

PREPARATION AND CHARACTERIZATION OF KAOLIN-CLAY BASED CERAMIC MICROFILTRATION MEMBRANE

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Abstract

This work highlights the preparation of ceramic membranes from a low-cost naturally occurring clay material with Kaolin. Additives like sodium carbonate, sodium metasilicate and boric acid was added in standard stoichiometric ratio with the processed clay material, imparting characteristic properties. Paste casting method was followed for fabricating circular disc shaped membranes with 55 mm× 6 mm dimensions. Sintering effects were studied by exposing the membranes at temperatures ranging between 600°C to 800°C in a programmable muffle furnace. The membranes fabricated were characterized using standard characterization techniques like Scanning Electron Microscopy (SEM) and Powder X-ray Diffraction Analysis (PXRD). Finally, water permeation studies were carried out in a standard membrane module within the microfiltration regime , obtaining a standard permeation flux and the data was used in calculating the porosity of the ceramic membrane.

1. Introduction.

Advantages of ceramic membranes include high temperature applicability, resistance to corrosive feed, consistency in high pressure application and long life. Early research on the preparation of ceramic membranes has utilized expensive α - Al_2O_3 as a precursor [1]. Afterwards γ - Al_2O_3 , zirconia, titania, and silica were used for membrane synthesis [2]. Recently some researchers have started to work with cheaper raw materials like apatite powder [3], fly ash [4], kaolin [5], clay [6] etc. to reduce the cost of the membrane. Due to the well-known structural adsorption, rheological and thermal properties of clay minerals, membranes from clays are gaining a lot of attention. Initial days of research on ceramic membrane preparation were concentrated on pillared clays; the preparation of ceramic membranes using pure clays has started very recently. The preparation of membrane by different process like pressing [7], paste casting [6] were reported, the paste casting method is simple to fabricate and in present work we used paste casting method for the preparation of ceramic membrane. Kaolin is added to decrease in pore size and uniform distribution in the membrane.

The objective of the present work is to prepare low-cost ceramic membranes using clay and kaolin mixture as main raw material. Three different membranes were prepared; four different membranes are with different sintering temperature. In addition to membranes are mixed with sodium carbonate, sodium metasilicate and boric acid. Characterization of all membranes were investigated by XRD (Bruker D8, advanced X-ray diffraction measurement system) to study the phase changes and SEM (Leo 1430 vp) to determine average pore size and pore size distribution. For the analysis of thermal transformations during the whole sintering process, thermo-gravimetric analysis (TGA). Water permeation experiments were carried out to evaluate the permeability and average pore size.

2. Materials and methods.

2.1 Raw materials.

After drying of the raw muddy clay from MIT Manipal campus at 100 °C, it was grinding in a ball mill and passed through 150 μm mesh screen. All the membranes were prepared with 150 μm mesh clay powder and Kaolin from (Rohm chemical Industries).

Chemicals:- Kaolin (Rohm Chemical Industries), Sodium meta-silicate (Nice Chemicals Private Ltd), sodium carbonate (Sarabhai M chemicals) and boric acid (SD Fine Chemical Limited) were used for membrane preparation. Kaolin provides low plasticity and

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high refractory to the membrane, Sodium meta-silicate increases mechanical strength by creating silicate bonds. Sodium carbonate improves dispersion properties, thereby creating homogeneity. Boric acid also increases mechanical strength by creating metaborates during sintering.

2.2 Membrane preparation.

The clay collected was made free from all the impurities such roots, plastic pieces and leaves, followed by drying in sunlight for 24 hours for complete moisture removal. Dry clay was fed into a ball mill for 2 hours to reduce particle size of soil so that paste made for membrane support preparation yield good viscous properties. The resultant fine powder was sieved with 150 μ m mesh screen. Composition of the membrane given in the Table.1

Table.1 Composition of membrane

Materials	Wet Basis
Clay (%)	60
Kaolin (%)	10
Sodium Carbonate (%)	3
Sodium Meta Silicate (%)	2
Boric Acid (%)	2
Water (%)	13

Membrane is prepared by paste casting method given in [5]. From the compositions given in Table 1. The materials were mixed with distilled water and the paste was casted over a gypsum surface in the shape of a circular disc of 60mm diameter and 10 mm thickness. After partial drying in room temperature for 48 h, the disc was removed carefully and heated at 100 °C for 8 h. eventually; the caste disc was heated step by step (100 °C in every 30 min) in a muffle furnace to the desired sintering temperature and kept in this temperature for 5 h. Then, the temperature of the muffle furnace was cooled gradually to room temperature. Finally, the membrane was polished with silicon carbide abrasive paper (C-180) to give a final shape of around 55mm diameter and 8 mm thickness as well as washed in distilled water and dried. Membrane where prepared three different temperature like 600°C, 700°C and 800°C. Called as Membrane A, Membrane B and Membrane C Respectively.

2.3 Membrane Characterization.

Characterization was performed using TGA, SEM, Powder XRD. The structural characterization of the membrane by thermogravimetric analysis(TGA). TGA of the sample mixture are conducted (TGA SDTA 851e, Mettler Toledo) to identify the various thermal transformations of the material during sintering condition. The membrane morphologies were observed via scanning electron microscopy (SEM, JEOL JSM-6480 LV) to determine average pore size and pore size distribution, Porosity. Prior to imaging, each sample was platinum coated in a specialized device to increase the conductivity for a better imaging. The synthesized samples were subjected to X-ray diffraction by a diffractometer (XRD, Philips Analytical, PW-3040) equipped with the graphite monochromatized CuK α radiation($\lambda=1.5406\text{\AA}$) in 2 θ angles ranging from 20o to 800 with a step size of 2 degree and scanning rate 1 minute. Water permeation experiments were carried out to evaluate the average pore size and permeability. Chemical stability of the membranes was checked by comparing the porosity, pore size.

2.4 Water permeability

Four membranes were subjected to water permeation experiments (Fig. 1) using distilled water. Hydraulic permeability (Lh) and average pore diameter (rl) were determined by the equation:

$$J = \frac{n\pi r^4 \Delta p}{8\mu l} = L_h \Delta p \quad (1)$$

Where, J is the liquid flux (m³m⁻²s⁻¹), ΔP is the transmembrane pressure (kPa), μ is the viscosity of water, and l the pore length (i.e. thickness of membrane, assuming the pores are cylindrical). Taking porosity, $\epsilon = (\text{saturated wt-dry wt}) / \text{saturated wt}$ Eq. (1) can be changed to

$$r_l = \sqrt{\left[\frac{8\mu L_h}{\epsilon} \right]} \quad (2)$$

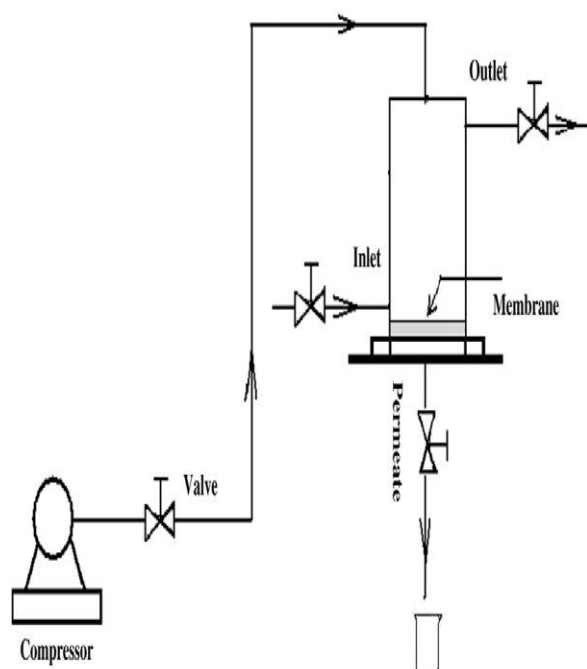


Fig.1: water permeation experimental setup

The porosity was figured out by simple pycnometric method using water as a wetting liquid. The Trans membrane pressure drop for these experiments was in the range of 10–325 kPa. Before the experiment, standard compaction tests were conducted at a pressure of 300 kPa which was above the operating pressure. The flux was initially high and reduced to a steady value. These data was taken by measuring the permeate of 250ml volume. In the next stage of the experiment, the flux through the membrane was measured with respect to 250kpa pressures. The hydraulic permeability (Lh) was obtained by Eq. (1). With this value and porosity value, the average pore radius was calculated by eq (2).

3. Results and discussion.

3.1. Thermo-gravimetric analysis.

Thermal Gravimetric Analysis or Thermogravimetric Analysis (TGA) is an analytic method. This measures the change of weight with respect to increase in temperature in a controlled. Atmosphere thus to predict the thermal stability of the material tested. The primary parameters measured during analysis include weight, temperature and rate of temperature change. These data are plotted after required

transformation before the results are interpreted. Based on the interpretation, this analysis gives information on absorbed moisture, proportion of organic and inorganic materials in sample, and solvent residue apart from degradation temperature. A typical experiment involves placing a known weight of sample in the crucible and gradually raising the temperature which can be programmed according to our requirement.

The data acquisition system automatically plots the relation between temperature and weight.

This is finally smoothened to find the exact point of inflection. Each point of inflection may be interpreted as temperature of maximum weight loss which indirectly provides us information on its degradation.

TGA of the Kaolin-clay membrane shown in Fig.2 when subjected to thermogravimetric analysis by heating the dry inorganic mixture in a α -alumina crucible from room temperature to 825 °C at a heating rate of 10 °C/min.

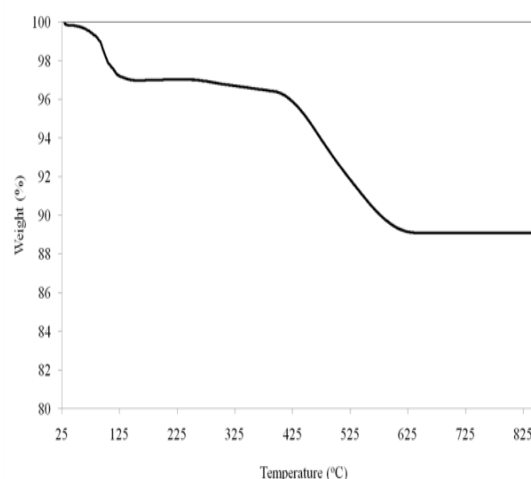


Fig.2 TGA of Clay-Kaolin Membrane

During the first phase of heating the mass loss of membrane up to 90 °C was 0.23% and up to 150 °C the mass loss of membrane had shown a mass loss of 2%. These mass losses can be attributed to the loss of loosely bound water molecules. The higher mass loss was due to the presence of some hygroscopic materials (like sodium metasilicate, boric acid). At temperatures up to 650 °C, it was observed that the higher mass loss of membrane is occurred Between 300 °C to 600 °C. This phenomenon may be attributed to the fact that the boiling point of boric acid as a component in membrane is around 300 °C. After 650°C for the

compositions, mass change was marginal. Thus, the minimum sintering temperature for the membranes should be above 650 °C.

3.2 Powder X-ray diffraction analysis.

From the XRD analysis fig.3 and fig.4 we can find crystallinity of the membrane and composition of membrane by JCPDS software.

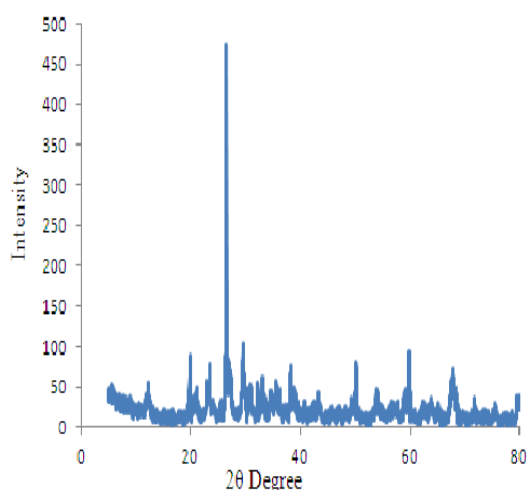


Fig.3 X-ray diffraction of Membrane B

From the TGA analysis it is observed that above sintering temperature of 650 °C almost no significant weight loss occurred. To verify this hypothesis XRD analysis of membrane structure at temperature higher than 600 to 800 °C is done.

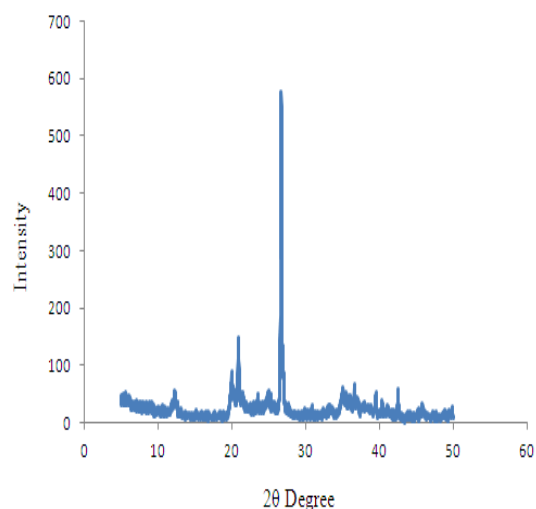


Fig.4 X-ray diffraction of Membrane C

From XRD analysis the compositions of membrane before sintering reflections of illite, kaolinite and quartz were observed in the mixture of kaolin-clay material. In the sintered samples, no reflection of kaolinite was found due to transformation to metakaolinite. For membrane at 700°C and 800 °C, reflections of illite, mullite, quartz and nepheline ($\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$) were found but at 800°C quartz, mullite and nepheline a reflection was detected. Quartz reflections did not change significantly. A critical observation of the peaks at higher temperature reveals that there is significant phase transformation occurs at 800°C. This signifies that the membrane skeletal structure constitutes mainly metakaolinite, quartz and nepheline. From the XRD analysis it all so can be concluded that the sintering temperature of 800°C is sufficient for membrane fabrication. All XRD diffraction graphs indicate no change in the peak trends corresponding to quartz thereby inferring that quartz phase is not at all affected by sintering of inorganic materials within the temperature considered in this work. Therefore the sintering temperature up to 800°C considered in this work.

3.3 Scanning Electron Microscope (SEM) analysis.

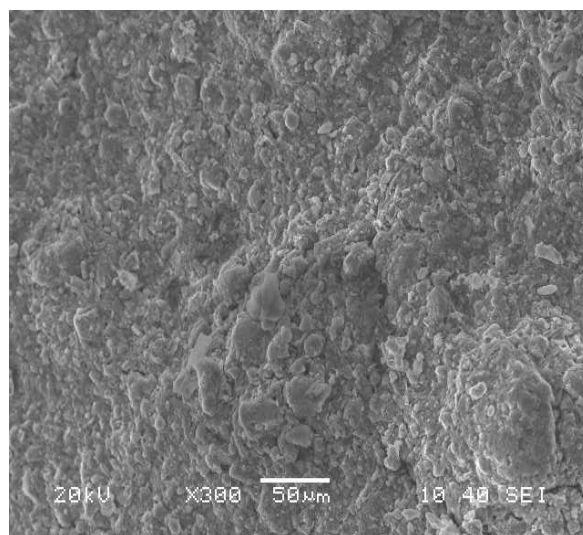


Fig.5 SEM of Membrane B

SEM pictures for the membrane sintered at two different temperatures considered in this work. All the membranes showed a surface with rough morphological structure. The ceramic substrates sintered at lower temperature shows

highly porous structure. the membrane sintered at 800°C are more consolidated due to the fact that for sintering temperature over 750°C the particles agglomerate together creating more dense ceramic body. As a result the porosity of the membrane decreases with increase in sintering temperature (25-15%). A superficial observation of the SEM indicates that the membrane did not have any pinholes cracks and the maximum observable pore size of the surface is about $6\mu\text{m}$.

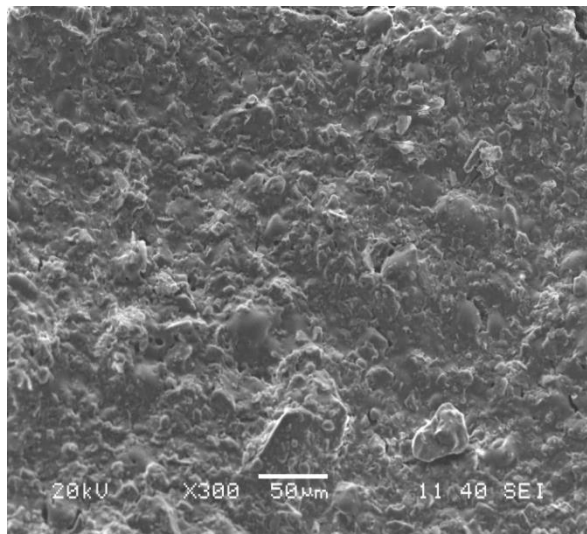


Fig.6 SEM of Membrane C

3.4 Permeation experiment

The inorganic membranes are subjected to liquid permeation test using distilled water in batch mode operation. The hydraulic permeability, average pore diameter and porosity of the membrane are determined experimentally. Transmembrane pressure drop for water permeation test is maintained at 0-250kpa (microfiltration range). Before using each fresh membrane, membrane compaction has been conducted using deionized water at a Transmembrane pressure 300kpa. During these experiments, the membrane flux was observed to be high initially and reduced to a steady state. At beginning flux of $1.96 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ which reaches to steady state value of $4.23 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ shown in fig.7. These data was taken by measuring the permeate of 250ml volume. The hydraulic permeability and average pore radius of the membrane can be estimated according to

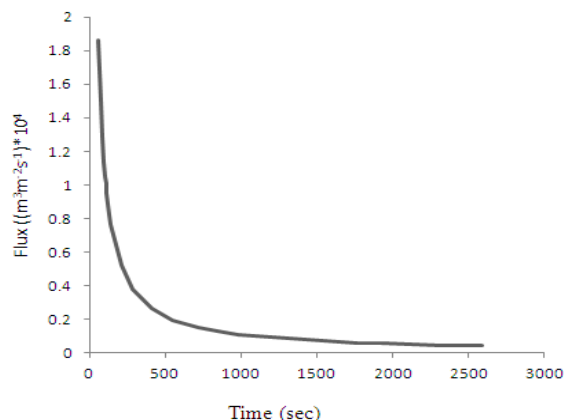


Fig.7. permeate flux of membrane C

the Eq.1. The average pore radius of the membrane is evaluated by assuming presence of cylindrical pores in the membrane matrix using the Eq.2. The porosity of the membrane is determined by pycnometric method using water as wetting liquid. The membrane porosity is decrease from 28% to 18% when sintering temperature varies from 600°C to 800°C . this is due to the fact that increase in sintering temperature densification of the porous structure occur and thereby allow for an decrease in the membrane porosity.

4. Conclusion.

Microfiltration membranes were prepared from locally available clay collected from MIT Manipal campus. The study indicates that with the addition of a small amount of sodium carbonate, sodium metasilicate and boric acid, a high flux ceramic microfiltration membrane can be prepared. This study indicates that a defect-free ceramic membrane can be fabricated with high content of clay and low content of expensive precursors. The thermal characterization and XRD study inferred that the appropriate sintering temperature for the chosen composition of membrane is 800°C . The observable maximum pore size of the membrane is $6\mu\text{m}$. the distribution of pore size based on SEM and physical interpretation is good and only 28-18% of porous structure contribution towards the transport studies. TGA of ceramic membrane shows that the loss of weight at 800°C is maximum.

5. References.

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