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Novel ceramic hollow fibre membranes contactor derived from kaolin and zirconia for ammonia removal and recovery from synthetic ammonia

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ABSTRACT

The adverse effects of ammonia found in wastewater streams lead to the development of advanced water treatment technology, i.e. membrane contactor (MC). In this study, single layer hollow fibre membrane (SLZK) and dual layer hollow fibre membrane (DLZK) were prepared from zirconia and kaolin and modified into hydrophobic membrane through simple grafting process via fluoroalkylsilane (FAS) agent. The properties of membranes such as morphology, surface roughness, mechanical strength, wettability and liquid entry pressure were analysed through scanning electron microscopy (SEM), atomic force microscopy (AFM), 3-point bending strength, contact angle and LEPw setup. Finally, the performance of the membranes was also investigated towards ammonia removal via membrane contactor system. Our findings showed that hydrophobicity properties significantly improved for both SLZK and DLZK membranes after grafting modification process as indicated by the increase of contact angle value from 5° and 1° to 132.7° and ~180.0° respectively. Based on the morphological analysis, the surface of DLZK showed more porous structure as compared to the SLZK. In addition, DLZK also displayed the highest mechanical strength and contact angle reading of 125 MPa and ~180° respectively. This suggests that the DLZK showed an excellent membrane contactor performance with highest value of mass transfer coefficient (3.77 x 10-5 ms^{-1}) and almost complete removal of ammonia removal (91%). Overall, these results implied that dual layer ceramic membrane developed from kaolin and zirconia could provide the basis for the development of alternative ceramic membrane with excellent properties for membrane contactor system.

1. Introduction

Amidst a rapid global population growth and the improvement of living standards, excessive and uncontrolled human activities have caused an imbalance to the cycle of nature. Increased conversion of inert nitrogen will guarantee the generation of several reactive forms, that, at high concentrations will cause hazards to the environment [1].

Unbeknownst, the ammoniacal nitrogen, NH_3–N (the combination of ammonium ions, NH_4^+, and ammonia, NH_3) is the main compound contributing to reactive nitrogen which are introduced into natural waters by industrial, domestic, and agricultural wastewater approach. Therefore, it is the target of most nitrogen removal processes [2]. Ammonia, especially in gaseous state appeared to be one of the main pollutants comprised in natural water from industrial, domestic and

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agricultural wastewater discharge. Therefore, scientists are currently researching the use of advanced technologies and approach to eliminate ammonia because the accumulation of such pollutants consumes oxygen for nitrification, which increases water toxicity and subsequently harms aquatic organisms such as fish. For this reason, various techniques have been studied to remove dissolved ammonia [3].

Previous studies have proven that apart from ammonia removal, ammonia from wastewater can also be recovered and reused as an alternative source for ammonia production such as from landfill leachate by Kurniawan et al. [4,5] as well as domestic wastewater by Lee et al. [6]. One of the emerging techniques for the removal and recovery of ammonia from wastewater is by membrane contactor (MC). MC is a technology that uses hydrophobic and microporous membranes to complete the mass transfer between two phases without dispersion. These phases could be gas/liquid or liquid/liquid. The physical and/or chemical properties of the membrane and osmotic components allow the transportation or separation of certain components. In the case of full pores, for liquid/liquid applications with two polar phases, the basic principles for separation are: first, at the entrance of each membrane pore, next is the mass transfer at the interface where the two phases are in contact, and finally, the diffusion process inside the irregular pores taken place. Compared to conventional contactor methods (such as scrubbers), the use of membrane contactors has several advantages including operational flexibility, reduced capital costs and easily predictable design [7,8].

With respect to their technological strength, MC membranes that typically exist in hollow fibre configuration allow any volatile species such as ammonia gas (converted from high pH of ammonia solution) to be transferred through the hydrophobic porous wall of the membrane (feed) and an acid such as sulphuric acid is flowed counter-currently on the lumen side (permeate) of the membrane in order to react with the ammonia gas to create ammonium sulphate. The high pH of ammonia liquid converted to ammonia gas is used in the application [9]. Hydrophobicity is important to prevent wet-out where water is repelled by the hydrophobic membrane surface, unless a pressure exceeding the breakthrough pressure is applied.

Another novelty of the mode of MC operation is that the membrane must be porous enough for ammonia gas to pass through the pores of the hydrophobic membrane. Once the ammonia gas transfers through the hydrophobic membrane, it will disturb the ammonia-ammonia balance on the shell side, because such ammonium substances are expected to be converted into ammonia gas and generate protons (hydrogen ions), thereby reducing the pH of the solution.

Hydrophobic polymeric membranes, such as polyvinylidenefuoride (PVDF), polytetrafuoroethylene (PTFE) and polypropylene (PP), are commonly employed for MC because of their low surface energy and high hydrophobicity. However, polymers have disadvantages, which are unable to act in harsh conditions such as high temperature and non-chemical resistance, which are crucial properties for membranes in MC. Ceramic membranes are able to alleviate this problem, as they can withstand harsh conditions due to their excellent mechanical stability, chemical stability and thermal resistance. Usually, alumina is the most common material for ceramic membrane fabrication. Unfortunately, alumina-based ceramic membranes revealed some drawbacks due to high sintering temperature of up to 1500°C, apart from the high cost of the alumina powder making the overall cost of ceramic membrane fabrication extremely expensive. In fact, when a high sintering temperature is used, the fabrication process will be prolonged. Nevertheless, these ceramic membranes possess hydrophilicity behaviour that inhibits their application in membrane contactor systems [10].

Nowadays, the utilization of alternative ceramic material such as clays and industrial wastes have gained popularity in ceramic membrane towards several applications [11]. Among all alternative ceramic materials, kaolin has been widely used in alternative ceramic membrane fabrication [12]. This particular material possesses a few advantages, which are cheap and abundantly available in many countries such as United States, China, Germany, India and Malaysia. In addition, the issue of ceramic membrane hydrophilicity of kaolin can be solved by simple modification process via FAS grafting method. Not only it is superhydrophobic, but it improves the porosity of the membrane. In a ground-breaking work, Hubadillah et al. [13], pioneered the fabrication of ceramic hollow fibre membrane from kaolin towards oily-wastewater separation and obtained high flux and oil removal. Meanwhile, Abdulhameed et al. [14] and Mohtor et al. [15] fabricated composite ceramic hollow fibre membrane from kaolin and alumina for carbon dioxide capture and dye removal from water, respectively. They reported that the addition of alumina in kaolin ceramic membrane improved the pore size and porosity of the ceramic hollow fibre membrane. Another study conducted by Aziz et al. [16] used FAS to modify mullite membrane to produce omniphobic membranes. Their major findings reported high performance of desalination in membrane distillation proved the effect of FAS to remove oil.

To align with the UN Sustainable Development Goal (SDG) [17,18], No 3 and 6 “good health and well-being” and “clean water and sanitation”, this work aims to reuse ammonia to maintain the nitrogen balance cycle in the nature as well as recover high ammonia concentration in wastewater. Pradhan et al. [19] mentioned that SDGs no 3 and 6 were included in the top 10 of global ranking of SDG pairs with high shares of synergies.

To the best of our knowledge, no study has been reported on the application of ceramic hollow fibre membrane derived from kaolin towards the ammonia recovery/removal via membrane contactor system. Hence, in this study, a hydrophobic ceramic hollow fibre membrane derived from the natural material was fabricated and modified to investigate the feasibility of the membrane to be used for ammonia removal via membrane contactor system. Ceramic membrane was used in this study to provide information and investigation on the application of ceramic membrane as an alternative material, as compared to conventional membrane contactor system for ammonia recovery, which is normally dominated by polymeric membrane.

In addition, the configuration of the ceramic membrane with mixed composite kaolin-zirconia dual-layer hollow fibre membrane used in the membrane contactor application for ammonia recovery has never been done before. Practically, the kaolin membranes exhibited low chemical stability when in contact with high concentration of ammonia and this hinders the use of kaolin membrane in membrane contactor system. Therefore, there is a need to develop composite ceramic hollow fibre membrane derived from kaolin and zirconia.

Based on our previous studies of using kaolin and zirconia composite membrane [20,21], zirconia has been chosen to be fabricated together with kaolin in order to reduce the dissolubility of the ceramic membrane in high alkaline condition. In the first attempt, hydrophobic single layer hollow fibre membrane derived from kaolin and zirconia was prepared and tested towards ammonia removal through membrane contactor. Then, dual layer hollow fibre membrane in which the inner layer derived from kaolin and zirconia, whereas the outer layer derived from zirconia alone was prepared. It should be stated that the study on dual layer hollow fibre membrane was conducted to compare the performance of membrane contactor. Two different types of membranes were chosen to be compared in this study. Initially, the effects of different particle on the surface of the membranes toward the reaction with FAS agent were investigated. Subsequently, the effects of different membrane’s surface in different concentration of ammonia in membrane contactor application were studied.

It is anticipated that this work would enable the use of ceramic material which is kaolin, an environmental-friendly material to recover/remove dangerous pollutant of ammonia via MC which can be seen previously dominated by the polymeric membrane group. Furthermore, this work has the potential to be used in for treatment of wastewater laden with ammonia, leading to the UN SDGs no 3 and 6 such as providing good well-being and clean water.

2. Materials and methods

2.1. Materials

Kaolin powder was purchased from BG Oil Chem Sdn Bhd, Malaysia and zirconium (IV) oxide (ZrO_2) was obtained from Acros Organics, (Thermo Fisher Scientific New Jersey, US) as the ceramic material. N-methyl-2-pyrrolidone (NMP) was purchased from AR grade, QRëC™, Selangor, Malaysia and used as solvent. Polyethersulfone (PESf) as polymer binder was provided by Radal A300, Ameco Performance, Greenville, SC, USA and Arlacel 135 (polyethyleneglycol-30 dipolyhydroxystearate, Uniqema, East Yorkshire, UK) used as dispersant to hold the dope suspension in a homogenous suspension. The kaolin powder and the Arlacel 135 were heated up to 60°C in an oven to remove moisture and were used later without any purification process. Then, tap water was used as a non-solvent coagulant bath. Ammonium hydroxide (NH_4OH) and sodium hydroxide (NaOH) from QRëC™ were used to prepare - alkaline solution while sulphuric acid (H_2SO_4) was for acid solution preparation. 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (97%), with a chemical formula of $C_8F_{17}C_2H_4Si(OC_2H_5)_3$, was used as the grafting agent (Sigma Aldrich,USA). While ethanol, used for hydroxylation and grafting (C_2H_5–OH) was purchased from Merck, Germany.

2.2. Fabrication of hydrophobic SLZK and DLZK

Based on our previous work [20], two types of hollow fibre membranes with different configurations were prepared. These were single layer hollow fibre membranes derived from zirconia and kaolin (SLZK), via phase inversion/sintering technique and dual-layer hollow fibre membrane derived from kaolin and zirconia for inner layer, while neat zirconia on the outer layer (DLZK) [21] was prepared via co-extrusion/co-sintering phase inversion technique. The membranes were sintered/co-sintered at 1300°C. Table 1 depicts the dope suspension and spinning parameters for the membranes' fabrication process. To start, the preparation of dope suspension was initiated by mixing zirconia and kaolin powder and gradually adding n-methyl-2--pyrrolidone (NMP) and Arlacel P135 in a ceramic jar. The dope suspension was then milled by using rotary ball mill at 192 rpm for 96 h. During 48 h, polyethersulfone (PESf) was added. Then the dope suspension was subjected to spinning process where the parameters of the spinning process are presented in Table 1. The membrane precursor was then straightened and cut into desired length prior to sintering process about 15 cm long. The sintering process was conducted in two steps in high-temperature tubular furnace (XY-1700 MAGNA). The intention behind using two different types of ceramic hollow fibre membrane is to investigate the effect of different surface materials i.e., zirconia only and kaolin-mixed zirconia to the performance of the membranes toward membrane contactor application and a comparison study on which membrane showed a relatively better performance to remove/recover ammonia.

Table 1
Compositions of the dope suspension and spinning parameters for SLZK and DLZK.

	SLZK [20]	DLZK [21]	
		Inner Layer	Outer Layer
Dope composition (wt%)			
Kaolin	30	35	–
Zirconia	10	10	40
NMP	54	48.4	54
PESf	5	5.6	5
Arlacel P135	1	1	1
Spinning parameters			
Viscosity at 20 s^{-1} (cP)		2160	37,500
Extrusion rate (ml/min)	10	10	8
Bore fluid rate (ml/min)	10	10	–
Air gap (cm)	5	5	5

In this study, hydrophobization process was prepared using the immersion-grafted technique [11,22–24]. Prior to grafting method, the SLZK and DLZK were immersed in a solution containing ethanol and water in a ratio of 1:2, respectively, for 24 h to allow hydroxylation. After the immersion, the membranes were transferred into a grafting solution, which was prepared by mixing 2 wt% of FAS and 98 wt% of ethanol solutions at room temperature. The immersion time was set at 24 h to allow complete reaction of hydroxyl groups between the membrane surface and FAS solution. Thereafter, the grafted membranes were rinsed to remove unreacted FAS on the membrane surface. Finally, the grafted membranes were dried at 100°C in an oven, overnight. Fig. 1 displays the schematic diagram of two membranes structure in this study where the green, yellow and blue dots represent zirconia particles, kaolin particles and FAS particles, respectively.

2.3. Characterization of hydrophobic SLZK and DLZK

The surface morphology as well as surface roughness of hydrophobic SLZK and DLZK were measured by using Scanning Electron Microscopy (SEM) (TM 3000, Hitachi) and atomic force microscopy (AFM, Park XE-100, Korea), respectively. The contact angle of the ceramic hollow fibre membranes was measured at the surface before and after hydrophobization by the sessile drop technique using a goniometer (Model: OCA 15 EC, Dataphysics, Germany) by dropping 2 μL deionized water as the contact liquid on the membrane surfaces.

Liquid entry pressure (LEPw) was used to measure the wettability properties of the grafted membranes. By using the same set-up from Hubadillah et al. [22], about 5 cm membrane length were potted on an adaptor and the end of the membranes were sealed with epoxy, which was later plugged-in to a tank containing distilled water equipped with diaphragm pump and pressure gauge. Then, distilled water from the tank circulates through the lumen side of the membranes while the pressure in the system was gradually increased by adjusting the valve connected to the pressure gauge. The experiment continued until the first droplet of water was observed on the entire shell side (surface) of the membrane. The experiment was replicated for at least five independent measurements at different spots of each sample of fibre. The pressure at which the water droplets started to appear on the membrane's surface is referred as the liquid entry pressure of water (LEPw) for a given membrane sample. The value of LEPw was determined and recorded in bar unit at increasing 0.5 bar interval.

The mechanical strength of the membranes before and after grafting was examined via the three-point bending test using a tensile tester (Instron model 5544), provided with a load cell of 1 kN. Membranes were fixed on the sample holder at a 30 mm distance. The mechanical strength was calculated using Equation (1):

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

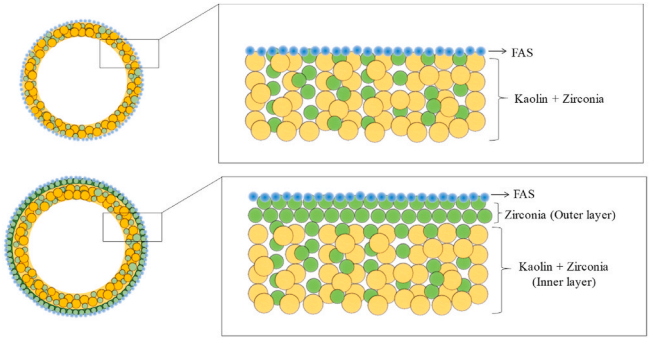

Fig. 1. Schematic diagram of SLZK and DLZK configurations.

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

2.4. Ammonia recovery/removal via membrane contactor (MC)

The MC test was carried out on a laboratory-scale setup, as illustrated in Fig. 2. The setup consists of two tanks containing 500 mL of 5 and 10 M of NH_4OH solution at the feed tank, while 500 mL of 0.1 M of sulphuric acid, H_2SO_4 at permeate tank. The initial pH for 5 M and 10 M of ammonia solution were kept at 9–11 [25,26] and 11–13 [9,27], respectively, while initial concentration of the ammonia was 20 g/L for both pH. Throughout the experiment, the pH decreased to a certain extent. Hence, in order to adjust the pH steadily, 5 M of NaOH solution was added dropwise to the feed tank until the pH ranged from 9 to 11 for 5 M of NH_4–OH and from 11 to 13 for 10 M of NH_4OH. An in-house designed SLZK and DLZK membrane modules equipped with 10 (15 cm) randomly packed fibres (prepared separately) was connected between the tanks with an average surface area of 0.0354 m^2 per module. The module was assembled in a vertical position where the feed (ammonia) was sourced inwards through the side of the membrane module and exited the opposite side of the module, whereas the permeate was directed from the top and flows to the bottom of the membrane module. Epoxy was used to connect the fibres in the module. Table 2 lists the membrane contactor module configuration used in this study while Table 3 depicts the operating condition for the membrane contactor application system.

The pressure of the system was fixed at 1 bar for the whole experiment. The feed flowed through the intertubular space or the shell side of the fibres, whereas the permeate flowed inside the capillaries (lumen side) at 0.5 mL/min of flow rate for both tanks. The pH of the acid and alkaline solution was measured using pH meter (Milwaukee MW101 PRO pH Meter) and the pH before and after the experiment were recorded.

The reduction of ammonia concentration in feed tank and increment in ammonia concentration in permeate tank was measured by using DR5000 HACH Spectrophotometer, based on Ammoniacal Nitrogen HACH Salicylate Method (Method 10,031, APHA). The percentage of ammonia recovered/captured was calculated based on the difference between the respective and initial NH_3–N concentrations of ammonia solution based on the increasing of the NH_3–N concentrations for 180 min of run per experiment in acid solution (permeate tank), while the percentage of ammonia removal was determined based on the difference between the respective time and initial NH_3–N concentrations in the feed tank based on the decreasing of NH_3–N concentrations between the consecutive time and initial according to Equation (2) as follows:

$$NH_3 - N = \frac{C_i - C_o}{C_i} \times 100\% \quad (2)$$

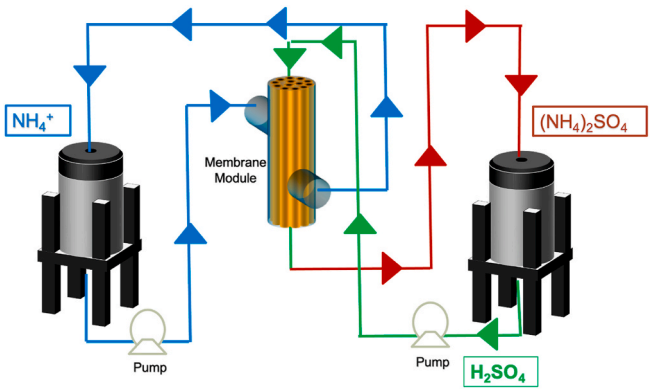

Fig. 2. Schematic diagram for membrane contactor set-up.

Table 2
Specifications of the hollow fibre membrane module.

	SLZK	DLZK
Contactors Material	Acrylic	
i.d. (mm)	20	
o.d. (mm)	22	
Length (mm)	150	
Hollow Fibres Material		
- Inner layer	Kaolin Zirconia	Kaolin/Zirconia
- Outer layer		Zirconia
i.d. (mm)	0.883	1.03
o.d. (mm)	1.36	1.58
Effective length (cm)	10	10
Pore dimensions (μm)	2.774	0.418
Number of fibres	12	12
Mass transfer area based on i.d. (m^2)	0.0354	0.0354
Porosity, ε (%)	13	20

Table 3
Operating condition of membrane contactor.

Operating Condition	NH_4	H_2SO_4
Temperature (°C)	Ambient	
Duration time (min)	180	
Fluid flow rates (ms^{-1})	0.5	
Pressure (bar)	1	
Initial concentration (mg/L)	20,000	9000
pH	9–11, 11 - 13	4

where C_i and C_o are initial and consecutive concentration of NH_3–N, respectively.

1 mL of aliquot was taken out from the tank by using 1000 μL micropipette (Thermo Fisher Scientific, USA) and the sample was diluted at dilution factor of 1000 prior to be read using the spectrophotometer for the first 100 min, the interval of each sample was collected for every 5 min while after 100 min, the interval of sample collected was increased to 30 min making a total of 180 min. The second step of the experiment was performed based on the results obtained on the first stage. The effects of the pH and the extraction solution concentration on the overall mass transfer coefficient (K) were examined. The flow rate was set at 0.5 $Lmin^{-1}$ for both tanks while the temperature was kept at room temperature. The overall mass transfer coefficient, K was determined experimentally according to Equation (3):

$$K = \frac{V}{At} ln \frac{C_o}{C_i} \quad (3)$$

where: K, V, At, C_i and C_o are the overall mass transfer coefficient, total volume of feed solution (L), membrane surface area (m^2), concentration of ammonia (mg/L) at initial time and final time in the feed solution, t, respectively. The overall mass transfer coefficient was determined to understand the optimum condition that favoured the removal and recovery of ammonia. The purity of $NH_4)_2SO_4$ salt was evaluated by using Attenuated Total Reflection Fourier transform infrared (ATR-FTIR, Shimadzu Corporation, Japan) spectrometer. About 5 mL of the liquid salt sample was transferred into a glass petri dish and left to dry in an oven at 100°C overnight for drying prior to characterization.

2.5. Statistical tests

In order to statistically compare the results of recovery and removal of ammonia from the MC by using SLZK and DLZK, the Prism – GraphPad software (U.S.A) was used to calculate the t-test from the two results based on two tailed paired t-test [28]. The paired sample t-test was used when the observations on the two populations of interest were collected in pairs according to Equation (4) as follows; where, the differences were considered significant when $p < 0.05$ in one tailed value, if the p-value

was less than 0.001 ($p < 0.001$), the pairing was of significance. Two-sample *t*-test was used when the data of two samples were statistically independent, while the paired *t*-test was used when the data were in the form of matched pairs [29]. The *t*-test was calculated based on the final ammonia concentration indicating the amount of ammonia recovered at the permeate tank.

$$t = \frac{\overline{X}_1 - \overline{X}_2}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \quad (4)$$

3. Results and discussion

3.1. Morphology and hydrophobicity

Fig. 3 depicts the SEM images at the outer surface of the ceramic membranes SLZK and DLZK before and after grafting method was applied to the membranes' surface at magnification of 3000x. Based from the images, after grafted membranes presents an FAS coated layer, which can be clearly observed based on the shape of the particles, which appeared glassier, as compared to before grafting. The particles presence in these two membranes were different where SLZK consists of kaolin mixed zirconia while DLZK consisted of only zirconia on the membrane's surface (wall), hence, the morphology of these two membranes also appeared different. It can be clearly seen in Fig. 3 that SLZK displayed bigger particle size on its surface as compared to that of DLZK due to the contribution from kaolin, which has a larger particle size than zirconia alone. Kaolin predominantly occupied the surface morphology of SLZK whereas DLZK surface morphology only consisted of zirconia particles (white particles). With respect to its surface, it can be seen that DLZK possessed a more porous structure compared to SLZK as kaolin possessed platelet-like structure, which allowed small particles of zirconia to be included in between the kaolin porous structure. According to Hubadillah et al. [24], theoretically, amorphous silica particles tend to result in a denser ceramic due to better densification of amorphous structure during sintering. Kaolin contained high composition of silica, made up about 60 wt%, therefore it induced the densification process of kaolin resulting in less porous SLZK morphology, as compared to DLZK. The average pore size of SLZK on the surface was 2.774 μm [20], while that of DLZK was 0.418 μm [21] and this value was calculated based on our previous studies.

The presence of the FAS agent on the surface of the membranes before and after grafting could be detected by using 3D AFM images as shown in Fig. 4. As stated by Yusof et al. [30], based on the AFM images, bright regions portrayed the protrusions at the surface, which represented the lotus-like structure, while the dark depressions represented pores. As can be seen from the images, the bright region increased after grafting process for both membranes indicated that after grafting, the membranes possessed more lotus-like structure which was related to the hydrophobicity of the membrane surface.

It is important to note that the value of surface roughness measurement (R_a) for both grafted membranes also increased. DLZK showed the highest R_a value, which was 0.354 nm compared to that of SLZK (0.206). This value of R_a increased after grafting where the value for SLZK and DLZK non-grafted were 0.149 and 0.254 nm, respectively. Based on the increasing value of R_a for both membranes after grafting, the grafting of FAS agent on the surface increased the surface roughness of the membrane and hence enhancing the hydrophobicity of the membrane, which corresponded to the study undertaken by Bayat et al. [31].

Kaolin and zirconia particles with surface grafted fluoroalkylsilane (FAS) molecules for both membranes but did not polymerize to form a continuous layer due to the limited number of –OH groups left on the ceramic membrane surface after sintering at high temperature. This explained why the value of R_a after grafting for DLZK was higher compared to SLZK. Aissaoui et al. [32] stated that the most common route of functionalization of FAS to the surface of SiO_2 surface was to attach alkylsilane through the formation of Si–O–Si bonds between the silanol groups present on the oxidized silicon surface and the hydrolyzed organosilane molecules. In fact, the mechanism of silane attached to the membranes' surface by lateral reaction and the interaction of hydrogen bonding during the hydroxylation process, which later formed the siloxane structure explained the hydrophobicity of the membrane, as shown in Fig. 5. Due to the different ceramic materials on which the FAS was applied, this process depends on the nature of the reactive moieties in the organosilane, typically Cl or an alkoxy group. In fact, according to Ciampi et al. [33], this reaction was complex and the silane retention and organization on the surface have been under debate. However, it is believed that the hydrophobic structure on the membranes' surface was formed due to various interfacial processes such as covalent binding to the surface, lateral polymerization of adsorbed silanes, and three-dimensional polymerization.

Boussu et al. [34] stated that although AFM was widely used to characterize surface roughness of membranes, it was difficult to

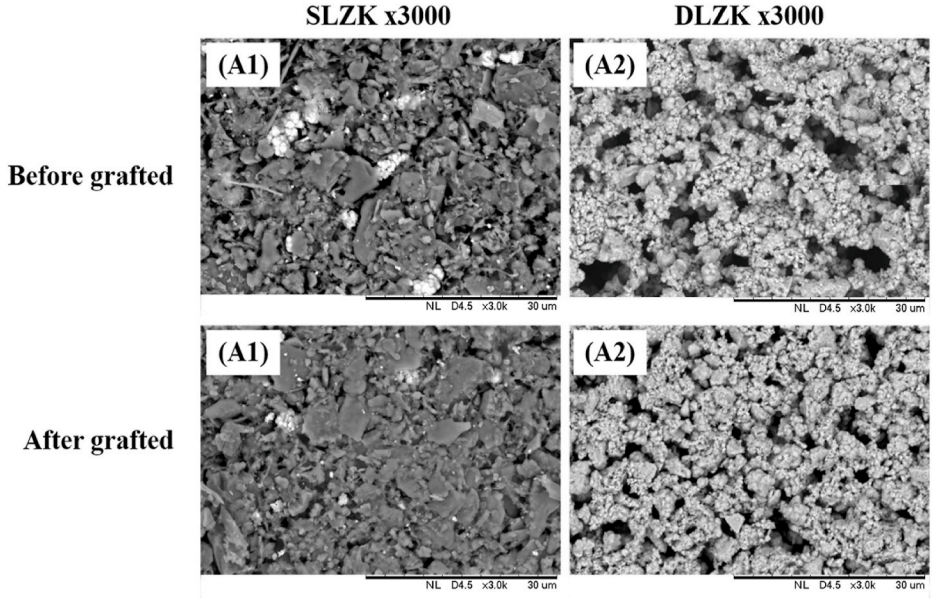

Fig. 3. SEM images of surface of grafted and non-grafted SLZK and DLZK at x3000 magnification.

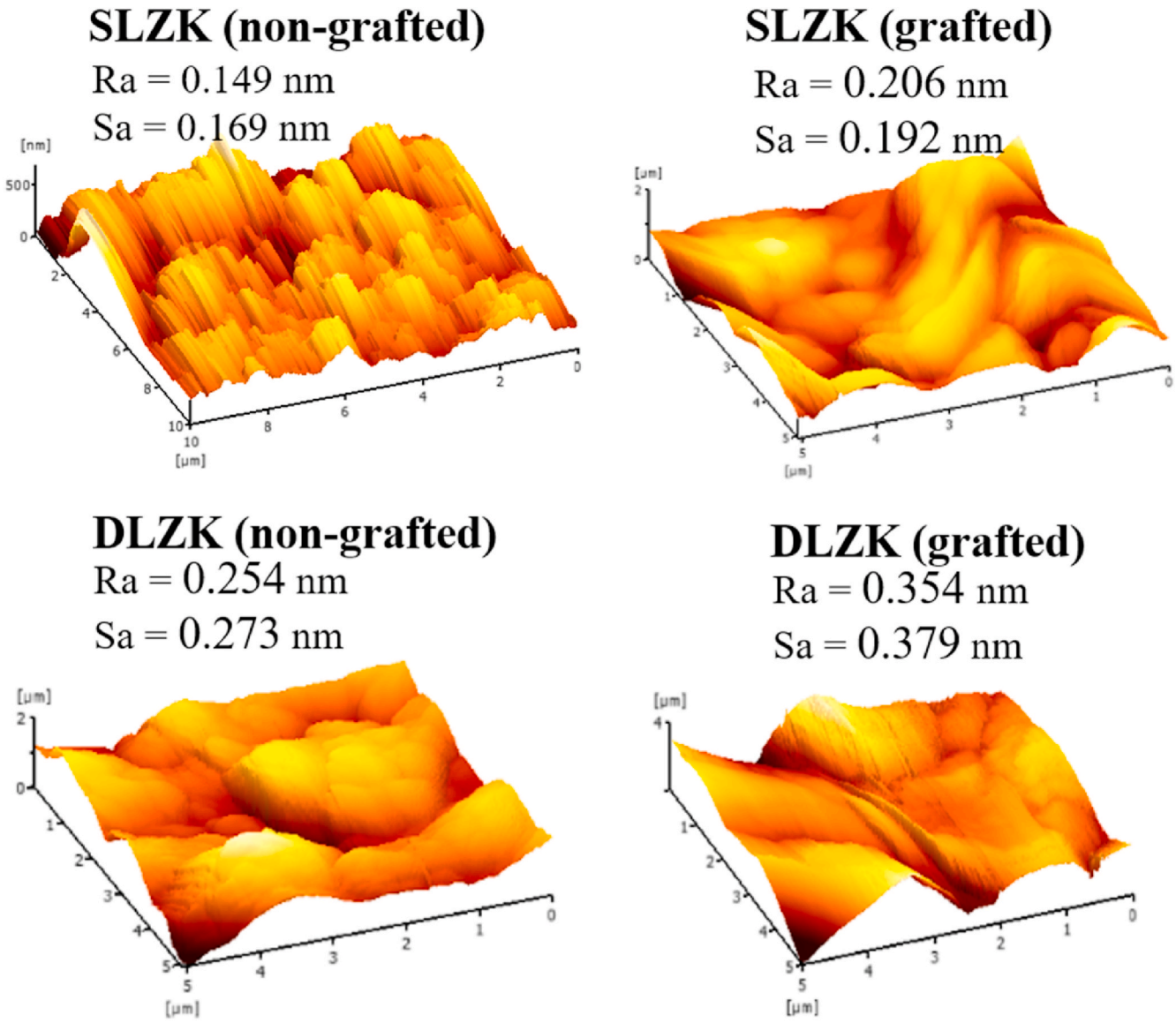

Fig. 4. Roughness of grafted and non-grafted SLZK and DLZK.

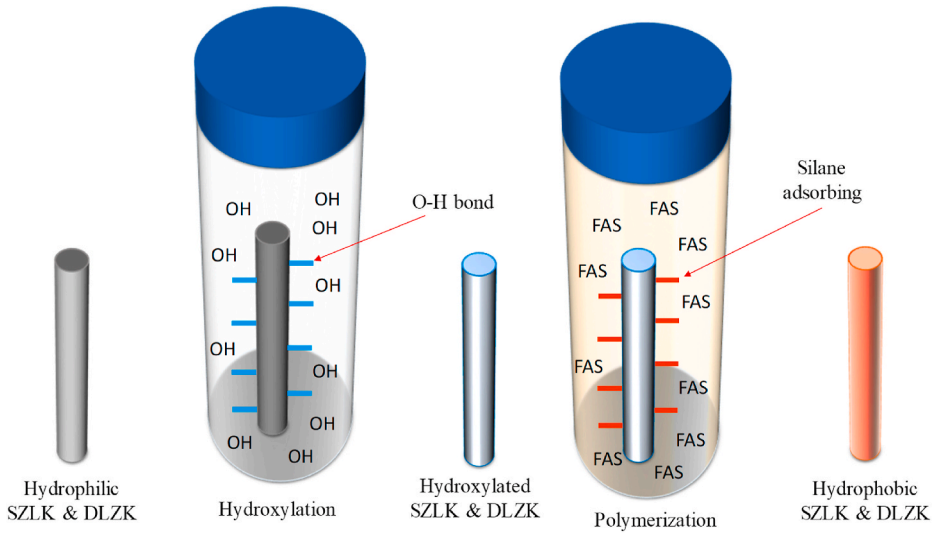

Fig. 5. Immersion-grafting process mechanism of SLZK and DLZK.

compare the roughness of overall membranes or the uniformity of the grafted areas as the roughness values were normally obtained by several modes and at different scan areas. Hence, in order to investigate the uniformity of the grafting, Fig. 6 depicts the actual picture of the hydrophobicity of the membrane before and after having grafted with FAS for SLZK and DLZK. As expected, the membranes grafted with FAS denoted as FAS-SLZK and FAS-DLZK appeared to be floating on the dye solution without any reaction/absorption of dye onto the membranes. On the other hand, both ungrafted membranes (pristine SLZK and DLZK) appeared to be sinking in the petri dish dye solution, while absorbing its colour, eventually turning the membrane visually blue. Both membranes were compared to grafted kaolin only membrane as control and it seemed that the kaolin membrane half floated in the petri dish dye solution, as compared to the FAS-SLZK and FAS-DLZK. Based on the observation at the level of the immersion of the membranes, it can be said that the FAS agent has successfully grafted on the surface of the membranes. The uniformity also can be proven by the value of contact angle which will be discussed in the next sub-topic.

3.2. Wettability behaviour and mechanical strength

In order to determine the effectiveness of grafting process on the SLZK and DLZK surfaces, the wettability properties of the membranes were measured in terms of contact angle value. Table 4 presents the values of contact angle of SLZK and DLZK before and after grafting. The low contact angle values of less than 10° were obtained for the samples before grafting with FAS. This was attributed to the high hydrophilic character of the membranes as a consequence of the high density of the hydroxyl group on the membrane's surface. After grafting, the contact angle value of SLZK increased exceeding 132°, which confirmed that the grafted SLZK possessed a hydrophobic character. Similar results were also obtained by most previous study in ceramic hydrophobization with FAS silane agent by [22,35,36]. The hydrophobicity of the grafted membrane was then evaluated by using contact angle as shown in Table 4. The contact angle measurement was repeated for at least 5 different spots to prove the uniformity of the grafted areas. Notably, DLZK showed the highest value of contact angle value, which can be considered superhydrophobic due to the value of contact angle obtained reached almost 180°. This can be concreted by proof from the morphology analysis, SEM where DLZK obtained a micro-textured or micro-patterned surface, which enhanced hydrophobicity. (Fig. 3). This is because, DLZK surface was made up of only zirconia, and the particle size of zirconia were smaller than kaolin, which is platelet-like. Additionally, zirconia particle also showed rougher surface or higher Ra value, as compared to that of SLZK as shown in Fig. 4.

The wettability properties of the membranes were further characterized using liquid entry pressure with water (LEPw) (Table 4). The LEPw for SLZK was lower than DLZK. As stated by Kujawa et al. [35], LEPw increased with the decreasing membrane pore diameter, which was also obtained in this study. DLZK possessed smaller pore size than SLZK at the surface, which explained the reducing of pore size eventually leading to increase of LEPw in lumen. A higher LEPw for DLZK was obtained in this study (2 bar). This value was comparable to the LEPw of polymeric membrane [37]. The values of LEPw for both membranes also showed lower values from inner to outer due to the pore size for DLZK for inner layer relatively larger due to the presence of kaolin and zirconia.

Table 4
Characteristics of SLZK and DLZK for average 3 samples per membrane.

	SLZK	DLZK
Contact Angle (°)		
- Before Grafted	5 ± 1.5275	1 ± 0.5773
- After Grafted	132.7 ± 2.5501	~180.0 ± 1.5275
		
Mechanical Strength (MPa)		
- Before Grafted	25 ± 2.0816	119 ± 2.5166
- After Grafted	35 ± 1.000	125 ± 2.000
LEPw of Grafted Membrane (bar)		
- lumen	1.5 ± 0.2887	2.0 ± 0.2889

Meanwhile, in order to evaluate the change of the mechanical strength of SLZK and DLZK by grafting, a three-point bending test was conducted on the membranes before and after grafting. The results are presented in Table 4. Both membranes showed an increase in mechanical strength after grafting, where mechanical strength of SLZK was increased from 25 to 35 MPa whereas DLZK increased from 119 to 125 MPa. As discussed before, DLZK possessed a smaller pore size and closer grains due to the condensation of silane groups as a function of grafting process, thus leading to higher mechanical strength. In this regard, two conclusions can be made as a function of grafting process. Firstly, the mechanical strength can be enhanced due to the chain entanglement between the silane agent and hydroxyl group on the membrane surface. Secondly, no defects such as cracks or holes formation can be seen as the mechanical strength is enhanced, which is important for practical applications.

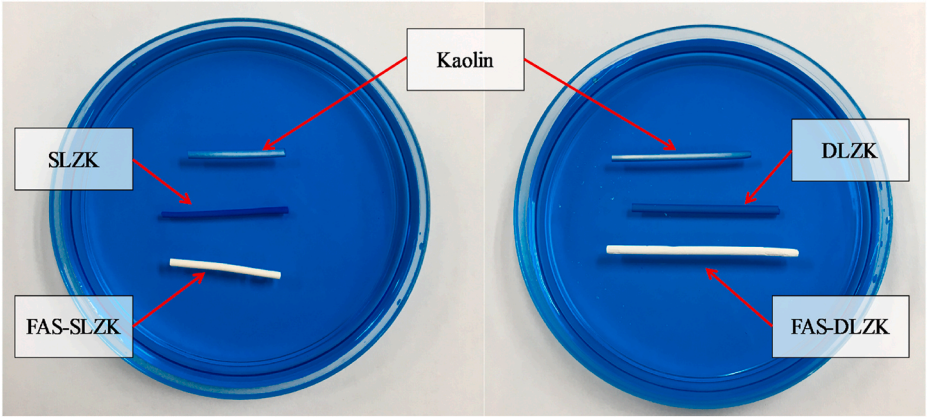

Fig. 6. FAS grafted and ungrafted of SLZK and DLZK as well as kaolin membrane in dye solution.

3.3. Membrane contactor performance

To justify their technical feasibility, the performance of the modified hydrophobic ceramic hollow fibre membranes was evaluated in membrane contactor application for the reaction of ammonia (in free ions, NH_4^+ or NH_3) from ammonium hydroxide (NH_4OH) and reacted with sulphuric ions (SO_4^{2-}) from sulphuric acid (H_2SO_4). The reaction is shown in Equation (5) below and the mechanism can be observed in Fig. 7. Eventually, the reaction of these two chemical substances can evidently produce ammonium sulphate $(NH_4)_2SO_4$, which can be used as a fertilizer.

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq) \quad (5)$$

During operation of a membrane contactor for ammonia removal it may be necessary to regularly adjust the solution pH by addition of an appropriate alkaline (NaOH) in order to maintain the driving force for the membrane separation process [37]. The most important phenomenon relating to membrane contactors is the mass transfer driven by vapour pressure or concentration difference across the membrane. When one of the fluids is water or an aqueous liquid, it is critical that the membrane is not wetted beforehand due to effects of surface tension. Wettability is controlled by chemical composition (modification with FAS reagent from hydrophilic to hydrophobic) of the membrane and geometry of the pores.

Referring to the statement above, this study was conducted by fixing the initial concentration of ammonia to 20 g/L while the velocity or flow rate of the system for both tanks were fixed at 0.5 L/min and concentration of sulphuric acid, H_2SO_4 at 0.1 M or pH 4 for all runs. The flow rates were kept constant as this study adapted a similar method from a study conducted by Tan et al. [9], and Zhu et al., [27]. Fig. 8 shows the concentration of ammonia at the permeate tank over duration of 180 min. The membranes were air filled at the prior to be used and there was a delay in the first minutes, which could reflect some differences in residence time distributions for the modules due to difference porosity of the membranes as well as its impact on displacing the fluids initially in the module. The SLZK showed some delay, as compared to the DLZK due to the difference of porosity of the membranes. The SLZK possessed lower porosity compared to the DLZK, which induced the delay on the beginning of the experiment. Based on the previous experimental study, Tan et al. [9] used PVDF membranes, and the time taken to conduct the experiment was 100 min. However, most studies used a longer time as it provided more data on the ammonia gas capturing process such as the study done by Hasanoğlu et al. [37], where they increased the contact time from 30 to 180 min. Hence, this study took the approach to extend the contact time up to 180 min. Due to the high concentration of ammonia used in the feed tank, it should be noted that the process might

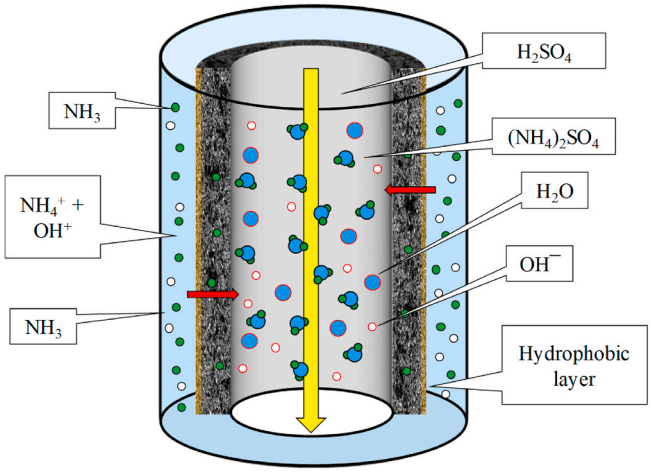

Fig. 7. Membrane contactor mechanism.

be rapid. From Fig. 8 (a), by using 5 M of ammonia solution at pH 9, the DLZK showed a steady increase at the first hour (60 min), starting from the 15th minute until the end of experiment. However, the SLZK showed constant signs of increased ammonia after 1 h of operation. Fig. 8 (b) shows that when 10 M ammonia solution of pH 13 was used, the SLZK started to show a rapid increase for the first hour and gradually slowed down until the end of the experiment, whereas the DLZK showed a steady rise in ammonia concentration over the course of 3 h of contact time. Ashrafizadeh and Khorasani [25] uncovered that the effects of the pH in the ammonia feed increased as the time passed by. These results were explained by the fact that as time increases, the ammonia concentration in the feed solution decreased and the percentage of ammonia converted into free ammonia (FA), which itself depended on feed pH, became the dominant factor in ammonia removal. The same reason applied to this study, i.e., as the pH of the feed changed, the contact time also changed due to the conversion of ammonia solution, ionized ammonia (liquid) to free ammonia, FA (gas).They eventually explained why the spike of increasing ammonia concentration was different at the two different pHs.

In order to evaluate the data shown in Fig. 8, the properties of the membrane were taken into consideration. The difference in membrane material (at the surface contact with ammonia at shell wall) became a factor as the SLZK consisted of mixed kaolin-mixed zirconia while DLZK only consisted of zirconia particle. Fig. 3 showed that the pore size distribution for DLZK showed more uniform distribution that that of the SLZK as the particle size of kaolin looked bigger than zirconia. Here, this implied that different particle sizes provided different mass transfer. In an agreement with the study conducted by Tan et al. [9], the experiments also showed that as the contact time increases, ammonia recovery could potentially increase in the permeate tank due to the possibility of elongated recovery period.

3.3.1. Ammonia removal

To evaluate the ammonia removal at the feed tank, the percentage of removal was calculated based on the increased concentration of ammonia at the permeate tank. Assuming that the reduction of ammonia in feed tank was due to free ammonia that was transferred through the porous membrane or by how the amount of FA that was captured or absorbed to permeate tank, Fig. 9 (a) and (b) shows the percentage pf ammonia removal was calculated based on Equation (2).

Fig. 9(a) depicts the reduction percentage of ammonia captured for the SLZK and the DLZK at 5 M of ammonia solution from feed tank. Ultimately, the SLZK showed the lowest percentage of ammonia inside the feed tank after the duration of 3 h, which was 9% as compared to the DLZK (28%). The SLZK displayed the highest ammonia absorbed/captured from feed tank to permeate tank, in which 91% of ammonia was capable to pass through the wall of the SLZK during the 3 h of study. Meanwhile, the DLZK showed a relatively high percentage of ammonia absorbed at 72% from the feed tank, but comparatively lower than the SLZK. As a result from lower pH, less free ammonia was released as gas state. With respect to the morphological structure, the pore size of DLZK was considered smaller compared to that of SLZK. This explained the reduction of ammonia capture by using the DLZK as compared to that by the SLZK.

Meanwhile, Fig. 9 (b) depicts the percentage of ammonia concentration reduction at feed tank at 10 M of ammonia concentration. No significant difference at the ammonia removal percentage was observed. The percentage for both SLZK and DLZK were 77% and 80%, respectively. As compared to 5 M (Fig. 9 (a)), the difference of percentage for both SLZK and DLZK was almost 20%. This might be due to at high pH (alkaline), the diffusion rate for the free ammonia to pass through the porous membrane increases. Likewise, the reduced amount of ammonia capture shows the stability of the DLZK, as compared to the SLZK, which was affected by different membrane pore sizes. The DLZK possessed narrower pore size distribution than the SLZK.

In order to examine the recovery and removal data obtained

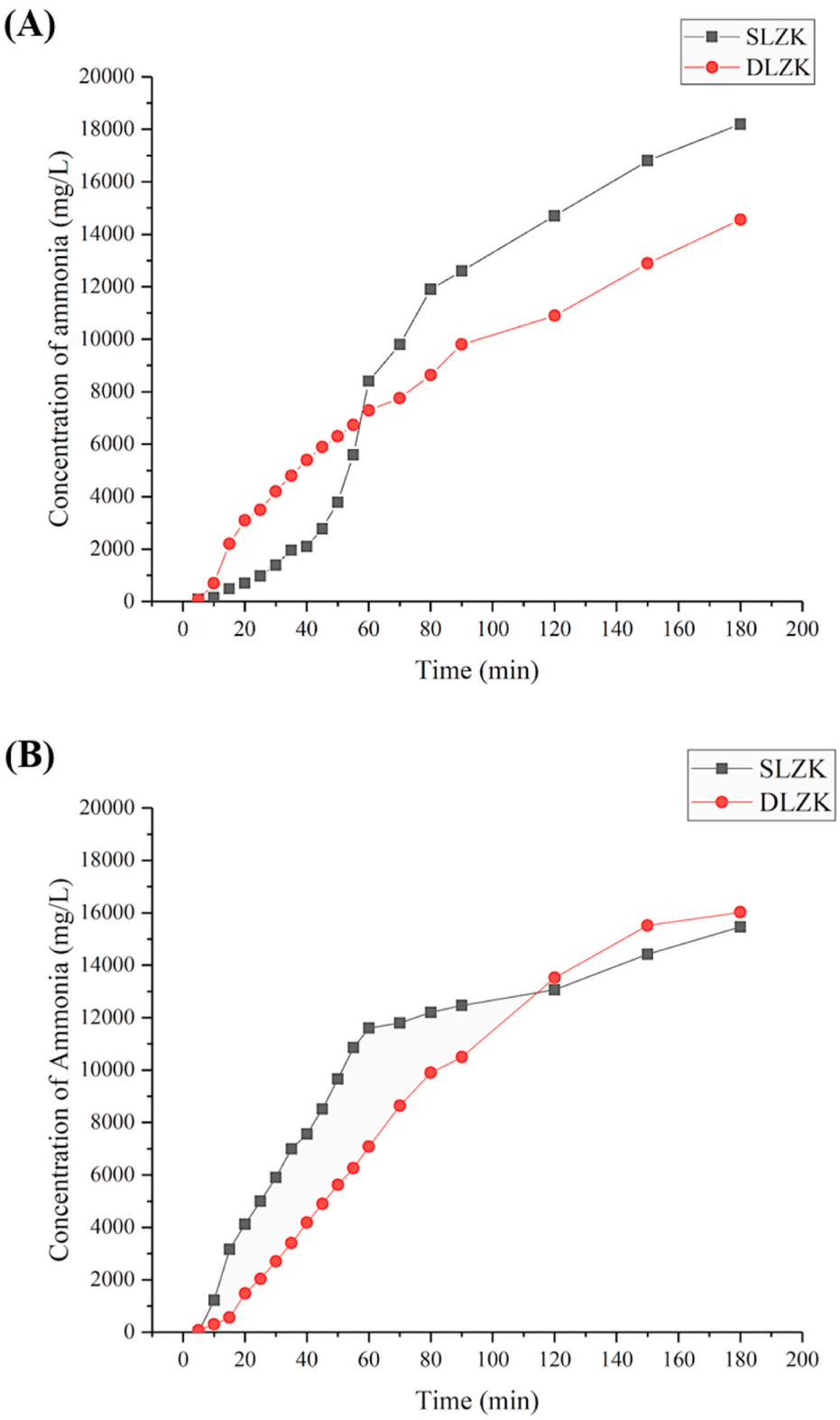

Fig. 8. Concentration of ammonia during membrane contactor test at a) 5 M (pH 9–11) and b) 10 M (pH 11–13) using SLZK and DLZK membrane at permeate tank.

statistically, the data were statistically compared by using two paired sample *t*-test for both comparisons i.e. the difference in type of particles on the membrane's surface as well as the difference in pH of ammonia used. Gerald [28] stated that *t*-tests can be used when there were two groups or two sets of data. According to Xu et al. [29], two samples could be considered independent if the selection of the individuals or objects that made up one sample did not influence the selection of the individuals or subjects in the other sample in any way. In fact, the two-sample *t*-test should be applied to compare the mean values of two samples. On the other hand, if the observations in the first sample are coupled with some particular observations in the other sample, the samples are considered to be paired.

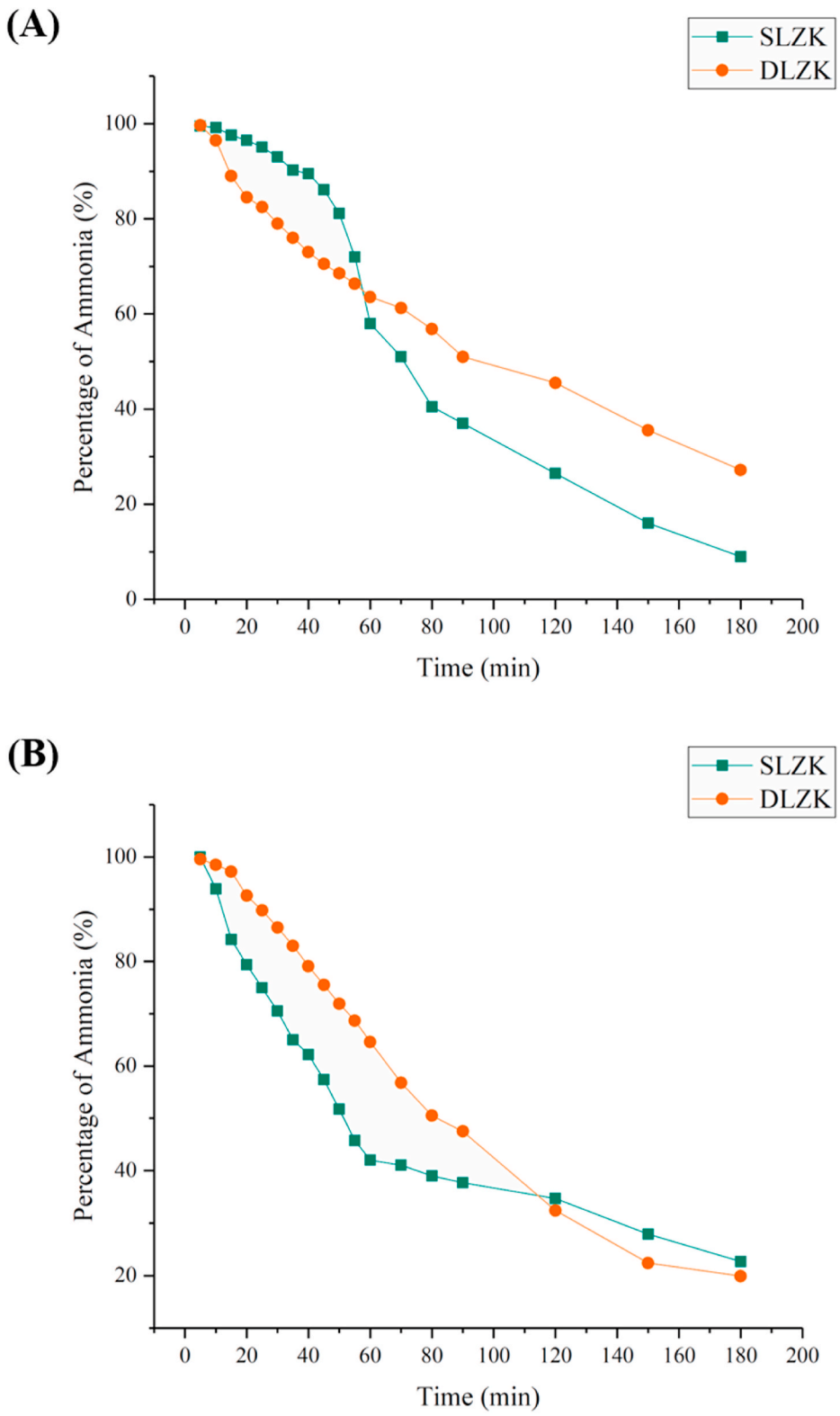

Fig. 9. of ammonia in feed tank at a) 5 M (pH 10) and b) 10 M (pH 13).

Since both membranes, SLZK and DLZK were grafted using similar material and concentration, FAS (2 wt%), it was appropriate to use the two-sample *t*-test to compare the membranes in terms of the effects of FAS grafting layer towards the ammonia recovery as these membranes are considered to originate from the same population. Based on the results obtained via the software, the *p*-value for the recovery of ammonia using the SLZK and DLZK in both 5 M and 10 M of ammonia obtained values of less than 0.001 ($p < 0.001$). This indicated that the effectiveness of comparing these two membranes were significant with R^2 of 0.9540 for 5 M of ammonia. When comparing the SLZK and DLZK in 10 M of ammonia, similar correlation coefficient value can be seen with R^2 of 0.9372. Both ammonia concentration showed splendid significance for their correlation coefficient value.

By comparing the data from the two-tailed *p*-value, the *p*-value

obtained for 5 M was 0.8458. This value was considered insignificant as the value obtained was greater than 0.05. When calculating the *p*-value of membranes based on 10 M of ammonia, the *p* value was less than 0.05, which indicated its significance. The comparison between the SLZK and DLZK in 5 M of ammonia indicated further effects on the performance of MC. This claim could be validated by the data of mass transfer coefficient (Kms^{-1}), which induced the recovery and removal of ammonia in 5 M, while the value of mass transfer coefficient obtained was slightly less than that of 10 M of ammonia. Based on statistical perspectives, having two different membranes surfaces affected the recovery or removal of ammonia in different ammonia pH (concentration).

According to Hasanoğlu et al. [37], the reaction between ammonia and sulphuric acid was considered to be instantaneous when the acid concentration was greater than the ammonia concentration. Under this condition, the reaction took place on the interface of the membrane and consequently the concentration of ammonia on the interface essentially dropped to zero. The boundary layer resistance on the receiving solution could be considered negligible because the protonation reaction of ammonia was supposed to be instantaneous. Therefore, only the feed solution boundary layer and the membrane resistance have to be taken into account in the derivation of model equation. According to Zhu et al. [27], the driving force for ammonia transfer across the membrane was either the difference in the partial pressure of ammonia, or the difference in the concentration of ammonia, on each side of the membrane. As free ammonia continuously transported across the membrane, ammonia concentration in the feed solution decreased, resulting in a lower pH value in the feed solution, if the feed solution was not buffered. Subsequently, the change in the pH values would potentially modify the relative concentrations of ammonia in the feed, affecting the recovery and the flux of ammonia. Instead of the total concentrations of VCs, it may be suitable to use the equilibrium concentrations of volatile species (VCs) to estimate mass transfer coefficients, removal efficiency and flux of easily ionized VCs. This is due to the fact that only volatile species could pass through the membrane barrier. Fig. 9 depicts the concentration of ammonia at permeate when the concentration reached equilibrium to calculate the mass transfer.

Ammonia exists as both un-protonated and protonated ammonia in aqueous solution where the transport of these unsteady ammonia and ammonium ions in the shell side was governed by axial diffusion, radial diffusion, and convection process. Mandowara et al. [38] suggested a three-step transport method, which could take place sequentially during the ammonia removal for further explanation. The first (1) step is radial diffusion of both un-protonated ammonia and ammonium ions to the internal surface of the hollow fibre. The second (2) step is the diffusion of ammonia inside the membrane pores. Finally, (3), ammonia in gaseous form reaches the interface (located at the pore exit of the hydrophobic membrane) and instantaneously reacts with the extract phase (sulphuric acid present at the lumen side). Ammonia is highly soluble in sulphuric acid, therefore there is no formation of reaction zone; it reacts only at the interface.

However, Nagy et al., stated that there are five process for permeation through a homogeneous membrane, which are (1) transportation or diffusion of the solute molecules through the liquid (or gas; in this case, the mass transfer resistance of the boundary layer in the latter is negligible, consequently this step can also be ignored) film of the feed phase adjacent to the surface of the solid membrane; (2) dissolution of the solute molecule in the upstream surface of the membrane matrix; (3) diffusion of the dissolved species across the membrane matrix; (4) desorption of the solute molecules in the downstream side (permeate side) of the membrane; and (5) diffusion through the boundary layer of the permeate phase into the bulk permeate phase. The first and fifth steps can be omitted as there are no mass transfer resistances between the continuous fluid and membrane phases. This can be the case for gas permeation or liquid permeation with high volumetric flow rates [39].

Therefore, both SLZK and DLZK were considered homogeneous membranes even though SLZK consist of mixed kaolin and zirconia particles because the zirconia particles have dispersed evenly in the dope solution due to the effect of Arlacel, which acted as a dispersant. Thereby producing uniform membranes from the phase inversion process. Here, the diffusion of free ammonia has taken placed because mass transfer occurs.

According to Imai et al. [40] and Qi et al. [41], various resistance affected the mass coefficient transfer in hollow fibre membrane gas contactor application such as pH, concentration, and pore size of the membrane itself. In this paper, major parameters studied includes pH and concentration varying at 5 and 10 M and pH 11 and 13, respectively. Evidently, the change in pH and concentration affected the mass coefficient transfer of the membrane contactor. Semmens et al. [42] reported that the difference in pore size of membrane affected the separation of the volatile solutions, while major findings found that porous membranes enhanced the mass transfer.

The investigation on multiple pH value by Aligwe et al. [43], also revealed that pH value significantly affected the mass coefficient transfer as high pH yielded a higher coefficient value. Another work conducted by Aligwe et al. [44] also shows the effects of using different module configuration and flow in the membrane contactor system. Different module configuration influenced the value of mass coefficient transfer. In this case, the acid flows on the shell side, whereas the ammonia flows in the bore (lumen) side as the feed. Our findings reported that water vapour partial pressure on the sulphuric acid side was likely to be lower than that on the feed side. Thereby allowing water vapour to be transported through the membrane pores to the feed side. This claim was supported by Ulbricht et al. [45] in which the value of mass coefficient transfer was influenced by this multicomponent transport situation between ammonia, air, and water vapour.

The term "TransMembraneChemiSorption" proposed by Ulbricht et al. [46] defined a separation technique, which used a membrane device to strip a gas species from a liquid feed phase and captured it using a liquid receiving phase that chemically reacted with the gas species. However, Aligwe et al. [43], and Ulbricht et al. [45] found that to obtain the mass transfer coefficient, the water vapour partial pressure on the sulphuric acid side was likely to be lower than that on the feed side, resulting in water vapour transported through the membrane pores to the sulphuric acid side. This might affect the value of k_m when dealing with a multi-component transport situation between ammonia, air, and water vapour. It increased the ammonia feed concentration and introduced predictive uncertainty. The acid-base reaction at the receiving gas-liquid interface was exothermic and led to local increase in temperature, which affected the Henry's law constant and the reabsorption rate of ammonia. Based on the previous case studies, we did not foresee any problem with the use of sulphuric acid due to its low concentration. Therefore, the osmotic pressure difference between the two sides of the membrane can be neglected.

According to Table 5, the mass transfer coefficient of the DLZK at 10 M or pH 13 showed the highest value parallel with obtaining the highest ammonia recovery at 99.5%. This data corresponded to the statistics of Norddahl et al. [26], who reported that a higher pH subsequently resulted in a free ammonia (FA) fraction close to unity. Thereby yielding the best results in terms of ammonia mass transfer.

Another study done by Qu et al. [47] also reported similar findings in agreement with this study in which the ammonia removal efficiency reached 99.5% when the pH value was higher than 12. This could be

Table 5
The ammonium sulphate recovered from membrane contactor (sample number = 3).

	Mass Transfer Coefficient (K) (m s^{-1})	Ammonia Recovered (%)
SLZK 5 M	$0.81 \times 10^{-5} \pm 4.8 \times 10^{-7}$	99.3% ± 0.0472
SLZK 10 M	$2.72 \times 10^{-5} \pm 4.8 \times 10^{-7}$	99.4% ± 0.0251
DLZK 5 M	$3.54 \times 10^{-5} \pm 2.8 \times 10^{-7}$	99.5% ± 0.0493
DLZK 10 M	$3.77 \times 10^{-5} \pm 2.1 \times 10^{-7}$	99.5% ± 0.0251

attributed to the ammonia dissociation in aqueous solution, as illustrated in Equation (6):

$$NH_4^+(aq) + OH^-(aq) \leftrightarrow NH_3(g) + H_2O(aq) \quad (6)$$

Based on Equation (6), by increasing the pH value of the aqueous solution (feed tank), the dissociation equilibration shifts towards yielding NH_3, the only form of ammonia that can be stripped to the permeate. Therefore, the NH_3 enriched aqueous solution was formed as opposed to NH_4^+, which resulted in higher ammonia removal efficiencies. Table 5 shows that as the pH increases, the mass coefficient also increased parallel with the removal of ammonia efficiency. The mass coefficient transfer for free ammonia (FA) concentration was calculated based on the ratio of final concentration over the initial concentration of ammonia in the feed tank with respect to its flow rates, effective area of the membrane and time (Equation (3)). We surmised that the higher the value mass coefficient, the faster and the more ammonia can be transferred to the permeate tank, which later reacted to produce ammonium sulphate in the permeate tank.

In this work, ceramic membranes were used in MC and have shown splendid performance in terms of highest mass coefficient, as compared to previous works, which were predominantly controlled by polymeric membranes. The mass transfer coefficients obtained in this work were compared with those of previous works in Table 6. The table shows that membranes fabricated using ceramic alternative based material enhanced the performance of MC in terms of mass coefficient transfer as well as the stability of the membranes in high concentration of ammonia. In addition, the alternative of material proves to be another contributing factor for future commercialization, as compared to the cost of other commercial ceramic membrane materials such as alumina and silica, which is considered as high as the cost of polymeric membrane.

The stability test for both membranes was done prior to this experiment, where the membranes were immersed and shaken at 250 rpm for 72 h in high concentration of ammonia (20 g/L) [20,21]. Based on the observation, the current membranes had similar characterization to the membranes from the previous studies. Contact angle test was done after the experiment to the membranes (Fig. 10). The SEM images of the SLZK (a2) and the DLZK (b2) where the contact angle was lower than before MC test (a1 and b1). However, the value did not decrease. This implied that the membranes were still stable even after the experiment was completed.

Previously, surface modification has been extensively conducted in ceramic membranes to modify hydrophilic properties to achieve hydrophobic behaviour by using materials such as alumina, zirconia or a combination of few materials particularly in the membrane distillation (MD) application, which required the use of hydrophobic membranes. Ceramic membranes used in membrane contactor also have been studied in the use of carbon dioxide capture rather than ammonia recovery. Table 7 depicts previous studies using ceramic membrane with modification for MD and MC application in terms of the permeate flux and membrane configuration. However, it should be noted that the outcome of these applications was different. Nonetheless, the flux for this study had similar range to that of previous studies using polymeric membrane in membrane contactor for ammonia recovery (Table 5).

The representative spectra collected in $(NH_4)_2SO_4$ solution by the FTIR-ATR for the SLZK and the DLZK are depicted in Fig. 11. According to Kadam et al. [54], a broad absorbance region was observed at approximately 3500–2700 cm^{-1}, which consisted of an O–H stretch absorption at 3500–3000 cm^{-1} range, along with an overlapping band for the N–H stretch at 3300–2700 cm^{-1}. The broad absorption band were due to the solute–solvent interactions. At 1640 cm^{-1} a band due to water bending was observed. The bands at 1450 and 1000 cm^{-1} were due to N–H bending and sulphate, S–O [55,56]. Fig. 11 shows that the difference in term of intensity or transmittance for the SLZK was slightly lower than the DLZK due to the presence of OH^- from the feed tank. After a period of time, the ammonia gas has been converted to ammonium sulphate. Therefore, the balance of H^+ induced hydration process as reported by Nadykto et al. [57], who also explained the effect of ammonia on the thermochemical stability of common atmospheric hydrogensulphate $(HSO_4)^-$ ion, under atmospheric conditions. The presence of NH_3 did not enhance the thermochemical stability of $HSO_4^-(H_2O)^n$ and ammonia was unlikely involved in the gas-phase hydration of hydrogen sulphate ion, which explained the presence of water after the ammonia gas was successfully converted into the salt. Hence, the purity of this salt or ammonium sulphate demonstrated its ability to be used as a fertilizer, indicating a successful ammonia recovery from feed solution.

Table 6
Comparison of mass transfer coefficient obtained in this study with the literatures.

Membrane Type	Membrane Material	Membrane Configuration	Mass Transfer Coefficient (K) ($m\ s^{-1}$)	Ref.
Polymeric	Polyvinylidene fluoride	Single layer hollow fibre	1.52×10^{-5}	[9]
Polymeric	Polypropylene	Single layer hollow fibre	1.29×10^{-5}	[27]
Polymeric	Polypropylene	Single layer hollow fibre	1.46×10^{-5}	[26]
Polymeric	Polypropylene	Single layer hollow fibre	1.7×10^{-6}	[48]
Polymeric	Polyvinylidene fluoride	Single Tube	8.33×10^{-6}	[40]
Polymeric	Polypropylene	Single layer hollow fibre	0.44	[42]
Polymeric	Polypropylene	Single layer hollow fibre	7.2×10^{-6}	[44]
Polymeric	Polypropylene	Single layer hollow fibre	2.5×10^{-6}	[43]
Ceramic	Alumina/Silica	Tubular	7.62×10^{-7}	[49]
Ceramic	Kaolin-Zirconia	Dual layer hollow fibre	3.77×10^{-5}	This study

4. Conclusion

This study has demonstrated that single layer hollow fibre membrane (SLZK) and dual layer hollow fibre membrane (DLZK) derived from kaolin and zirconia were successfully prepared and converted into hydrophobic membranes using simple grafting method via FAS grafting agent. In fact, the membrane properties such as morphology, surface roughness, bending strength and pore size distribution were significantly improved after the grafting process. The surface roughness of SLZK and DLZK were improved from 0.149 to 0.254 nm to 0.206 and 0.354 nm, respectively. It is important to note that the highest contact angle of ~180° and mechanical strength of 125 MPa were achieved by the DLZK, for which wettability and strength were among the most crucial requirements for ceramic membrane to be operated in membrane contactor system. The key finding of this study was that the highest value of mass transfer coefficient (3.77×10^{-5}) obtained by the DLZK was comparable to those of previous works. Ammonia was also successfully converted into ammonium sulphate and can be used as fertilizer.

This study has the potential to be used for treatment of ammonia-containing wastewater. The use of kaolin as an alternative material for ceramic membrane fabrication in this work also brought new perspectives in membrane separation application for ammonia recovery/removal, which not only created an environmental-friendly condition due to its non-toxicity and abundantly availability worldwide, but also provided an attractive alternative raw ceramic material for membrane fabrication.

Author statement

Mohammad Arif Budiman Bin Pauzan: Data curation, Writing-

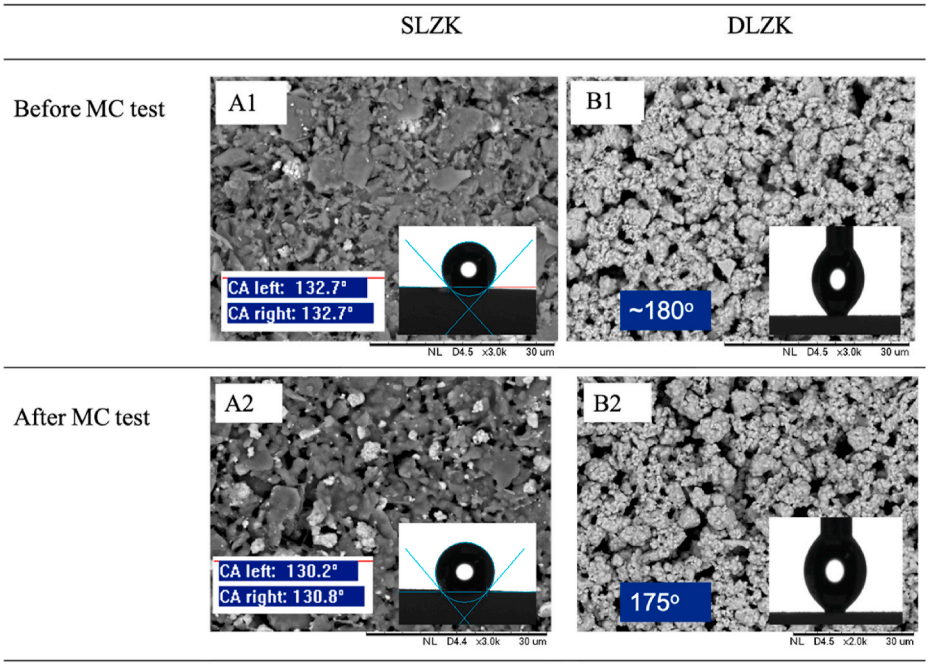

Fig. 10. SEM images and contact angle value of SLZK and DLZK, (a1, b1) before MC test and (a2, b2) after the MC test.

Table 7
Previous studies of ceramic membrane where hydrophobic ceramic membrane was applied.

Year	Material	Membrane Configuration	Type	Flux/Mass transfer coefficient	Ref.
2004	Alumina/Zirconia	Tubular	MD	0.5–8.4 L/m^2h	[50]
2006	Alumina/Zirconia	Tubular	MD	0.7–7.0 L/m^2h	[51]
2007	Alumina/ Aluminosilicate/ Zirconia	Tubular	MD	0.8–5.3 L/m^2h	[52]
2016	Alumina/Kaolin	Hollow fibre	MD	0.2–4.1 L/m^2h	[53]
2019	Kaolin	Hollow fibre	MD	28 kg/m^2.h	[13]
2017	Alumina/Kaolin	Hollow fibre	CO_2 MC	0.18 mol/m^2s	[14]
2021	Kaolin/Zirconia	Hollow fibre	NH_3 MC	3.77 x 10^{-5} Kms^{-1}	This study

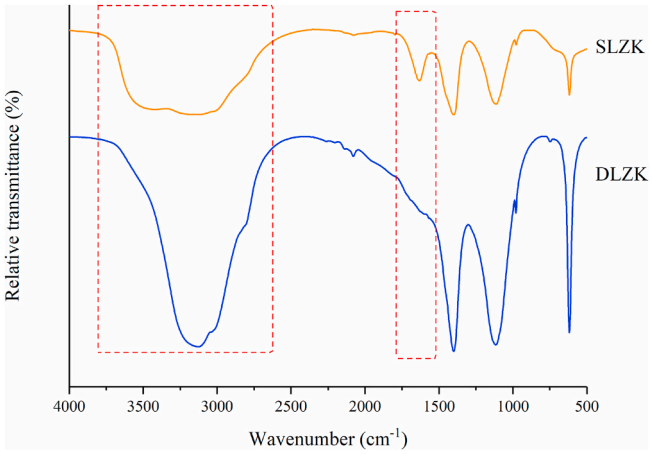

Fig. 11. ATR-FTIR spectra of $(NH_4)_2SO_4$ from MC by using SLZK and DLZK at pH13.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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