RESEARCH ARTICLE

Development of hydrophobic metakaolin hollow fibre membrane for membrane distillation application

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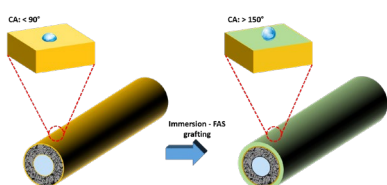*   Corresponding author: hafiz@petroleum.utm.my

Graphical abstract

Abstract

Metakaolin hollow fibre membranes (MHFM) was prepared by a combined phase inversion and sintering method for direct contact membrane distillation (DCMD) application. Four hydrophobic metakaolin hollow fibre membranes (h-MHFM) sintered at different temperatures (1200ºC to 1500ºC) were successfully prepared by grafting 1H,1H,2H,2H-perfluorodecyltriethoxysilane on the MHFM. Prior to the grafting process, the MHFM was hydrolysed with a mixture of ethanol and water with the ratio of 1:2 for 24 hours. The effectiveness of the hydrophobization on each MHFM was assessed using contact angle measurement, scanning electron microscopy (SEM) and three-point bending test. It was found that the increasing sintering temperature improved the mechanical strength from 117.6 MPa to 182.3 MPa. Further increment in mechanical strength was also observed after the modification with fluoroalkylsilane (FAS). The contact angle of the membrane was enhanced up to 120˚ after modification. In general, the membrane prepared at low sintering temperature of 1200°C exhibited the highest DCMD performance with the water vapor flux of 17.5 kg/m^{2}h due to the sufficient pore size for the vapor to pass through the membrane structure.

Keywords: Ceramic membrane, metakaolin, perfluorodecyltriethoxysilane, hydrophobic

INTRODUCTION

In recent years, a great deal of research has been devoted to the development of membrane separation technology. Membrane separation is known as a "worldwide technology" especially in water treatment applications due to several advantages such as cost effective, simple operation, long-life term and less energy consuming [1]. Nowadays, hydrophobic membranes such as polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and polypropylene (PP) have received wide attention in advanced membrane separation technologies, including membrane distillation (MD). Munirasu *et al.* (2017) prepared the superhydrophobic PVDF membranes via phase inversion for the MD application [2]. The membrane exhibited high contact angle value of 164˚ and mean pore size in the range of 0.1 to 0.3 μm. A high salt rejection of 99.999% with 80 LMH flux were obtained. Zhang *et al*. (2016) modified the PVDF membranes with fluorographite for seawater desalination using direct contact membrane distillation (DCMD) [3]. The FESEM images showed that the fluorographite particles were randomly located on the modified membrane which enhanced the contact angle value from 109˚ to 122˚. Interestingly, the liquid entry pressure (LEP$_w$) was also enhanced from 0.9 to 1.3 bar. Recently, Zhang *et al.* (2016) evaluated the desalination performance of the commercial PTFE membranes through vacuum membrane distillation (VMD) [3]. The commercial PTFE membranes were supplied by three different companies, and exhibited the contact angles of 136.1˚ to 145.9˚, LEP$_w$ of 3.2 to 3.6 bar and mean pore sizes of 0.1052 to 0.1495 μm.

MD is a membrane separation process in which two solutions of different temperatures are separated by a hydrophobic porous membrane [4]. The hot water at the feed side vaporizes and passes through the membrane pores. The vapor then condenses at the cold side of the membrane as pure permeate [5]. Fig. 1 shows the schematic diagram of the MD mechanism. The feed temperature drops across the boundary layer adjoining the membrane surface at the feed side. Thereby, the feed water vaporizes, and the vapor transports through the hydrophobic membrane pores to the permeate side. Simultaneously, the heat also transports through the hydrophobic membrane to the cold permeate side. This mechanism is called as heat transfer. There are two steps involved during heat transfer:

1. Heat transfers as sensible heat and latent heat, which creates the temperature difference between the boundary layer and bulk flow.
2. Heat transfers from the bulk flow of the hot feed side to the boundary layer through heat convection.
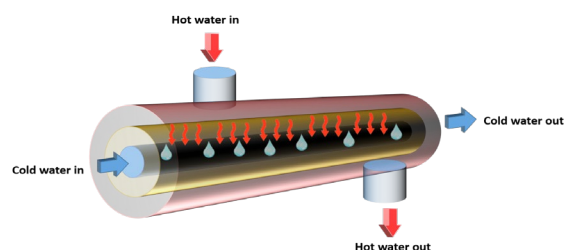

Fig. 1 Schematic diagram of MD mechanism

However, the long-term performance of the polymeric membranes has been doubted due to their weak endurance towards harsh operating conditions [6]. For example, the sensitivity towards high temperature or swelling phenomenon of the polymeric membranes

results in short working life. Whereas, ceramic membranes show excellent resistance towards temperature, pressure and chemical. This opens up the possibility of using ceramic membranes for treating various feed solutions at different operating conditions [7, 8]. Unfortunately, ceramic membranes cannot be used directly for MD due to their hydrophilicity nature. The modification of the hydrophilic ceramic membrane into hydrophobic has widely been reported. Krajewski *et al.* (2006) modified the commercial tubular zirconia membranes with alumina support using 1H,1H,2H,2H-perfluorodecyltriethoxysilane at various soaking times [9]. After modification, the contact angles were in the range of 142° to 148°. Huang *et al.* (2016) applied a similar grafting process on alumina flat sheet membrane and successfully modified the hydrophilic ceramic membrane into hydrophobic with the contact angle of 158° [10]. However, it is worth to mention that these commercial membranes were fabricated using the expensive starting materials (alumina, zirconia, etc.) and require high sintering temperature, making them less cost competitive. Accordingly, low-cost ceramic membranes derived from clay have been developed and modified for the MD applications. For instance, Khemakhem *et al.* (2011) developed a novel ceramic membrane from Tunisian clay and modified the membrane with triethoxy-1H,1H,2H,2H-per-fluorodecylsilane [11].

Due to the superior advantages of ceramic membranes for MD application, the development of cost competitive ceramic membranes is critically in need. Hence, this study aims to develop a low-cost hydrophobic ceramic membrane for MD application. In our previous work [12], we studied the development of the high strength and low-cost metakaolin ceramic hollow fibre membrane at various sintering temperatures ranging from 1200°C to 1500°C. However, the prepared membrane was hydrophilic, hence, not suitable to use for MD application. Therefore, in this study, the metakaolin hollow fibre membrane was hydrophobized with fluoroalkylsilanes (FAS). The properties of the modified membranes were determined and tested for MD application.

EXPERIMENTAL

Materials

Metakaolin was produced through the calcination of kaolin powder (purchased from Bg Oil Chem Sdn Bhd, Penang, Malaysia) at 700°C for 3 hours. Polyethersulfone (PESf, Radel A-300, Ameco Performance, USA), N-methyl-2-pyroolidone (NMP, QRëC™) and Arlacel P135 (polyethyleneglycol 30-dipolyhydroxystearate, CRODA) were used as the polymer binder, solvent and dispersant, respectively for the preparation of the ceramic suspension. Tap water was used as the bore fluid and coagulant bath during the fabrication of the ceramic hollow fibre membrane. 1H,1H,2H,2H-perfluorodecyltriethoxysilane (97%), which has the chemical formula of $C_8F_{17}C_2H_4Si(OC_2H_5)_3(C8)$ was used as the grafting agent (Sigma Aldrich, USA) while ethanol (C_2H_5OH) and sodium chloride (NaCl) were purchased from Merck, Germany.

Preparation and modification of metakaolin hollow fibre membrane

In this study, metakaolin hollow fibre membranes (MHFM) were prepared via phase inversion and sintering technique at various sintering temperatures, as reported in our previous work [12]. Prior to the fabrication process, a ceramic suspension consisting of metakaolin as ceramic material, dispersant, binder and solvent was prepared. 1 wt% of Arlacel P135 was added to 49 wt% of NMP solvent with gentle stirring prior to the addition of metakaolin powder (45 wt%). The mixture was then ball milled for 48 hours at 150 rpm. 5 wt% of PESf was then added to the suspension as binder and the suspension was ball milled for another 48 h. After that, the suspension was degassed for 1 hour and immediately transferred into a stainless-steel syringe. Table 1 shows the fabrication conditions of MHFM. After extrusion, the MHFM precursors were soaked in water overnight to remove the residual solvents followed by drying in oven. Finally, the precursors were sintered in a high-temperature tubular furnace (XY-1700 MAGNA) under air atmosphere. During sintering, the

temperature was increased from room temperature to 600°C at a heating rate of 2 °C/min. The temperature was then kept constant for 2 hours to remove the polymer binder. Subsequently, the temperature was further increased to the desired temperature at a rate of 3 °C/min and held for 3 hours. Finally, the temperature was cooled down to room temperature at a rate of 5 °C/min. Prior to grafting, the membranes were rinsed with a solution of distilled water and ethanol in the ratio of 2:1 followed by drying at 100°C in an oven. Then, the MHFMs were immersed in the grafting solution containing 2 wt% of FAS and 98 wt% of ethanol for 24 hours. After that, the MHFMs were rinsed with distilled water and dried in oven before assembling into membrane module. The hydrophobic metakaolin hollow fibre membranes were denoted as h-MHFM.

Table 1 Dope composition and spinning condition.

Dope composition (wt%)	
Metakaolin powder	45
N-methyl-2-pyrrolidone (NMP)	49
Polyethersulfone (PESf)	5
Arlacel	1
Spinning parameters	
Bore fluid	Tap water
Coagulant fluid	Tap water
Bore fluid flow rate (mL/min)	10
Air gap (cm)	5
Spinneret: Outer diameter (mm)	2
Spinneret: Inner diameter (mm)	1

Characterization of hydrophobic metakaolin hollow fibre membrane

The surface morphology of MHFM and h-MHFM was studied through scanning electron microscopy (SEM, Hitachi model TM3000, Japan). The contact angles of MHFM and h-MHFM were determined using the contact angle goniometer (CA, OCA 15EC Dataphysics, Germany) with deionized water as the contact liquid. 2 µL of water droplet was dropped on the membrane surfaces for the contact angle measurements. The LEP_w of the h-MHFM was also investigated using a permeation system. Prior to the measurement, the h-MHFM was potted on an adaptor and the end of the h-MHFM was sealed with epoxy resin. Then, the water was circulated through the lumen side of the h-MHFM. The system pressure was slowly increased by adjusting the pressure gauge. The experiment was stopped when the first drop of water was seen on the shell side of the membrane. The minimum pressure at which the water started to pass through the membrane was taken as the LEP_w. Three-point bending tests were carried out to determine the mechanical strength of the MHFM and h-MHFM using INSTRON 3342. The mechanical strength (σ_F) was calculated using Eq. (1) (Hubadillah *et al.*, 2017a; Hubadillah *et al.*, 2016; Hubadillah *et al.*, 2017b):

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

(1)

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

Direct contact membrane distillation application

DCMD tests were carried out on a laboratory-scale setup as illustrated in Fig. 2. The setup consisted of the feed and permeate thermostatic cycles, which were connected to a membrane module. The membrane module was assembled using a brass connector consisting of two tee-shaped and a 3/4" hex nipple connectors. The system was designed to equip with two circulating streams, i.e. the hot stream, also known as feed stream, that circulated through the

membrane shell-side, and the cold stream that was fed through the lumen-side of the h-MHFM. Deionized water was employed as the feed and permeate. Both solution temperatures were controlled using coiled heater (830, PROTECH) and chiller (S&A CW-5000 Water chiller), respectively. The feed and permeate solutions were circulated throughout the DCMD process. Four liquid digital thermometers (Extech 392050, Dial Thermometer) were attached on the DCMD system to measure the temperature of the feed and permeate flows. In this study, the feed and permeate temperatures were fixed at 50°C and 10°C, respectively. Meanwhile, the cross-flow velocities of the hot and cold streams were both set at 0.023m/s. The permeate flux, J_v in the form of water vapor was collected at the permeate tank at which the weight of the tank with permeate was measured using a weighing balance (Model WA-K, WJ) and was then calculated using eq. (3):

$$J_V = \frac{\Delta W}{A \Delta t}$$

(3)

where ΔW (kg) is the weight of the permeate water vapor collected over a predetermined time, t (hours) and A (m^2) is the effective membrane area.
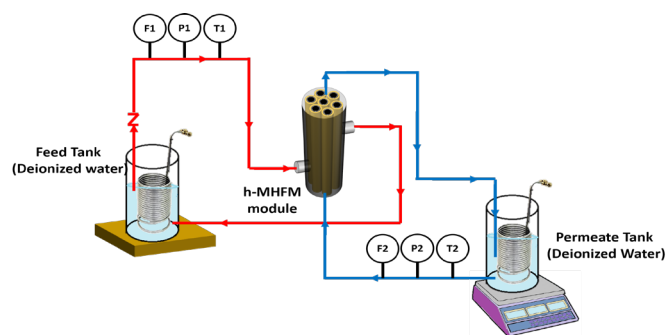

Fig. 2 DCMD setup.

RESULTS AND DISCUSSION

Microstructure of metakaolin hollow fibre membrane before and after hydrophobization

Fig. 3 shows the SEM images of the outer surface of the metakaolin hollow fibre membranes before (MHFM) and after modification (h-MHFM) prepared at different sintering temperatures. Two different trends could be observed. Firstly, the surface became denser with the increasing of sintering temperature from 1200°C to 1500°C. This mechanism is widely reported in literatures on the preparation of ceramic membranes at increasing sintering temperatures [13, 14]. According to Darcovich and Toll (2017), the densification of the ceramic particles in the membrane matrix occurs more rapidly when the sintering temperature increases. As shown in Figure 3, the densification process began to occur at the sintering temperature of 1300°C. At the sintering temperature of 1500°C, the metakaolin particles changed to rod shape, indicating that the metakaolin was converted into mullite. Mullite forms at 1000°C due to the crystallographic relation of Al–Si spinel phase and metakaolinite, in which the c axis of mullite crystal is parallel to the orientation of the Al–Si spinel phase, where the Al–Si spinel phase requires the collapse of the metakaolinite structure. The mullite growth is accelerated by instantaneous nucleation process and the short distance diffusion [15]. Chakroborty (2016) also stated that this rod-shaped started to develop at the sintering temperature of 950°C to 1000°C and appeared as cubic with 10 to 60 nm in sizes.

Secondly, the membrane structure changed after modification with FAS. As observed, the pore size of the MHFM and h-MHFM showed significant changes at the sponge-like region (membrane surface structure) as shown in Fig. 4. A close observation on the SEM images showed that there were nodules forming on the ceramic

particles in the membrane matrix. These nodules are the FAS polymer layer attached on the h-MHFM surface after grafting process (Fig. 5).
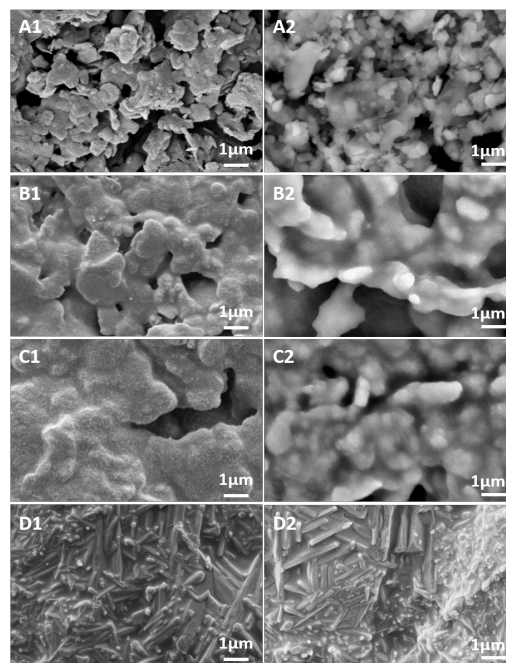

Fig. 3 SEM images of (1) MHFM and (2) h-MHFM prepared at different sintering temperatures; (A) 1200°C, (B) 1300°C, (C) 1400°C, and (D) 1500°C
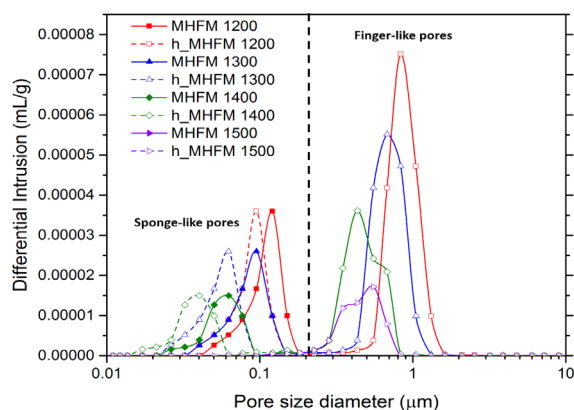

Fig. 4 Pore size distribution of metakaolin hollow fibre membrane prepared at different sintering temperatures before (MHFM) and after grafting (h-MHFM).

Fig. 6 presents the mechanical strength of metakaolin hollow fibre membranes before (MHFM) and after modification (h-MHFM) prepared at different sintering temperatures. As discussed in our previous work [12], the mechanical strength increased with increasing sintering temperature due to the densification mechanism. At the increasing sintering temperatures, the pore size of MHFM reduced which improved the mechanical strength of MHFM. In this study, an improvement of membrane mechanical strength was also observed after surface modification with silane agent (h-MHFM). However, the improvement gap was in between 10 to 20 MPa, which was probably due to the formation of polymer layer coated on the surface. For example, for the MHFM and h-MHFM sintered at 1200°C, the mechanical strength was increased from 117.6 MPa to 122.3 MPa. Interestingly, there is no other studies reported on the mechanical strength performance of ceramic membrane before and after surface modification. Therefore, this study offers an advantage by providing the information on the mechanical strength for the ceramic membrane before and after modification. In addition, the enhanced mechanical strength performance also proved that the prepared h-KHFM did not suffer from any crack or defect during the grafting process.
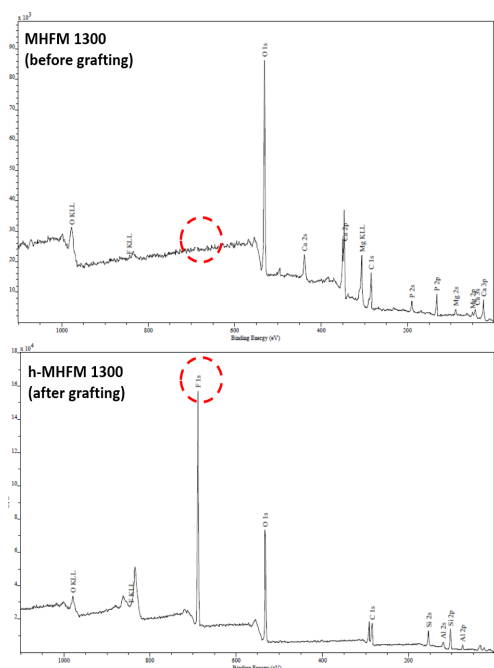
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Fig. 5 XPS analysis for h-MHFM sintered at 1300˚C before and after grafting
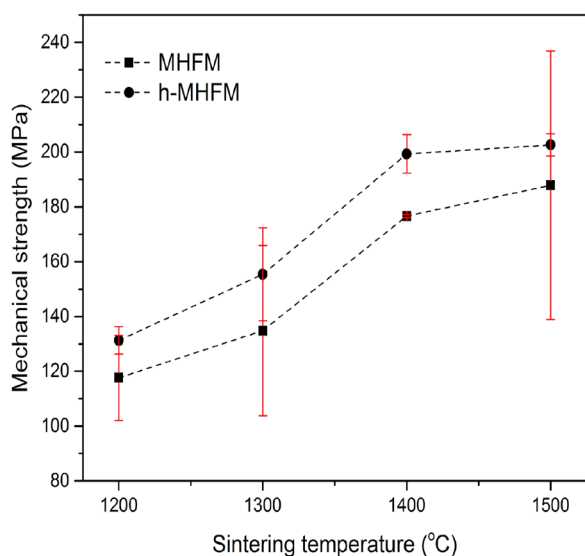
Fig. 6 Mechanical strength results of MHFM and h-MHFM.

Fig. 7 Contact angles of MHFM and h-MHFM prepared at different sintering temperatures; (A) 1200˚C, (B) 1300˚C, (C) 1400˚C, and (D) 1500˚C.

Fig. 8 Schematic diagram for water droplet mechanism on modified membranes.

Wettability properties of metakaolin hollow fibre membrane before and after modification

Fig. 7 illustrates the contact angle results for metakaolin hollow fibre membrane before (MHFM) and after modification (h-MHFM). As expected, the contact angle was successfully improved to above 90˚. For MHFM, the contact angle showed an increasing trend from 5˚ to 39˚ at increasing sintering temperatures, indicating the hydrophilic properties of MHFM. After modification, the contact angle demonstrated an increasing trend from 153˚ to 165˚ at increasing sintering temperatures, but the value was decreased when the sintering temperature was 1500˚C. This was probably due to the rod-shaped surface structure of the h-MHFM that decreased the contact angle value. Figure 8 illustrates the schematic diagram of the water droplet on the h-MHFM prepared at different sintering temperatures. For the membrane sintered at 1500˚C, the contact angle reduced as a result of the flatter surface structure due to the formation of rod-shaped particles as a function of mullitization at higher sintering temperature [16].
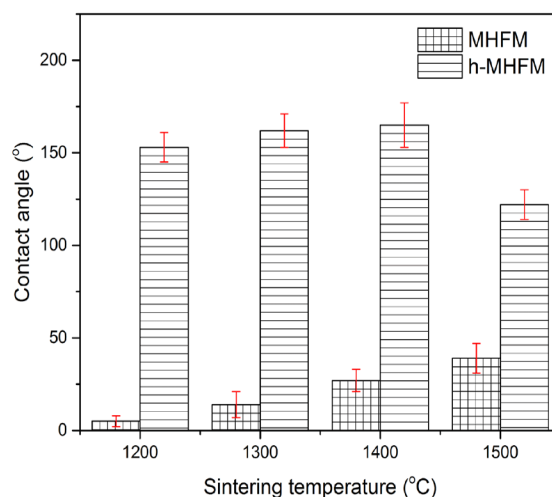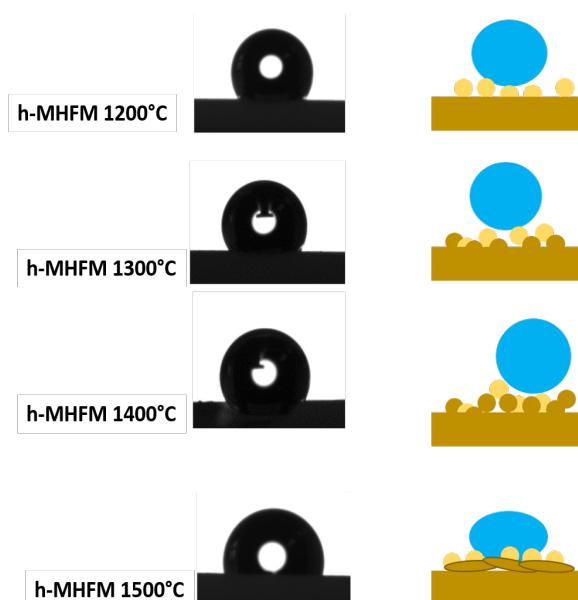
Direct contact membrane distillation performance

Fig. 7 shows the DCMD water vapor flux of the modified metakaolin hollow fibre membranes (h-MHFM) for 120 minutes testing period. As can be seen, the h-MHFM sintered at 1200˚C, which exhibited the third highest contact angle, possessed the highest water vapor flux of 17.5 kg/m²h at the first 10 minutes. The flux started to become stable after 50 minutes with value in range of 16.1 to 16.5 kg/m²h. Increasing sintering temperature would reduce the water vapor flux due to the pore size reduction. At the sintering temperature of 1500˚C, the water vapor flux was the lowest with value in the range of 5.3 kg/m²h. This trend can be explained by the decrease of pore size as the function of sintering temperature. Accordingly, further pore size reduction was observed after grafting (Fig. 4). A similar trend was also observed in a work by Gu *et al.* (2016) [7]. In addition, the flux performance of the membranes in this study was lower than that obtained by the polymeric membrane [17]. In this study, it was found that the membrane pore size is also a main factor towards the water vapor flux of MD apart from the membrane hydrophobicity. Future study will be conducted on the use of the prepared h-MHFM for the treatment of contaminated wastewater using MD process. Table 2 shows the comparison of the permeate water vapor flux obtained in this study with literature for DCMD process.
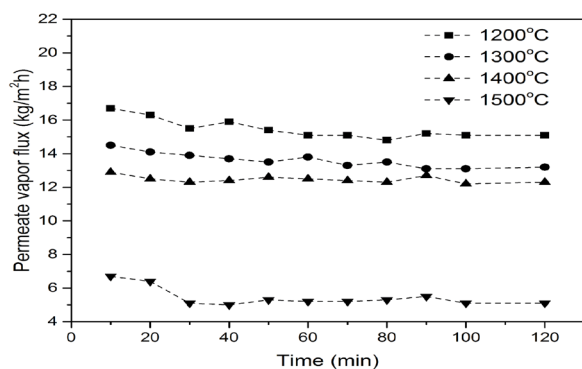
Fig. 9 DCMD water vapor flux for h-MHFM prepared at different sintering temperatures.

Table 2 Comparison of the permeate water vapor flux obtained in this study with literature for DCMD process.

Type of hollow fibre membranes		Permeate water vapor flux, J_V (kg/m²h)	Ref
Polymeric membranes	PVDF-PP	8-11	[18]
	PTFE	17.2	[19]
Ceramic membranes	Beta-Sialon	12.2	[20]
	h-MHFM 1200	16.5	This work
	1300	13.2	
	1400	12.9	
	1500	5.3	

CONCLUSIONS

Metakaolin hollow fibre membranes at different sintering temperatures were successfully developed and modified to acquire hydrophobic properties for the MD application. The prepared membranes experienced a pore size reduction at increasing sintering temperatures. In addition, the metakaolin particles converted to mullite phase with rod-shaped structure at the sintering temperature of 1500˚C. The modification of the metakaolin hollow fibre membranes with fluoroalkylsilanes successfully converted the membrane into superhydrophobic. Furthermore, the mechanical strength of the metakaolin hollow fibre membranes was also enhanced after modification. Excellent water vapor flux performance was obtained for the modified metakaolin hollow fibre membrane prepared at the sintering temperature of 1200˚C. It was revealed that the membrane hydrophobicity and membrane pore size are the main factors in MD application. A future study on the membrane thermal stability and treatment on the contaminated wastewater will be studied.

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