres were cut to a length of 30 cm and dried at an ambient temperature for 2 to 3 d. After that, the dried hollow fibres were sintered in air in the high-temperature tubular furnace (XY-1700 MAGNA). The temperature was increased at a heating rate of 2°C/min from room temperature to 600 °C, at which point the temperature was kept constant for 2 h to remove the polymer binder. The temperature was then increased to 1,300 °C at a rate of 5 °C/min, where it was held for 6 h. Finally, the temperature was brought down to room temperature at a rate of 5°C/min.

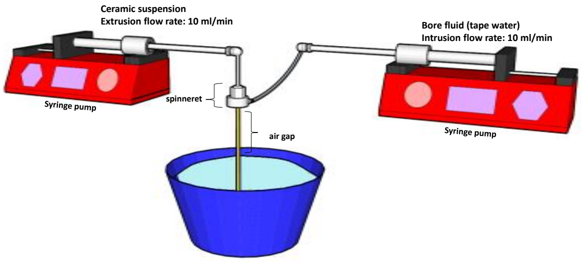


Figure 1 Schematic representation of phase inversion technique for ceramic membrane fabrication

Table 1 Composition of the ceramic suspensions

Fibre/ Materials	A	B	C
Kaolin (wt.%)	35	37.5	40
NMP (wt.%)	59	57.5	54
PESf (wt.%)	5	5	5
Arlacel P135 (wt.%)	1	1	1

3.0 RESULTS AND DISCUSSION

Figure 2 shows the viscosity of ceramic suspensions at shear rates between 5 to 100 s^{-1} containing 35 wt.%, 37.5 wt.% and 40 wt.% kaolin contents. As shown, the viscosity increases with increasing kaolin content. Moreover, the viscosity pattern obeyed the shear thinning behavior, where the viscosity of suspension decreased with an increase in shear rate.

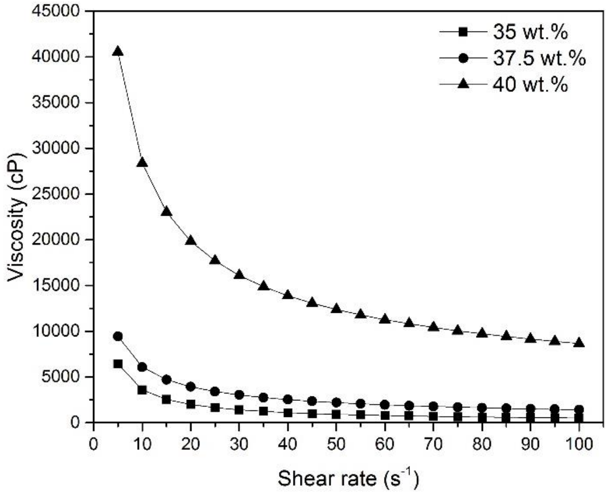


Figure 2 Viscosity of ceramic suspension containing kaolin/NMP/Arlacel P135 with different kaolin contents

A similar pattern can be observed by Kingsbury's work who used alumina as ceramic material [14]. The viscosity of the ceramic suspensions in this work were determined at a shear rate of 30 s^{-1}, and gave a value of 1416 cP, 3039 cP and 16111 cP for kaolin contents of 35 wt.%, 37.5 wt.% and 40 wt.% respectively.

Figure 3 shows the SEM image of overall view, cross section and porous structure on kaolin hollow fibre membranes (KHFMs) prepared using three different contents of kaolin powders. It can be seen in Figures 3(A1 and A2) that at 35 wt.% kaolin content, finger-like voids extend across approximately 70% of the fibre cross section with the remaining 30% consisting of a sponge-like region. Increasing kaolin content from 35 to 37.5 % results in a large reduction in finger-like void length to approximately 20% of the fibre's cross section, as shown in Figures 3(B1 and B2). Thereby, no finger-like voids could be observed with increasing kaolin content at 40 wt.% as shown in Figures 2-C1 and 2-C2.

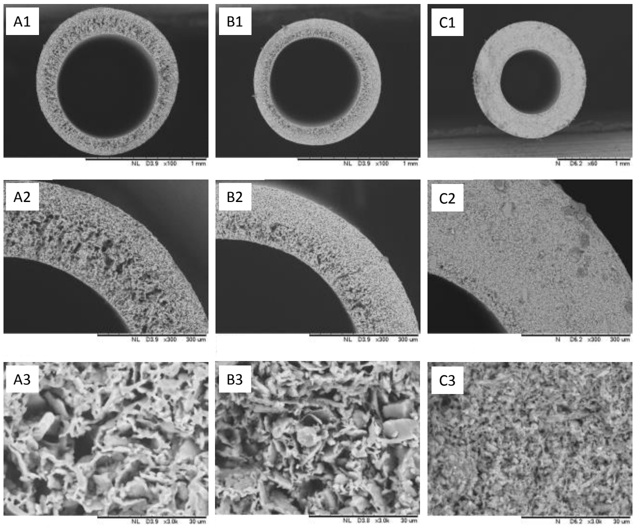


Figure 3 SEM images of the (1) overall view; (2) cross section; and (3) porous structure at high magnification of KHFMs at different kaolin contents; (A) 35 wt.%; (B) 37.5 wt.%; and (C) 40 wt.%

According to Kingsbury and Li [14], the viscosity was a dominating factor for finger-like formation. Moreover, they suggested that an increase in suspension viscosity inhibits viscous fingering at both the inner and outer surfaces of the fibre and that finger-like void length is reduced. Interestingly, they found a critical viscosity value of 12,100 cP at a shear rate of 30 s^{-1} which stood as a threshold for finger-like formation in ceramic membrane. This critical value for viscosity promoted a ceramic hollow fibre membrane structure without any finger-like voids. A similar finding has been discovered in this work, shown by a ceramic suspension with a viscosity value of 16,111 cP at 30 s^{-1} for fibre C. Whereas for fibres A and B, finger-like voids formation is due to the viscosity being below 12,100 cP, namely 1416 cP and 3039 cP, respectively.

The mechanical strength of the KHFMs was also tested. The results showed that the mechanical strength of the fibres increased from 16 MPa to 75 MPa when the kaolin content was increased from 35 wt.% to 40 wt.% as shown in Figure 4. Most previous studies also reported a similar trend. According to Othman *et al.* [15], high mechanical strength was possessed by fibres with less finger-like voids, which increases the integrity of the sponge-like voids structure in the fibre. Moreover, this mechanism could be explained by an increase in the mass of the kaolin particle, leading to the growth of necks between the kaolin particles. It is clearly observed from the SEM image shown in Figures 3(A3, B3 and C3). Fibre C with 40 wt.% not only possessed morphology without finger-like structures, but reduced the size of sponge-like voids in the fibre structure. Conversely, fibres A and B have a similar size of sponge-like voids. Thereby, it is concluded that ceramic content (kaolin) is a major factor to the formation of finger-like voids in the fibre's structure, while at the same time, diminishing the membrane's mechanical strength.

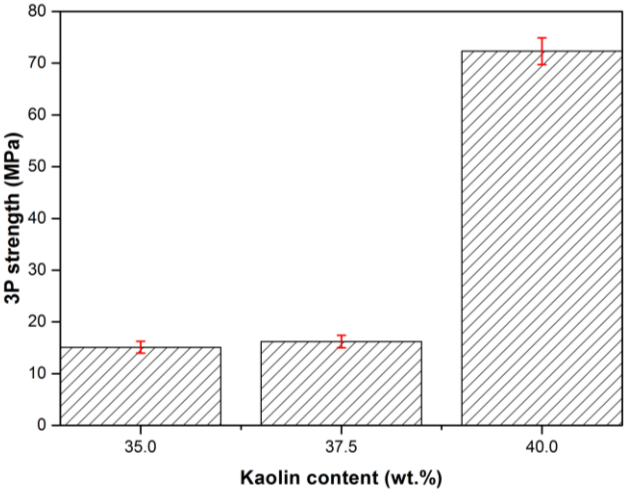


Figure 4 The mechanical strength of kaolin hollow fibre membranes (KHFM) prepared at different kaolin contents

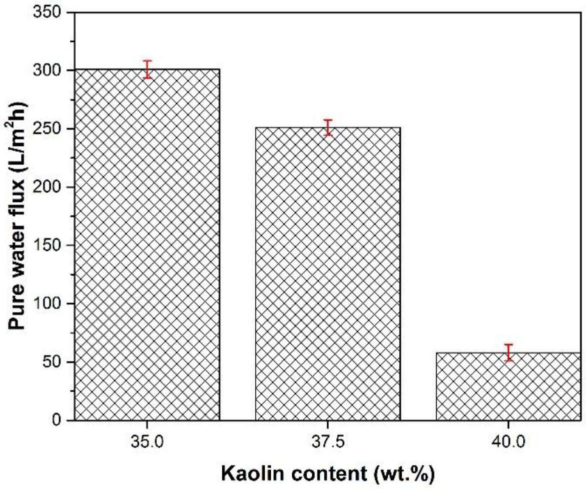


Figure 5 The pure water flux of kaolin hollow fibre membranes (KHFM) prepared at different kaolin contents

Figure 5 indicates the pure water flux (PWF) of KHFMs prepared at different kaolin contents. As shown, the PWF decreases from 301 L/m^{2}h to 58 L/m^{2}h with increasing kaolin content from 35 wt.% to 40 wt.%. This is expected because increasing the kaolin content reduced the pore sizes in the fibre's structure. It is important to mention that there is a huge gap of PWF value for fibre B (37.5 wt.%) and fibre C (40 wt.%) compared to fibre A (35 wt.%) and fibre B (37.5 wt.%). This can be explained based on the SEM image (Figure 3). Fibre A has the longest finger-like voids whereas Fibre C does not have any finger-like voids and possesses the smallest sponge-like voids. Therefore, it is suggested that longer finger-like voids could help in producing membranes with high flux. Although the mechanical strength of the fibre is significantly low, it could still be used for water separation application.

4.0 CONCLUSION

Three KHFMs with different morphologies have been successfully prepared by varying the kaolin content from 35 wt.% to 40 wt.% through the combined phase inversion and sintering techniques. From the morphologies of the obtained KHFMs, it can be observed that by reducing the kaolin content, the viscosity of ceramic suspension becomes lower and suppresses the formation of finger-like voids. Conversely, by increasing the kaolin content, symmetric KHFMs with small sponge-like voids have been obtained. In studying the effect of kaolin content, it can be seen that the fibre with longer finger-like voids has lower mechanical strength but higher pure water flux. Therefore, it can be concluded that the presence of finger-like void structures in KHFMs structure strongly affects the mechanical strength and pure water flux, and consequently would be significantly suitable for further study in water separation.

Acknowledgement

The authors gratefully acknowledge financial support from the Ministry of Education Malaysia under the Higher Institution Centre of Excellence Scheme (Project 7 Number: R.J090301.7846.4J192), Universiti Teknologi Malaysia under the Research University Grant Tier 1 (Project number: Q.J130000.2546.12H25) and Nippon Sheet Glass Foundation for Materials Science and Engineering under Overseas Research Grant Scheme (Project number: R.J130000.7346.4B218). The authors would also like to thank Research Management Centre, Universiti Teknologi Malaysia for the technical support.

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