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Preparation of Kaolin Based Tubular Ceramic Membrane: Effect of Sintering Temperature.

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ABSTRACT

In comparison with polymeric membranes, ceramic membranes have better combination of thermal, chemical and mechanical stability, longer life and apparently its ability to stand against various organic solvents. Amidst various types of ceramic membrane, ceramic membranes based on kaolin are more promising because of their lower material and sintering cost. In this work, tubular ceramic membranes were prepared using low cost inorganic raw materials such as kaolin, quartz and calcium carbonate by extrusion technique. The ceramic membranes were sintered at various temperatures (850-1100 °C) in order to examine its effect on the characteristics of the membrane. The research findings clearly indicated that the porosity of the membrane decreased from 52.6 to 47.9% with increasing temperature (850-1000 °C). All the membranes displayed better chemical stability in both acid and alkali solution. Pure water permeation flux increased with an increase in the applied pressure as well as sintering temperature. The pore radius of the membranes is estimated to be 0.217, 0.253, 0.304 and 0.336 µm for the sintering temperature of 850, 900, 950 and 1000 °C, respectively. The optimized sintering temperature for membranes has been decided as 950 °C because at this temperature, the membranes were found to be almost straight and the porosity as well as pore size were also satisfactory.

Keywords: Ceramic membrane; Pore size; Porosity; Kaolin.

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INTRODUCTION

Membrane separation processes have been found to be advantageous and promising separation technology compared to other separation technology such as distillation, adsorption, extraction and crystallization processes. Moreover, lesser capital cost, compact design, high separation factors and exclusion of secondary separation units are regarded as the primary advantages of membrane technology. The usage of membranes has become a standard procedure during the last two decades due to these reasons. Recently, there has been larger interest in the preparation and practice of ceramic membrane technology for the diverse field of application. Ceramic membranes have advantageous features over polymeric membrane, such as better thermal stability, mechanical stability and capability to withstand organic solvents, better cleaning property and longer life span [1]. However, ceramic membranes are more costly as compared to polymeric membranes because of their expensive raw materials and sintering cost. Commonly, most of the ceramic membranes accessible in the market are prepared from expensive materials such as alumina, silica, titania and zirconia materials, which increase its material as well as sintering cost [2, 3]. Therefore, preparing ceramic membrane from low cost materials is a challenge for upcoming researchers. There are variety of module configuration and membrane geometries, which are appropriate to a wide range of applications. Membranes are commonly supplied in tubular or hollow and flat sheet arrangements. Tubular membranes have numerous advantages over flat membranes. These membranes are suitable for handling viscous liquids with higher extent of suspended solids and can be cleaned easily either chemically or mechanically. For the preparation of membrane, there are various fabrication techniques available, including tape casting, slip casting, isostatic pressing, dip coating, extrusion, sol-gel process and chemical vapor deposition. Amongst these techniques, extrusion process is best suited for the preparation of tubular ceramic membrane for large scale as well as batch wise production. The required condition for extrusion process is that, the precursors should exhibit rheological as well as plastic characteristics.

The main disadvantage of ceramic membrane is its higher cost. In order to overcome this limitation, few researchers have reported the production of ceramic membrane using cheap materials, for example Moroccan clay, pyrophylite, ball clay, dolomite, and kaolin, etc.[4-7]. Bouzerara *et al.* prepared the ceramic support from kaolin and kaolin-dolama mixtures. Four different processing routes were investigated with two different configurations (tubular and flat). The tubular support was prepared by extrusion technique, whereas flat support was prepared by both dry pressing and roll pressing. Their research indicated that the membrane with a uniform pore size of 28 µm and porosity of 43 % was obtained at a higher sintering temperature of 1250 °C. They recommended that the fabricated membrane can be employed in UF and MF processes [4].Saffaj *et al.* used Moroccan clay as a basic material for preparing membrane support by extrusion technique. The mechanical and structural properties of prepared membrane support were suitable for the applications of membrane [5]. Vinoth *et al.* prepared the tubular ceramic membrane from low cost clays (kaolin, ball clay, pyrophylite and feldspar) using extrusion method. The ceramic membrane was sintered at 950 °C. They obtained the membrane with porosity of 53%, mechanical stability of 12MPa, water permeability of 5.93×10^{-7} m/s kPa and an average pore size of 0.309 µm [6]. Vasanth *et al.* fabricated circular disk type ceramic membrane from cheap materials (kaolin clay, calcium carbonate and quartz) by the use of uniaxial dry compaction method. They examined the consequence of sintering temperature (in the temperature range of 900-1000 °C) on the characteristics of membrane such as pore size, porosity, chemical stability, flexural strength, and pure water flux. It was observed that the membrane sintered at 900 °C was having porosity, flexural strength and average pore size of 30%, 34 MPa and 1.30 µm, respectively [7].

After critical analysis of available literature, it is observed that there are still much work which has to be done in the field of low cost ceramic membranes [8-10].Therefore, the research focuses on the preparation of ceramic membrane with tubular configuration using inexpensive materials that could play a key role to achieve feasibility for industrial use with good performance characteristics. For this work, low cost materials (kaolin, quartz and calcium carbonate) were selected and then tubular membranes were prepared by using extrusion process. The performance of membrane was examined through various characterization techniques. Depending upon the various parameter, such as pore size, porosity, chemical stability and permeate flux, the application of prepared membrane will be decided.

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MATERIALS AND PREPARATION TECHNIQUES

The materials used for the preparation of the ceramic membrane (i.e. kaolin and quartz) were of mineral grade, which are locally available. Characterization results of these base materials were earlier reported in our study by Vasanth *et al*. (2010) [6] and Vinoth *et al*. (2015) [10].

Calcium carbonate was delivered by Merck (I) Ltd, Mumbai. The main raw material for preparing the membrane was Kaolin clay in terms of composition. This provides high refractory property and low plasticity to the membrane, which also fulfills the condition of extrusion process by providing plasticity. Quartz contributes for higher thermal and mechanical stability to the membrane. Calcium carbonate acts as a pore former and supports in the sintering process as well. During sintering process, calcium carbonate dissociates into calcium oxide (CaO) and releases CO_2 gas, track followed by the free CO_2 gas thus creates the porous structure in the ceramic membrane.

Table 1: Composition of materials along with their significance for preparing membranes

Raw Materials	Composition (wt. %)	Significance
Kaolin	50	Low plasticity and high refractory property
Quartz	25	Increases mechanical and thermal stability
Calcium carbonate	25	Pore forming agent

Preparation of Tubular Membrane

The tubular shaped ceramic membrane was prepared with outer and inner diameter of 11.5 and 5.5 mm, respectively and the length of 105 mm. For preparing tubular shaped ceramic membrane, the composition of clay powders along with its significance is given in Table 1. The materials were precisely weighed as their composition and were mixed manually to make homogeneous mixture. Then dough type paste was prepared using optimized amount of Millipore water. Any organic additives were not used for preparing paste. After that, a significant amount of the paste was fed to the extruder, where the paste was forced by the piston and extruded through a hollow cylindrical (tubular) die in horizontal direction to make a tubular shaped membrane. After which, the extruded membranes were subjected to four steps of heat treatment successively. In first step of heat treatment, the membranes were naturally dried for 12h. In the second step, the membranes were dried at 100 °C for 12h in a hot air oven. Third step of heat treatment involved drying of membranes at 200 °C for 12h in box furnace. These above stated controlled process of drying confirms the maximum exclusion of moisture from the membrane and also decreases the possibility of thermal stress. Afterwards, in the last step of heat treatment, the membranes were taken to the sintering process and sintered at different temperatures (850 – 1100 °C) with a heating rate of 0.5 °C/min for 6h in a box furnace. This kind of restricted heat treatment will dodge the formation of bends and cracks in the membrane. After the sintering process, the sintered membrane obtained hard and porous texture. To make the surface smooth, the prepared membranes were polished using abrasive paper of grade 220. For removing the free particles stuck on the surface during polishing, the membranes were sonicated in Millipore water for 15 min. Finally, the obtained membranes were dried at 100 °C for further characterization. Figure 1 represents the schematic diagram of the fabrication process.

Characterization of Membrane

The characterization technique includes the XRD analysis which was conducted to calculate the degree of phase transformations and crystallinity before as well as after the sintering process. The peaks were evaluated in a Bruker AXS instrument using CuKα as a source of radiation. The peaks were acquired for the 2θ range of 1-80° using a scan speed of 0.05 °/s. The average porosity of ceramic membrane was measured by Archimedes' principle with Millipore water as a soaking agent. Chemical susceptibility of the membrane was valued in terms of weight loss of the membrane after treating the membranes in aggressive medium. The membranes were treated in acidic (H_2SO_4, pH = 1.1) and alkaline (NaOH, pH = 13) solution for consecutive seven days and then chemical susceptibility of the membrane was measured by calculating change in weight of the membrane. Hydraulic permeability of the membrane has been measured by calculating pure water flux of the prepared membrane by applying pressure. For this, the cross flow micro-filtration system was employed to

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calculate water flux. The in-house setup was used for calculating water flux. The setup consists of feed tank, pressure gauge, membrane module, pump and three control valves to control inlet flow, retentate flow and bypass flow. The experimental setup is easy to operate and it is designed in such a manner that the cross flow velocity and pressure of the system can be altered and fixed.

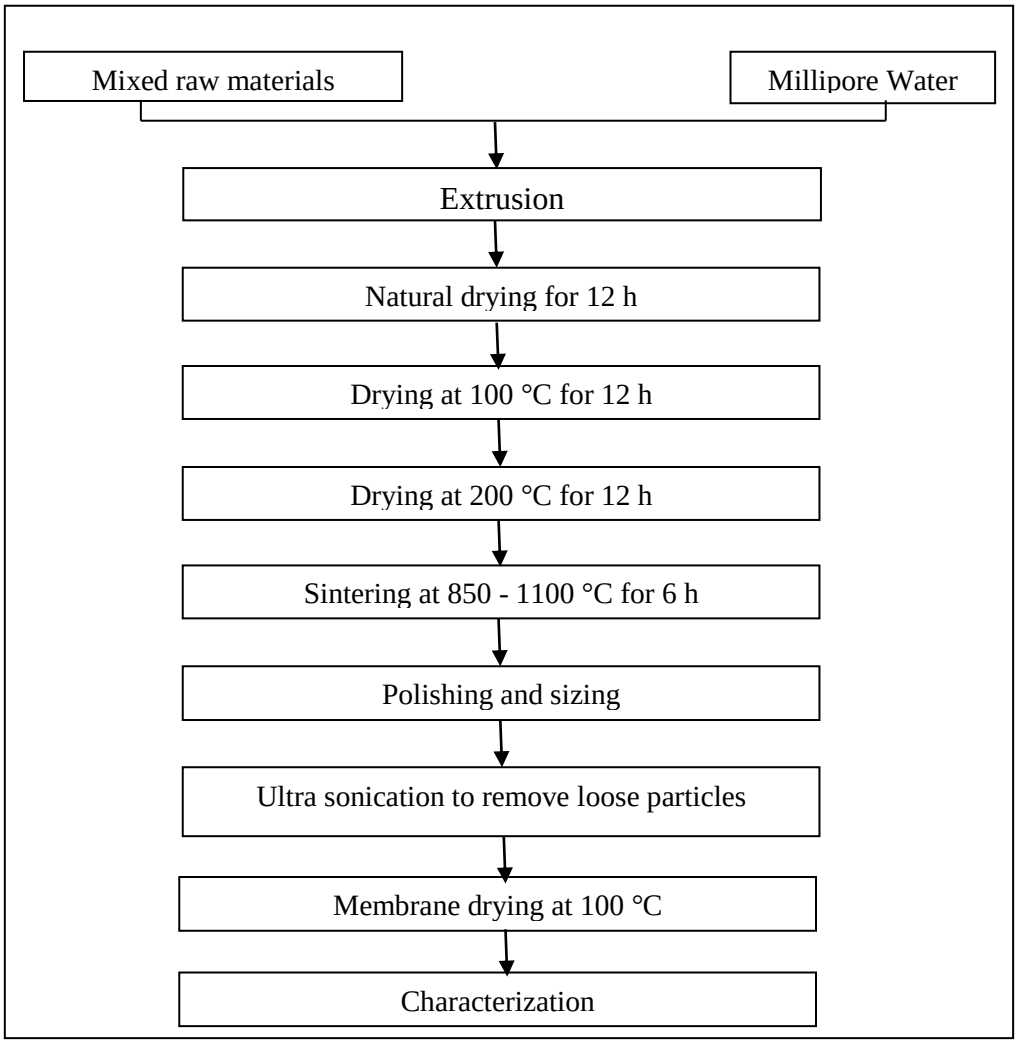

Figure 1: Schematic representation for the fabrication of tubular shaped ceramic membrane

RESULTS AND DISCUSSION

Characteristics of Membrane

The XRD analysis has been done to detect the phase transformation characteristics and crystallinity of the membrane during sintering. Figure 2 shows the XRD patterns of the membranes after and before sintering at different temperatures.

Sintering process permits the membrane to go through phase transformation, hence few new phases have been observed. From XRD profile, it is observed that the peaks of the mixture of raw clays correspond to quartz, kaolin and calcium carbonate, which are the three components of raw materials. In the entire XRD pattern, the peaks corresponding to quartz are not changed. This confirmed that quartz has not affected even at the higher sintering temperature, indicating higher thermal stability of the quartz. The peak corresponding to kaolinite (kaolin) vanished because of the conversion of kaolinite to metakaolinite. Some new phases have also been observed that are Anorthite ($CaO.Al_2O_3.2SO_2$) and Wollastonite ($CaSiO_3$). This might be because of the reaction between amorphous silica and CaO[7].

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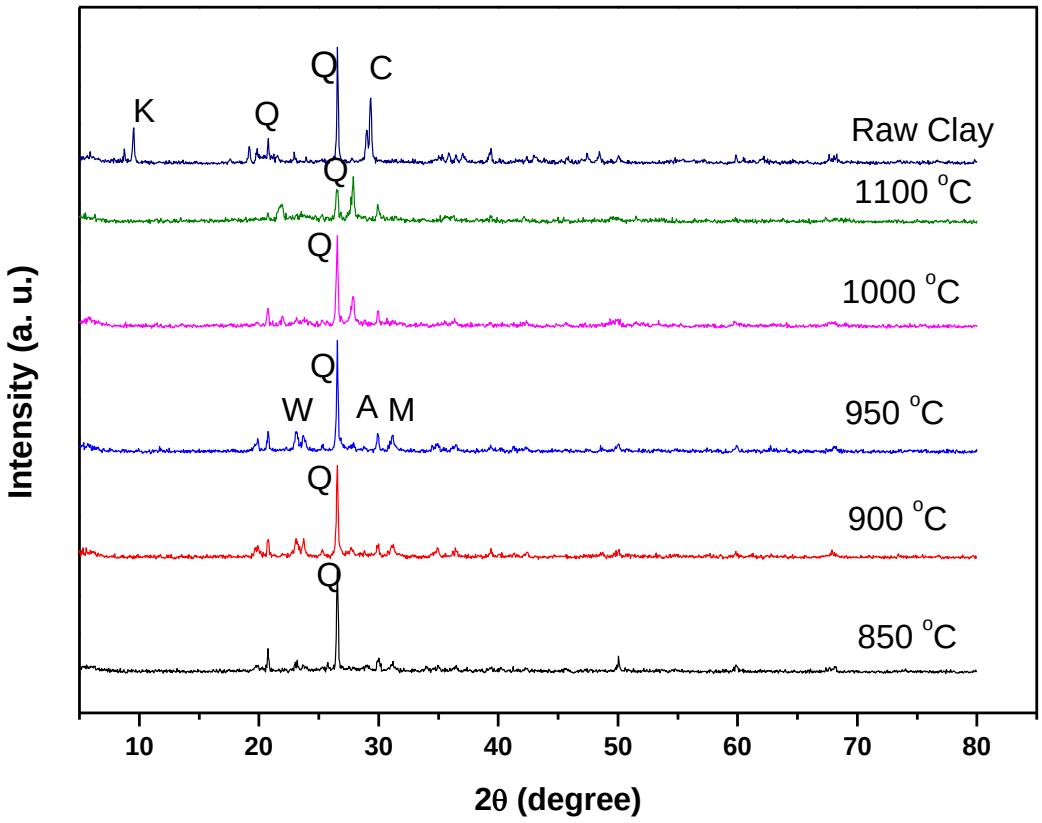

Figure 2: XRD peaks of ceramic membranes at different temperatures (K-Kaolin, Q-Quartz, C-Calcium Carbonate, M-Mullite, A-Anorthite, W-Wollastonite)

The crystal size of membranes at the different sintering temperature can be evaluated using Scherrer's formula [7].

$$d_{XRD} = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

The crystallite size of membrane is found as 53, 51, 46, 42, 41 nm for the sintering temperature of 850, 900, 950, 1000 and 1100 °C, respectively. It is observed that as sintering temperature increases, crystallite size decreases. This is probably due to the densification of the membrane.

FESEM analysis has been done to study the surface morphology of the membrane and to detect the cracks and defects on the surface.

From the images (see Fig.3), it is clear that there are few pores on the inner and outer surface as well and the surface is rough but defects free.

The porosity of the ceramic membranes has calculated using Archimedes' principle [6]. Water is used for the analysis of porosity at various sintering temperature. The porosity of the ceramic membrane has been calculated using the following expression:[11]

$$Porosity\,(\varepsilon(\%)) = \left[\frac{W_W - W_D}{\rho_{water}}\right] \times \frac{100}{V_{mem}} \quad (2)$$

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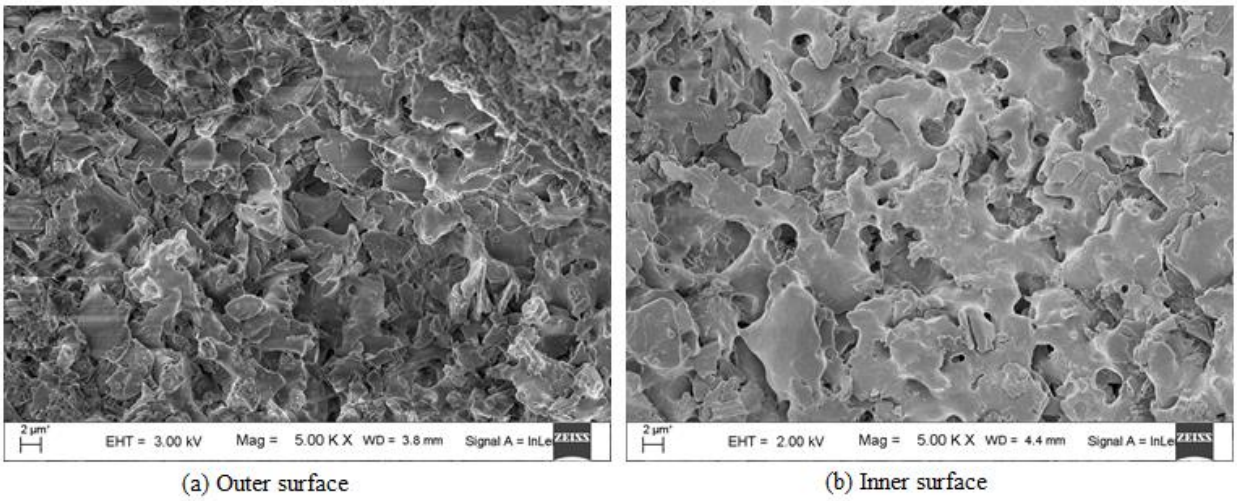

Figure 3: FESEM images of outer and inner surface of membrane sintered at 950 °C (optimized temperature)

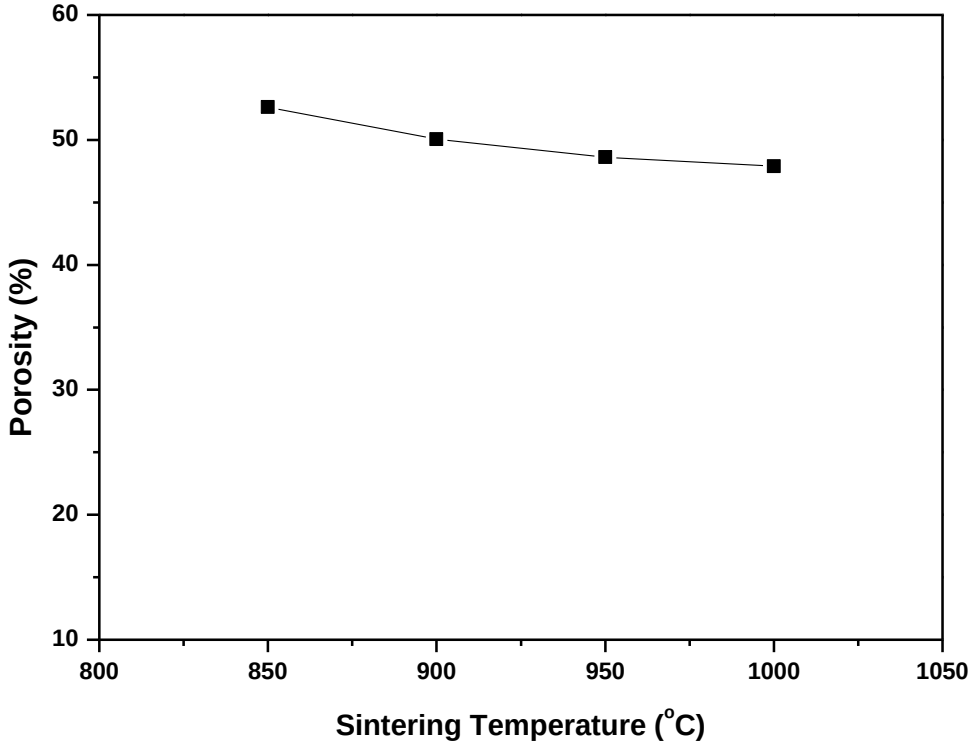

Figure 4: Variation of average porosity of ceramic membrane with sintering temperature

Figure 4 shows the variation of average porosity with change in the sintering temperature. It is detected that the porosity of the ceramic membrane decreased from 52.6 to 47.9 % with increasing temperature from 850-1000 °C. It is caused by denser texture of ceramic membrane because at high temperature, the particles aggregate with themselves to attain a further solidified structure.

The chemical susceptibility of the ceramic membrane has been calculated in terms of weight loss once treating them in acidic (H_2SO_4, pH = 1.1) and alkaline (NaOH, pH = 13) solution separately for one week at

ambient atmosphere. The change in weight has been estimated after a period of one week. Figure 5 depicts the weight loss in acidic and alkaline solution.

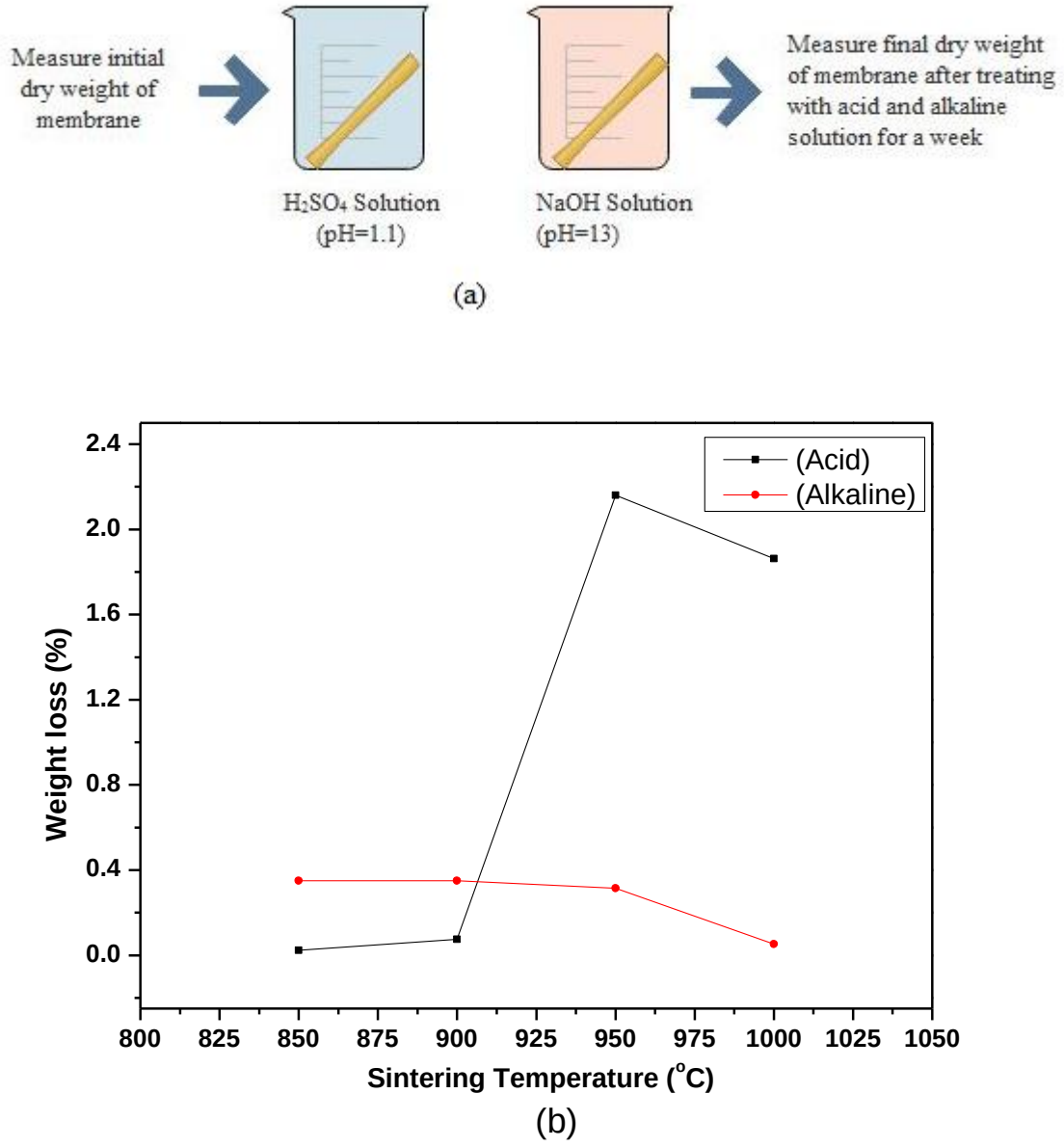

Figure 5: (a) Process of finding chemical susceptibility and (b) Variation of chemical susceptibility in terms of weight loss with sintering temperature after treating with acid and alkaline solution

The obtained results indicated that there was no major weight loss in these solution and mainly in alkaline solution. The loss in acidic medium was 0.024, 0.075, 2.161, and 1.863 % and in alkaline it was 0.351, 0.35, 0.314 and 0.053% for the membranes sintered at 850, 900, 950 and 1000 °C, respectively. For acidic medium, it is less than 2 % and for alkaline it is less than 1% for a period of seven days. It means that ceramic membranes are exhibiting a good corrosive resistance in both acidic and alkaline medium.

The water flux is evaluated by using the following expression:

$$J_W\,(flux) = \frac{Q}{A \times t} \qquad (3)$$

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Figure 6 displays the water flux of membranes at different temperatures as a function of time and applied pressure. It is observed that as the applied pressure increases, the water flux also increases. In early stage at constant pressure, the flux is high, then it decreases and becomes constant after some time.

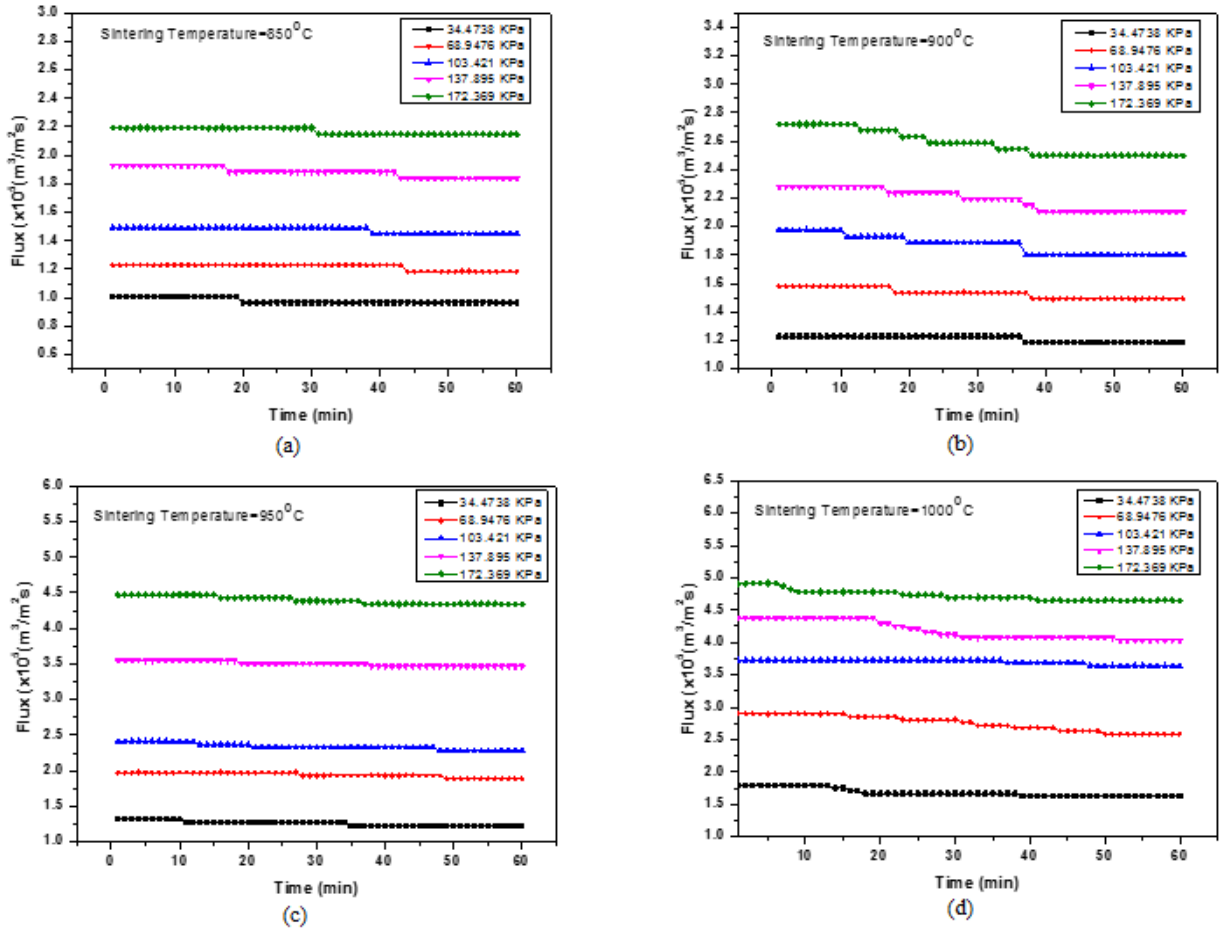

Figure 6: Deviation of pure water flux with applied pressure at constant cross flow rate of 50 LPH over the span of 1hr for different sintering temperature (a) Variation of flux for 850 °C (b) Variation of flux for 900 °C (c) Variation of flux for 950 °C (d) Variation of flux for 1000 °C.

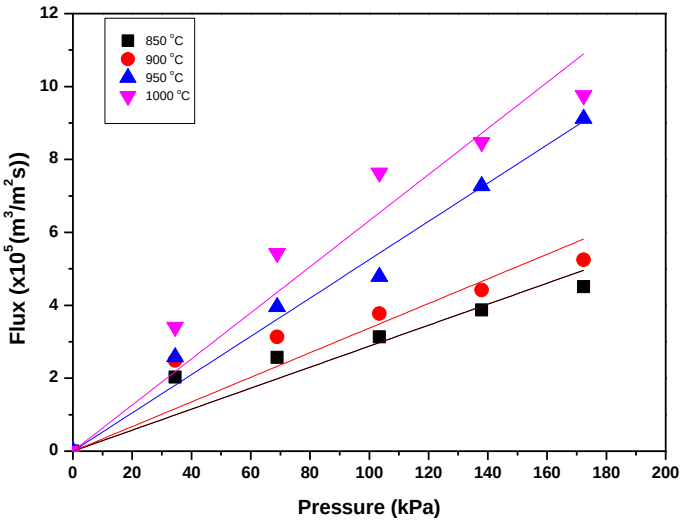

Figure 7: Flux variation with applied pressure

Moreover, it has been observed that the water flux increased when the sintering temperature enhanced. This is perhaps as a result of increase in the pore size of membrane. Pore size has been evaluated with Hagen-Poiseuille equation [6, 11]. First, permeability was determined by calculating slope of the curve of flux versus pressure (Figure 7) for each sintering temperature. Using the permeability value (slope of flux versus pressure plot) in Hagen-Poiseuille equation, the pore size of each membrane has been calculated. The pore size of the tubular ceramic membrane is found to be 0.217, 0.253, 0.304 and 0.336 µm for the sintering temperature of 850, 900, 950 and 1000 °C, respectively (See Table 2).

Table 2: Characterization parameters obtained for ceramic membranes

Sintering Temperature (°C)	Porosity (%)	Permeability (m/s kPa)	Pore Size (µm)
850	52.6	2.88×10^{-7}	0.217
900	50.1	3.37×10^{-7}	0.253
950	48.6	5.25×10^{-7}	0.304
1000	47.9	6.32×10^{-7}	0.336

CONCLUSIONS

In this work, tubular shaped ceramic membrane has been prepared using low-priced raw material by extrusion method. The optimized sintering temperature has been decided as 950 °C because at this temperature the prepared membrane offers better combination of porosity, flux and pore size. The membrane sintered at 950 °C has water permeability of 5.25×10^{-7} m/s kPa with average pore radius of 0.370 µm and average porosity of 48.6 %.An increase in sintering temperature from 850 to1000 °C increased the pore size and pure water flux while the porosity of the membrane reduced. The prepared membranes have shown better chemical stability indicating that these membranes can be used in the industrial process. Considering its pore size in account, it could be utilized for microfiltration applications as well as support for the preparation of nanofiltration and ultrafiltration membranes.

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NOMENCLATURE

ε	Porosity of the membrane (%)
W_D	Dry weight of the ceramic membrane (g)
W_W	Wet weight of the ceramic membrane (g)
ρ_{water}	Density of water (kg/m^3)
V_{mem}	Volume of tubular ceramic membrane
σ_c	Compressive strength of membrane (MPa)
F	Force applied on the membrane while measuring compressive strength (KN)
A	Cross sectional area over which force is applied (m^2)
J_w	Water permeability flux (m^3/m^{2}s)
Q	Volume of water permeated (m^3)
t	Time to collect permeate (s)
d_{XRD}	Crystallite size of membrane particles (nm)
K	Shape constant

α	Wavelength of the CuKα radiation (Å)
β	Full-width at half-maximum
θ	Diffraction angle (degree)

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