Pretreated aluminium dross waste as a source of inexpensive alumina-spinel composite ceramic hollow fibre membrane for pretreatment of oily saline produced water

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ABSTRACT
Pretreatment of produced water using ceramic membrane is considered promising due to its excellent separation performance and thermal and mechanical stabilities, however, the high cost of ceramic membranes discourages industries for large scale applications. The purpose of this work is to fabricate ceramic hollow fibre membranes from alumina-spinel composite powder synthesized from low-cost aluminium dross waste for the pretreatment of oily saline produced water. The hollow fibre membranes were prepared via phase inversion-based extrusion and sintering technique. Aluminium dross (less than 50 µm) was subjected to pre-treatment via water leaching and calcination, resulting in alumina (Al₂O₃) and spinel (MgAl₂O₄) as major constituents. Subsequently, the as-prepared alumina-spinel composite powder was used as a ceramic material in fabricating the hollow fibres. The effect of sintering temperatures on the morphology, crystalline phase, pore size and porosity, mechanical properties, and removal efficiencies of the alumina-spinel composite hollow fibre membranes were investigated. The microfiltration test of the hollow fibres was assessed using produced-water feed of 200 mg L⁻¹ at 1 bar. The hollow fibre sintered at 1275 °C offers 92.41% rejection percentage of oil, the highest after 50 min of stable flux. Furthermore, turbidity was found to decrease from 378 NTU to 28.5 and 22.5 NTU for hollow fibres sintered at 1250 and 1275 °C after 2 h of filtration. In this work, the alumina-spinel composite hollow fibre membranes are found to be an effective tool as an alternative for the pretreatment of oily saline produced water.

1. Introduction

Oil and gas have been historically and are still the world’s most commonly used conventional energy sources despite of the rising interest on renewable energy. During the extraction of oil and gas, a large volume of by-product termed as produced water is generated, which is a real threat to the environment and therefore requires to be treated before it is discharged or reused [1]. The produced water is typically a complex mixture of organic, inorganic, and saline water and is considered to be the largest waste stream in the oil and gas industry that accounts for a volume to product ratio of 3:1 [2]. The concentration range of oil and grease in global produced water production varies from 2 to 565 mg/L depending on one field or another [3]. Conventional produced water treatment techniques such as flotation systems, hydrocyclones, and mixed media filters have limitations for efficient separations of solids, oil, and grease particles smaller than 5.0 µm [4]. To encounter this limitation, membrane technologies are emerged as one of the most promising options and have proven their huge potential to be highly effective in treating feed streams, with high separation efficiency and relatively ease of operation to meet the environmental regulations and standards imposed on the petroleum industry [5].

The pretreatment of produced water is usually needed prior to desalination process via membrane technology (i.e. reverse osmosis (RO) and membrane distillation) because contaminants such as oils and other organic materials adversely affect membrane performance during desalination [6]. Therefore, mitigation of fouling is vital for the long-term operation of desalination facilities. Microfiltration using ceramic membranes is a reliable and feasible alternative to the pretreatment of produced water prior to the desalination process due to their robustness and idealness in harsh environments [7]. In comparison, classical

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methods such as coagulation and flocculation generate a significant amount of sludge and require extra chemical consumption and therefore, likely to be more expensive [8].

Over the past few years, ceramic membranes have caught a significant attention over polymeric membranes because of their robustness in harsh environments (i.e. having excellent mechanical strength, highly resistant to chemicals, thermally stable, insensitive to swelling, and easy to clean) [9,10]. To date, ceramic materials such as alumina (Al2O3), zirconia (ZnO), and titania (TiO2) are the common materials in fabricating ceramic membranes. Non-oxide ceramics such as silicon nitride (Si3N4) and silicon carbide (SiC) have also been well-documented by previous studies [10,11]. However, they are well-known to be expensive and generally, the application cost of ceramic membranes for industrial purposes is one- and three-orders of magnitude more per unit of polymeric membrane [12]. Therefore, some efforts have been made by researchers to fabricate inexpensive ceramic membranes synthesized from natural occurring alumino-silicate minerals such as pozzolan [8], kaolin clay [13], bentonite [14], bauxite [15], and even industrial wastes like fly ash [16] and rice husk ash [17].

Aluminium dross, a residual waste from the aluminium processing industry could also be a good candidate in manufacturing low cost ceramic membranes. This waste is generated as a by-product due to aerial oxidation during aluminium smelting [18]. Currently, most of this waste eventually ends up in landfills, which is potentially harmful to the human health and environment. Indeed, utilizing this waste to make low-cost ceramic membranes can be a promising alternative to waste reduction and recycling and therefore, this enormous burden on the aluminium processing industry may be at least partially preventable. The unique properties of aluminium dross such as abundantly available and contains a fraction of valuable elements such as Al2O3, aluminium nitride (AlN), magnesium oxide (MgO), iron oxide (Fe2O3), etc. make this material an attractive option for low cost ceramic membranes [15,19]. At present, aluminium dross has been applied successfully to synthesise valuable ceramic materials such as pure Al2O3 and Al2O3-MgAl2O4 (alumina-spinel composite) [20,21]. However, as far as the authors concern, the recycling of aluminium dross to fabricate ceramic hollow fibre membranes for oilfield produced water treatment has yet to be reported in literature.

In this study, aluminium dross waste was utilized not only to reduce its environmental impact but also to produce a novel alumina-spinel composite hollow fibre membrane for the pretreatment of oily saline produced water. Ceramic alumina-spinel composite powder was prepared via water leaching and calcination method while the hollow fibres were fabricated using phase inversion-based extrusion and sintering technique. The obtained powder and hollow fibres were characterized in terms of their physical properties and subsequently, the hollow fibres were applied for the filtration of produced water as a pretreatment process for desalination. The effect of sintering temperature on the performance of the hollow fibre membrane (rejection and flux) was carried out in detail.

2. Experimental

2.1. Preparation of alumina-spinel composite powder

In this work, aluminium dross waste was used as a starting material to prepare alumina-spinel composite powder and subsequently hollow fibre membranes. The sample was obtained from an aluminium processing plant in Pasir Gudang, Johor, Malaysia and was in a gray to blackish colour. The received aluminium dross was subjected to sieving to obtain fine powder of less than 50 µm, which is rich in oxides, whilst removing most of the metals found in the original material. The powder was then involved with water leaching using a cross-water ratio of 1:4 for 8 days to eliminate soluble impurities such as chloride salt as much as possible [22]. Then, the mixture was filtered and dried in an oven at 100 °C overnight. After drying, the powder was ground with a mortar and then was calcined at 1100 °C for 90 min. The calcined powder was further ball milled for 24 h at 200 revolutions per minute (rpm) and was sieved to gain a particle size less than 36 µm.

2.2. Preparation of hollow fibre membrane

The combined phase inversion-based extrusion method and sintering technique was used to prepare hollow fibre membranes. Suspension was prepared by mixing Airlac P135 (Polyethyleneglycol 30 Dipropyleneoxyxtreeatrate, CRODA) (1 wt%) and aluminium dross powder (50 wt%) in an N-methyl-2-pyrrolidinedione (NMP, QR6®) solvent (7.14 wt%). Afterwards, the mixture was rolled/milled at 200 rpm for 48 h. Poly (ether sulfone) (PES, Radel A300, Amoco Performance, USA) was added later as a binder and further rolled/milled for another 48 h. Prior to extrusion, the suspension was degassed for 1 h to remove any entrapped air bubbles. The degassed suspension was then transferred to a stainless steel syringe and was extruded through a spinneret into tap water at a constant speed of 10 ml/min with bore fluid (tap water) of 10 ml/min. An air-gap of 5 cm was applied during the extrusion of hollow fibre precursor into tap water. After the phase inversion process was completed, the hollow fibres were cut to 2 cm and then were dried at room temperature overnight. The hollow fibres were then placed into a tubular furnace (XY-1700 MAGNA) and were sintered at a target temperature ranging from 1200 to 1300 for 5 h. The temperature was first increased to 600 °C at a rate of 2 °C min⁻¹ to remove any remaining liquids and held for 2 h for the removal of organic polymer binder and dispersant. Next, the temperature was further increased to the target temperature at a rate of 5 °C/min to consolidate the ceramic membrane. The membrane was then cooled down to room temperature at 5 °C/min.

2.3. Characterization

Thermogravimetric (TGA) and differential (DTA) thermal analyses were carried out in a METTLER TOLEDO (TGA/SDTA851) in order to investigate the thermal stability of the aluminium dross. The samples were tested to a range of temperatures from 30 °C to 1000 °C, at a heating rate of 5 °C/min in atmospheric air. X-ray fluorescence, XRF (Rigaku, NEXCG EDXRF) analysis was carried out to determine the oxides composition of raw aluminium dross powder. X-ray diffractometer, XRD analysis (Rigaku Smartlab) was carried out to investigate the phase transformation behaviour of the raw aluminium dross waste, the treated aluminium dross waste and the sintered hollow fibres. The profiles were recorded in the 2θ range from 3° to 100° with a scanning resolution of 0.02°. The particle size distribution of the alumina-spinel composite powder was determined using a laser particle size analyzer (MasterSizer 3000, Malvern Panalytical).

The morphology of the aluminium dross, the as-prepared alumina-spinel composite hollow fibre membranes and composition of inorganic deposited on the membrane surface after microfiltration were examined using scanning electron microscopy, SEM and energy dispersive spectroscopy, EDS (TM 3000, Hitachi). The porosity and pore size distribution of the hollow fibres were estimated through image processing of SEM pictures using ImageJ software (Java(TM) Platform SE binary). SEM images were turned into white and black regions, which represent particles and pores, respectively. The porosity of the hollow fibre membrane was determined by calculating the percentage of black pixels to total pixels [15]. The area average pore diameter from SEM analysis of the hollow fibre membrane was estimated by assuming cylindrical porous texture of the membrane [23]. The flexural strength of the sintered hollow fibres from 1250 to 1300 °C (three test specimens) was determined by using a three-point bending apparatus with a load cell of 1 kN. The bending strength was measured as follows [9]:

\[ \phi = \frac{8FD_L}{\pi(D^2_0 - D^2_1)} \]  

(1)
where, $F$ is the force at which the fracture of specimen takes place, $L$ is the span, which was kept at 43 mm and $D_o$ and $D_i$ are the outer and inner diameter of the hollow fibres, respectively.

2.4. Microfiltration experiment

2.4.1. Preparation of synthetically hypersaline produced water

Synthetic oily saline produced water with a concentration of $200 \text{mgL}^{-1}$ was prepared by mixing seawater with crude oil using a rapid mixer (food processor). The mixing process was conducted for four minutes at a constant speed rate, which is well-described elsewhere [1]. The average oil droplet size of $20 \mu\text{m}$ was obtained using the Malvern Mastersizer analyzer (Mastersizer 3000) as shown in Fig. 1. The real seawater in this study was received from Port Dickson, Negeri Sembilan, Malaysia with a salinity of $33.7 \text{mS}$. It is worth mentioning that the actual wavelength of the synthetic-made oily saline produced water was measured to be $285 \text{nm}$. The turbidity of synthetic-made oily saline produced water was $378 \text{NTU}$.

2.4.2. Microfiltration application

In this work, a lab-scale of cross-flow microfiltration system was employed. The produced water was flowed across the membranes at a transmembrane pressure of 1 bar at room temperature for a period of 120 min. Prior to that, the hollow fibres were subjected to deionized water for 10 min at 1 bar. The water flux was determined using the following equation [24]:

$$J_W = \frac{V}{At}$$

where $J_W$ is the water flux ($\text{L/m}^2\text{h}$), $V$ is the volume of permeate ($\text{L}$), $A$ is the effective area of membrane ($\text{m}^2$) and $t$ is the time taken for the water to pass through the membranes (h).

After performing microfiltration, the oil removal efficiency, permeate flux, conductivity and turbidity were evaluated respectively. The conductivity of the produced water samples before and after filtration were analyzed by a conductivity meter (model 4520, JENWAY). The oil concentration at feed and permeate were analyzed using ultraviolet-visible spectrophotometry at a wavelength of $285 \text{nm}$. Turbidity was measured using turbidity meter (Hach, ratio/xr Turbidimeter). The rejection was calculated using the expression below [24]:

$$R(\%) = \left(\frac{C_f - C_p}{C_f}\right) \times 100\%$$

where, $C_f$ is the concentration in the feed and $C_p$ is the concentration in the permeate.

3. Results and discussion

3.1. Properties of aluminium dross powder

3.1.1. Thermal analysis

The thermal stability study of the raw aluminium dross is shown in Fig. 2. As can be seen from the TGA thermograms, a weight loss of 1.7% can be detected at a temperature between 30 and $530 \degree\text{C}$, which is likely to be due to the loss of structural water and decomposition of organic matters from raw dross [21]. A small exothermic peak at 200°C is observed, suggesting the decomposition of bound water. Whereas, the exothermic peak observed below than 200°C is due to the loss of absorbed water. In contrast, it is apparent that there is a substantial weight increment after heating at a temperature of more than $530 \degree\text{C}$. The increase in weight could be attributed to the oxidation of raw dross to oxides in the atmospheric air as supported by a sharp endothermic effect at the maximum temperature of $720 \degree\text{C}$ [25].

3.1.2. Mineralogical and chemical composition

The chemical composition of raw and calcined aluminium dross measured in weight percent (wt%) using XRF is given in Table 1. The identification of various phases that exist before and after the treatment of aluminium dross are depicted in Fig. 3. Al$_2$O$_3$ (reference code: 01-089-7716, 01-088-0826) and MgAl$_2$O$_4$ (reference code: 01-087-0345, 01-078-6063) composites were successfully synthesized from aluminium dross after water leaching and calcination at $1100 \degree\text{C}$. Initially, the main phases present in the raw dross were aluminium nitride (AlN, reference code: 01-080-6097), alumina, spinel, and minor constituents of aluminium (Al, reference code: 00-004-0787) and sellaite (MgF$_2$, reference code: 01-070-8281). During the leaching process, most of the dissolved compounds were removed while releasing some polluted gases such as ammonia and hydrogen, which was attributed by the hydrolysis reaction of dross. Ammonia gases were generated through hydrolysis of AlN via reaction 4 and similarly, hydrogen was produced as a result of the reaction of Al with water (see reaction 5) [26]. During the leaching process, besides the loss of those gases, hydrated alumina, Al(OH)$_3$ (reference code: 01-080-6432) was also formed at the same time. This is confirmed from the XRD analysis of washed aluminium dross and was identified as a major phase.

$$\text{AlN} + 3\text{H}_2\text{O} \leftrightarrow 2\text{Al(OH)}_3 + 2\text{NH}_3$$

$$2\text{Al} + 6\text{H}_2\text{O} \leftrightarrow 2\text{Al(OH)}_3 + 3\text{H}_2$$

Fig. 1. Particle size distribution of oil droplet of synthetically made oily saline produced water.

Fig. 2. TGA and DTA analysis of raw aluminium dross.
As can be seen, there is a significant increase in peak intensity and decrease of peak width after calcination process, indicating high crystallinity of the Al₂O₃ and MgAl₂O₄, which can be attributed to the thermally promoted crystallite growth. The increase in intensity of alumina and spinel could also be related to thermal decomposition of hydrated alumina (Al(OH)₃) and the reaction between Al₂O₃ and MgO at high temperature as proposed below [21,22]:

\[
\begin{align*}
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} & \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \\
\text{Al}_2\text{O}_3 + \text{MgO} & \rightarrow \text{MgAl}_2\text{O}_4
\end{align*}
\]

(6)

(7)

3.1.3. Morphology

SEM photographs of raw and pre-treated aluminium dross are shown in Fig. 4(a-b). The obtained alumina-spinel composite powder (Fig. 4(b)) was obtained from the pretreatment of raw dross through water leaching and calcination at 1100 °C. The raw dross (Fig. 4(a)) is large and irregular in shape; however, after the milling of treated dross for 24 h, the obtained particle size of the alumina-spinel composite powder is remarkably reduced and more homogenous. Clearly, from the observation of the SEM image in Fig. 4(b), the as-prepared alumina-spinel composite powder is composed of agglomerate particles and it is challenging to determine the individual particle units. Nevertheless, the medium value of the particle size distribution (D50) of the as-prepared alumina-spinel composite powder shows a particle size of 0.0943 µm. Even though the particle size distribution shows three main distribution peaks, the alumina-spinel composite powder exhibits a relatively narrow distribution of particle size, ranging from 0.02 to 10 µm as shown in Fig. 5.

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\text{Al}_2\text{O}_3 + \text{MgO} & \rightarrow \text{MgAl}_2\text{O}_4
\end{align*}
\]

(6)

(7)
In colour was due to the oxidation of a small fraction of Fe$_2$O$_3$ contained in the hollow fibres turn out to be pale-yellow to dark-brown. The transition after the aluminium dross treatment via water leaching and calcination and therefore, are not included in this work. The starting material of the ceramic loadings sintered at various temperatures starting from 1225 to 1300 °C, from left to right. It is noteworthy that the hollow fibres sintered at 1225 °C and lower were too brittle and were subjected to failure and therefore, are not included in this work. The starting material of the alumina-spinel composite powder appears to be in a pale-gray colour after the aluminium dross treatment via water leaching and calcination at 1100 °C (insert SEM images in Fig. 4(b)). However, the final sintered hollow fibres turn out to be pale-yellow to dark-brown. The transition in colour was due to the oxidation of a small fraction of Fe$_2$O$_3$ contained in the aluminium dross as a starting material, as supported by the XRF analysis in Table 1 [27]. Under SEM analysis, the hollow fibres have an average outer diameter (OD) and inner diameter (ID) of 1360 µm and 938 µm at 1250 °C sintering temperature, OD and ID of 1310 µm and 837 µm at 1275 °C sintering temperature, and OD and ID of 1200 µm and 837 µm at 1300 °C sintering temperature. The increase of radial shrinkage of the sintered hollow fibres at relatively 11.8% from 1250 to 1300 °C was attributed to densification, which is accompanied by neck growth through diffusion between particles in the hollow fibres [15].

As can be seen in Fig. 4(d), the alumina-spinel composite hollow fibre membrane shows a typical asymmetric structure that consists of macro-voids on the inner side and with relatively dense sponge-like structures on the outer side. At increased magnifications shown in Fig. 6(a–c), macro-voids regions occupy approximately 45% of the fibre cross section, extending from the lumen side for all hollow fibres. The macro-voids structure was a result from the interfacial instabilities between the ceramic suspension and coagulant during the phase inversion process. This naturally occurring phenomenon could be attributed to many different mechanisms as a result of the difference in viscosity, density, or interfacial tension and so forth between two fluids, which destabilizes the interface due to acceleration on the interface during the phase inversion process [28]. The acceleration on the interface occurred on the lumen side first as a result of the 5 cm air-gap during the extrusion of the precursors, which brought about periodical invasion of non-solvent of bore fluid into the ceramic suspension, initiating macro-voids from the inner surface.

In terms of the membrane microstructures shown in Fig. 6(d–i), it can be observed that many individual particulates of alumina-spinel exhibit less formation of interconnected particles at a sintering temperature of 1250 °C (Fig. 6(d,g)). As the sintering temperature increases, the number of interconnected particles increases and more significantly with more homogenous and compact microstructures at 1300 °C as shown in Fig. 6(f,i). Nevertheless, a uniform porous microstructure embedded with grown alumina-spinel grains was formed, especially for hollow fibres sintered at 1250 and 1275 °C, which is appropriate in fabricating a porous separation membrane.

In this work, alumina-spinel composite hollow fibre membranes have been successfully prepared using aluminium dross as a starting material. Based on the SEM analysis as confirmed by the XRD data shown in Fig. 7, there were two main phases detected, mainly an alumina-rich phase which could be distinguished by its light grey colour and a spinel-rich phase with a grey-coloured appearance (Fig. 6) [29]. Al$_2$O$_3$ and MgAl$_2$O$_4$ are predominantly identified in all the sintered hollow fibre membranes, indicating that no change of its major phase even after sintering of the hollow fibre precursors. The sintered hollow fibre membranes at 1250 and 1275 °C have almost equal intensity and maintained high crystallinity of Al$_2$O$_3$ and MgAl$_2$O$_4$. However, the peak intensity begins and somewhat to reduce at 1300 °C which could be attributed to the intensified interdiffusion of alumina and spinel [30]. Alumina-spinel, as a composite ceramic material, usually has a desirable combination of mechanical, chemical and thermal properties [31].

### 3.2. Properties of hollow fibre membranes

#### 3.2.1. Morphology and phase composition

Fig. 4(c) shows a picture of the hollow fibres with 50 wt% of ceramic loading sintered at various temperatures starting from 1225 to 1300 °C, from left to right. It is noteworthy that the hollow fibres sintered at 1225 °C and lower were too brittle and were subjected to failure and therefore, are not included in this work. The starting material of the alumina-spinel composite powder appears to be in a pale-gray colour after the aluminium dross treatment via water leaching and calcination at 1100 °C (insert SEM images in Fig. 4(b)). However, the final sintered hollow fibres turn out to be pale-yellow to dark-brown. The transition in colour was due to the oxidation of a small fraction of Fe$_2$O$_3$ contained in the aluminium dross as a starting material, as supported by the XRF analysis in Table 1 [27]. Under SEM analysis, the hollow fibres have an average outer diameter (OD) and inner diameter (ID) of 1360 µm and 938 µm at 1250 °C sintering temperature, OD and ID of 1310 µm and 837 µm at 1275 °C sintering temperature, and OD and ID of 1200 µm and 837 µm at 1300 °C sintering temperature. The increase of radial shrinkage of the sintered hollow fibres at relatively 11.8% from 1250 to 1300 °C was attributed to densification, which is accompanied by neck growth through diffusion between particles in the hollow fibres [15].

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porosity as shown in Fig. 8. The flexural strength improves more dramatically when the sintering temperature increases to 1300°C, which can be ascribed to the completely dense and interlocked alumina-spinel crystals. The porosity of the outer surface of the hollow fibre sintered at 1300°C is only 4.23% (Fig. 6(i)), much lower than that of the hollow fibre membranes sintered at 1250 and 1275°C. For comparison, the alumina-spinel hollow fibres prepared in this study involved sintering temperatures lower than 1300°C instead of higher than 1500°C, which is required if pure Al₂O₃ is the raw material used to fabricate ceramic hollow fibre membranes [15]. The presence of impurities in the aluminium dross starting material such as Fe₂O₃ and SiO₂ that were not removed even after pre-treatment of powder, have a strong influence on the sinterability properties of the alumina-spinel composite hollow fibre membranes. During the sintering process, those impurities were thought to favor the bridging between the grains and membrane densification and therefore acted as sintering aids in decreasing sintering temperature, which make aluminium dross a promising raw material for a low cost ceramic membrane [15,33]. A direct evidence of this is provided by the SEM characterization in Fig. 9(b–d). The mechanism of the formation of liquid phase and the dissolution of oxide impurities from aluminium dross during hollow fibre fabrication is proposed as in Fig. 13.

Fig. 6. Cross sectional SEM image at different sintering temperatures: (a) 1250 °C, (b) 1275 °C and (c) 1300 °C with enlarged magnification of (d-f) fractured surface and (g-i) outer surface of the alumina-spinel composite hollow fibre membranes.

Fig. 7. XRD analysis of sintered alumina-spinel composite hollow fibre membranes at (a) 1300 °C (b) 1275 °C (c) 1250 °C.
3.3. Microfiltration performance

In this work, the microfiltration test of alumina-spinel composite hollow fibre membranes was employed as a pretreatment of oilfield saline produced water for desalination. The efficiency of hollow fibre membranes prepared at different sintering temperatures was investigated in terms of flux, oil rejection and turbidity at transmembrane pressure of 1 bar during 120 min. Fig. 14 shows the water permeate flux as a function of microfiltration time. The total permeate flux of the membrane sintered at 1250 and 1275°C in 2 h were 314.80 and 239.47 L/(m².h), respectively. It is worth mentioning that the permeate flux decreases continuously as the filtration progresses. There was no permeate flux observed during the crossflow filtration of the hollow fibre sintered at 1300°C as the edge of the membrane outer surface was too dense (see Fig. 9(a)). A sharp reduction in permeate flux is observed between the first 10–20 min of filtration. This drop in flux is likely to be due to the concentration polarization effect, which is caused by the formation of organic and inorganic fouling layer on the surface of the alumina-spinel composite hollow fibre membranes as oil concentration in the feed solution increases with time [27]. The fouling layer caused by oil in the feed solution has resulted in additional hydrodynamic resistance, therefore resulting in performance deterioration [27]. In addition, salt deposition occurred on the membrane surface over time,

Fig. 8. Surface area porosity of the fractured surface and the outer surface of alumina-spinel composite hollow fibre at different sintering temperatures using SEM analysis via imageJ.

Fig. 9. Local enlarged cross-sectional SEM image of (a) the outer edge of alumina-spinel composite hollow fibre membrane sintered at 1300 °C and fractured surface alumina-spinel composite hollow fibre membranes sintered at (b) 1250 °C (c) 1275 °C and (d) 1300 °C.

Fig. 10. Pore size diameter distribution of fractured surface of sintered alumina-spinel composite hollow fibre at 1250 and 1275 °C using SEM analysis via imageJ.
which has resulted in reduction of the effective membrane surface consequently permeate flux. The SEM images of membrane after 2 h of filtration with produced water reveals salt deposition that were build-up on the membrane surface. The composition of the salt was determined by EDS analysis and is shown in Fig. 15. Nevertheless, a more stable flux performance is achieved after a period of 50 min for both alumina-spinel composite hollow fibre membranes sintered at 1250 and 1275 °C.

Fig. 15. Composition of salt deposited on the membrane surface.

Fig. 16 presents the rejection of oil in synthetically-made oily saline produced water with time using the alumina-spinel composite hollow fibres. Clearly, the oil rejection is higher for hollow fibre sintered at 1275 °C. This occurs due to the fact that a membrane sintered at a higher temperature results in a reduction of membrane pore size, which provides better size-exclusion separation characteristics. It is noticed that oil rejection is more stable after 50 min of filtration test for both membranes. The alumina-spinel composite hollow fibre membrane sintered at 1275 °C shows the highest rejection of 92.4% after 50 min of stable rejection. Even though the rejection was slightly lower than that previous studies [27, 34], the as-prepared alumina-spinel composite hollow fibre membranes have comparable mechanical properties and was successfully fabricated at lower sintering temperature (below 1300 °C) using a low-cost material particularly aluminium dross waste. The removal efficiencies of turbidity for hollow fibre sintered at 1250 and 1275 °C were 92% and 94% after 2 h of filtration, with an effluent turbidity of 28.5 and 22.5 NTU. In this work, no significant effect of alumina-spinel hollow fibre membrane on conductivity was observed. The conductivity for both membranes sintered at 1250 and 1275 °C was approximately 31.6 and 30.8 mS, no significant rejection over the initial salinity (33.7 mS).

In order to reduce membrane fouling, a periodic backflushing of the hollow fibre membrane sintered at 1275 °C was applied to further investigate membrane regeneration. Permeate flux recovery of the membrane is shown in Fig. 17. During this step, 0.1 wt% NaOH aqueous solution was employed through the membrane pores, resulting in an effective removal of oil and salts from membrane surface. The hydraulic backwash process is in accordance with the previous study [27]. The restoration of 43–56% was observed for the initial flux of the hollow fibre membrane, while maintaining a steady final permeate flux of 101.06–110.43 L/m² h during three runs of cycle. The permeate flux recovery of the hollow fibre membrane was attributed to the nature of ceramic, which is hydrophilic, resulting a weak bonding between membrane surface and foulants, therefore it can be detached rapidly. In summary, a low-cost alumina-spinel composite hollow fibre membrane holds a huge potential as a competitive candidate for the pre-treatment of oily saline produced water prior to desalination facilities. Besides, the recycling of industrial solid aluminium dross waste can help in lessening the impact on the environment.
4. Conclusion

In this work, a novel and low-cost alumina-spinel composite hollow fibre microfiltration membrane was fabricated and therewith for pretreatment of synthetic oily saline produced water. The membrane was successfully fabricated via phase inversion and sintering technique. The sintering process was carried out at temperatures ranging from 1225 to 1300 °C. The sintered hollow fibre at 1275 °C was found to be more efficient in removing oil droplets in produced water. The hollow fibre possesses an average pore diameter, fractured surface porosity, and outer surface porosity of 0.49–0.55 µm, 23.77% and 20.01% respectively. In addition, 92.41% rejection of oil has been achieved at feed concentration of 200 mg/L after 50 min of stable flux using hollow fibre sintered at 1275 °C. The results obtained from this study have laid an important platform for the aluminium dross waste to be recycled and reused as ceramic hollow fibre membranes. These findings are expected to not only solve environmental problems associated with aluminium dross but also produce a high-valued alumina-spinel composite hollow fibre membrane for the pretreatment of produced water prior to desalination.

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