PREPARATION AND CHARACTERIZATION OF CERAMIC MEMBRANES FROM FLY ASH AND KAOLIN

Dissertation

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MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING

by

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CERTIFICATE

This is to certify that the dissertation work entitled "**Preparation and characterization of ceramic membranes from fly ash and kaolin**" submitted by **Manju Rawat (Roll No. 601511002)** in partial fulfillment for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, Punjab, has been carried out under my supervision. This work has not been submitted partially or wholly to any other university or institute for the award of this or any other degree or diploma.

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DECLARATION

I hereby declare that the work being presented in the thesis report entitled **"Preparation and characterization of ceramic membranes from fly ash and kaolin"** by me in partial fulfillment of the requirements for the award of the degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, is an authentic record of my own work carried under the supervision of **Dr. Vijaya Kumar Bulasara** (Assistant Professor, ChED) during January – June 2017. The matter presented in this thesis has not been submitted in any other University/Institute for the award of any degree/diploma.

Date: 17/8/2017

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ABSTRACT

Kaolin has been identified as a low-cost raw material for the preparation of ceramic microfiltration membranes. In order to reduce the membrane cost further, fly ash has been studied for its suitability as a raw material. However, the fly ash based membranes had large pore size (> 2 µm), low porosity (< 30%) and low strength (< 20 MPa). In a view to decrease the membrane cost without compromising upon these parameters, the present work uses mixtures of fly ash and kaolin for preparation of ceramic membranes. Ceramic microfiltration membranes have been prepared using five different compositions (labeled as M1–M5) formulated with different amounts of fly ash and kaolin. A sintering temperature of 900°C has been chosen based on the thermogravimetric analysis (TGA) of the raw material mixtures. The SEM analysis of the sintered membranes evidenced a large amount of small pores on the surface and the XRD analysis revealed the presence of metakaolin, quartz and nepheline in kaolin rich membranes. The water permeation study indicated that the porosity of the membranes increases and pore size decreases with increasing the kaolin content in the raw materials mixture. The mechanical strength and chemical stability also increased with increasing the kaolin content. The M4 membrane has been selected for further use since it has a good combination of pore size (0.885 µm), porosity (42.7%), mechanical strength (43.6 MPa), and chemical stability (< 3% weight loss in acid and 0.02% in base). Aqueous solution of humic acid was prepared with a concentration of 50 mg/L and used as feed for microfiltration experiment with M4 membrane at two different transmembrane pressures (1 bar and 2 bar). It was noticed that a pressure difference of 2 bar resulted in superior flux, while, a pressure difference of 1 bar resulted in better rejection of humic acid (98.46%) and good permeate quality (0.77 mg/L). Therefore, the membrane M4 has been successfully applied in the separation of humic acid from water.

Keywords: Fly ash, Ceramic membrane, Preparation, Characterization, Microfiltration.

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Chapter 1

INTRODUCTION

1.1 Definition of membrane

The word membrane originated from the Latin word *membrana* which means a skin [1]. Membrane keeps things separated in the living world and passes materials selectively. Although it is difficult to give an exact definition of a membrane, a general definition could be: 'a membrane is a thin barrier, placed between two phases, or media, which allows one or more solutes selectively to pass from one medium to the other in the presence of a suitable driving force.' The term 'selective' is inherent to a membrane or a membrane process. The membrane processes are the combination of two unit operations i.e., mass transfer and momentum transfer. Figure 1.1 below shows membrane based separation process [2]. In a membrane separation process, the solute rich phase is called retentate and the solvent rich phase is called permeate. In a dead-end filtration, the retentate mixes with the feed and solute concentration increases on the feed side resulting in fouling of membranes. The increase in solute concentration near the membrane surface due to accumulation of solute particles is called concentration polarization, in which case, the surface concentration of solute is higher than the bulk concentration or feed concentration.

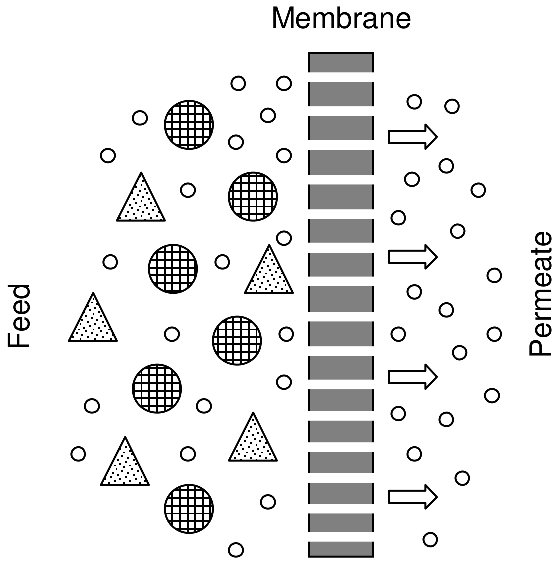

Figure 1.1: Membrane based separation process

1.2 Classification of membrane separation processes

The membrane based separation processes have a very important role in process industries. These processes differ mainly on the basis of the size of species or particles and the driving force for separation. The most commonly used membrane separation processes include microfiltration (MF), ultra-filtration (UF), nano-filtration (NF), reverse osmosis (RO), electrolysis, dialysis, electro-dialysis etc.

The classification of different membrane processes is shown in Table 1.1. The most relevant processes technically and commercially are the pressure driven processes namely microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Apart from these, concentration gradient and electrical potential also act as driving force in some of the membrane processes.

Table 1.1: Classification of membrane separation processes [1]

Driving force	**Membrane process**	**Permeate**	**Retentate**	**Membrane type**
Pressure difference	Micro-filtration (MF) (0.5-2 bar)	Dissolved solutes, water	Suspended solids	Symmetric micro-porous
	Ultra-filtration (UF)	Small molecules, water	Polymers, proteins, micelles, colloid particles	Asymmetric micro-porous
	Nano-filtration (NF)	Monovalent ions, water	Small molecules, divalent sales	Thin-film membrane
	Reverse osmosis (RO)	Small polar solvents, salts, water	All solutes	Asymmetric skin type
	Pervaporation (PV)	Volatile small molecules, water	Low volatility species; species less soluble in the membrane	Asymmetric homogenous polymer
Concentration difference	Diffusion dialysis (DD)	Small molecules, water	Large molecules	Nonporous or micro-porous
	Membrane extraction (ME)	Gases, solutes, vapours soluble in the extractant	Components of feed insoluble in extractant	Nonporous or micro-porous
Electrical potential difference	Electro-dialysis (ED)	Ionized solutes, water	Non-ionic solutes	Ion-exchange membrane
Temperature difference	Membrane distillation (MD)		Molecules < 1 nm	Micro-porous

1.2.1 Microfiltration (MF)

This refers to membranes that have pore size in the range of 0.1 – 10 µm. It is used to filter suspended particulates, larger bacteria, yeast, large colloids having molecular weight greater than 5000 kDa from solution and the transmembrane pressure used in microfiltration is less than 2 bar.

1.2.2 Ultrafiltration (UF)

The membrane pore size is in the range of 2 – 100 nm. It is used to filter dissolved macromolecules such as proteins and polymers having molecular weight in the range of 5 – 5000 kDa and the transmembrane pressure is in the range of 1 – 10 bar.

1.2.3 Nanofiltration (NF)

The membrane pore size is in the range of 1 – 2 nm. It is used to filter larger molecules having molecular weight of 0.1 – 5 kDa such as sugar; and the transmembrane pressure is in the range of 3 – 20 bar.

1.2.4 Reverse osmosis (RO)

Osmosis is the tendency of solvent molecules to pass through a semi-permeable membrane from low concentration side to high concentration side. This can be reversed by applying pressures higher than the osmotic pressure. In reverse osmosis, the water travels from the higher solute concentration side to lower solute concentration side of a semi-permeable membrane because of high applied pressure (10 – 80 bar). The membrane pore size is less than 1 nm. It is used to filter the dissolved species (M.W. < 0.1 kDa) present in feed and allow water to pass through it.

1.3 Advantages of ceramic membranes

Ceramic membranes are generally made of various inorganic materials such as silica, alumina, titania, zirconia, kaolin etc. They are either dense or porous. The dense membranes are used in gas separation and porous membranes are used in liquid filtration. Ceramic membranes have more advantages over polymeric membranes. Compared to polymeric membranes, ceramic membranes offer the following features:

a) high chemical, mechanical and thermal stability
b) withstand high temperatures and pressures
c) long durability and can be regenerated.

Since these membranes do not get seriously affected by the frequency and nature of cleaning, they can be subjected to aggressive cleaning agents, which is very much prevalent in industrial chemical processing units [2].

Chapter 2

LITERATURE REVIEW

2.1 Preparation of ceramic membranes

Since the ceramic membranes are more expensive than polymeric membranes, research is focused mainly on reducing the overall cost by using cheaper raw materials such as kaolin, clay and fly ash with low sintering temperatures (< 1000°C) [3-7]. Kaolin is the most widely used clay mineral in the fabrication of ceramic membranes due to its high refractive properties, low cost and abundant availability [8-12]. Other inorganic materials used in the fabrication of ceramic membranes include quartz, sodium carbonate, calcium carbonate, boric acid and sodium metasilicate [7].

In general, the ceramic membranes are fabricated by two methods: *paste casting method* and *dry compaction method*. Of these two methods, the paste method is widely used in the fabrication of ceramic membranes on a laboratory scale [7].

2.1.1 Paste method

In the paste method (Figure 2.1), the membrane fabrication process involves mixing and grinding of raw materials followed by addition of distilled water to make a thick and uniform paste. The paste is then casted in a circular ring and the wet disks are dried at room temperature. Then, the casted membranes are heated to 100°C in a muffle furnace and kept there for about 12 h. The membranes are kept at the desired sintering temperature (≈900°C) for about 4 h. This is then followed by slow cooling from sintering temperature to below 100°C. After sintering, the membranes become hard and porous. The membranes are then polished using SiC abrasive paper to remove dense silicate layer and make the surface smooth. Thereafter, the membranes are sonicated in an ultrasonication bath to remove soluble impurities and/or loose particles [13].

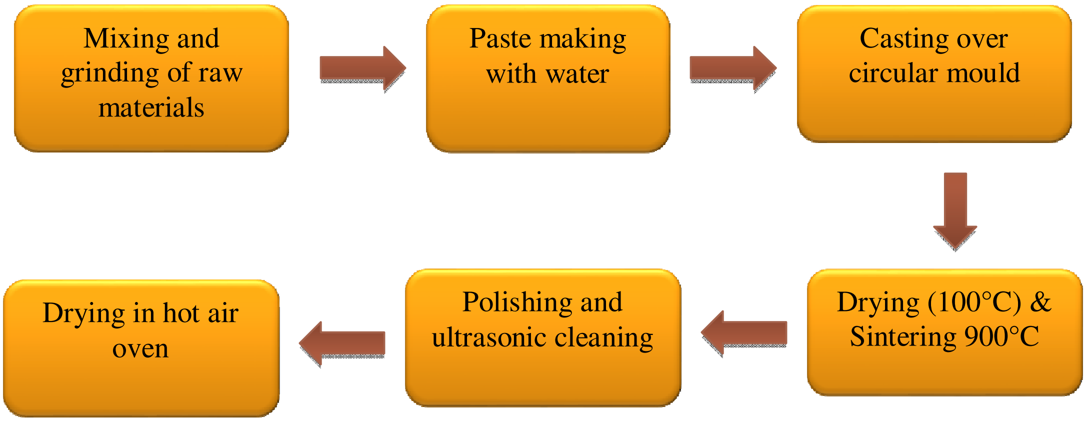

Figure 2.1: Paste casting method [7]

Manufacturing of kaolin based ceramic membranes by paste method became popular in 2008 when Nandi et al. [7] published a paper on the preparation and characterization of low cost inorganic membranes. In addition to kaolin, the authors also used some other raw materials such as quartz, sodium carbonate, calcium carbonate, boric acid and sodium metasilicate for membrane preparation and sintered their membranes at four different temperatures between 850 and 1000°C. They observed that the mean pore size increased from 550 nm to 810 nm, porosity decreased from 42% to 33%, mechanical strength increased from 3 to 8 MPa and the chemical stability was unaffected with increasing the sintering temperature. They estimated the raw-materials cost as $\$130/m^2$.

Later in 2009, Nandi et al. [5] used kaolin based ceramic membrane with an average pore size of 0.285 µm and porosity 23.6% for dead-end microfiltration (MF) of mosambi juice to remove high molecular weight pectic materials (cellulose/hemicellulose) and retain sucrose, citric acid, and flavor in the permeate. The authors observed that the pH and density of the permeate were the same as that of the original juice. They reported that the filtered juice can be stored under refrigeration for more than 30 days without any degradation of juice quality. They analyzed the flux decline by various pore blocking models.

In 2011, Jana et al. [3] used paste method to prepare circular shaped flat ceramic microfiltration membranes (50 mm diameter and 5 mm thickness) using different amounts of kaolin and clay, and sintered at 850–1000°C. They found that the mean pore size, permeability and mechanical strength increased, while, porosity (volume of pores ÷ total volume) and pore density (number of pores ÷ membrane area) decreased with increasing the sintering temperature. They also found that the pore diameter of membranes is inversely proportional to the ratio of kaolin to clay. The lowest mean pore size of 0.31 µm was obtained for the membrane prepared using 62% kaolin and 18% clay, and sintered at 1000°C. They also concluded that the particle size of raw materials controls the pore size of membrane.

Singh et al. [13] used fly ash as the main raw material along with other materials such as calcium carbonate and sodium metasilicate for economic fabrication of ceramic membranes and sintered at 800–1000°C. These membranes had moderate porosity (35–40%) and pore size (1.2–2.3 µm) with good chemical stability. They found that the sintering temperature of 900°C is optimum to achieve lowest mean pore size and uniform pore size distribution. They also showed the applicability of fly ash based membrane in microfiltration of oil-in-water emulsions with an oil rejection of 99.2%.

Kaur et al. [14] prepared kaolin based flat ceramic microfiltration membranes to use them as supports for cellulose acetate ultrafiltration membranes with different quantities of carbonates ($CaCO_3$ and Na_2CO_3) and sintered at 900°C. They noticed large pore size and low porosity for the supports that are prepared without using the carbonates. They found that addition of $CaCO_3$ increases the porosity of membrane with wider pore size distribution than those prepared with Na_2CO_3. They concluded that a small amount (10 wt%) of Na_2CO_3 can act as a pore modifier and results in small pores, whereas, excess amount (more than 20%) of Na_2CO_3 may block the pores due to the formation of sodium silicate layer.

Kaur et al. [15] studied the effects of carbonates compositions on the permeation characteristics of cost-effective ceramic membrane supports. They made kaolin based ceramic membrane supports using different quantities of calcium and sodium carbonates. They evaluated the mean pore size and water permeability in the range of 0.3–0.8 µm and 78–1027 L/h.m^2.bar, respectively. They obtained high porosity, permeability and chemical stability for calcium carbonate membranes, and high pore density and mechanical strength for sodium carbonate membranes. They concluded that 20 wt% $CaCO_3$ is optimum to achieve the best membrane having 0.5 µm pore size, 37% porosity and 48 MPa flexural strength, which can be used for microfiltration of oil-in-water emulsions.

Nandi et al. [12] prepared low-cost ceramic microfiltration membranes from kaolin by paste method and used for treatment of oily wastewater with varying trans-membrane pressures (41–165 kPa) and achieved 97% rejection for 50 mg/L crude oil concentration at 165 kPa transmembrane pressure. They modelled the permeate flux decline by intermediate pore blocking (for the first 10 minutes) followed by cake filtration (up to 30 minutes). They stated that the prepared membrane can be applied for the treatment of oil/water emulsions on industrial scale.

Nandi et al. [6] used kaolin based ceramic membrane with an average pore size of 0.285 μm and porosity 23.6% for dead-end microfiltration (MF) of orange juice and evaluated the fouling mechanism. They observed that the pH, acidity, total soluble solids and density of the juice were unaffected by microfiltration. However, they observed a significant improvement in juice color and clarity. They concluded that the enzyme treatment followed by microfiltration is highly effective for preservation/storage of orange juice.

Jana et al. [16] prepared clay based low-cost ceramic membranes to remove chromate ions from their aqueous solution by micellar enhanced microfiltration using cetylpyridinium chloride (CPC) as the surfactact and observed 100% separation of chromate ions at a feed ratio (surfactact/chromate) of 10. They found that the mean mechanical strength, permeability and pore size increased, while, porosity and pore density decreased with increasing the sintering temperature. The membrane sintered at 1000°C had 4.58 μm pore size, 42% porosity, 2.06×10^{10} m^{-2} pore density and 11.55 MPa of flexural strength. They estimated the raw materials cost of the membrane as \$19/m^2.

The above literatures are summarized and shown in Table 2.1.

Table 2.1: Summary of literature on paste method.

Author(s)	**Raw materials used**	**Sintering temperature**	**Membrane properties**	**Application**
Nandi et al. (2008)	Kaolin, calcium carbonate, boric acid	850–1000°C	Pore size: 0.55–0.81 µm Porosity: 33–42%	N.A.
Jana et al. (2010)	Clay, kaolin, sodium carbonate, boric acid	1000°C	Average pore size: 4.58 µm Porosity: 42%	N.A.
Nandi et al. (2009)	Kaolin, feldspar, sodium carbonate, boric acid	900°C	Average pore size: 0.285 µm Porosity: 23.6%	Filtration of mosambi juice
Jana et al. (2011)	Clay, kaolin, sodium carbonate, sodium metasilicate, boric acid	1000°C	Average pore size: 0.31 µm Porosity: 22%	Oil-water separation, fruit juice clarification
Singh et al. (2013)	Fly ash, sodium carbonate	900°C	Average pore size: 1.2-2.3 µm Porosity: 35-40%	Useful for microfiltration application
Kaur et al. (2015)	Kaolin, calcium carbonates, boric acid	900°C	Average pore size: 0.52 µm Porosity: 35%	N.A.
Kaur et al. (2016)	Kaolin, calcium carbonates, boric acid	900°C	Average pore size: 0.3-0.8 µm Porosity: 37%	Separation of oil-in-water emulsion
Nandi et al. (2010)	Kaolin, quartz, feldspar, sodium carbonate, boric acid, sodium metasilicate	900°C	Average pore size: 0.285 µm Porosity: 23.6%	Clarification of orange juice
Nandi et al. (2009)	kaolin, quartz, calcium carbonate, boric acid, sodium metasilicate	850°C	Average pore size: 0.55 µm Porosity: 42%	Treating oily waste water with low-cost ceramic membrane

2.1.2 Dry compaction method

In the dry compaction method (Figure 2.2), the membrane fabrication process involves mixing and grinding of raw materials followed by addition of poly-vinyl alcohol (PVA) as a binder. After mixing with PVA, a known amount of the raw materials powder is placed in a circular mould and compacted at a high pressure (50 MPa). Then, the casted membranes are heated to 100°C in a muffle furnace and kept there for about 12 h. The membranes are kept at the desired sintering temperature (≈900°C) for about 4 h. This is then followed by slow cooling from sintering temperature to below 100°C. After sintering, the membranes become hard and porous. The membranes are then polished using SiC abrasive paper to remove dense silicate layer and make the surface smooth. Thereafter, the membranes are sonicated in an ultrasonic bath to remove any loose particles and/or soluble impurities [8].

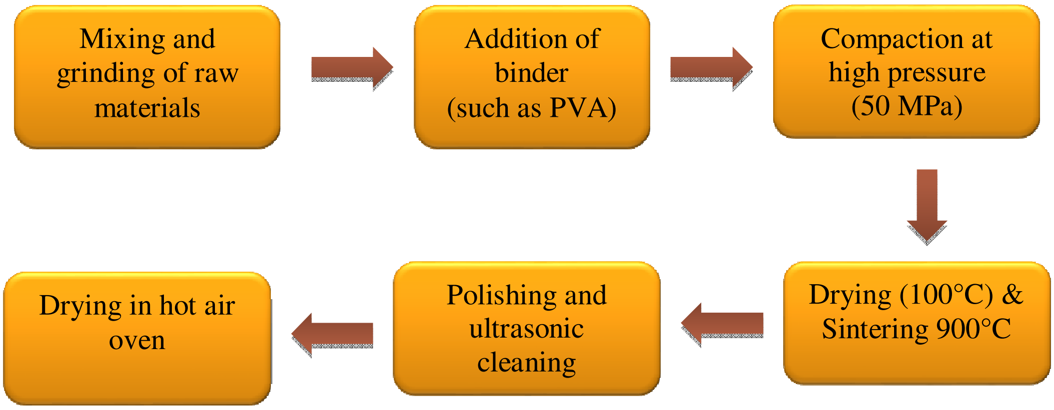

Figure 2.2: Dry powder compaction method [8].

Vasanth et al. [8] prepared kaolin based low-cost macroporous ceramic membrane supports by the dry compaction method using PVA as the binder and sintered at different temperatures in the range 900–1000°C. They found that the pore size and flexural strength of the membrane can be increased by increasing the sintering temperature. These membranes were found to have porosity in the range 22–40% with good mechanical strength and chemical stability.

Vasanth et al. [9] prepared low-cost ceramic membranes by the dry compaction method using mixtures of clays in different amounts and sintered at 900°C. They found that the raw materials composition had a significant impact on the membrane properties such as porosity (23–30%), pore size (0.45–1.30 μm) and flexural strength (10–34 MPa). All the prepared supports were found to be stable in both acidic and basic solutions. Further, they studied the performance of these supports for treatment of oil-in-water emulsions and achieved considerable oil rejection of 96% for 200 mg/L of oil concentration.

Kaniganti et al. [4] prepared kaolin based ceramic membranes by dry compaction method using PVA as binder and sintered at 900°C for the separation of bacteria (*E. coli*) from aqueous solution. They fabricated membranes with 39.4–19.3% porosity and 0.7–4.5 μm average pore size. The authors achieved very good bacterial removal efficiency (> 99%) with the membranes having large pore diameter (4.5 μm) and low porosity (19.3%).

Monash et al. [17] prepared ceramic microfiltration membranes by dry compaction method using different inorganic materials such as ball clay, feldspar, pyrophyllite, kaolin, quartz and calcium carbonate along with PVA as a binder and sintered at four temperatures (850–1000°C). They found that the membranes showed good chemical stability in 20 wt% solutions of HCl, H_2SO_4 and NaOH. They found that the pore size and mechanical strength increased, while, porosity decreased with increasing the sintering temperature. They considered the membrane sintered at 950°C having 44% porosity, 28 MPa flexural strength, and 1.01 μm pore size as the best one suitable for microfiltration applications.

Emani et al. [11] prepared kaolin based ceramic membranes by dry compaction technique using different compaction pressures (29, 39 and 49 MPa) and sintered at 900°C for the microfiltration of mosambi juice. They obtained moderate values of pore size (1.69–0.72 μm), porosity (35.4–39.4%) and flexural strength (7.81–11 MPa). They studied the filtration performance of the membrane compacted at 49 MPa in clarification of mosambi juice and achieved satisfactory results.

Emani et al. [10] studied the cross flow microfiltration of oil-in-water emulsions using kaolin based membranes. They prepared flat ceramic membranes by dry powder compaction method and obtained the higher average pore sizes (3.06–2.16 μm) and porosities (30.1–37.4%) which is used for cross flow MF studies. They conduct cross flow runs using a feed oil concentration of 400 mg/L of for various combinations of transmembrane pressures (138–207 kPa) and cross-flow velocities (Re = 3417–6835). They observed the flux decline data which refers to existence of one of the pore blocking phenomena (complete/intermediate/standard pore blocking) during the first 10 min of experimental run followed with cake filtration for the data obtained for later time periods. They obtained the steady state flux and rejection were

11.58%, 22.14 $\times 10^{-6}$ $m^3 m^{-2}$ s and 98.52%, respectively, at trans-membrane pressure (ΔP = 207 kPa), fabrication pressure (73 MPa) and minimal cross flow velocity (Re = 3417).

The above literatures are summarized and presented in Table 2.2.

Table 2.2: Summary of literature on compaction method.

Author(s)	**Raw materials used**	**Sintering temperature**	**Membrane properties**	**Application**
Vasanth et al. (2011)	Kaolin, sodium carbonate, boric acid	850–1000°C	Pore size: 550–810 nm Porosity: 33–42%	N.A.
Vasanth et al. (2013)	Kaolin, calcium carbonate, titanium dioxide	900°C	Pore size: 0.45-1.30 μm Porosity: 23-30%	N.A.
Kaniganti et al. (2015)	Kaolin, calcium carbonate, boric acid, polyvinyl alcohol (PVA)	900°C	Pore size: 0.7–4.5 μm Porosity: 39.4-19.3%	Bacteria separation from water
Monash et al. (2011)	Clay, kaolin, feldspar, quartz, calcium carbonate, poly vinyl alcohol	850–1000°C	Average Pore size: 1.01 μm Porosity: 41-46%	Microfiltration membrane for industrial use
Emani et al. (2013)	Kaolin, quartz, calcium carbonate, boric acid, poly vinyl alcohol	900°C	Average Pore size: 1.85-0.89 μm Porosity: 35.4-39.4%	Clarification of mosambi juice
Emani et al. (2014)	Kaolin, quartz, calcium carbonate, boric acid, poly vinyl alcohol	900°C	Average Pore size: 3.06-2.16 μm Porosity: 30.1-37.4%	Oil water emulsions

2.2 Applications of ceramic membranes

2.2.1 Separation of oil-water emulsion

Ceramics membranes have been used for separating oil-in-water emulsions [9,10,12,18]. The membrane acts as a barrier to oil droplets in the aqueous stream, due to their smaller pore size (relative to droplets' size) and chemical inertness. The separation of oil/water emulsions by ceramic microfiltration membranes is mainly due to the oil droplet size, which is greater than the membrane pore size. Up to 90% removal of oil has been achieved by Nandi et al. [12].

2.2.2 Removal of bacteria

Cross flow micro filtration can be used for removing bacteria and spores from skim milk. Ceramic membranes are typically tolerant to stronger detergents and higher temperatures than normal organic membranes. This is a beneficial feature when working with high concentrations of bacteria. Kaniganti et al. [4] applied kaolin based ceramic membranes for removal of bacteria from synthetic solutions.

2.2.3 Removal of dyes

Most ceramic membranes have slightly negative charge and they can be used for the ultrafiltration of dye solutions. When certain salts are added, the presence of ions in the solution (such as Na^+ or Cl^-) cause shielding of membrane charge by the counter ions, lower the electrostatic repulsions and allow passage of anionic low molecular weight dyes through the membrane pores. Nowak and Skowron [19] used ceramic ultrafiltration membranes for removal of anionic dyes of molecular weight above 600 Da and obtained good rejection of dyes (> 85%).

2.2.4 Removal of heavy metals

Jana et al. [17] used polymer enhanced ultrafiltration (PEUF) with ceramic membrane to remove Hg(II) and As(III) using polyvinyl alcohol (PVA) as the chelating polymer and investigated the effect of concentrations of PVA, arsenic and mercury on the removal efficiency of these heavy metal ions. They found that the heavy metal removal increased with the increase in polymer concentration and decreased with the increase in metal ion concentration in the feed.

2.3 Literature gap and objectives

In most of the studies reported in the literature, kaolin was used as the major raw material for the fabrication of cost-effective ceramic membranes having submicron range pores. In order to decrease the membrane cost further, fly ash was used as the no-cost raw material in some studies for fabrication of inorganic membranes. However, fly ash based membranes had larger pore size (> 2 μm), lower porosity (< 30%) and lower strength (< 20 MPa) than kaolin based membranes. Mixing of fly ash with kaolin may produce low cost membranes with good physical and pore characteristics. No studies have been reported on the fabrication of inorganic membranes using mixtures of fly ash and kaolin so far. Therefore, a combination of these two materials is studied in this work with an objective to reduce the cost of kaolin based membranes without compromising upon the permeation properties and strength.

The objectives of the present work are as follows:

1. Preparation of ceramic membranes using fly ash and kaolin in different compositions.
2. Characterization of membranes by TGA, SEM, and XRD.
3. Estimation of pore size and porosity of membranes by permeation test.
4. Determination of mechanical strength and chemical stability of the membranes.
5. Application of an optimized membrane for microfiltration of humic acid from water.

Chapter 3

MATERIALS AND METHODS

3.1 Raw materials

The main inorganic raw materials used in this work are fly ash, kaolin, calcium carbonate, sodium carbonate, boric acid and sodium metasilicate (Table 3.1). Of these materials, kaolin provides low plasticity and high refractory properties to the membrane. The physicochemical properties of fly ash such as surface area, water holding capacity, porosity, particle size, and bulk density make it suitable for ceramic membrane preparation. Calcium carbonate acts as pore forming agent. Boric acid acts as a colloidal agent and improves dispersion properties. Sodium metasilicate acts as a binder as it forms silicate bonds to impart high mechanical strength to the membranes.

All chemicals (sodium carbonate, calcium carbonate, kaolin, boric acid and sodium metasilicate) except fly ash were obtained from CDH India Ltd. Sodium carbonate, calcium carbonate, boric acid and sodium metasilicate were graded at least 99.5% pure and were used without any pre-treatment.

Table 3.1. Different raw material compositions used in membrane preparation.

Raw materials	**Amount used (wt.%) in different membranes**				
	M1	**M2**	**M3**	**M4**	**M5**
Fly ash	75	50	37.5	25	0
Kaolin	0	25	37.5	50	75
$CaCO_3$	15	15	15	15	15
Na_2CO_3	5	5	5	5	5
Boric acid	2.5	2.5	2.5	2.5	2.5
Na_2SiO_3	2.5	2.5	2.5	2.5	2.5

3.2 Membrane preparation

Five different ceramic membranes were prepared by paste casting method with different amounts of fly ash and kaolin. The compositions of different raw materials used are shown in Table 3.1. The procedure adopted in the membrane preparation is shown in Figure 3.1.

Firstly, the raw materials were accurately measured and then grinded properly in a ball mill. The grinding of fly ash with other raw materials takes an hour and the grinding of kaolin powder with other raw materials takes only ten minutes. Then, a measured quantity of distilled water was used to prepare a uniform and thick paste. The paste was pressed in a circular mould of 5 mm height and 50 mm diameter. Then, they were dried openly at ambient conditions for 12 h followed by drying at 100°C before sintering. Then, the membranes were placed in a muffle furnace for heating, and the furnace temperature was slowly increased to 250°C and again to 900°C. After reaching the sintering temperature (900°C), the membranes were kept for four hours and then cooled to below 100°C. The membranes were then polished with Silicon carbide abrasive papers C-220 and C-100 to obtain a smooth surface and cleaned in ultrasonication bath.

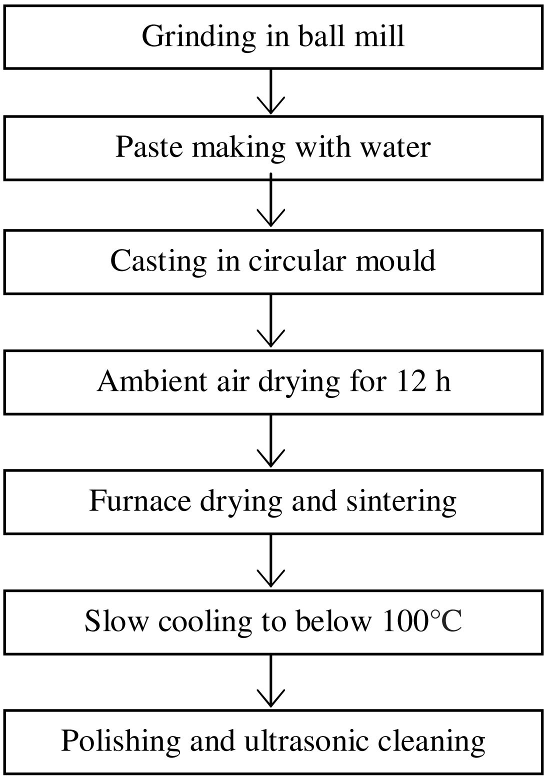

Figure 3.1. Methodology followed for membrane preparation

3.3 Characterization techniques

The characterization techniques include the thermo-gravimetric analysis (TGA), X-ray diffraction (XRD) and morphological study by scanning electron microscopy (SEM), permeation study, chemical stability test, strength determination using a UTM machine as described below.

- TGA of the raw material samples was done at IIT Roorkee to determine the weight loss of samples and select appropriate sintering temperature.
- XRD analysis of sintered membranes was done at SAI Labs, Thapar University, Patiala to identify various phase transformations.
- SEM analysis was done at SAI Labs, Thapar University, Patiala to study the morphology and to check pores and defects on the surface of the membranes.
- Porosity of the membranes was determined by the gravimetric method using water as wetting liquid.
- Pore size and permeability of membranes were determined from water permeation experiments.
- Chemical stability of the membrane was checked by subjecting membranes to HCl (pH 1) and NaOH (pH 13) solutions for 7 days.
- Mechanical strength was determined by a UTM machine at Chandigarh University to find out the flexural strength of the membranes.

3.4 Microfiltration of humic acid and regeneration of membrane

The microfiltration of aqueous solution of humic acid of concentration 50 mg/L was done on a selected membrane (M4) at two different transmembrane pressures (1 bar and 2 bar). The humic acid concentrations were estimated from the absorbance values obtained from a UV spectrophotometer at a wavelength of 254 nm [20] with the help of a pre-calibrated curve. The used membrane was regenerated (after using it for 20 min, i.e., when the flux became half of the initial flux) by cleaning the membrane using a surfactant solution manually, followed by back-flushing with distilled water.

3.5 Repeatability of data

Each experiment was conducted five times and the average values are reported. The repeatability was found to be good because the maximum error and standard deviation were less than 5% and 4%, respectively.

Chapter 4

RESULTS AND DISCUSSION

4.1 Physical observations

Five different sets of membranes were prepared using five compositions given in Table 3.1 with varying amounts of fly ash and kaolin as major raw materials along with 15% $CaCO_3$, 5% Na_2CO_3, 2.5% boric acid and 2.5% sodium metasilicate as other constituents.

The physical appearance of the membranes changed with changing the composition as shown in Figure 4.1. It was noticed that the membrane made of fly ash (i.e. M1) was fully textured in greyish colour and the one prepared using kaolin (M5) was whitish in color, while, those prepared using mixtures of these two materials (M2, M3, and M4) were partially textured.

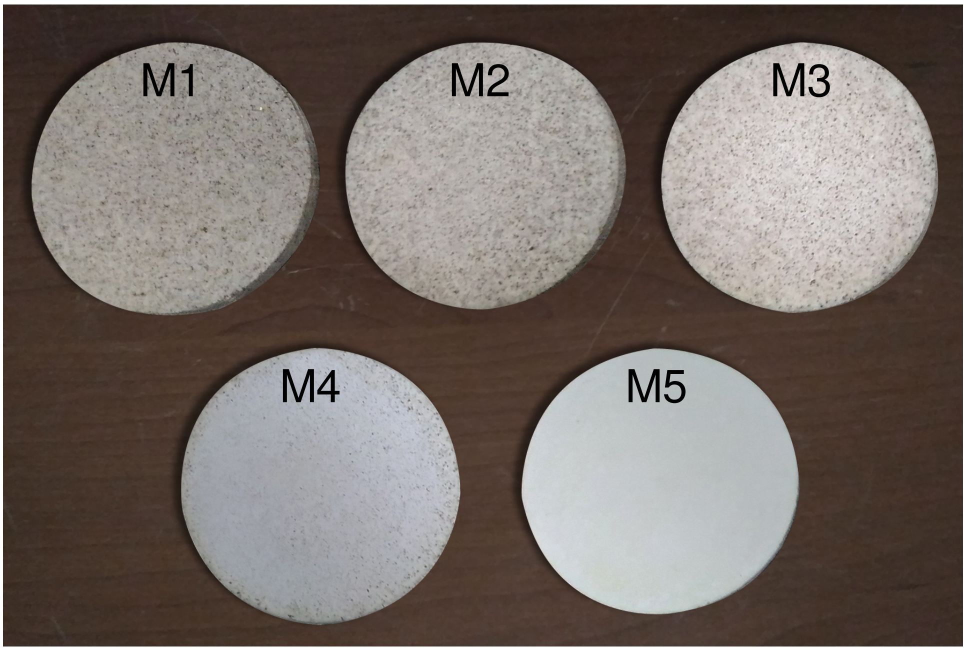

Figure 4.1. Photographs of membranes of different compositions.

4.2 Thermo-gravimetric analysis

The aim of thermo-gravimetric analysis (TGA) is to identify weight loss with increment of temperature that is from 20°C to 1000°C at a heating rate of 10°C/min. With increase of temperature, several phase transformations occur in the membrane. It is very useful to identify the optimum sintering temperature and analyze the porosity results. TGA of different raw material mixtures was conducted (under N_2 atmosphere) at IIT Roorkee to identify the thermal transformations of the material at sintering conditions. Figure 4.2 shows the TGA curves of five different compositions used in this work.

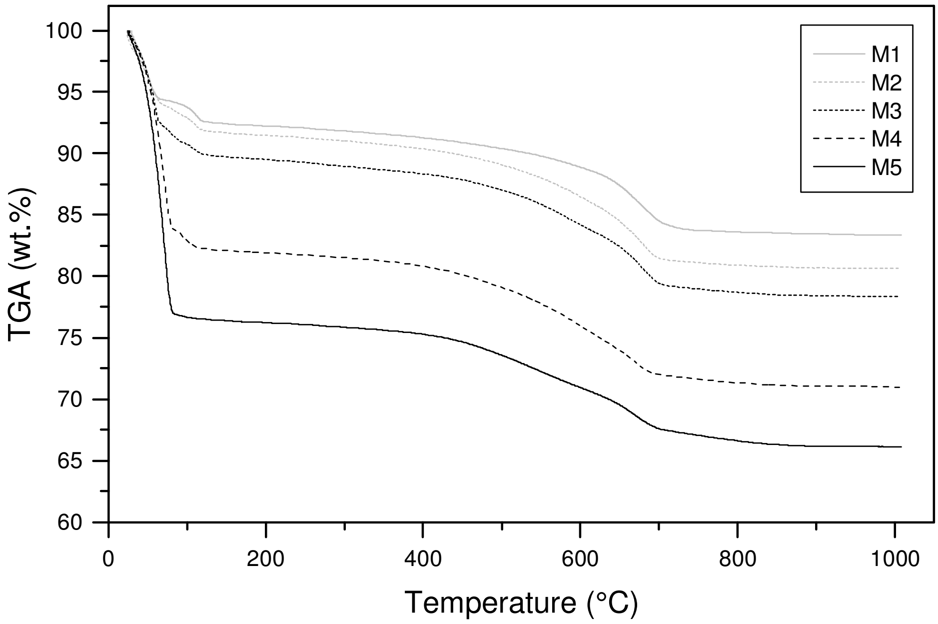

Figure 4.2. TGA curves of different raw material mixtures.

As shown in Figure 4.2, the initial weight loss noticed up to 120°C was due to the evaporation of free moisture (i.e. water added for paste making) and a little weight loss between 120 and 250°C was due to the evaporation of bound moisture (i.e. moisture present in the particle structures of kaolin, sodium metasilicate and other raw materials). The initial weight loss was the lowest for M1 and highest for M5 as kaolin mixture requires more water to be added than fly ash mixture for making a uniform paste. The weight loss between 400 and 600°C is due to the phase transformation of kaolin ($Al_2Si_2O_5(OH)_4$) to metakaolin ($Al_2Si_2O_7$) accompanied by release of water, which induces mechanical strength as well as porosity to the membranes. The weight loss in this region was negligible for fly ash membrane (M1) and it increased with increasing the kaolin content. Further, weight loss between 600 and 800°C observed in all the five compositions was due to the decomposition of calcium carbonate into calcium oxide. This is accompanied by the release of carbon dioxide and increases porosity. The total weight loss was the highest for kaolin membrane (M5) and lowest for fly ash membrane (M1).

4.3 Surface morphology

The prepared membranes are analyzed by scanning electron microscopy (SEM) and corresponding images are shown in Figure 4.3. The SEM pictures indicated that no cracks are present in all five membranes and that the membrane surface is free from any defects.

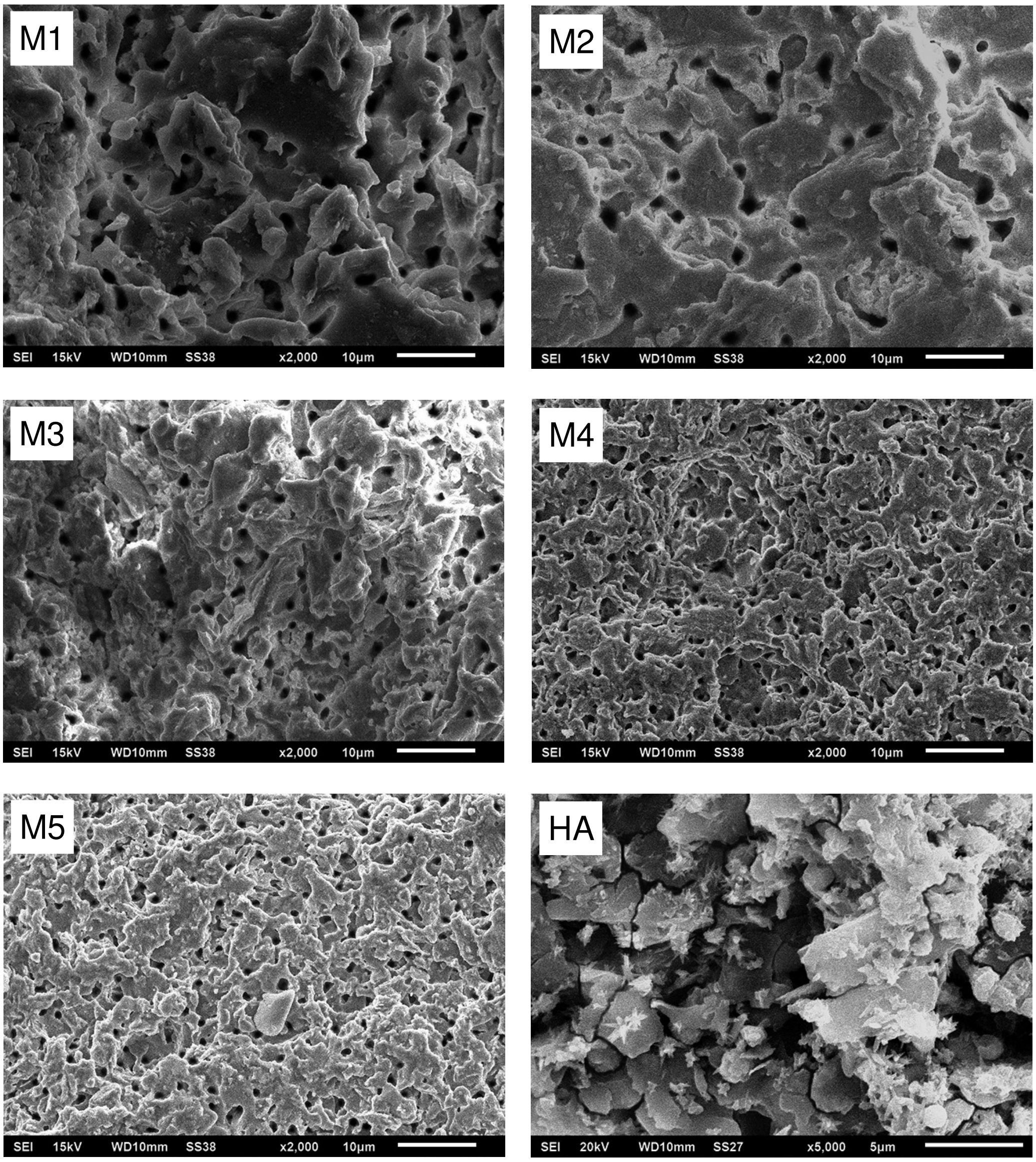

Figure 4.3: SEM pictures of different membranes (M1–M5) and humic acid particles (HA).

It can be observed from these pictures (Figure 4.3) that the surface morphology changed gradually with changing composition and a small number of large pores are evident for fly ash rich membranes (M1 and M2) whereas a large number of small pores are present on the surface of kaolin rich membranes (M4 and M5).

4.4 Phase identification by X-ray diffraction analysis (XRD)

X-ray diffraction (XRD) analysis was used to identify various phase transformations during the sintering process. The XRD patterns of five membranes are shown in Figure 4.4 and the minerals identified are listed in Table 4.2. As shown in the figure, anorthite, which is formed by the interaction of CaO with alumina and silica structures during the sintering stage, is present in all the membranes in moderate amounts.

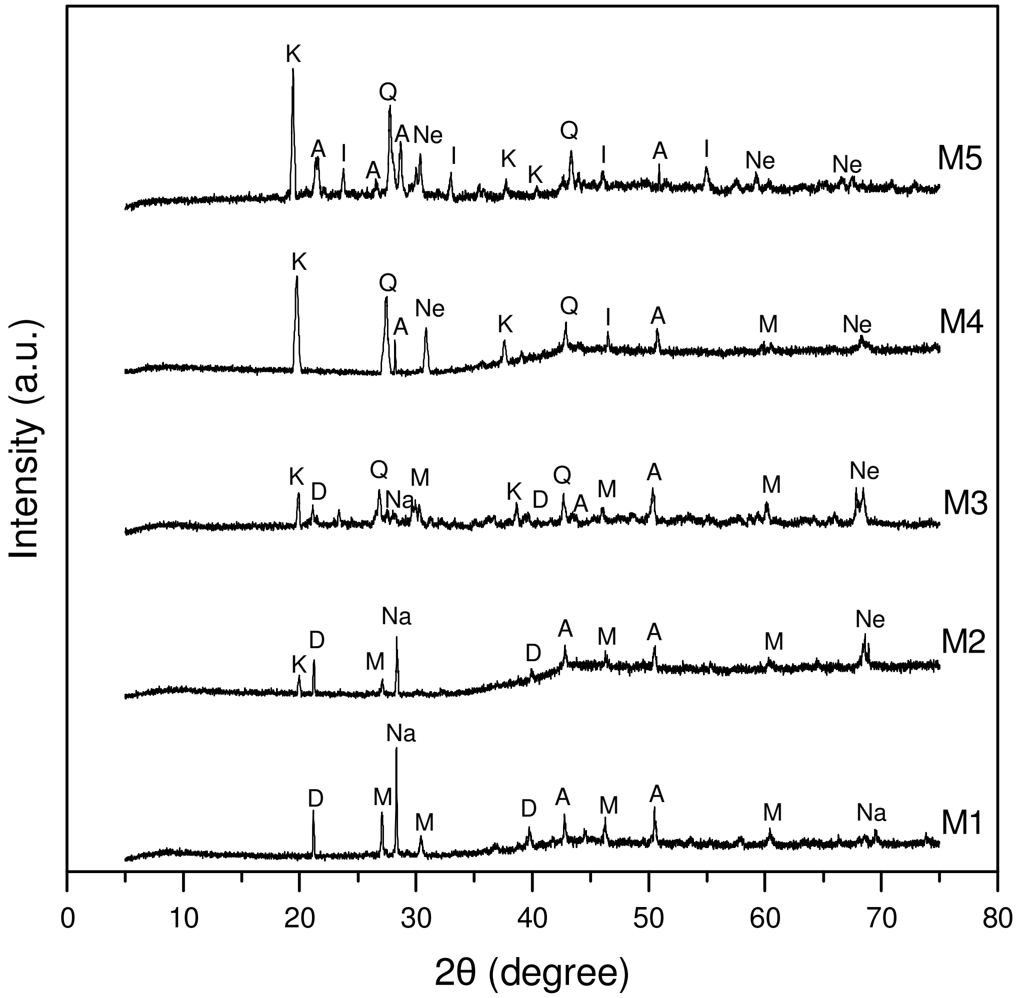

Figure 4.4: XRD analysis of different membranes.

The fly ash based membrane (M1) mainly contained nacrite and dickite along with traces of mullite. The kaolin based membrane (M5) contained metakaolinite and quartz in high amounts along with nepheline in moderate amount. However, the membranes prepared using mixtures of fly ash and kaolin (M2–M4) contained all of these minerals in different proportions. The amounts of nacrite, dickite and mullite decreased, while the amounts of meta-kaolinite, quartz and nepheline increased with increasing the kaolin/fly ash ratio (from M1 to M5). The hardness values of all these minerals are presented in Table 4.2.

Table 4.2: List of minerals identified by XRD analysis.

Notation used	**Name of the mineral**	**Chemical formula (repeating units)**	**Mohs hardness (1–10 scale)**
A	Anorthite	$CaAl_2Si_2O_8$	6.0
D	Dickite	$Al_2Si_2O_5(OH)_4$	1.5–2
I	Illite	$K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$	1–2
K	Meta-kaolinite	$Al_2Si_2O_7$	4–5
M	Mullite	$Al_6Si_2O_{13}$	6–7
Na	Nacrite	$Al_2Si_2O_5(OH)_4$	2–2.5
Ne	Nepheline	$NaAlSiO_4$	6
Q	Quartz	SiO_2	7

4.5 Water permeation results

The pore size and hydraulic permeability of the membranes was determined from water permeation experiments. The porosity was determined by gravimetric method using water as the wetting medium. Initially, the thickness and diameter of membranes were measured at different locations and their average values were determined for calculating the total volume. Then the dry weights of the membranes were estimated. The membranes were dipped in water and sonicated in an ultrasonic bath for 15 minutes and their wet weight was estimated. The volume of the pores was calculated as the difference between the wet and dry weights of the membranes divided by the density of water. Then the porosity was calculated as the ratio of pore volume to the total volume.

The water permeation tests were conducted for all the five membranes using a permeation setup shown in Figure 4.5. Initially the cell was filled with water and compacted for about two hours. Then, different pressures were applied by means of an air compressor and the corresponding flowrates of permeated water were noted for each pressure. The average pore size or mean pore diameter (d_p) and permeability (L_h) are determined from water permeation (J versus ΔP) using the following correlations [7].

$$\text{Porosity, } \varepsilon = \frac{\text{pore volume}}{\text{total volume}} \tag{4.1}$$

$$\text{Flux, } J = \frac{n\pi r^4 \Delta P}{8\mu l} = L_h \Delta P \tag{4.2}$$

$$\text{Pore size, } \mathrm{d_p} = 2r = 2\times\left[\frac{8\mu l L_h}{\varepsilon}\right]^{0.5} \tag{4.3}$$

The water flux values (J) of different membranes at different transmembrane pressures (ΔP) are shown in Figure 4.6. The slopes of these plots represent the hydraulic permeability of the membranes. As shown in the figure, the permeabilities of membranes decreased with increasing the kaolin content. The highest value (3369.5 L/m^2.h.bar) was oberved for fly ash based membrane (M1) and the lowest value (780.7 L/m^2.h.bar) was observed for the kaolin based membrane (M5).

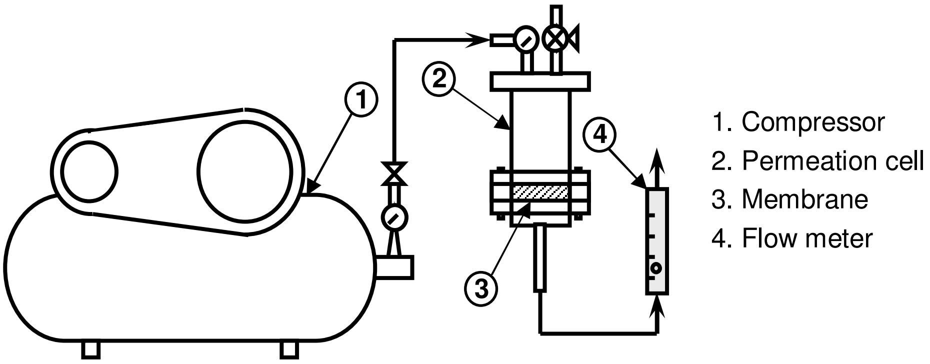

Figure 4.5. Setup used for water permeation experiments.

The calculated values of pore size and porosity of the five membranes are plotted in Figure 4.7. As shown in this figure, the porosity was lowest for fly ash based membrane (M1) and highest for kaolin based membrane (M5) and it increased with increasing the kaolin content from M2 to M4. This can be correlated to the results of thermogravimetric analysis (discussed in section 4.2), which indicated maximum weight loss for M5 and minimum weight los for M1 because of the transformation of kaolin to metakaolin accompanied by the release of water vapor. The porosity of the membranes was proportional to the total weight loss observed during the sintering process. Also, the pore size of the membranes decreased gradually with increasing the kaolin content (from 2.3 μm for M1 to 0.73 μm for M5). Therefore, it can be concluded that an increase in kaolin content leads to decrease in pore size and increase in porosity of membrane.

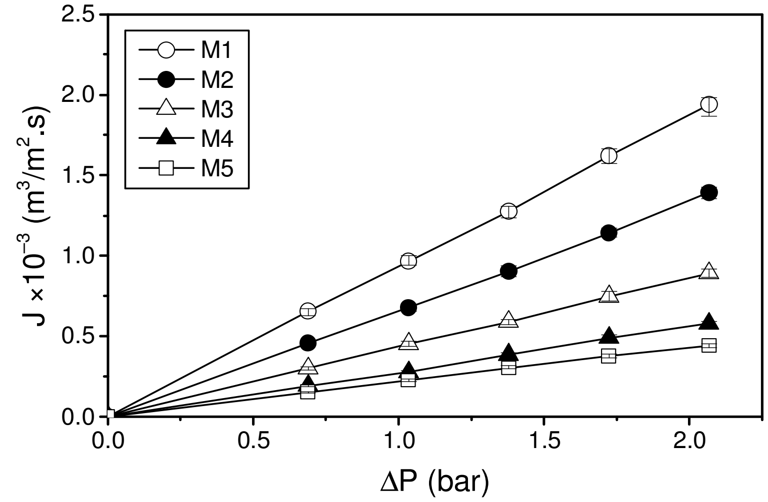

Figure 4.6. Water permeation data of different membranes.

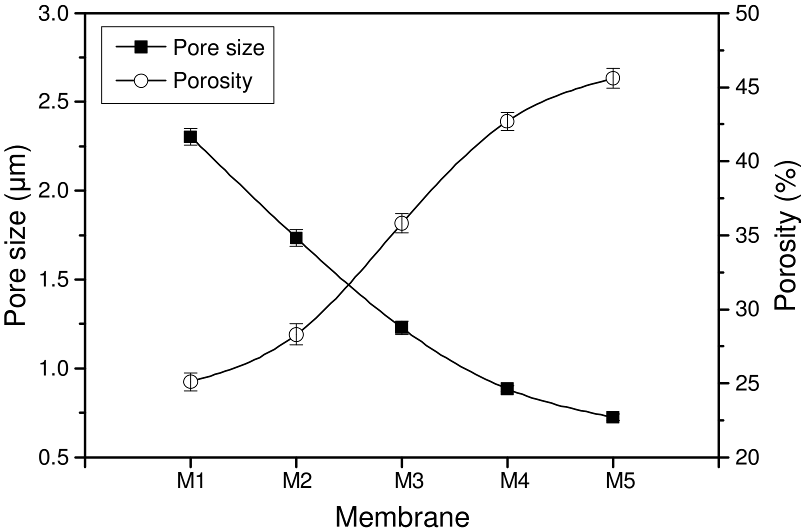

Figure 4.7. Pore size and porosity versus membrane composition.

4.6 Mechanical strength

A good ceramic membrane should have a high mechanical strength (> 30 MPa) to use it as a support for ultra- and nano-filtration applications. The mechanical strength testing was done by three point bending method as per ASTM C1161-13 standard on a universal testing machine (UTM) available at Chandigarh University. The mechanical strength is generally expressed in the terms of flexural strength (σ) which is calculated using the formula:

$$\sigma = \frac{3Fl}{2bt^2} \tag{4.4}$$

where, F (N) is the load (force) at fracture point, l (mm) is the span length, t (mm) is the thickness and b (mm) is the width of the specimen. Samples are subjected to a preload of 0.5 N at a test speed of 10 mm/min. The results (Figure 4.8) showed that the mechanical strength increases proportionally with increasing the kaolin content. The fly ash based membrane (M1) had the lowest strength (19.5 MPa) as it contained low hardness minerals nacrite and dickite (refer to XRD results discussed in section 4.4). The kaolin based membrane (M5) had the highest strength (48.2 MPa) due to the presence of high hardness minerals metakaolin, quartz and nepheline.

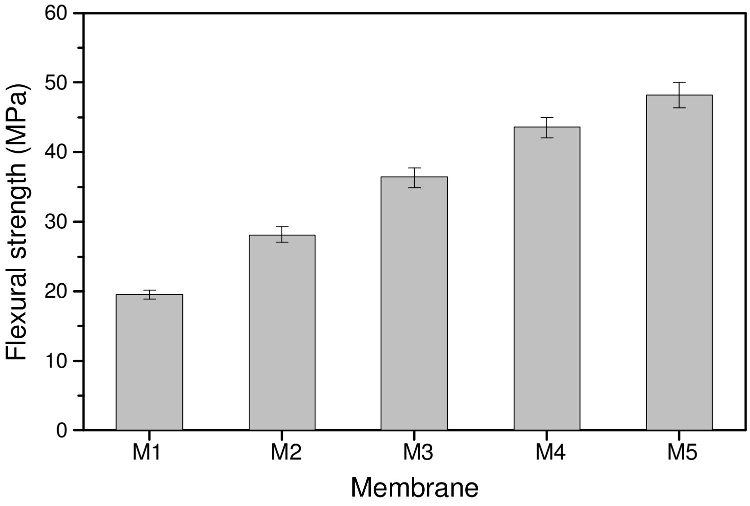

Figure 4.8. Mechanical strength of different membranes.

4.7 Corrosion test results

Figure 4.9 shows the weight loss (%) of different membranes in acidic (HCl, pH = 1) and basic (NaOH, pH = 13) solutions. Membranes were kept in HCl and NaOH solutions for seven days to determine the chemical stability. The weight loss (%) of the membranes was determined by measuring the dry weights before and after soaking in these solutions. Below figure (Figure 4.9) shows that all the membranes have very good chemical stability against basic solutions, with negligible weight loss. However, in acidic solution, the weight loss of M1 and M2 (> 4%) is considerably higher than that of the other membranes M3, M4 and M5. Hence, the membranes M1 and M2 are not suitable for microfiltration of acidic solutions.

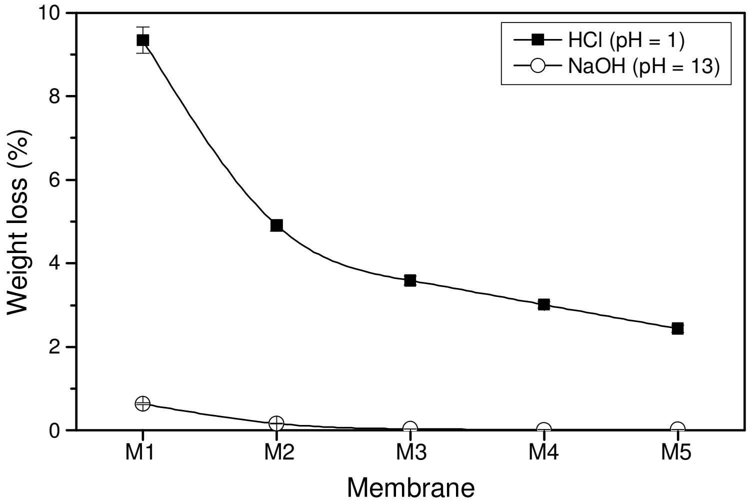

Figure 4.9. Weight loss (%) versus membrane composition.

4.8 Selection of optimum composition

Based on the results discussed in the above sections, membranes M4 and M5 have the desirable characteristics in terms of pore size (< 1 μm), porosity (> 40%), mechanical strength (> 40 MPa) and chemical stability (< 3% weight loss). Both these membranes are equally good. However, M4 membrane is relatively less expensive as it contains 25 wt% fly ash and 50 wt% kaolin than M5 membrane, which contains 75 wt% kaolin. Therefore, the membrane M4 was chosen as the best low-cost membrane and also used for separation of humic acid from its aqueous solution.

4.9 Microfiltration of humic acid solution

The optimized membrane (M4) has been used for microfiltration experiments to separate humic acid (an essential component of fertilizers used to improve water holding capacity of soils) from its aqueous solution. It has been reported in literature that humic acid is found in surface water up to a concentration of 50 mg/L. and the environmental protection agency (EPA) has imposed a limit of 2 mg/L in drinking water. In general, the particle size of humic acid ranges from 1 – 50 μm with flaky structure (see Fig. 4.3). Hence, it can be separated by using microfiltration membranes. The permeation setup shown in Figure 4.5 was used for the microfiltration of 50 mg/L aqueous solution of humic acid at two different transmembrane pressures (1 bar and 2 bar).

The plots of permate flux and humic acid rejection are shown in Figure 4.10. The permeate flux decreased with filtration time for both the transmembrane pressures as shown in Figure

4.10 (a). The observed flux decline was due to the pore blocking caused by the accumulation of humic acid particles near the pore openings. This phenomenon is quite common in dead-end filtration as the solute particles rejected by the membrane polarize near the membrane surface. The regenerated membrane also produced a permeate flux similar to that of the original membrane with only 5% loss.

As shown in Figure 4.10 (b), the M4 membrane was good enough to reject more than 90% of the humic acid from its aqueous solution. The rejection values for a transmembrane pressure of 1 bar ranged between 97.1 – 99.8% with an average rejection of 98.46%. The average concentration of humic acid in the permeate was 0.77 mg/L. This value is well below the permissible limit for drinking water standards (i.e. 2 mg/L). Therefore, the M4 membrane prepared in this work is useful for purification of water contaminated with humic acid for drinking purposes.

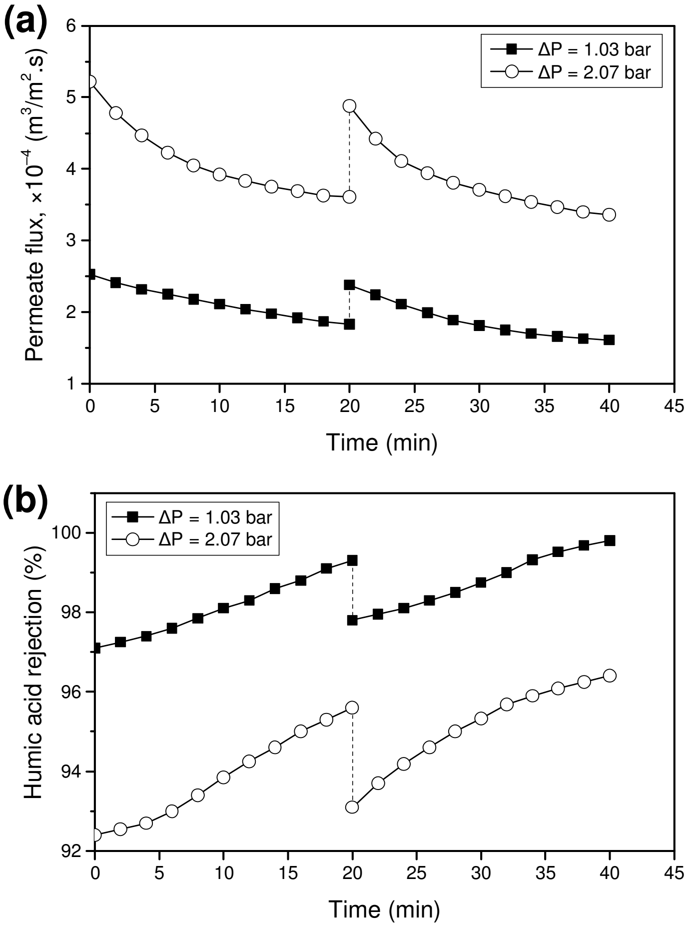

Figure 4.10: Flux (a) and rejection (b) profiles observed for membrane M4.

On the other hand, the rejection values at 2 bar pressure difference ranged between 92.4 – 96.4% with an average rejection of 94.49%. This corresponds to an average humic acid concentration of 2.75 mg/L, which is above the permissible limit. This is because of passage of solute through the membrane pores caused by breaking/folding of humic acid particles at high pressure. Though, high pressure results in increase of permeate flux, it compromises upon the permeate quality. Therefore, the M4 membrane should not be used at high transmembrane pressure (2 bar).

Chapter 5

CONCLUSIONS AND FUTURE SCOPE

Ceramic microfiltration membranes have been prepared using five different compositions formulated with different amounts of fly ash and kaolin. With the help of TGA of the raw material mixtures, the sintering temperature has been selected as 900°C. It was also observed from the TGA that the weight loss during the sintering process increases with increasing the kaolin content due to release of water in the transformation of kaolin to metakaolin. The SEM analysis of the sintered membranes evidenced a large amount of small pores on the surface of M4 and M5 membranes. The XRD analysis revealed the presence of metakaolin, quartz and nepheline in kaolin rich membranes. The water permeation study indicated that the porosity of the membranes increases and pore size decreases with increasing the kaolin content in the raw materials mixture. The mechanical strength and chemical stability also increased with increasing the kaolin content. The M4 membrane has been selected for further use since it has a good combination of pore size (0.885 μm), porosity (42.7%), mechanical strength (43.6 MPa), and chemical stability (< 3% weight loss in acid and 0.02% in base). Aqueous solution of humic acid was prepared with a concentration of 50 mg/L and used as feed for microfiltration experiment with M4 membrane at two different transmembrane pressures (1 bar and 2 bar). It was noticed that a pressure difference of 2 bar resulted in superior flux, while, a pressure difference of 1 bar resulted in better rejection of humic acid (98.46%) and good permeate quality (0.77 mg/L). Therefore, the membrane M4 has been successfully applied in the separation of humic acid from water.

There is a great scope for continuing this research (listed below), which can be taken as future work.

- The performance of M4 membrane can be compared with that of M1 and M5.
- The applicability of prepared membranes can be tested for separation of oil-water emulsions, bacteria solutions, clarification of fruit juices, removal of suspended particles and wastewater treatment.
- The prepared membranes can be used as supports for ultrafiltration and nanofiltration membranes.

References

[1] Mulder, M. (1992) Basic principles of membrane technology, 1st Ed., Kluwer Academic Publishers.

[2] Membrane technology – wikipedia, available at: http://en.wikipedia.org/wiki/ Membrane_technology (last accessed: June 2017).

[3] Jana, S.; Purkait, M.K.; Mohanty, K. (2011) Preparation and Characterizations of Ceramic Microfiltration Membrane: Effect of Inorganic Precursors on Membrane Morphology, Separ. Sci. Technol., 46, 33–45.

[4] Kaniganti, C.M.; Emani, S.; Thorat, P.; Uppaluri, R. (2015) Microfiltration of synthetic bacteria solution using low cost ceramic membranes, Separ. Sci. Technol., 50, 121–135.

[5] Nandi, B.K.; Das, B.; Uppaluri, R.; Purkait, M.K. (2009) Microfiltration of mosambi juice using low cost ceramic membrane J. Food Eng., 95, 597–605.

[6] Nandi, B.K.; Das, B.; Uppaluri, R. (2012) Clarification of orange juice using ceramic membrane and evaluation of fouling mechanism, J. Food Eng., 35, 403–423.

[7] Nandi, B.K.; Uppaluri, R.; Purkait, M.K. (2008) Preparation and characterization of low cost ceramic membranes for micro-filtration applications. Appl. Clay Sci., 42, 102–110.

[8] Vasanth, D.; Uppaluri, R.; Pugazhenthi, G. (2011) Influence of sintering temperature on the properties of porous ceramic support prepared by uniaxial dry compaction method using low-cost raw materials for membrane applications, Separ. Sci. Technol., 46, 1241–1249.

[9] Vasanth, D.; Uppaluri, R.; Pugazhenthi, G. (2013) Performance of low cost ceramic microfiltration membranes for the treatment of oil-in-water emulsions, Separ. Sci. Technol., 48, 849–858.

[10] Emani, S.; Uppaluri, R.; Purkait, M.K. (2014) Cross flow microfiltration of oil–water emulsions using kaolin based low cost ceramic membranes, Desalination, 341,61–71.

[11] Emani, S.; Uppaluri, R.; Purkait, M.K. (2013) Preparation and characterization of low cost ceramic membranes for mosambi juice clarification, Desalination, 317, 32–40.

[12] Nandi, B.K.; Uppaluri, R.; Purkait, M.K. (2009) Treatment of oily waste water using low-cost ceramic membrane: flux decline mechanism and economic feasibility, Separ. Sci. Technol., 44, 2840–2869.

[13] Singh, G; Bulasara, V.K. (2013) Preparation of low-cost microfiltration membranes from fly ash, Desalin. Water Treat., 53, 1204–1212.

[14] Kaur, H.; Bulasara, V.K.; Gupta, R.K. (2016) Preparation of kaolin-based low-cost porous ceramic supports using different amounts of carbonates, Desalin. Water Treat., 53 (5), 1204–1212.

[15] Kaur, H.; Bulasara, V.K.; Gupta, R.K. (2016) Effects of carbonate composition on the permeation characteristics of low-cost ceramic membrane supports, J. Ind. Eng. Chem., 44, 185–194.

[16] Jana, S.; Saikia, A.; Purkait, M.K.; Mohanty, K. (2011), Chitosan based ceramic ultrafiltration membrane: Preparation, characterization and application to remove Hg(II) and As(III) using polymer enhanced ultrafiltration, Chem. Eng. J., 170, 209–219.

[17] Monash, P.; Pugazhenthi, G. (2011) Development of ceramic supports derived from low-cost raw materials for membrane applications and its optimization based on sintering temperature, Int. J. Appl. Ceram. Technol., 8, 227–238.

[18] Vieira, T.M.; Souza, J.S.; Barbosa1, E.S.; Cunha, A.L.; Neto, S.R.F. (2012) Numerical study of oil/water separation by ceramic membranes in the presence of turbulent flow, Adv. Chem. Eng. Sci., 2, 257–265.

[19] Nowak, M.K; Skowron, K.J. (2011) Ceramic membrane behaviour in anionic dye removal by ultrafiltration, Desalin. Water Treat., 34, 367–373.

[20] Shamsuddin, N.; Das, D.B.; Starov, V.M. (2015) Filtration of natural organic matter using ultrafiltration membranes for drinking water purposes: Circular cross-flow compared with stirred dead end flow, Chem. Eng. J., 276, 331–339.