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Fabrication and characterization of robust zirconia-kaolin hollow fiber membrane: Alkaline dissolution study in ammonia solution

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Abstract−Kaolin has been found to be a more economical alternative in ceramic hollow membrane fabrication compared to alumina, silica, and zirconia despite having similar properties. However, it was discovered that apart from having high mechanical strength and the ability to withstand high operational temperature, the kaolin membrane has the tendency to dissolve in a high alkaline solution. Hence, in this study, zirconia (ZrO_2) was imposed to kaolin suspension as co-starting material due to its stable hexagonal properties with kaolin to overcome this drawback. To study the dissolution property of the modified kaolin-based membrane, a phase inversion technique was used to fabricate zirconia-kaolin hollow fiber membrane (ZKHFM) followed by immersion in ammonium hydroxide (NH_4OH) as an alkaline solution. Ammonia was aptly chosen for it being considered as one of the pollutants to be removed from wastewater. The mechanism, morphology and properties of the membrane were investigated in terms of sintering temperature, morphology, mechanical strength, pore size and porosity The results showed that ZKHFM with 10 wt% (ZK-10) with sintering temperature of 1,200 °C had the best performance in terms of having high mechanical strength (21 MPa), excellent permeation flux (~1,600 Lm^2/h) and lowest dissolution (0.01 g dissolute) at pH 13, indicating the ability of ZKHFM to be used in alkaline solution.

Keywords: Dissolution, Kaolin, Zirconia, Hollow Fiber Membrane, Ammonia

INTRODUCTION

Ammonia is considered water pollutant that needs to be treated for daily use. It usually comes as a by-product of fertilizers used in plantations and the production of the fertilizers itself is drained into rivers [1]. It can also originate from the anaerobic reaction from an anaerobic digester [2] or a by-product of radioactive waste [3]. Many treatments have been implemented to treat ammonia, including membrane filtration such as membrane contactor [4] and membrane distillation [5], in which the latter has attracted more interest due to its ability to filter ammonia from wastewater while at the same time recovering the ammonia to be turned into fertilizer [6]. Normally, ammonia originating from anaerobic digester and landfill leachate is usually in high concentration, which eventually might be in high alkaline condition with pH of more than 10. Hence, if membrane technology is intended to apply to treat this ammonia-rich wastewater, the membrane must be able to withstand the high concentration and pH of ammonia. The membrane also needs to be porous enough to allow ammonia to pass through the wall of the membrane and hence reduce the weakness of the membrane due to high alkaline condition of ammonia.

The recent exploration of new alternative materials for ceramic membranes has attracted many researchers to experiment with natural and low-cost materials, such as kaolin [7-9], natural ball clay [10], bauxite [11] and waste materials such as fly ash [12] and aluminium dross [13], which possess similar properties and characteristics as commercial ceramic membrane fabricated from silica, alumina, titania and zirconia, which are considered costly from a technical and economical perspective [14]. According to Hubadillah et al. [15], kaolin possesses unique physical properties such as

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low plasticity and high refractory properties, where these criteria are essential to producing a high-performance ceramic membrane. Moreover, high presence of aluminosilicate in kaolin makes it an ideal alternative raw material for ceramic membrane. Another study by Hubadillah et al. [7] discovered that kaolin could also be used as filtration membrane for oily wastewater removal. Furthermore, kaolin is known to have uniform pore channels, which is one important characteristic in membrane performance [15].

Nevertheless, despite having numerous advantages, kaolin does have a drawback. It was discovered that when used in high alkaline or basic solution, i.e., high pH of such as ammonium hydroxide (NH_4OH) solution, it will tend to dissolve. Technically, ammonia is a basic solution due to a lone pair present on the nitrogen, N atom, but it will react with -OH and later become high basic as the pH increases. Kaolin contains high composition of silica dioxide (SiO_2) in which this unstable silica negatively surface charged leads to highly polarized interatomic, Si-O. According to Niibori et al. [16], upon contact with water (OH-), SiO_4^+ (representing a part of SiO_2 framework), will react with water to form Si-OH, which will later turn to $Si\text{-}O^-$ in basic solution. They revealed that the presence of highly polarized interatomic Si-O bonds facilitates the detachment of Si in basic solution due to deprotonation of the O to negatively charged species such as $Si\text{-}O^-$.

Considering that zirconia has appeared to be used in ceramic membrane along with the use of other ceramic membranes fabricated from silica, alumina and titania, zirconia has been recognized to be a popular choice compared to polymeric membrane in microfiltration for wastewater due to its capability to withstand high temperature, pressure and chemical stability [14,15]. According to Yang et al. [17], zirconia membrane, particularly, has been one of the famous ceramic membranes due to its high chemical resistance, which allows steam sterilization and cleaning procedures at very high and low pH, excellent pure water permeability and high membrane flux in separation and filtration due to their specific surface properties as well as high thermal stability. However, owing to the fact that zirconia membrane requires a high melting point (~2,715 °C), this would lead to a higher cost of production.

Nishiyama et al. [18], prepared porous silica containing zirconia which has high resistant against water and alkaline solutions. They reported that a small amount of zirconia (~10 wt%) can effectively enhance the resistance against alkaline solution. Pure zirconia was found hardly dissolved in the alkaline solution, where it was suggested that the Zr-O-Zr network to be resistant properties in alkaline condition compared to Si-O-Si network, which makes the Si-O-Zr network stable in alkaline solution. Therefore, Nishiyama et al. [19] developed another study to add zirconia to bond with silica (MCM-48) to increase the chemical resistance. Normally, due to smaller particle size zirconia if to be compared to silica, the voids in the big pore channel present in kaolin will be filled by zirconia, which enhances the bond strength between these two materials with oxide bond. As confirmed by Rodič et al. [20], the Si-O-Zr bond is the strongest when seen in FTIR among other Si bonds.

Therefore, to the best of our knowledge, as no previous report on using ceramic membrane fabricated from mixed of zirconia and kaolin for microfiltration has been reported, thus we investigated the possibility of zirconia to be introduced in an ordered mesoporous silica containing kaolin powder by investigating the morphology of the fabricated membrane, which could later improve the resistance to high concentration of alkaline solutions. First, a study of the composite zirconia-kaolin hollow fiber membrane, namely ZKHFM, was done based on the effect of sintering temperature of the ZKHFM membrane to present the best sintering temperature for the membrane in terms of mechanical strength, average pore size, porosity and permeability of the membrane. Followed by on the effect of zirconia content in ZKHFM with the same criteria as mentioned. Lastly, the ability of the membranes to be used in high alkali condition was investigated by dissolution test. The ZKHFM membranes were fabricated in hollow fiber configuration via phase inversion and sintering technique with adaptation from a study by Hubadillah et al. [7]. The characteristics of the membrane were characterized and explored. Ammonia was chosen to be used in this study due to its properties to be basic or alkaline, especially in high pH, as well as ammonia is considered as one of the most crucial contaminants that need to be removed during wastewater treatment.

MATERIALS AND EXPERIMENTAL

1. Materials

Kaolin powder was purchased from BG Oil Chem Sdn Bhd, Malaysia and zirconia powder or zirconium (IV) oxide (ZrO_2) from Across were used as the ceramic material. N-methyl-2-pyrrolidone (NMP) was purchased from Merck and used as solvent. Polyethersulfone (PESf) as polymer binder was provided by Amoco Chemicals and Arlacel 135 (CRODA) was used as dispersant to hold the dope suspension in a homogeneous suspension. The kaolin powder and the PESf were heated to 70 °C in the oven before being used to remove any adsorbed moisture and were used without any purification process. Then, tap water was used as a non-solvent coagulant bath. Ammonium hydroxide (NH_4OH) used for alkaline solution was purchased from Merck, U.S.A and used without any pre-treatment.

2. Preparation of Zirconia-kaolin Hollow Fiber Membrane (ZKHFM)

In this work, the preparation of three types of zirconia-kaolin hollow fiber membrane (ZKHFM) were fabricated and labelled as ZK5, ZK7 and ZK10, indicated by the total composition (wt%) of zirconia powder added onto the mixed zirconia-kaolin membrane suspension. The amount of zirconia added corresponds to the study by Nishiyama et al. [18], where the amount was varied between the range of below 10 wt%, which was also used in other preliminary studies prior to this study. The idea of using less than 10 wt% was not only to reduce the cost of membrane materials but also to investigate the effect of not more than 10 wt% of zirconia towards the performance of the membrane. It was assumed if the wt% of zirconia content was more than 10%, the performance of the membrane would be hugely influenced by the zirconia, not kaolin itself as in this study, where the priority of this study is the kaolin hollow fiber membrane. The addition of zirconia was to enhance the kaolin hollow fiber membrane to be used in high concentration of alkaline/ammonia condition. Based on the preliminary studies previ-

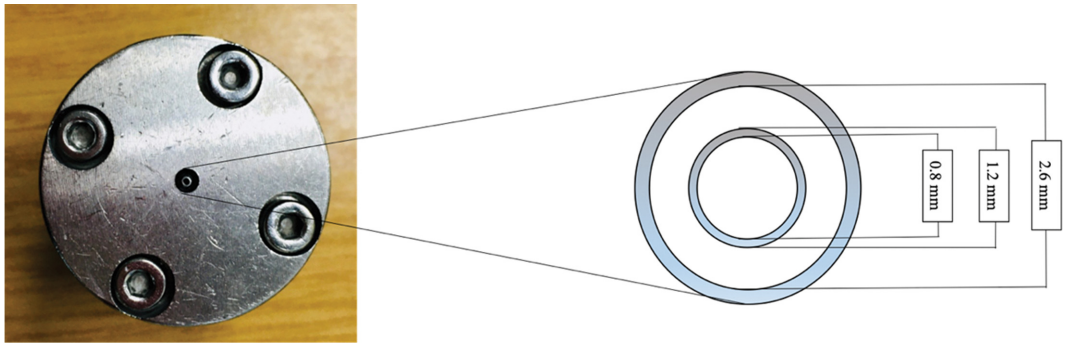


Fig. 1. Spinneret dimension for ZKHFM fabrication.

Table 1. Suspension composition for ZKHFM

Membrane	Composition (wt%)				
	Kaolin	Zirconia	NMP	PESf	Arlacel
ZK5	35	5			
ZK7	33	7	54	5	1
ZK10	30	10			

ously conducted, the addition of less than 5 wt% of zirconia revealed not so conducing results that enhanced the performance of the membrane in high concentration of ammonia; hence, the 5 to 10 wt% with 7 wt% at the middle were chosen. The detailed compositions of the dope suspensions are listed in Table 1. First, the preparation of dope suspension was initiated by mixing n-methyl-2-pyrrolidone (NMP) and Arlacel p135 to the addition of zirconia and kaolin powder in a ceramic jar together with 2 (8 mm) and 2 (20 mm) alumina balls. The dope suspension was milled for 96 h by using rotary ball mill at 192 rpm where polyethersulfone (PESf) was added during 48 h. Prior to the extrusion, the suspension was degassed with stirring at 120 rpm for at least half an hour under vacuum condition at room temperature until no bubbles were observed. After that, ZKHFM was prepared via dry/wet phase inversion/sintering technique with 10 ml/min for ceramic extrusion rate, 10 ml/min for bore-fluid extrusion rate, 5 cm air gap between the spinneret to the surface of coagulant water bath. The size of spinneret used in the ZKHFM fabrication is depicted in Fig. 1. The suspension was immediately immersed into the water bath at room temperature and solidified ceramic support was left to dry for 24 h. The membrane precursor was then straightened and cut into the

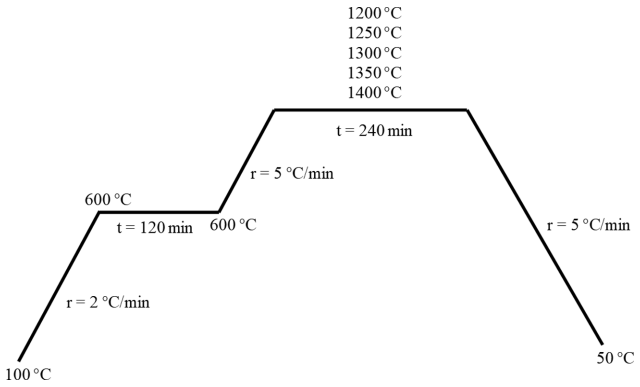


Fig. 2. Sintering profile for ZKHFM.

desired length prior to the sintering process about 15 cm long. The sintering process was done in two steps in a high-temperature tubular furnace (XY-1700 MAGNA); firstly, sintering temperature was set up at 600 °C at a rate of 2 °C/min and held for 120 min so that the binder would be burned off. Then, the sintering temperature was increased to 1,200-1,400 °C at a rate of 5 °C/min and held for 240 min. The final sintering temperature will be chosen depending on the performance of the membrane, which will be discussed in detail in the next sub-topic section. Finally, the temperature was then reduced to room temperature at a rate of 5 °C/min. The sintering profile for the sintering process of ZKHFM is shown at Fig. 2, while the schematic of fabricated ZKHFM is illustrated in Fig. 3.

3. Characterization of Zirconia-kaolin Powder and ZKHFM

The chemical composition of the kaolin powder was characterized using X-ray fluorescence (XRF) to determine the kaolin's ele-

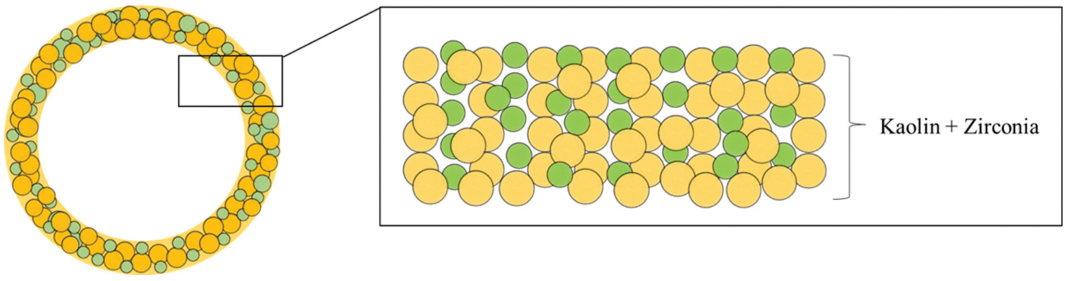


Fig. 3. Schematic diagram of ZKHFM.

ment composition. For the characterization of the crystallinity of kaolin and zirconia powder, X-ray diffraction (XRD) with Cu-Kα radiation (RINT, Ultima III, Rigaku Corp.) and Raman Spectroscopy (Raman) spectra were used.

3-1. Morphological and Pore Characteristics of ZKHFM

In membrane fabrication via phase inversion, the structure of the ceramic membrane is an important element to be analyzed. In this study, the structure of successfully prepared ZKHFM membranes was examined using scanning electron microscopy, SEM (JEOL JSM 7600F) and energy dispersive spectroscopy (EDAX) for mapping. The membrane samples were cut into 1 cm size and placed on a metal holder, which was then sputtered by platinum under vacuum before testing. The images were captured at a few magnifications to examine the overall cross-section and surface of the fabricated membrane.

ImageJ software (National Institutes of Health (NIH), U.S., Public Domain) was used to estimate of the average pore size distribution and porosity of the fabricated membrane. According to the software, the average pore size distribution and porosity of the ZKHFM were recognized based on the representation of black and white areas located from SEM images (surface image) by conducting some adjustment to the threshold of the image. The black region represents the pores, while the white region represents the represented particles. Then, the porosity was determined by calculating the percentage of the black regions, while the average pore diameter was determined by assuming cylindrical porous texture of the membrane.

3-2. Mechanical Strength of ZKHFM

The mechanical strength of the fabricated ZKHFM was examined by three-point bending test using a tensile tester (Instron 5544) provided with a load cell of 1 kN. DLZK was fixed on the sample holder with a 30 mm distance. The bending strength, σF (MPa) was calculated using Eq. (1) as follows:

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

where F is the measured load at which fracture occurred (N), and L, D_o, and D_i, are the length (m), the outer diameter (m), and the inner diameter of the hollow fiber (m), respectively.

3-3. Water Flux Permeability Test

The laboratory scale for the water flux permeability test implemented in this work was done as shown in Fig. 4 in a crossflow/dead-end permeation system. 5 cm of ZKHFM was placed in a stainless-steel carter with the tip (one end) of the membrane blocked with epoxy. Distilled water was used as feed and the first drop of water flowing out from the membrane's module until the reading was constant was recorded for 100 minutes of test duration. The pressure of the permeation system was fixed at 1.0 bar throughout the experiment by fixing the permeation system gauge, while the retentate outlet pressure was open for atmospheric pressure. Water permeation flux, J ($L/m^2 \cdot h$) test was used to determine the effect of permeability of the membranes by using Eq. (3):

$$J = \frac{V}{At} \quad (3)$$

where V, A and t are the volume of the permeate (L), membrane area (m^2), and time (h), respectively.

3-4. Dissolution/Stability Test of ZKHFM in High Alkaline Condition

A dissolution test was carried out to investigate the capability of the ZKHFM in high alkaline condition. The three ZKHFM membranes, which are ZK5, ZK7 and ZK7, were then compared to other ceramic membranes, which were alumina (Al_2O_3) hollow fiber membrane fabricated by adapting study by Abdullah et al. [21], kaolin hollow fiber membrane by adapting study by Hubadillah et al. [7], which was later labelled as K40 indicating 40 wt% of kaolin was used and zirconia (ZrO_2) hollow fiber membrane, which was fabricated using the same parameter in this study (40 wt% of zirconium dioxide powder only). 0.3 g of each consecutive membrane was weighed and later dipped in 10 mL of 10 M~pH 13 of ammonium hydroxide (NH_4OH) solution in 50 mL centrifuge tube and agitated on a digital orbital shaker (Intertek, Heathrow Scientific. LLC, USA) at 250 rpm for 72 h as shown in Fig. 5. The tip of the membrane was blocked with epoxy at both ends to investigate

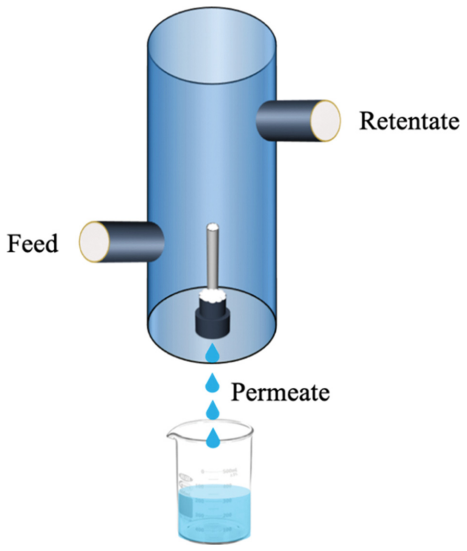


Fig. 4. Water flux permeability test set-up.

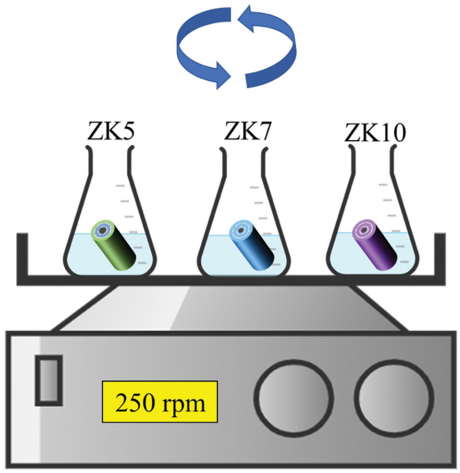


Fig. 5. Dissolution test of ZKHFM at average three samples per membranes shaken on an orbital shaker.

the effect of dissolution which had taken place at the wall surface side of the membrane, not the lumen side. The initial and final concentrations of NH_4OH as well as the initial and final weight of the membranes were recorded. The rate of membrane dissolution was determined by calculating the percentage of weight loss at the end of the test. The ability of the membrane to sustain its original weight indicates its ability to perform well in a harsh condition. The ammonia concentration was measured using DR5000 HACH Spectrophotometer, USA with HACH Ammoniacal-Nitrogen (NH_3-N) Reagent Set, HACH Salicylate Method, 0.4 to 50.0 mg/L NH_3-N (HR) Test 'N Tube™ Vials (Method 10031) and APHA method, while the pH of NH_4OH was measured by pH meter (Thermo Scientific ELITEPCTS Pocket pH/Conductivity Meter, U.S.A). Three samples of membranes were used for each consecutive membrane as replicates and the average value was calculated and recorded.

3-5. Statistical Tests on ZKHFM

The performance of ZKHFM to other membranes, i.e., alumina, zirconia only and kaolin only membranes, was compared statistically by using Prism - GraphPad software (U.S.A) according to one way analysis of variance (ANOVA) for the multiple comparison of means and tests. The variances of the groups were calculated according to Eq. (4) as follows, where $\overline{Y}_i$ is the mean of the group i, n is the number of observations of the group i; $\overline{Y}$ is the overall mean; K is the number of groups [22]. The differences were considered significant when $p<0.05$, whereas if the p-value is less than 0.001 ($p<0.001$), the comparison is significant with F statistic is the ratio of intergroup mean sum of squares to intragroup mean sum of squares [23].

$$\Sigma_{i=1}^{K} n_i(\overline{\overline{Y}}_i - \overline{Y})^2/(K-1) \quad (4)$$

RESULTS AND DISCUSSION

1. Chemical Composition of Kaolin and ZKHFM

The chemical composition of the kaolin powder used in this work evaluated by XRF is shown in Table 2. From the table, SiO_2 appears to be the major component in kaolin followed by Al_2O_3. These data correspond with data from other studies where SiO_2 content in kaolin was 48 wt% [24], 49 wt% [25], 53 wt% [26] and 55 wt% [27], where the content of SiO_2 indicates the highest percentage compared to other components. As known, SiO_2 and Al_2O_3 are the most common materials used in ceramic membrane. However, due to high content of SiO_2 which is approximately half of the composition of the kaolin, then the kaolin will tend to follow similar characteristics as SiO_2 based ceramic membrane.

According to Hubadillah et al. [7], and [9], the best kaolin hollow fiber membrane configuration is when kaolin content is at 35 wt% with dope extrusion rate at 10 mL/min and bore fluid flow rate of 10 mL/min, with ratio of ceramic to polymer binder (PESf) of 1 : 8 showing the most stable hydrodynamic force and sintered at 1,300 °C. The parameters from the previous study were adapted in this study; however, with different compositions of zirconia and kaolin, which make total ceramic composition to be 40 wt%. This composition was determined based on our preliminary study prior to this study because the composition from the Hubadillah et al. [7] study failed to produce a perfectly shaped zirconia-kaolin hollow fiber configuration with the assumption of some interaction between kaolin and zirconia being incapable of tolerating the combination with ceramic to PESf ratio. Hence, by reducing the kaolin content from 35% to 30% with the same amount of zirconia (10 wt%), similar to a study by Nishiyama et al. [18], a more stable composition of both kaolin and zirconia was established for this study. The reason for choosing zirconium (IV) oxide powder for the source of zirconia instead of yttria-stabilized zirconia (YSZ) powder by Paiman et al. [14], zirconium propoxide (ZrPr) by Park et al. [28], or zirconium oxychloride hydrate ($ZrOCl_2$) by Zhu et al. [29], Martí-Calatayud et al. [30] and Su et al. [31] was due to all the materials mentioned having to be dip coated with on alumina as support when preparing the membrane. Whereas, in this study, the zirconia powder was mixed with kaolin to form a sole single hollow fiber membrane. Even though YSZ has been known to be the most stable zirconium state [32], however, in this study, further investigation on the interaction between the Zr-O bond with Si-O bond was intended due to these bonds being assumed to be the main influence in dissolution of kaolin in alkaline solution. YSZ possesses less Zr-O bond due to the structure having combined with yttria. The mechanism of the proposed structure will be further explained later in next sub section. Hence, zirconium (IV) oxide (ZrO_2) was chosen due to this zirconia; ZrO_2 possesses the most Zr-O apart from being more cost effective compared to other zirconium; apart from this, zirconium is in powder form, which is easier to be used in ceramic membrane dope suspension. The schematic diagram of showing Zr-O and Si-O in kaolin (aluminosilicate) is depicted in Fig. 6.

2. Effect of Sintering Temperature of ZKHFM

Subsequently after the fabrication of ZKHFM, the membrane precursor of ZKHFM with zirconia content of 10 wt% by following the wt% from study by Nishiyama et al. [18] was sintered at different sintering temperatures to study the effect of sintering temperature of the membrane. Zirconia and kaolin have different melting point, where the melting point of zirconia is higher than kaolin. The sintering temperatures were varied from 1,200-1,400 °C. One

Table 2. Chemical composition of the kaolin used (wt%)

SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	CaO	TiO_2	
59.096	34.726	0.942	0.814	2.916	0.104	0.713	This study
47.85	37.60	0.83	0.17	0.97	0.57	0.74	[24]
48.57	35.05	0.6	0.77	0.08	1.34	1.19	[25]
53.2	27.3	1.9	0.07	1.92	0.3	-	[26]
55.080	29.041	2.813	0.172	1.422	0.010	0.066	[27]

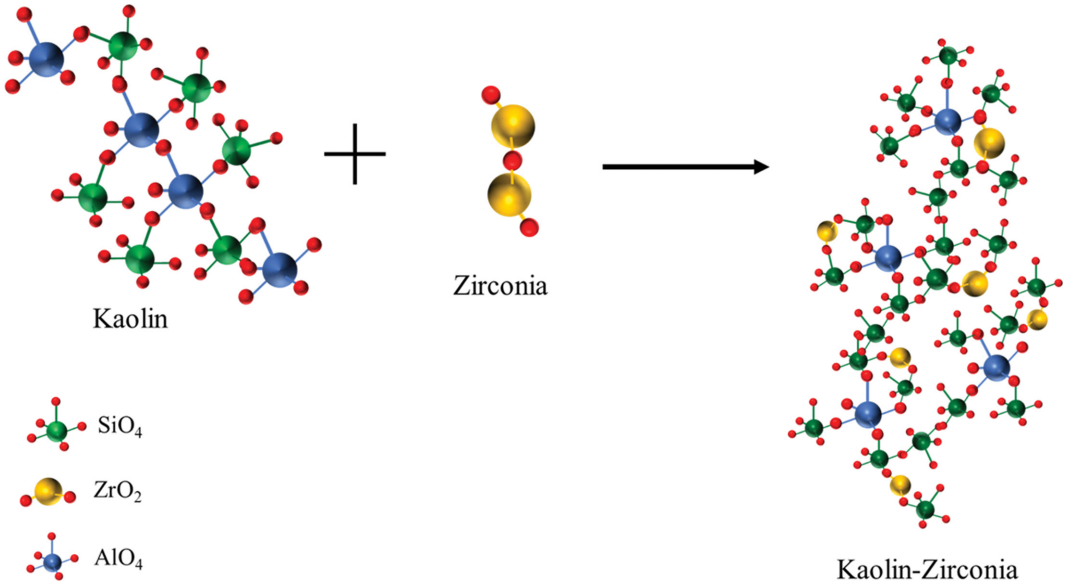
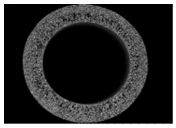
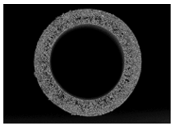
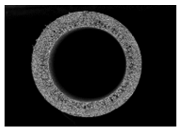
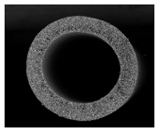
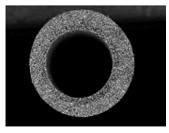
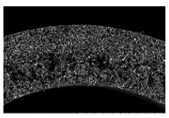
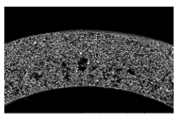
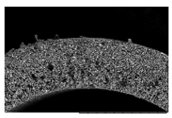
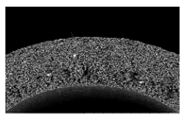
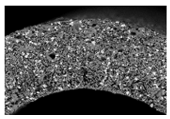


Fig. 6. Schematic mechanism of zirconia and kaolin (aluminosilicate) in ZKHFM.

Table 3. ZKHFM (zirconia loading of 10 wt%) morphology sintered at 1,200 to 1,400 °C

Sintering temperature (°C)	1,200	1,250	1,300	1,350	1,400
x80					
x30					
Tickness (μm)	1,100	1,010	953	904	846
Outer diameter (mm)	1.58	1.42	1.36	1.34	1.30
Inner diameter (mm)	1.03	0.915	0.883	0.888	0.877
Mechanical strength (MPa)	20.81	21.06	31.46	32.86	35.31

of the advantages of the phase inversion technique is the formation of micro-void structure which enhances the permeation process using the membrane. As can be seen in Table 3, the formation of the micro-void structures was obvious at 1,200 °C and the formation was reduced, i.e., became more sponge-like/dense structure as the temperature increased. The formation of zirconia seems to be agglomerated; however, it was discovered the structure does not have any impact on the performance of the membrane. The addition of Arlacel as dispersant to disperse the particle is assumed to be the reason for the well distributed zirconia particles.

Likewise, as the sintering temperature increased as shown in Table 3, the mechanical strength of the membrane also increased due to kaolin structure that also started to melt, hence allowing the membrane to form a denser structure, as stated by Jamaluddin et al. [33] supported by SEM images at 3000 magnifications on the ZKHFM surface in Fig. 7. As the temperature increased, the thickness of the membrane also reduced due to the dense structure of the membranes where the pore size was reduced. This finding is expected because as stated by Gitis and Rothenberg [34], when the thickness of ceramic membrane decreases, the mechanical strength decreases correspondingly. However, in this study, interestingly, due to the melting of the kaolin when sintered at higher temperature, i.e., 1,300 °C and above, leads to denser structure of the membrane, which eventually leads to higher mechanical strength even though the thickness of the membrane was decreased. Another aspect to be considered is the grain growth which occurred during sintering process, which altered the grain boundaries between pores leads to shrinkage of the membrane [35]. Another study by Kolstov et al. [36], where alumina-zirconia nanocomposite membranes were fabricated by hydrothermal synthesis where they claimed were due to the interaction of alumina and zirconia at certain degrees, which induced reducing grain growth as well as stabilized the membrane in sintering temperature up to 1,400 °C as well as increasing the mechanical strength of the membrane.

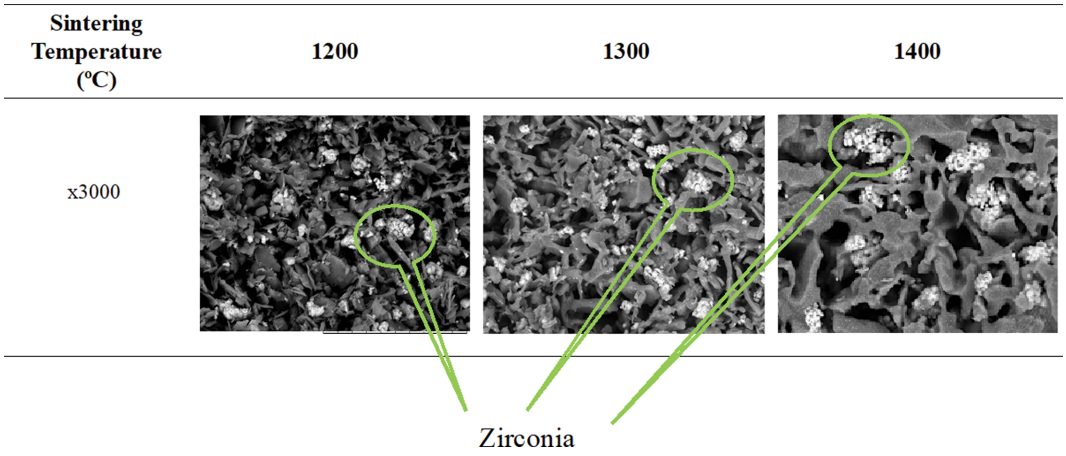


Fig. 7. SEM images of magnification of x3,000 for ZKHFM (zirconia loading of 10 wt%) sintered at 1,200, 1,300 and 1,400 °C.

Furthermore, from the magnified SEM images at 3000 magnifications as shown in Fig. 7, which show the platelet-like structure of kaolin has started to melt at sintering temperature 1,300 °C and a clear version of the melting can be seen at sintering temperature 1,400 °C. This melting was assumed to be the root behind the higher mechanical strength of ZKHFM. However, due to different melting point, the zirconia structure (white color), was maintained. Remarkably, the mechanical strength of ZKHFM from this study corresponds to a study by Hubadillah et al. [7] and [9], which is ~20 MPa and increased as sintering temperature increased. Moreover, particle packing also could be related or contributed to the effect of mechanical strength of the ZKHFM. It was discovered, the number or the formation of the micro voids was reduced as the sintering temperature increased. This could be related to the particle packing where the particles have filled the voids as the result of melting due to high sintering temperature.

Another theory which impacted the value of mechanical strength in ceramic hollow fiber membrane is microcracking or micromechanics which occurs during the sintering process, especially after a temperature of more than 1,200 °C. Previous studies by Sobhani et al., and Wang et al., on porous alumina membrane where microcracking was investigated, due to high content of alumina as well as high sintering temperature which causes the microcracking. However, in this study, the formation of microcracking was not obvious; instead, the formation of micro voids was obvious can be seen due to different particle sizes of silica and zirconia as well as due to phase inversion for membrane fabrication technique which caused the formation of voids in the membrane. As mentioned, the content of alumina is low in ZKHFM and hence it was assumed there was no microcracks was formed, which impacted the mechanical strength of ZKHFM.

2-1. Water Permeability Test of ZKHFM

Apart from investigation on the morphology, permeability is also one of the most important parameters in the performance of a membrane [37]. Investigation on the effect of the sintering temperature towards ZKHFM in terms of its permeability was done based on water permeation flux. As can be seen in Fig. 8, the ZKHFM sintered at 1,200 °C shows the highest water flux collected, which is 1,646 L/m^2·h with ZKHFM sintered at 1,400 °C showing

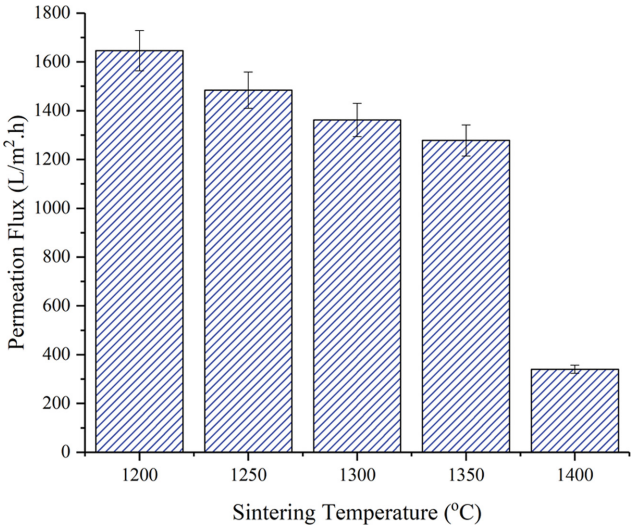


Fig. 8. Water flux versus sintering temperature of ZKHFM (zirconia loading of 10 wt%) sintered at 1,200 to 1,400 °C at average three membranes for each sintering temperature.

the lowest water flux, which is 340 L/m^2·h followed by 1,484, 1,362, and 1,278 L/m^2·h for ZKHFM sintered at 1,250, 1,300 and 1,350 °C, respectively. A significant trend can be seen which is that as the sintering temperature increased, the water flux was decreased. This is because at the beginning of the filtration, it was assumed that a partial pore size reduction and the deposit of a loose particle layer at the surface was taking place by interaction of the water particles with the membrane material entailing the rapid decrease of the permeation flux. When this stage is completed, the filtration flux reaches a level that is only dependent on the transmembrane pressure. It is also interesting that the constant permeated rate is reached more quickly when the pressure is high [24]. Plus, in this study, the membrane trans-pressure was standardized at 1 bar to reach equality corresponding to study by Hubadillah et al. [7] which used the same pressure. However, in this study the flux was higher due to the different particles because of the presence of zirconia which induced a different outcome.

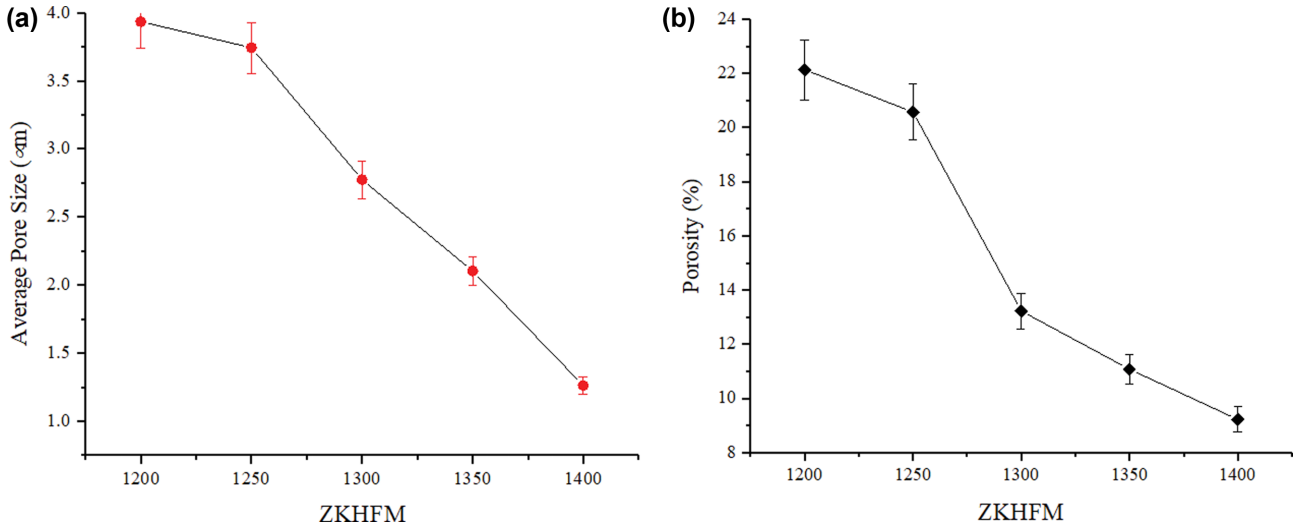


Fig. 9. (a) Average pore size and (b) porosity of ZKHFM (zirconia loading of 10 wt%) at sintering temperature 1,200 to 1,400 °C.

2-2. Average Pore Size and Porosity of ZKHFM

To investigate the average pore size distribution and porosity of ZKHFM, ImageJ software was used. According to Kingsbury and Li [38], there is a correlation between sintering temperature of ceramic membrane towards its permeability as well as pore size distribution and porosity of a membrane. As depicted in Fig. 9, as the sintering temperature increased, it induced the reducing of average pore size and porosity of the ZKHFM. Increasing the temperature reduces pore size and increases the densification of the membrane and eventually reduces the porosity. As can be seen from SEM images in Fig. 7, the void between kaolin particles can be seen to be filled with zirconia particles. This induced the different pore size and porosity of ZKHFM. Due to the melting of kaolin, the melted part closed the gap between the particles which reduced the average pore size of ZKHFM sintered at 1,200 °C from 3.935 μm to 1.262 μm for ZKHFM sintered at 1,400 °C followed by 3.743, 2.774 and 2.104 μm for ZKHFM sintered at 1,250, 1,300 and 1,350 °C, respectively as can be seen in Fig. 9(a). The reduced pore size also induced low porosity as can be seen in Fig. 9(b) where the porosity of ZKHFM sintered at 1,200 to 1,400 °C was reduced from 22.128 to 9.227% with 20.574, 13.227 and 11.084% for ZKHFM sintered at 1,250, 1,300 and 1,350 °C, respectively, in between. This study also corresponds to a study by Hubadillah et al. [9] where a similar trend was obtained.

From this finding, it can be concluded that, the addition of zirconia in kaolin membranes definitely helps in fabricating a perfect hollow fiber membrane configuration, with ZKHFM sintered at 1,200 °C showing the highest average pore size and porosity compared to other sintered temperature. Though having thre lowest mechanical strength, which is 21 MPa compared to the highest sintering temperature in this study, 1,400 °C, which is 35 MPa, however, in terms of permeability, ZKHFM sintered at 1,200 °C still possessed the highest water permeation flux which is up to 1,600 $L/m^2 \cdot h$ compared to 340 $L/m^2 \cdot h$ for ZKHFM sintered at 1,400 °C. High permeability is one of the important characteristics to be looked for in membrane performance. Instead possessing the lowest mechanical strength compared to other sintering temperatures, the membrane showed a similar result to a study by Emani et al. [39], where the result of 25 Mpa was chosen as the best configuration for low-cost material in membrane fabrication. Also, if to be compared to study by Usman et al. [40] also where the kaolin hollow fiber membrane sintered at 1,350 °C showed similar result of 20 Mpa. In terms of cost, Li et al. [41] stated that higher sintering temperature is more costly in ceramic membrane fabrication; hence this study showed that even at low sintering temperature, the membrane can work best for microfiltration purposes, high permeability. Not only does it save more energy for the sintering process due to lower temperature, but the ZKHFM sintered at 1,200 °C showed similar performance to kaolin membrane sintered at higher sintering temperatures by Usman et al. [40] and Emani et al. [42]. Also, this study showed that the kaolin hollow fiber membrane sintered at 1,200 °C showed higher mechanical strength compared to study by Hubadillah et al. [7] and Mohtor et al. [43] where the mechanical strength of the membrane sintered at 1,200 °C was 5 and 15 MPa, respectively Hence, through this finding, ZKHFM sintered at 1,200 °C was chosen as the best sintering temperature for ZKHFM.

The basic motivation of this study is to provide alternative knowledge on the use kaolin-based membrane with hollow fiber membrane configuration in harsh condition, i.e., high alkaline condition. This study in particular investigated the performance of kaolin hollow fiber membrane in high concentration/pH of ammonia. As to the best of our knowledge, no studies have been conducted on the performance of kaolin hollow fiber membranes used in high concentration of ammonia condition. However, it was discovered that during the permeation test of high concentration of ammonia using kaolin hollow fiber membrane, the membranes were dissolved. Hence, by adapting the study by Nishiyama et al. [18], by adding certain amount of zirconia, it was discovered the new modified kaolin hollow fiber membrane was able to solve the problem. Even though the addition of zirconia (conventional ceramic material) which is considered high in cost if to be compared to low cost of kaolin, it should be noted that the addition of zirconia

in this study was limited up to 10 wt%. Plus, the cost for the material of zirconia, which is zirconium oxide powder (ZrO_2), used in this study was considerably lower than the other zirconia type used for membrane fabrication, such as zirconyl chloride octahydrate or zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$), yittria-stablized zirconia (YSZ), zirconium (IV) butoxide, ZrTB (solution) and zirconium propoxide (ZP). Plus, previously, zirconia-based ceramic membranes were normally fabricated either by depositing the zirconia on the surface of a membrane support or via sol-gel or hydrothermal method as membrane coating, which is not considered a cost-saving method. To the best of our knowledge, there is no study of using zirconium oxide powder in the membrane fabrication which mixes both silica and zirconia as one dope suspension or to as a single mixed hollow fiber membrane. In this study, the zirconium oxide powder was mixed with the kaolin dope suspension and proceeded to phase inversion method, which is a single step of membrane fabrication. This study also was intended to investigate the effect of addition of zirconia powder added to the kaolin mixed zirconia dope suspension for an ideal weight percentage (wt%) of zirconia based on the weight percentage proposed by Nishiyama et al. [18], which is 10 wt%. Moreover, the effect of addition of zirconia wt% which is lower than the proposed by the study, which are 5 and 7 wt%, was also being investigated for a purpose of lowering the cost for zirconia used in the mixed zirconia-kaolin membrane fabrication in the future.

3. Effect of Zirconia Content in ZKHFM

For the purpose of verifying the effectiveness of zirconia addition in kaolin, the amount of zirconia content in ZKHFM fabrication was varied from 5, 7 and 10 wt%. The reduced amount of ZKHFM was divided by three types, namely ZK5, ZK7 and ZK10, where the number behind (ZK) corresponds to wt% of zirconia used. As for the sintering temperature which was set at 1,200 °C, which is considered the best as mentioned in the previous subsection, the membrane showed the best performance in water flux permeation as well as the highest average pore size and porosity. Not only can it save more energy, but the membrane can also perform without any huge difference to increased sintering temperature. The reason for the content of zirconia limit up to 10 wt% is due to our preliminary work, increase in zirconia content more than 10 wt% failed to produce a perfectly shaped hollow fiber configuration, which requires more study in the future. Fig. 10 depicts

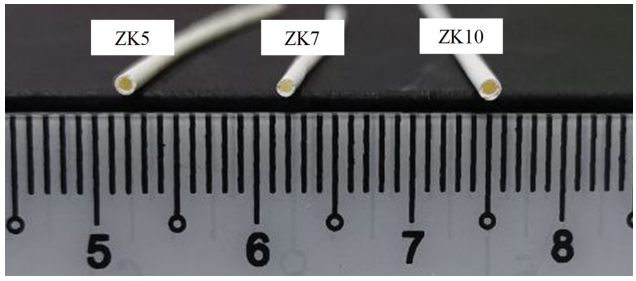


Fig. 10. Image of ZKHFM membranes, ZK5, ZK7 and ZK10 with different zirconia content sintered at 1,200 °C.

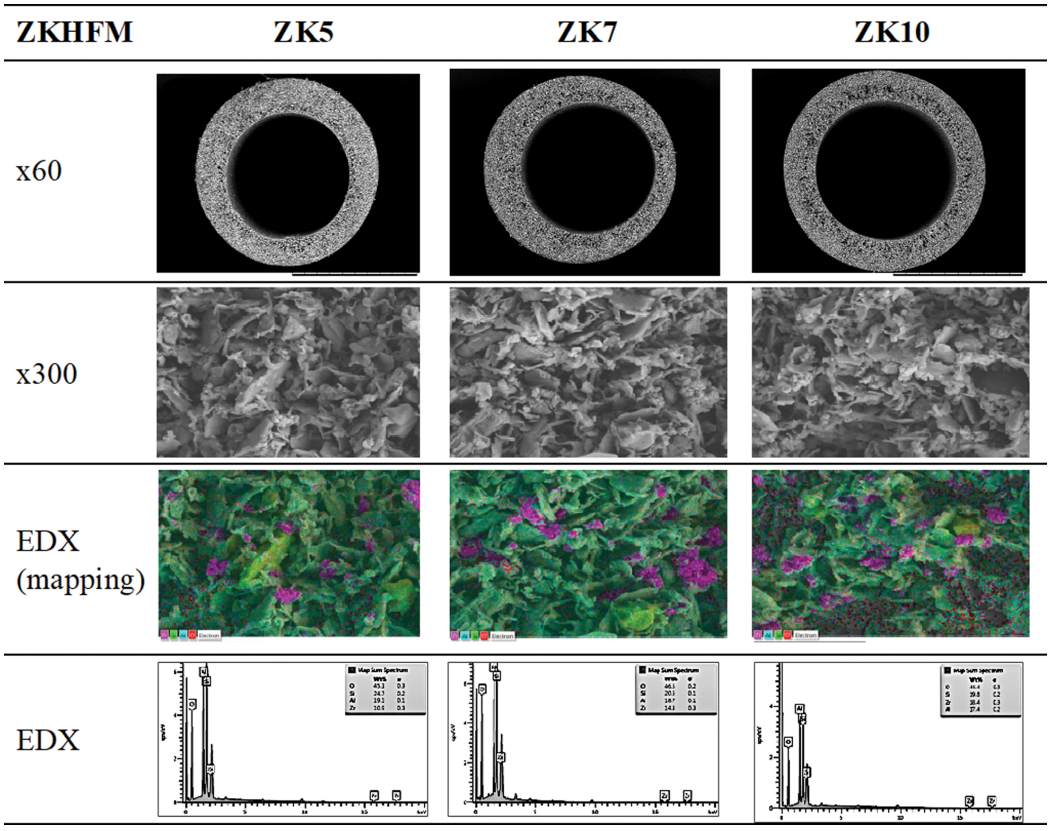


Fig. 11. SEM and EDX images of ZKHFM at different zirconia content sintered at 1,200 °C.

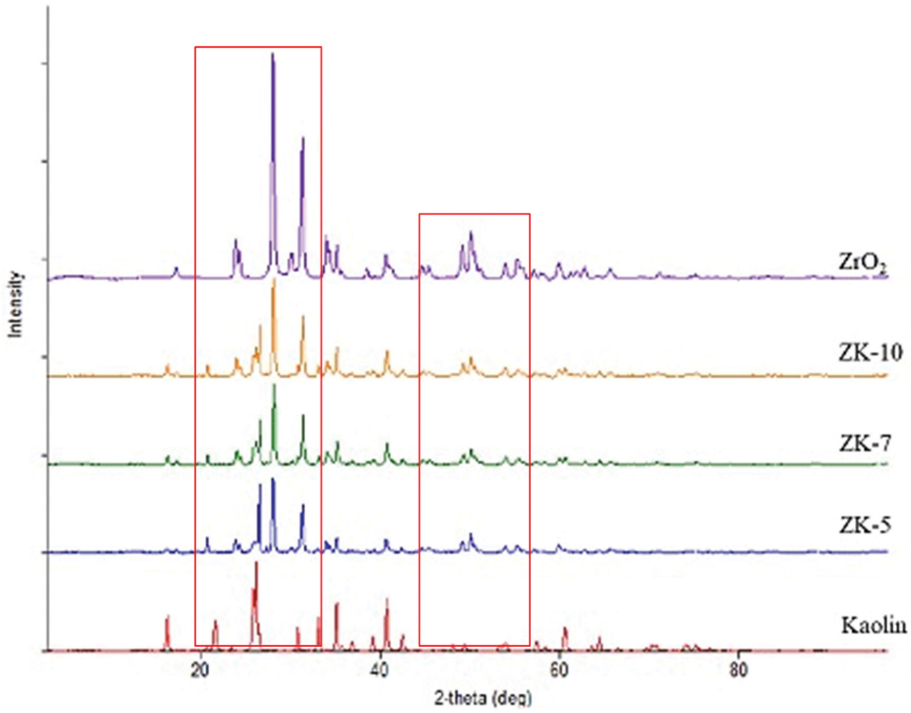


Fig. 12. XRD pattern for ZKHFM sintered at 1,200 °C.

the image of successfully fabricated ZKHFM with different zirconia content and sintered at 1,200 °C.

On the other hand, Fig. 11 describes the SEM and EDX images of ZKHFM membrane for ZK5, ZK7 and ZK10 sintered at 1,200 °C, which revealed platelet hexagonal structure of the kaolin. An asymmetric structure of micro voids near to the lumen side of the hollow fiber surface occupies about 20% of the hollow fiber thickness, with the remaining hollow fiber region occupied by a sponge-like layer. This asymmetric micro void structure increased in size when the weight percentage of zirconia content increased. The formation of the micro voids was assumed to help permeability of the membrane as stated by Li [44]. EDX was used to determine the presence of zirconia particles where it can be seen filling the void or big pore created from kaolin. The purple color in the image indicates that the presence of zirconia particle did fill the pore left by kaolin particles. Despite ZK7 presenting different thickness, based on the findings which will be discussed later in next sub-topics where ZK7 still follows the trend of properties for other ZK5 and ZK10, the thickness does not affect much the performance of the membrane.

3-1. Characteristics of ZKHFM at Different Zirconia Loading

To verify the structure of the ZKHFM especially in terms of its crystallinity, XRD was done to identify the correlation between Zr and Kaolin (SiO_2) spectra. According to Puthai et al. [45], XRD can be used to determine the crystallinity of the ZKHFM by investigating the interaction between SiO_2-ZrO_2, and whether the SiO_2-ZrO_2 powders are composite or simply a mixture of SiO_2 and ZrO_2. XRD patterns of each patent of ZKHFM prepared by phase inversion technique are compared with kaolin and zirconia as in Fig. 12. XRD patterns show that the structural characteristics of the prepared ZKHFM compared perfectly to ZrO_2 especially at the 2θ of 28° where a significant difference in peak intensity can be seen. This indicates that ZrO_2 structure was preserved even after the phase inversion process. The intense peak of silica in kaolin at 2θ of 25° decreased due to the reaction between silica and zirconia having taken placed. At peak 2θ of 50°, the peak of Zr was found at those ZK5 to ZK10 indicating that there monoclinic Zr was found in the membranes [46].

X-ray diffraction (XRD) has often been used for the study of the kaolin-zirconia phase transitions where the crystallinity of the mixture was studied. Plus, the use of RAMAN spectroscopy was also implemented to study the interaction between the Si-Zr bond

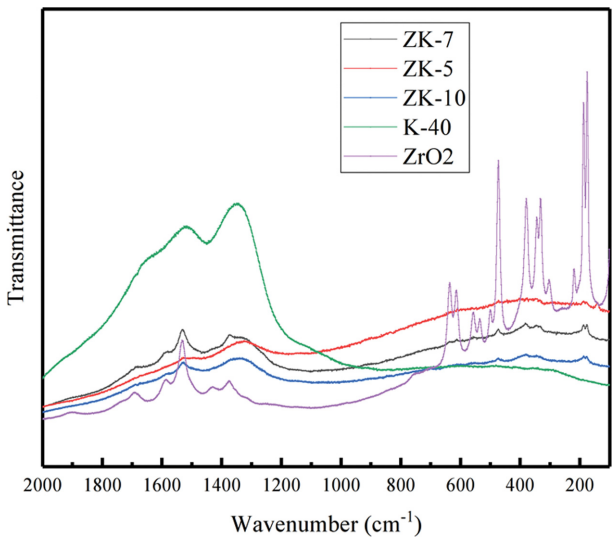


Fig. 13. Raman spectra for ZKHFM sintered at 1,200 °C.

or Al-Zr bond in the mixture in terms of hydroxyl removal. Because kaolin existed mainly as aluminosilicate (Al_2SiO_5), there is the possibility the removal of water or hydroxyl group is then replaced by Zr ion especially in powder form. Based on Fig. 13, from the Raman spectra of ZKHFM, a comparison was done to evaluate the membrane's spectra towards kaolin membrane (K40) and zirconia powder spectra. At wavenumber of 1,600 cm^{-1}, there is significant peaks for ZK10. As kaolin also contains alumina, the significant peak is due to interaction of alumina with ZrO_2 as proven by Boullosa-Eiras et al. [47]. However, at wavenumber of around 1,300-1,400 cm^{-1}, the significant peak for SiO_2-ZrO_2 was observed and this is confirmed by Lee and Condrate [48].

3-2. Mechanical Strength of ZKHFM at Different Zirconia Content

Park et al. [19] stated that zirconium ions occupy the interstices of the silica networks and increase their packing density. Furthermore, the zirconium ions in the interstices of the silica networks strengthen the electrostatic bonds and weaken the polarization of the non-bridged oxygen ions. Fig. 14 illustrates that ZK10 shows the highest mechanical strength due to the high weight percentage of zirconia in the membrane structure, which is 21 MPa. The higher the quantity of zirconia added, the higher the mechanical strength. If to be compared to other ceramic membranes, especially alumina-based membrane, the value of mechanical strength (MPa) of ZKHFM was considerably low, which may due to the composition of the suspension itself considered quite low, which is only 40 wt%. It was discovered, if high ceramic composition was used, then the dope failed to be extruded. Even though the composition is considerably low, other aspects should be taken into account such as the permeability, cost and the performance of the membrane itself. On the other hand, the value of MPa for ZKHFM was increased from 11 MPa (ZK5), 13 MPa (ZK7) to 21 MPa (ZK10) due to Zr ions which occupied the void between Si ions, hence increasing the bond between these two ions, which enhanced the strength of the membrane [28]. As added by Paiman et al. [14], as the mechanical strength of ceramic membrane increases with the increasing ceramic content due to the mass transport mechanism during the sintering process, leading to the growth of necks between the ceramic particles. Another theory which impacted the value of mechanical strength in ceramic hollow fiber membrane is microcracking or micromechanics which occur during the sintering process, especially after the temperature is more than 1,200 °C [49]. Previous studies by Sobhani et al. [50] and Wang et al. [51] on porous alumina-titania membrane where microcracking was investigated, due to this microcracking, especially due to the presence of alumina (high content in kaolin) affects the mechanical strength of ZKHFM. By reducing the zirconia content, which reduces the intermixing of particles as proposed by Koltsov et al. [36], which influences the reduction. In fact, there is also the possibility due reduction of particle packing mechanism because of less particles of zirconia also reducing the intensity of the grain growth between each pores, which leads to the reducing of mechanical strength at ZKHFM equipped with fewer zirconia content.

3-3. Water Permeation Flux of ZKHFM at Different Zirconia Content

Apart from instrumentation analysis, a water flux permeation test using distilled water was done to investigate the permeability of the membrane. As shown in Fig. 15, as the amount of zirconia content was reduced, so was the water flux permeation. ZK10 shows the highest permeability among those ZKHFM membranes, which is 1,646 L/m^2·h followed by 1,586 and 1,462 L/m^2·h for ZK7 and ZK5, respectively. This obtained data represent that the zirconia content does not affect much the permeability of the ZKHFM as the water flux is still considered high compared to study by Hubadillah et al. [7-9], where from their study the highest water flux was less than 1,000 L/m^2·h. To support the data, average pore size distribution and porosity of the ZKHFM will be explained in the next sub-chapter to correlate the permeability of the ZKHFM.

In addition, based on SEM images in Fig. 11, where the lack of asymmetric micro void structure for ZK5 might be the reason why the water flux was low compared to other ZKHFM. It was assumed the formation of sponge-like/denser structure at ZK5 which de-

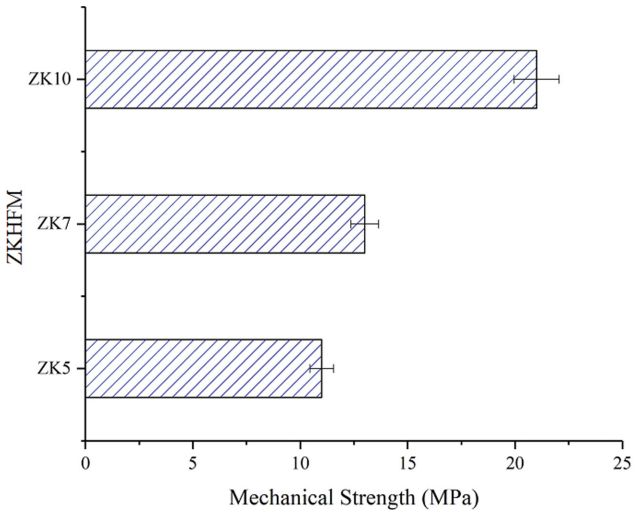


Fig. 14. Average of mechanical strength of ZKHFM sintered at 1,200 °C at different zirconia content for three samples per membrane test.

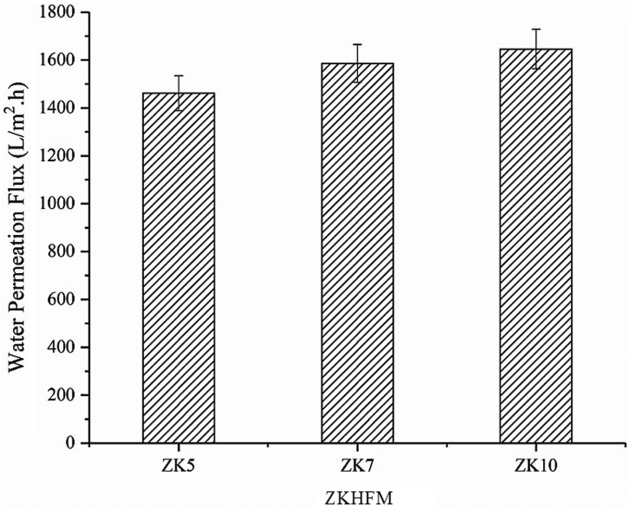


Fig. 15. Water permeation flux test of ZKHFM sintered at 1,200 °C at average three membrane samples for each trial.

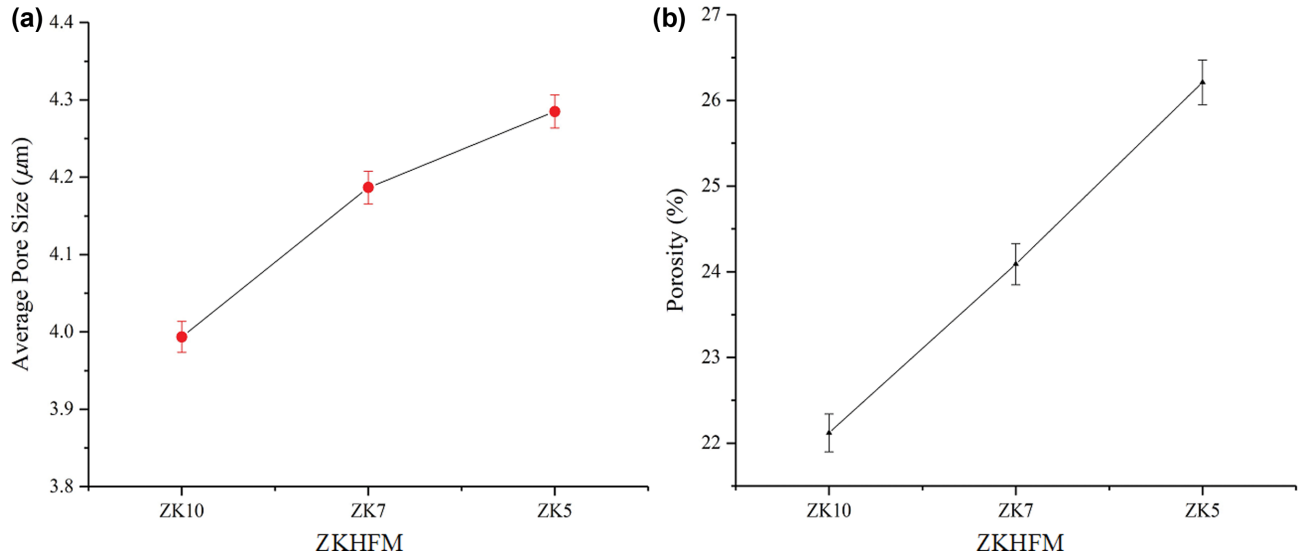


Fig. 16. (a) Average pore size (b) porosity of ZKHFM sintered at 1,200 °C at different zirconia content for average of three membranes per run.

creased the permeation of water if to be compared to ZK10.

3-4. Average Pore Size and Porosity of ZKHFM on the Effect of Zirconia Content

ImageJ software was used to validate the data to investigate the average pore size and porosity of ZKHFM on the effect of zirconia content. As can be seen in Fig. 16(a), the difference among the three ZKHFM membranes was not really significant as the ZK5 possesses the smallest average pore size, which is 3.99 μm followed by 4.18 and 4.28 μm for ZK7 and ZK10, respectively. Meanwhile, according to Fig. 16(b), the highest porosity was obtained by ZK10 at 26% followed by 24 and 22% for ZK7 and ZK5, respectively. This data obtained corresponded to the water flux permeation data obtained earlier. This explains the reason ZK10 showed the highest water flux permeation due to highest porosity as well as the biggest average pore size. Added by the data from SEM images at Fig. 11, where the structure of the membrane itself has shown that the present of micro voids did affect the porosity as well as permeability of the membrane as stated by Li [44].

3-5. Dissolution of ZKHFM in Alkaline Solution

The motivation of this study was to investigate the dissolubility or stability of ZKHFM in high alkaline of ammonia solution. Kaolin, having the aforementioned composition of silica (~60%) caused it to have low endurance in basic or alkaline solution. Since ammonia in high concentration or pH is very basic, the issue of using kaolin only membrane will result in it being dissolved in such solution. To verify the claim, a dissolution test was done by shaking the ZKHFM membranes in NH_4OH solution or immersion and shaking process. The final weight of the ZKHFM after test is shown in Fig. 17 and compared to alumina membrane, kaolin membrane (K40 indicated by 40 wt% of kaolin) and zirconia membrane (zirconium (IV) oxide only). As can be seen, the ZKHFM represented by ZK10 shows that this membrane was able to withstand the harsh alkaline solution as far as alumina and zirconia membrane, which is the weight loss only 6% lost from original weight. Meanwhile, kaolin membrane (K40) lost almost 100%,

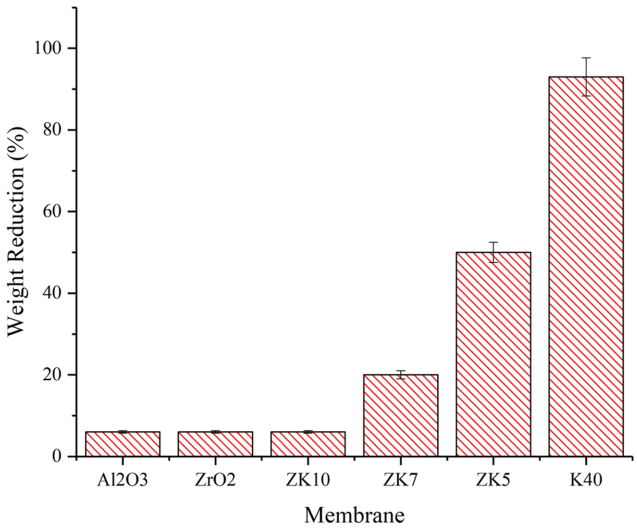


Fig. 17. Weight loss of ZKHFM, alumina, kaolin and zirconia only membrane in NH_4OH solution.

which is 93% from original weight, followed by ZK5 which lost half of its original weight, which is 50%. Last, ZK7 lost almost 20% from its original weight.

A clear image of the comparison of the dissolution of the ZKHFM in high alkaline ammonia solution is shown in Fig. 18. Due to the alumina and zirconia membranes producing similar result with ZK10, the image of the membranes was not included. Based on the image, the clear water of ammonia turned cloudy white, indicating that the kaolin membrane (K40) was dissolved in the solution. Compared to ZKHFM membrane, ZK5 showed the obvious half dissolved as the membrane lost half of its original shape. ZK10 shows the best performance in terms of dissolution as no white cloudy solution was discovered and the original shape of the membrane was maintained.

Fig. 19 depicts the flow of silica bond (in kaolin) to be break

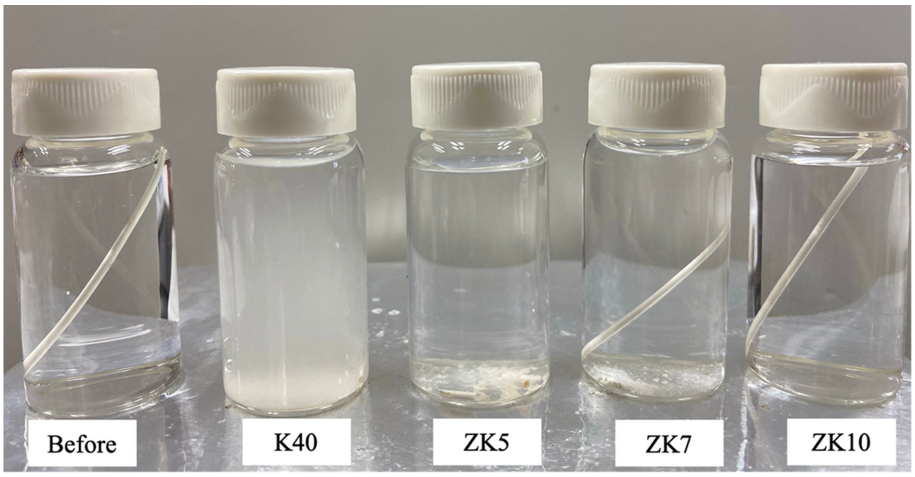


Fig. 18. Before and after dissolution test for ZKHFM and kaolin membrane (K40).

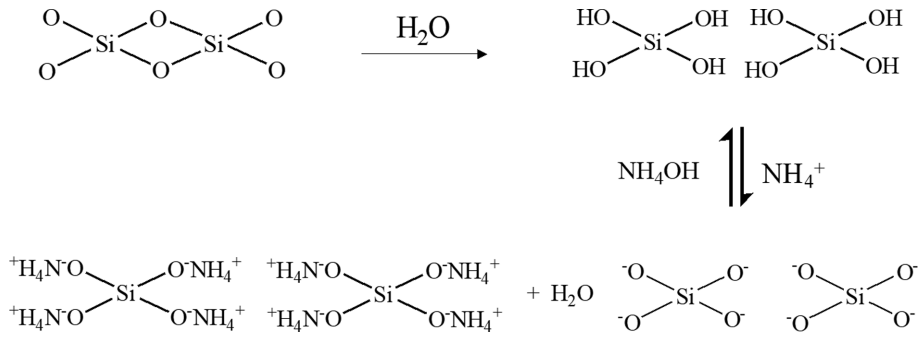


Fig. 19. Proposed mechanism of SiO_4 in alkaline solution.

down in high basic/alkaline condition to explain the mechanism of this reaction. This mechanism was illustrated by Niibori et al. [16], where they elaborated that as kaolin or SiO_2 contacted with water (OH-), SiO_4^+ (representing a part of SiO_2 framework) will react with water to form Si-OH, which will later turn to Si-O^- in basic solution. They revealed that the presence of highly polarized interatomic Si-O bonds facilitates the detachment of Si in basic solution due to deprotonation of the O to negatively charged species such as Si-O^-.

Kaolin composition mostly is dominated by aluminosilicate, Al_2O_3-SiO_2. Hence, the interaction of the aluminosilicate and zirconia could become a new network as Al_2O_3-SiO_2-Zr. Since the composition of alumina, Al_2O_3 in kaolin as shown in Table 2 is 35%, whereas silicate, SiO_2 was made up of 60% of total composition of kaolin used in this study. Due to silicate being predominantly composing the kaolin, which induced the dissolubility of

Table 4. Comparison of kaolin/alumina/zirconia membranes with previous studies

Materials	Type of membrane	Mechanical strength (MPa)	Flux ($L \cdot m^2/h$)	References
Malaysian kaolin (1,200 °C)	Hollow fiber	16	300	[7]
Malaysian kaolin+/TiO_2 (1,200 °C)	Hollow fiber	52	165	[54]
Malaysian kaolin (1,200 °C)	Hollow fiber	9	Not stated	[40]
Tunisian kaolin	Flat sheet	60	Low	[26]
Tunisian kaolin/starch	Flat sheet	28	65	[24]
Chinese kaolin+Al_2O_3	Hollow fiber	14	3,700	[55]
Indian kaolin	Flat sheet	73	206	[42]
ZrO_2/a-Al_2O_3	Flat sheet	Not stated	93	[17]
ZrO_2-Al_2O_3	Nanocomposite	60	Not stated	[36]
yttria-stabilized zirconia	Hollow fiber	336	Not stated	[14]
Kaolin/Zirconia	Tubular	Not stated	1,204	[27]
Malaysian kaolin with addition of 10 wt%/zirconia	Hollow fiber	21	1,600	This study

the material in high concentration of ammonia, there was the possibility the alumina particles were also affected by the exposure to the ammonia, but can be neglected due to the less composition of alumina compared to silicate.

Apart from that, according to Cormier et al. [52] and Ficheux et al. [53], the addition of zirconia in aluminosilicate not only will enhance the glass properties but also improve chemical durability or mechanical resistance, increasing viscosity and decreasing thermal expansion. Zirconia, indeed, is an efficient nucleating agent which will create a nucleation to the aluminosilicate structure, which to stabilize the glass structure. Based on their finding, explaining the addition of zirconia content in kaolin improves the stability of the membrane in high alkaline ammonia solution. Table 4 presents a summarized comparison of using kaolin/alumina/zirconia membranes from previous studies in terms of the mechanical strength and flux. The results from this study were discovered to be comparable to other studies where the highest flux was recorded and the mechanical strength of the ZKHFM was still considered the best to be used for microfiltration purpose. As there are not many studies of using silica and zirconia to be compared, the most similar study of using tubular membrane was by Boussemghoune et al. [27]; still, this study did not mention any performance of the membrane in high concentration of ammonia.

3-6. Statistical Comparison on ZKHFM

The results of performance of mechanical strength, permeability, pore size distribution and porosity for ZKHFM sintered at different sintering temperatures, which is 1,200 to 1,400 °C, ZKHFM with different zirconia content, which is ZK5, ZK7 and ZK10 sintered at 1,200 °C and dissolution of ZKHFM, alumina, zirconia only and kaolin (K40) hollow fiber membranes in ammonia were compared with each other statistically by comparing the means of the aforementioned results by one way ANOVA method. As proposed by the software used, it was discovered that *F* distribution value was the biggest in terms of the comparison on means of the dissolution of the membranes in the alkaline solution. This was due to the data not being sampled from populations with the same mean, which can be described as that the data was taken from different population (different type of membranes). Meanwhile, *p* value of $p<0.001$ indicating the outcome from the comparison does not affect the measuring of the data and R^2 close to value of 1 which is 0.999, indicates that the comparison is valid and the difference is significant as tabulated in Table 5 [56]. This means that the hypothesis can be accepted to avoid any type 1 error where the comparison from the means of performance of ZKHFM was valid. According to Kim [23], type 1 error occurs if there are comparisons on means of three groups that are mutually independent satisfying the normality and equal variance assumptions. Hence, by following the suggestion by the software, it was discovered the comparison was valid in terms of means variance, which indicated that there was a significant difference in comparing the membranes.

CONCLUSION

Kaolin based ceramic hollow fiber membrane has been successfully fabricated with the addition of zirconia, namely ZKHFM. Kaolin was used as an alternative material for commercial ceramic membrane such as alumina (Al_2O_3) and silica (SiO_2) due to its high cost. To overcome kaolin's tendency to dissolve in high alkali surrounding, zirconia was added because zirconia is known to be resistant in high alkali condition. The morphology and performance of the ZKHFM was investigated and membrane with 10 wt% Zr content, namely ZK10 sintered at 1,200 °C possesses the best characteristics in terms of high mechanical strength (21 MPa), high permeation flux (~1,600 $L \cdot m^2/h$), which also indicates low dissolution rate as well as obvious formation of asymmetric finger-like void on the membrane to enhance filtration process. As the sintering temperature increased, the weight percent of Zr reduced but the morphology of ZKHFM also changed as the membranes became denser, eventually reducing the particle size of the membrane and increasing the particle packing.

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Table 5. One way ANOVA for performance of ZKHFM

	Sintering temperature	Zirconia content	Dissolution
F	27.75	816	2517
P value	<0.0001	<0.0001	<0.0001
P value summary	****	****	****
Significant diff. among means (P<0.05)	Yes	Yes	Yes
R squared	0.9922	0.9967	0.999

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