Comparative study of Malaysian and Nigerian kaolin-based ceramic hollow fiber membranes for filtration application

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INTRODUCTION

Alumina and zirconia are extensively used for fabrication of ceramic membrane for various filtration applications. However, these materials are relatively expensive. In the past five years, kaolin has been gathering more attention among researchers as the ceramic material for the manufacturing of membranes (Emani et al., 2014; Hubadillah et al., 2016a; Hubadillah et al., 2016b). Hydrophilicity is the main required property for filtration applications. Kaolin has the inherent property of hydrophilicity, good mechanical, thermal, and chemical stability (Mittal et al., 2011). These properties are required for the filtration membranes for better performance. Another, Kaolin is rich of hydrophilic group of silica and alumina and cost-effective material.

Phase inversion is a well-adopted method for the fabrication of polymeric asymmetric membranes. It is a complex phenomenon which relies on solvent, polymer, and non-solvent. A similar method is also extended for the fabrication of ceramic membranes. Flat sheet, tubular, and hollow fiber membranes are the different modules available in the commercial market. Fouling is the main drawback in membrane technology. Hollow fiber membrane shows better filtration performance as it delivers higher flux with better selectivity due to the higher surface area.

Lately, kaolin is used in fabrication of ceramic hollow fiber membranes for various filtration application such as oily wastewater treatment (Emani et al., 2014; Hubadillah et al., 2017), desalination (Kazemimoghadam et al., 2007), natural organic matter treatment (Shamsuddin et al., 2015) and gas separation (Hubadillah et al., 2016b). From the literature, kaolin has well miscibility with solvents, additives, and binders. Kaolin is abundant in many countries, and the properties of kaolin also varied with respect to various geographical locations. The properties such as chemical composition, particle size and its distribution can influence the formation of membranes. The particle size are chief properties in the packing density of pores during membrane fabrication and sintering process (Hubadillah et al., 2016). Hence, two kaolins such as Nigerian kaolin (NK) and Malaysian kaolin (MK) were considered to compare the properties on membrane preparation and filtration applications. The main objectives of the study are: (i) Characterization of NK and MK, (ii) Fabrication of NK and MK ceramic hollow fiber membranes at two different loading concentrations of 34 and 37 wt. % and various sintering temperature of 1200, 1350, 1400, and 1500 °C; (iii) Water flux testing of NK and MK ceramic membranes.

Keywords: Ceramic hollow fiber membrane, kaolin, sintering, phase-inversion, water flux

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**EXPERIMENTAL**

**Materials**

The Malaysian kaolin clay powder samples were purchased from BG Oil Chem Sdn. Bhd. in Malaysia meanwhile the Nigerian kaolin clay was collected from Kankara local Government area of Katsina state in Nigeria. These samples were kept in the oven overnight before use to remove any trace amount of moisture. The solvent used was N-2-methyl-2-pyrrolidone (NMP) because of its non-volatility in preparing the kaolin-based ceramic membrane (KBCM). Arlacel P135 (polyethylene glycol 30-dipolyhydroxystearate) purchased from Uniqema was chosen as the dispersant. Polyethersulfone (PESF) purchased from Amoco chemical was used as the polymer binder during the suspension preparation.

**Kaolin-based hollow fiber membrane fabrication**

Prior to the membrane fabrication, the kaolin dope suspension was prepared according to Table 1. The KBCM were prepared using the technique of phase-inversion and sintering of the membrane (Fig. 1). Oven-melted Arlacel P135 gel was dissolved in NMP by stirring, followed by the addition of kaolin clay powder. The mixture was milled in an NQM-2 planery ball mill for 48 h for complete homogeneity of the mixture. Next, PESF was added to the mixture as a binder and then milling was continued for another 48 h. After that, the homogenized spinning suspension was degassed for 10 min using a vacuum pump, then the degassed suspension was transferred into a stainless-steel syringe for extrusion. The kaolin dope suspension was then extruded through the spinneret at a flow rate of 10 mL/min and temperature of 25 °C. The bore fluid rate was delivered alongside the feed solution at a flow rate of 10 mL/min to remove any trace amount of moisture. The solvent used was N-2-methyl-2-pyrrolidone (NMP) because of its non-volatility in preparing the kaolin-based ceramic membrane (KBCM). Arlacel P135 (polyethylene glycol 30-dipolyhydroxystearate) purchased from Uniqema was chosen as the dispersant. Polyethersulfone (PESF) purchased from Amoco chemical was used as the polymer binder during the suspension preparation.

Finally, the furnace temperature was reduced to room temperature at a heating rate of 5 °C/min.

**RESULTS AND DISCUSSION**

**Characteristics of raw Kaolin powders**

Fig. 2 shows the particle size distribution of the MK and NK powders. From the figure, unimodal distribution can be observed on both MK and NK. In general, the higher particle size distribution of ceramic leads to less packing structure and resulting in the production of the membrane with more porous structures (Hubadillah et al., 2016a). The size ranges of NK and MK were found to be from 700 to 2000 nm and 950 to 2700 nm, respectively. The wide range of particle size of MK is presumably due to the presence of mixture oxides which composed by kaolinite and some impurities.

![Fig. 2 Particle size distribution of the two-country kaolin sample.](image)

From XRD result shown in Fig. 3, the predominant phase of kaolinite is observed with minor quartz impurity. Both kaolin diffraction pattern agrees with KAOLINITE JCPS no. 01-089-6538 database and the intensity of kaolinite is found to be higher for MK. Also, the patterns are consistent with earlier literature (Nandi et al., 2009; Zhu et al., 2010). Moreover, metal oxides percentage by weight composition using XRF analysis for MK and NK are 55.21 % of SiO₂ and 40.33 % of Al₂O₃ for MK and 56.76 % of SiO₂ and 41.97 % of Al₂O₃ for NK.

![Fig. 3 XRD patterns of the raw kaolin samples.](image)

Thermogravimetric analysis was also performed on the two kaolin samples to identify the thermal stability. Fig. 4 shows the TGA and

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**Table 1. The composition of kaolin dope suspension and water flux.**

| Membrane | MK (wt. %) | NK (wt. %) | PESF (wt. %) | NMP (wt. %) | Flux (L/m² h) 1350°C 1400°C 1500°C |
|----------|------------|------------|--------------|-------------|---------------------------------|
| MK-37    | 37         | -          | 5            | 57          | 275.5 155.50 110.50             |
| NK-37    | -          | 37         | 5            | 57          | 210.29 144.27 76.93             |
| MK-34    | 34         | -          | 5            | 60          | 565.06 268.07 150.63            |
| NK-34    | -          | 34         | 5            | 60          | 460.56 184 124.02               |

The dried membrane precursor was sintered at different sintering temperatures between 1200 to 1500 °C in the tubular furnace (XY-1700 MAGNA). The temperature was maintained for 2 hours from room temperature to 600 °C at a heating rate of 2 °C/min to remove the residual liquid and to add organic binder and dispersant. Then, the furnace temperature was further increased to the target temperature at a heating rate of 5 °C/min and was then kept constant for 5 hours.
DTA of MK and NK powder samples. The total weight loss of MK was higher (15.9%) than NK. The TGA of MK possesses two distinct stages due to its high dehydroxylation of the kaolinite. This results also coincide with DTA endothermic peak at 510 °C for both samples (Fig. 4). Overall, the two types of kaolin hold similar crystallite structure with different thermal and pore size distribution properties. The influence of the two types of kaolin on ceramic hollow fiber membrane for fabrication and characterization are discussed in following sections.

Characteristics of sintered hollow fibre membranes

Fig. 5 shows the effect of sintering temperature on the mechanical strength of the MK and NK membranes. The desired property of ceramic membrane should have the higher mechanical strength for pressure-driven operation.

From Fig. 5, the mechanical strength of the membrane increases with the increase of sintering temperature from 1200 to 1500 °C. The higher mechanical strength was observed for ceramic hollow fiber membrane fabricated at a sintering temperature of 1500 °C. Among the membranes, MK-37 hold higher mechanical strength of 73 MPa for 1500 °C sintered made kaolin membrane. MK showed resilient in both the loading concentrations of 34 and 37 wt.% of ceramic hollow fiber membranes. It is mainly due to the particle size and distribution of MK. During sintering, MK particles are arranged into formation of ordered pore structure which eventually leads to formation of defect-free stable kaolin membrane. As can be seen in Fig 5, two distinct phases were noticed. The mechanical stability increases slowly at the sintering temperature range of 1200 to 1350 °C. The mechanical strength increases rapidly from 1400 to 1500 °C for both 34 and 37 wt% loading concentrations. Furthermore, the increase in loading of kaolin concentration increases the mechanical stability in both NK- and MK-based hollow fiber membranes. This is due to the formation of high packing density of kaolin particles in hollow fiber membranes.

Fig. 6 and 7 show the cross-section morphology of kaolin hollow fiber membranes sintered at various temperatures starting from 1200 to 1500 °C. It is worth mentioning that the morphology of the membrane fibers sintered at 1200 °C could not be measured as they were too brittle and subjected to failure. All membranes exhibit a typical asymmetric structure consisting of macro-voids on the outer side and relatively dense sponge-like structures on the inner side. The cross-section morphology of lower NK-34 and MK-34 membranes display a porous structure with irregular arrangement. It is due to the lower concentration of kaolin which leads to instantaneous formation of membrane. However, dense pores were observed in case of NK-37 and MK-37 kaolin membranes. It is mainly due to the delay in the exchange rate of solvent and non-solvent during phase inversion. The membrane formation was also varied with the effect of sintering temperature and it is evident in cross sectional analysis. The thick skin layer observed in the higher sintering temperature made ceramic membranes. This is owing to the increase of sintering temperature which allows the kaolin to form interconnected arrangement. In terms of membrane microstructures, it can be observed that there is less formation of interconnected particles at 1350 °C sintering temperature while at an increased temperature, there is increase in interconnected particles which result in compact microstructures and become more homogenous at the highest temperature (1500 °C). The result is comparable with the report of Silva et al. (2015) that an increase in sintering temperature leads to membrane densification and thus increases the mechanical strength.
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