Fabrication and characterization of composite hollow fibre membrane derived from hydroxyapatite cow bone and kaolin

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Abstract. Due to its superior behaviour, membrane separation has been applied widely towards water and wastewater treatment. Compare to polymeric counterparts, ceramic membrane has become innovation technology nowadays as it can be used both separation and adsorption application. The conventional ceramic membrane made from alumina, however, in view of its high-cost output. As a result, exploring to a cheap ceramic material derived from clay and waste is gaining attention. In this study, hydroxyapatite derived from cow bone waste and kaolin were used as the main materials for the fabrication of ceramic hollow fibre membrane via phase inversion and sintering technique. The membrane composition was varied through kaolin:hydroxyapatite ration into three composition (40:0, 0:40, 20:20). Result showed the ceramic membrane fabricated from 20 wt% kaolin and 20 wt% hydroxyapatite induces excellent performance at water flux of 10168.5 L/m².h and mechanical strength at 13.33 MPa.

1. Introduction

Water become the world’s most valuable resource because of rapidly growing populations, rising demand of water and the depletion of the quantity and quality of water supplies. Over the last century, the world’s population has grown over and will increase by about 45% over the next 50 years. As long as it is properly handled, freshwater is a valuable resource of world which will be pursue to be sustainable. To secure the sustainability of local growth, the prevention of pollution from industrial, domestic and agriculture activities should be done [1]. Therefore, through treating and reusing waste water, a lot of researchers concentrated on suitable systems for receiving fresh water, the method of removing unpleasant agents, such as organic, chemicals and biological pollutants from water is water purification.
There are numerous technologies utilized, for example, adsorption, ion exchange, coagulation, and membrane technology to remove contaminants from water. Among these technologies, membrane technology is a favored technology in expelling contamination from water. Membrane technology has been identified as the primary technology for the isolation of pollutants from contaminated sources in the treatment of water and wastewater [2]. This is because membrane technology has high efficiency, low utilization of energy and high filtration performance [3]. Throughout the water industry, membrane technology is used to enhance the water quality for usage, reuse or discharge into the environment. Membranes vary from finely porous to non-porous structures and can expel pollutants like bacteria and protozoa to ions [4].

Membrane technology made tremendous strides in the 20th century, and commercial markets expanded very quickly and globally. Thus, the 21st century is known as the "water century" [5]. In certain cases, the main attractions of membrane technology are reduction of the number of processing phases, high efficiency of separation, low consumption of energy and increased quality of the finished products. In comparison, membrane has been shown to be substantially simple, providing benefits over the traditional method due to low consumption of energy, mild temperature activity, avoiding of chemical products and preservation of nutrient and other desired compounds [6]. Increased water shortages, combined with fixed developments in membrane quality, costs and demand of energy, would result in stable growth in the water industry's membranes in the near future [4]. Phase inversion is one of the most desired and widely used techniques used by most researchers through immersion precipitation as a means of making membrane for microfiltration and ultrafiltration of polymer and ceramic membranes [7]. The interest in ceramic membranes for the treatment of industrial wastewater has recently increased due to their excellent properties compared with polymeric membranes. This is due to the ceramic membranes have high thermal stability, good mechanical strength and long lifetime compared with polymeric membranes.

In this study, both hydroxyapatite based cow bone and kaolin are the main material for the fabrication of ceramic membrane. Both kaolin and cow bone waste are example of alternative ceramic membrane material which is abundantly available in Malaysia. In this study, hydroxyapatite and kaolin are combined to develop membranes for a several reasons. One of the reason is hydroxyapatite cannot stand alone as the main material of membrane since it has disadvantages such as brittleness, low tensile strength and fracture toughness. So by mixing kaolin it can increase the mechanical strength of membrane since kaolin have high strength properties. The other reason is kaolin has low ion exchange capacity that can affect the performance of the membrane. This kaolin’s properties are opposite to the properties of hydroxyapatite. Due to the presence of phosphate and calcium, hydroxyapatite showed high ion exchange capacity [8].

It is possible to obtain hydroxyapatite from natural products such as egg shells, beef bones, and fish bones. Since hydroxyapatite is easily synthesized from waste materials, it is being highlighted as environment material from the aspect of the utilization of wastes [9]. Numerous studies have demonstrated hydroxyapatite’s adsorption features for industrial waste water filtration and aqueous solutions. Its particles can adsorb heavy metals from the earth such as cadmium, lead, arsenic, aluminum, and nickel. Hydroxyapatite are known for its properties such as high sorption ability and low water solubility. Fu et al. (2016) [10] stated that hydroxyapatite has a good thermal and chemical stability.

Due to its excellent chemical composition, mineralogical properties and particle size, kaolin is also a preferred substrate for ceramic membranes, making it easy and possible to create good membranes. Kaolin has the characteristics of low plasticity, high refractory properties and good chemical composition [11]. Furthermore, kaolin shows hydrophilic properties, which is highly desired for the fabrication of water filtration membranes. Due to its crystalline order, mineralogical features and composition of chemical, kaolin is a favoured raw substance for porous ceramic membrane. The outstanding of kaolin elements have encouraged research to produce low-cost ceramic membranes based from kaolin [12]. Therefore, in this work, cow bone hydroxyapatite (HAp) and kaolin will be used as the materials for the membrane. The fabrication process of ceramic hollow fibre membrane will be using both phase inversion and sintering technique.
2. Method

2.1. Materials
Kaolin were purchased from Kaolin Malaysia Sdn Bhd and cow bone hydroxyapatite (HAp) were obtained from previous work [13]. N-methyl-2-pyroolidone (NMP) (HPLC grade, Rathbone), polyethersulfone (PESf, Radel A-300, Ameco Performance, USA) and Polyethyleneglycol 30-dipolyhydroxystearate (Arlacel P135) were used respectively as solvent, polymer binder and dispersant. Tap water was also utilized as the coagulant bath and bore fluid.

2.2. Preparation of ceramic hollow fibre membrane derived from hydroxyapatite based cow bone and kaolin
Figure 1 shows the preparation of ceramic hollow fibre membrane derived from hydroxyapatite based cow bone and kaolin using both phase inversion and sintering method. Ceramic suspensions at different content were prepared by mixing kaolin, cow bone hydroxyapatite powder and Arlacel P135 with NMP. Three membrane compositions were formulated as summarized in Table 1. At 190 rpm, the suspension was subsequently ball-milled for 24 hours, using four and two zirconia milling balls with diameters of 6 and 12 mm, respectively. PESf was then be used as the binding agent, and continuously milled for another 48 hours.

The prepared suspension solution was degassed under vacuum with stirring method for one hour then followed by extrusion process by using stainless steel syringe. Infusion pumps (Harvard Apparatus, PHD 2000 Programmable and Chemyx Inc., Model Nexus 6000) regulated the flow rate of the suspension, while the bore fluid rate was controlled using the bore pump (AB, Japan). Both suspensions and bore fluid flow rates were set at 10 mL/min while the air gap was 5 cm. Before cutting to the length needed, the prepared membrane precursors were dried overnight. The precursors undergo sintering process at 1200 °C temperature in a tubular furnace. Finally, the membranes were cooled down at room temperature [13].
Table 1. The compositions for membrane fabrication.

| Compositions | Hydroxyapatite based cow bone (wt.%) | Kaolin (wt.%) | NMP | PESf | Arlacel |
|--------------|-------------------------------------|---------------|-----|------|---------|
| A            | 40                                  | 0             | 54  | 5    | 1       |
| B            | 0                                   | 40            | 54  | 5    | 1       |
| C            | 20                                  | 20            | 54  | 5    | 1       |

2.3. Characterization and performance of ceramic hollow fibre membrane derived from hydroxyapatite based cow bone and kaolin

The membrane’s surface and cross sectional morphology were analyzed by using scanning electron microscopy (SEM, TM 3000, Hitachi). The mechanical strength of the membrane was measured via three-points boning test using an Instron Model 5544 tensile tester provided with a load cell of 1 kN. With a 30 mm distance, the membrane was placed on the sample holder. The bending strength $\sigma_F$ was gained by using equation:

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

where $F$ is the measured load at which fracture happened (N), while $L$, $D_o$ and $D_i$ are the membrane length, the outer and inner diameters (m).

ImageJ software was used to determine the distribution of pore size and overall porosity of the membrane. The performance of separation was carried out under a pressure of 1 bar by a cross-flow filtration system.

$$
J = \frac{V}{A \times t}
$$

where $V$ is the permeate collected volume (L), $A$ is the membrane surface area (m²) and $t$ is the time of permeation (s) [14].

3. Results and discussion

The fabrication of composite ceramic hollow fibre membrane derived from hydroxyapatite based cow bone and kaolin were successfully developed at different composition ratio. Figure 2 illustrate the cross-sectional SEM image of composite ceramic hollow fibre membrane at different compositions with ratio cow bone:kaolin at A (40:0), B (0:40) and C (20:20) sintered at 1200 °C. Based on the SEM images, it was shown a significant change on the macrostructure of the developed ceramic membrane especially its pore size formation. For ceramic membrane prepared from cow bone waste (Figure 2) (A1 – A3), a clear finger-like voids are formed at approximately 70% of the cross section. Meanwhile, no finger-like voids was observed for ceramic membrane prepared from kaolin (Figure 2) (B1 – B3). Interestingly, a slight macrovoid formation can be observed for composite ceramic hollow fibre membrane prepared from cow bone waste and kaolin. At higher magnification of SEM images at 3000x magnification, the membrane can be linked through a process called particle packing. The unoccupied voids are filled when they reach at a point where they touch each other as more ceramic particles are introduced [15]. The particles look like bean structure and it occurred during the process of sintering. This is due to the particle of hydroxyapatite melt on the kaolin’s particles. All of the composition showed the almost the same structures. This result shows that shrinkage pores occur at a certain distance in the membrane after process of sintering. This distance inhibited the development of the vermicular structure by densification.
of the particles in the membranes [16]. From the study of Lai et al. [17] this situation is due to dope concentration that change of the precursors resulted into pore structured disordered.

![Figure 2](image2.png)

**Figure 2.** The SEM images for composite ceramic hollow fibre membrane at composition A, B and C; (1) overall cross section, (2) 300x and (3) 3000x.

Figure 3 shows the mechanical strength of composite ceramic hollow fibre membrane prepared at different composition A, B and C. The result showed that the membrane prepared from kaolin showed the highest mechanical strength of 37.18 MPa whereas membrane prepared from hydroxyapatite based cow bone showed the lowest (10.2 MPa). It should be noted here that the mechanical strength for composite ceramic hollow fibre membrane prepared from cow bone can be improved by addition of kaolin. This is according to the highest percentage of hydroxyapatite content (40 wt%) in the ceramic membrane matrix. Herein, the phenomenon occur as the brittleness properties of hydroxyapatite are the reason of this situation. In addition, this situation can be proven as composition C (20 wt% HAp and 20 wt% kaolin), showed high mechanical strength (13.33 MPa) than composition A. Since composition C contain kaolin (20 wt%) which functioning in increasing the mechanical properties of the membrane.

![Figure 3](image3.png)

**Figure 3.** Mechanical strength of membrane prepared with different composition at the sintering temperature of 1200 °C.
In order to evaluate the performance of ceramic membrane prepared from kaolin, cow bone and composite cow bone membrane, permeate flux was conducted and presented in Figure 4. As can be see, the permeate flux for all membrane is relatively higher with value more than 8000 L/m²h. In this study, the composite ceramic hollow fibre membrane prepared from kaolin and cow bone induced the highest permeate flux with value 10168.5 L/m²h. This situation can be explained due to the addition of hydroxyapatite because of the rising hydrophilicity of the membrane. In addition, previous work also found that hydroxyapatite can encourage increase productivity in term of high flux [18]. It is also well known that hydroxyapatite has great potential sorption ability [19]. Interestingly, kaolin also induce hydrophilicity which can improve the permeate flux of the composite membrane. Therefore, the highest permeate flux obtained by the composite ceramic hollow fibre membrane are due to the superhydrophilicity behaviour of combining hydrophilicity properties of both materials [20].

![Figure 4. Permeate flux of membrane prepared with different composition at the sintering temperature of 1200 °C.](image)

Nowadays, many researchers are focusing on the development of low-cost ceramic membrane from cheaper and more usable materials. Ceramic membranes have been developed from low-cost materials such as clays, animal bones waste, agricultural waste and industrial waste. There has been comprehensive research into the use of the alternative materials. Table 2 shows the comparison of ceramic membrane based from various alternative materials in this study with others previous work reported. As example for agricultural waste, Jamalludin et al. [16] successfully developed hollow fibre membrane green ceramic that made from sugarcane bagasse waste for water and oil separation due to bagasse make a good adsorbent for membrane. Hubadillah et al. [13] latest work has also successfully produced ceramic membrane in hollow fibre configuration using cow bone waste via phase inversion and sintering methods. The membrane with 60 wt% of cow bone waste hydroxyapatite resulted in highest mechanical strength (2020.5 MPa), stable flux (88.3 L/m²h) and a good removal performance.
Table 2. Comparison of ceramic membrane based from various alternative materials.

| Membrane                     | Ceramic content (wt%) | Bore fluid flowrate (mL/min) | Sintering temperature (°C) | Trans membrane pressure (bar) | Flux            | References   |
|------------------------------|-----------------------|------------------------------|----------------------------|-------------------------------|-----------------|--------------|
| Kaolin                       | 35                    | 10                           | 1200                       | 2                             | 320 L/m²h       | [21]         |
| Ball clay                    | 37.5 - 50             | 10                           | 1250                       | 1                             | 1286 L/m²h      | [22]         |
| Aluminum dross               | 50                    | 10                           | 1275                       | 1                             | 200 mg/L        | [15]         |
| Sugarcane bagasse           | 60                    | 10                           | 1000                       | 2                             | 466.2 L/m²h     | [16]         |
| Cow bone waste              | 69                    | 10                           | 1200                       | 2                             | 88.3 L/m²h      | [13]         |
| Composite kaolin and cow bone | 20                   | 10                           | 1200                       | 1                             | 10168.5 L/m²h   | This study    |

4. Conclusions
For fabrication of membrane, the ceramic hollow fibre membrane derived from hydroxyapatite-based cow bone and kaolin were successfully prepared in this research. The membranes were characterized by using SEM, mechanical strength, imageJ software, and performance by water flux. The membrane with composition C (20 wt% HAp, 20 wt% kaolin) have the mechanical strength (13.33 MPa) and it showed the highest flux with (10168.5 L/m².h) so the membrane showed its potential to be used in waste water treatment.

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