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An Overview of Production and Development of Ceramic Membranes

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Abstract

Ceramic membranes became one of the most important ceramic products because of their numerous benefits. Many attempts have been made by researchers to produce ceramic membranes with modified properties by varying their raw materials. Some of these attempts included incorporating wastes into their production process. Examples of such waste are fly ash wastes, glass waste, mud resulting from the hydro cyclone laundries, cortical bone animal, coal gangue, sawdust, construction waste and rice husk. An ideal waste would be priceless waste while at the same time assisting minimizing pollution. Such a situation deals with a dual economic and environmental aspect. This paper reviews the different methods used for ceramic membranes production using traditional raw materials or different types of wastes.

Keywords: ceramic membranes-waste recycling-membrane operations-membrane geometrical configuration.

INTRODUCTION

A membrane is a selective barrier that allows some components to pass while other components remain retain in the liquid phase. The feed stream is the influent stream to the membrane, the liquid that passes through the membrane is called permeate while the retentate is the liquid consisting of the retained constituents.

Membrane separation technologies are finding increased interest because of the increase in environmental regulations and the demand for desalinated water. Membranes reduce waste disposal expenditure and allow for material recovery and recycling resulting in an economic advantage. The usage of membranes has become a standard procedure during the last two decades due to the previous reasons. They can are widely used in micro-filtration, ultra-filtration and nano-filtration particularly in water and wastewater treatment.

According to the material of construction, the main types of membranes are polymer and ceramic membranes. These latter are fabricated from inorganic materials such as alumina oxides, zirconia, and titania. Ceramic membranes are usually more costly than polymer types because their starting materials are more expensive besides the complexity of their fabrication. However, ceramic membranes are characterized by long term durability, high mechanical strength, resistance to chemicals and solvents and thermal stability. Actually using ceramic membrane instead of conventional steps in water treatment (coagulation, sedimentation, and filtration) has proved to be more advantageous and effective [Gaulinger, 2007; Peng, 2008].

Ceramic membranes are generally composed of three layers. The inner layer is the porous supported layer which provides a high mechanical strength for the fabricated membrane. The second one is the intermediate layer which is coated over the supported layer and characterized by a lower pore size. Because of the difference in pore size between the support layer and the top layer, the intermediate layer acts as a bridge between these two layers. The last one is the top layer at which the separation takes place [Li, 2007; Peng, 2008; Synthetic Membrane, 2013].

There are various methods for fabricating ceramic membranes from their raw materials. These methods include slip casting, tape casting, pressing, extrusion, sol-gel process, dip coating, chemical vapour deposition, and anodic oxidation. The selection of any preparation method depends on the application and the desired membrane structure [Li, 2007].

TYPES OF CERAMIC MEMBRANES

Ceramic membranes can be categorized according to their structure into porous or dense membranes.

Porous membranes

A porous membrane is generally characterized by pore size, surface porosity and thickness. The pore size of these membranes is the only factor which controls the application in which the porous membranes can be used. Table (1) summarizes the different types of ceramic membranes used for separation according to their pore size [Li, 2007; Giwa and Ogunribido, 2012; Ceramic Membrane, 2013].

Porous membranes are typically used for solid-liquid and solid-gas separation. The structure of a porous ceramic membrane can be symmetric if its pores are more or less equally sized throughout its structure or asymmetric when pore size gradually decreases towards the surface where separation occurs. Separation mechanism in porous membranes takes place by molecular sieving [Tsuru, 2008; CSEM-UAE Innovation Center LLC, 2012].

Micro-filtration membranes are an excellent choice to remove suspended matter and bacteria. However, they fail to remove dissolved substances and some microorganisms. Thus, removing viruses and dissolved substances such as salt in seawater will required smaller pore size characteristic of nano-filtration [Gaulinger, 2007].

Table 1: Types of ceramic membrane

Type	**Pore size (nm)**	**Application**
Macro-porous	> 50	UF, MF
Meso-porous	2-50	UF, NF, GS
Micro-porous	< 2	GS
Dense	-	GS, reaction
UF: ultra filtration NF: nano filtration MF: microfiltration GS: gas separation		

Dense membranes

This membrane type has a very complex permeation principle and separation technique. It is used for gas separation, for example the oxygen transportation in zirconium oxide at high temperature. The separation technique of non-porous membranes takes place through a solution-diffusion mechanism at which the permeating molecules are first dissolved into the membrane, then diffuse and finally desorbs from the membrane [Tsuru, 2008; CSEM-UAE Innovation Center LLC, 2012].

Geometrical configuration of membranes

Plate and Frame (Pillow-shaped) membranes

Membranes that consist of flat plates are called pillow-shaped membranes (Fig. 1). The name pillow-shaped membrane comes from the pillow-like shape that two membranes have when they are packed together in a membrane unit. Inside the 'pillow' is a supporting plate, which attends solidity. Within a module, multiple pillows are placed with a certain distance between them, which depends on the dissolved solids content of the wastewater. The water flows through the membranes inside out. When treatment is done, permeate is collected in the space between the membranes, where it is carried away through drains [Baker, 2000; Li, 2007].

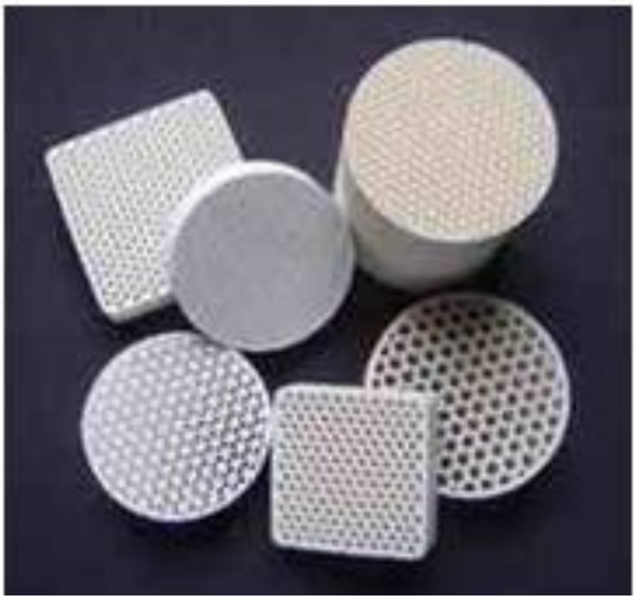


Figure 1: Plate and frame ceramic membranes

Tubular-shaped membranes

Tubular / straw membranes:

Generally used for viscous or bad quality fluids. These modules do not need a preliminary pre-treatment of the water. As the feed solution flows through the membrane core, the permeate passes through the membrane and is collected in the tubular housing. Tubular membranes is the most used membranes seen the costs and effect, shall not easily be polluted. Tubular membranes are not self-supporting membranes. They are located on the inside of a tube, made of a special kind of material. This material is the supporting layer for the membrane. Because the location of tubular membranes is inside a tube, the flow in a tubular membrane is usually inside out. The main cause for this is that the attachment of the membrane to the supporting layer is very weak. Tubular membranes have a diameter of about 5 to 15 mm. Because of the size of the membrane surface, plugging of tubular membranes is not likely to occur. A drawback of tubular membranes is that the packing density is low, which results in high prices per module. The following figure shows the shape of tubular / straw membranes [Baker, 2000; Li, 2007].

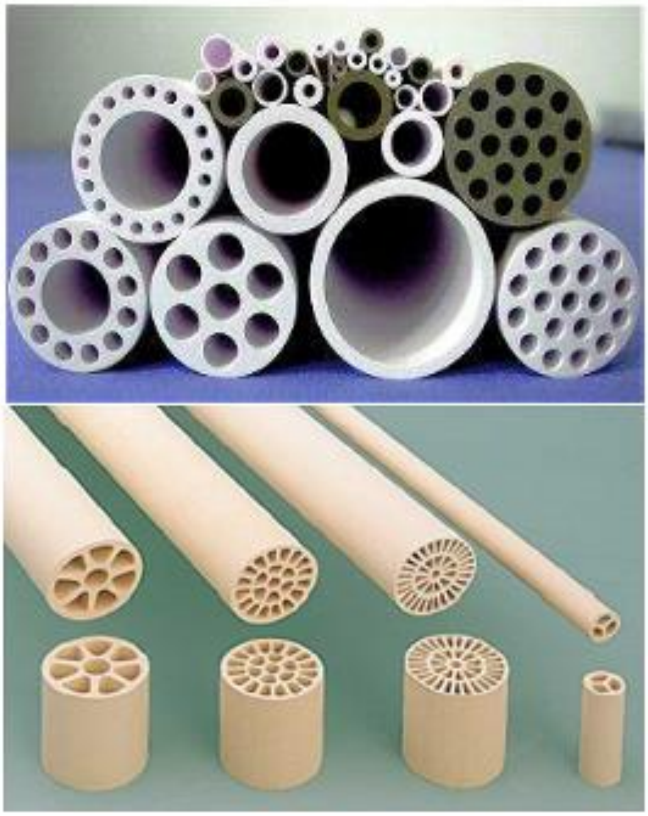


Figure 2: Tubular / straw membranes (diameter ≥ 5 mm)

Capillary membranes:
With capillary membranes the membrane serves as a selective barrier, which is sufficiently strong to resist filtration pressures. Because of this, the flow through capillary membranes can be both inside out and outside in. The diameter of capillary membranes is much smaller than that of tubular membranes, namely 0.5 to 5 mm. Because of the smaller diameter the chances of plugging are much higher with a capillary membrane. A benefit is that the packing density is much greater. Fig (3) shows the shape of capillary membranes [Baker, 2000; Li, 2007].

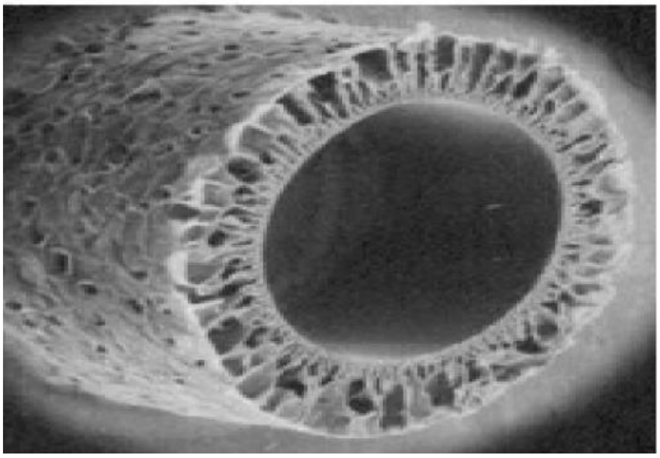


Figure 3: Capillary membranes (0.5 mm ≤ diameter < 5 mm)

Hollow fiber membranes:
Hollow fiber membranes are membranes with a diameter of below 0.5 mm. consequentially, the chances of plugging of a hollow fiber membrane are very high. The membranes can only be used for the treatment of water with low suspended solids content. The packing density of a hollow fiber membrane is very high. Hollow fiber membranes are nearly always used merely for nano-filtration and reverse osmosis (RO). As the feed solution flows through the open cores of the fibers, permeate is collected in the cartridge area surrounding the fibers. It can carry out the filtration in two ways, either “inside-out” or “outside-in”. The following figure shows the shape of hollow fiber membranes [Baker, 2000; Li et al., 2006, Li, 2007].

Figure 4: Hollow fiber membrane (diameter < 0.5 mm)

General Properties of Ceramic Membranes [PENG, 2008; Ceramic Membrane, 2013; Synthetic Membrane, 2013]

Advantages of ceramic membranes
As compared to most polymer and inorganic membranes, ceramic types offer many advantages such as:

a) They possess extremely high chemical, thermal, mechanical and physical stability. They can withstand elevated temperatures, extremes of pH (0 to 14), and high operating pressures up to 10 bar (145 psi) without concern for membrane compaction or swelling. This makes these membranes suitable for many applications where polymeric and other inorganic membranes cannot be used.
b) Their outstanding separation characteristics and their long working life.
c) They are ecologically friendly often much more favorable than other separation technologies.
d) No additives are necessary and the process temperature is not limited by an upper ceiling.
e) Filtration with ceramics is a mild, highly selective process without phase transformation.
f) Running costs can be minimized by closed production cycles and continuous processes.
g) Ceramic membranes are ideal for in-place chemical cleaning at high temperatures, while using caustic, chlorine, hydrogen peroxide, ozone and strong inorganic acids, and / or by using steam sterilization.
h) They possess a good ability for steam sterilization and back flushing.
i) They are characterized by a high abrasion resistance.

j) They allow for the use of high fluxes.
k) They are not deteriorated by the presence of bacteria which are responsible for degradation of some polymeric membranes.
l) They can be regenerated and dry stored after use.
m) One advantage of the structure of ceramic membranes is that the supports for the membrane elements are made from aluminum oxide or silicon carbide with open pores. This material can provide not only maximum permeability but also fulfills requirements relating to mechanical stability.

Disadvantages of ceramic membranes

One main disadvantage of ceramic membranes is their elevated density compared to polymers. Also, the production costs are higher owing to their expensive starting materials and more complicated fabrication process. Ceramic membranes also suffer from low membrane surface area per unit volume although this is generally compensated for by a long service life.

USES OF CERAMIC MEMBRANES

There are numerous applications of membranes in the field of water treatment, water desalination, micro-filtration, and ultra-filtration in which ceramic membranes have proved to be economically suitable due to their availability, high flux, and relatively low operating cost. Various ongoing research efforts aim to implement the use of ceramic membranes in various separation fields.

Refineries and metallurgical plants produce a huge amount of oily wastewater that should be treated before being discharged to the municipal sewage system. Ceramic membranes offer an efficient separation, low operational cost, and a compact design [Ebrahimi et al., 2009; Emani et al., 2014; Kumar et al., 2015].

Dense ceramic membranes are highly efficient in gas separation. Tong et al. [2015] used a ceramic carbonate membrane to directly separate CO_2 from flue gas in the temperature range 550-650°C. Some ceramic membranes are promising for application in high-temperature processes such as steam methane reforming due to their chemical stability [Polfus et al., 2015]. The application of hydrogen as energy source promoted the development of ceramic membranes that are used for gas separation [Li et al., 2015 a; Deibert et al., 2015].

Ceramic membranes also showed a good performance in food industries such as juice clarification [Vladisavljević et al., 2005; Emani et al., 2013] corn syrup clarification [Almandoz et al., 2010], clarification of raw rice wine [Lia et al., 2010] and treatment of the press liquor resulting from processing sardine fish [Pérez-Gálvez et al., 2011].

In particular, the importance of ceramic membrane has increased in the last two decades in the water treatment field. Using low-cost raw material is an attractive point for further research in the water treatment field using ceramic membrane [Nandi et al., 2008].

Seawater desalination is one of the promising channels for ceramic membrane usage [Larbot et al., 2004; Cui et al., 2011; 2013]. There are three membrane mechanisms that are made use of in water desalination:

- Reverse osmosis (RO): the membrane repels the salt ions and allows the passage of water molecules.
- Membrane distillation (MD): the porous membrane allows the passage of water vapour molecules after thermal treatment.
- Pervaporation: the membrane depends on water vapor pressure difference to allow the passage of water molecules through molecular sieves.

Currently, polymeric or ceramic membranes can be used in water desalination. Although polymeric membranes are widely used in this field, they suffer from swelling phenomenon, bio-fouling, and poor thermal and chemical stability. Ceramic membranes, on the other hand, show excellent thermal and chemical stability that make them a possible alternative to be used in water desalination process [Elma et al., 2012].

Zirconium dioxide was used as a pretreatment for RO desalination. It gave a good permeate quality and low fouling potential with high permeate [Xu et al., 2010].

Also, Elma et al. [2015] achieved 99.7 % salt rejection using silica membranes with high amount of tri-cobalt tetroxide (35 mol. %).

Zeolite membranes are a promising alternative to be applied in desalination due to their chemical and thermal stability and the high rejection rates obtained [Cho et al., 2011; Zhu et al., 2015].

Besides having long-term stability, Silicon nitride membranes also showed high mechanical strength and high salt rejection that could reach 99-100 % with high flux [Zhang et al., 2012; 2014]. The outstanding results obtained using silicon nitride membranes are promising for industrial and practical applications.

CHARACTERIZATION OF CERAMIC MEMBRANES

The performance of any ceramic membrane depends on a great extent on its morphology. A full investigation of the pore size and pore size distribution, shape, density, particle packing and membrane surface should be carried out in order to predict the quality of the membrane and therefore its performance for separation.

Characterization for ceramic membranes includes:

1) Morphology related tests.
2) Permeation related tests.

Morphology related tests

Morphology related tests are standard tests for ceramic membranes. The inspection is visual using optical or electron microscopes.

Usually surface roughness, grain size (and shape) and thickness of membrane cross section are to be determined by various techniques such as SEM and TEM.

Permeation related tests

As the name implies, permeation related tests give the required information about the permeability of the fabricated membrane according to the pore size that plays a vital role in the quality of the stream to be separated.

Those tests include, but not necessarily limited to the following tests:

- Permporometry.
- Gas absorption / desorption.

MANUFACTURE OF CERAMIC MEMBRANES

There are several methods for the preparation ceramic membranes such as slip casting, extrusion, pressing, etc. The following steps generally summarize the preparation procedure:

- Suspension preparation: Where the starting powders are mixed with a suitable binding liquid.
- Forming: This includes shaping of the prepared suspension according to some predetermined method.
- Heat treatment: This means using high temperatures to bind the membrane particles through a sintering process.

This firing step is the most important step in ceramic membrane preparation irrespective of ulterior preparation steps.

As for multi-layers membrane, they can be produced by coating a membrane support with the required layers (sol-gel, CVD, etc) before the firing step.

The fabrication of composite membranes is done by coating the membrane support then firing as illustrated in Fig (5). The following section reviews the different methods used in ceramic membrane fabrication [Li, 2007].

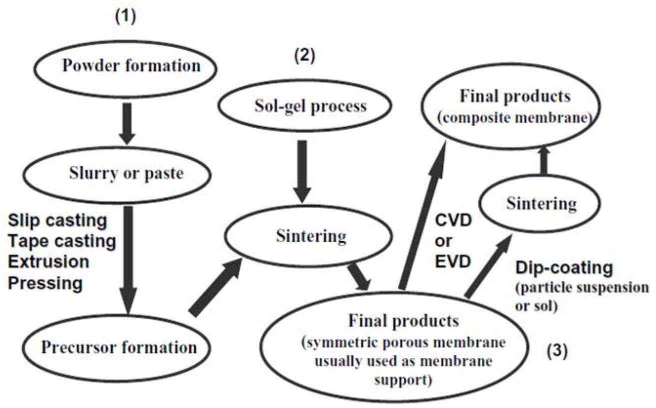


Figure 5: General ceramic membrane preparation procedures

Solid state method

This is the most conventional and one of the oldest methods for synthesis of ceramic compounds. In this regard, powders of the starting materials; oxides, carbonates, or salts, are mechanically mixed, followed by heat treatment at elevated temperatures; above 1000 °C for up to 24 hours. The extended heat treatment allows the diffusion of cations and anions in the solid state across the grain boundaries, ending up with the formation of the final ceramic product [Segal, 1997; Smart and Moor, 2005].

According to the concept of solid state reaction, it is always estimated to have dense ceramic membranes. And, using pore formers or pore generators (also known as porogens), porous ceramic membranes can be prepared by solid state processing of ceramic powders.

Examples of dense and porous ceramic membranes prepared by this method include alumina [Qin et al., 2014], mullite [Dong et al., 2008], silica [Gao et al., 2014], titania [Lin et al., 2015], and zirconia [Liu et al., 2007], as well as their combinations.

Slip casting method

It is the most commonly used method for membrane preparation. This method usually requires long casting time. Controlling the wall thickness during casting is difficult and the produced walls are usually thick.

The powder suspension is well mixed, then transferred into a porous mold so that the solvents can diffuse through the pores with the formation of a gel layer by particles precipitation on the internal surface of mold surface, to be followed by a consolidation step that must be very carried out rapidly to avoid penetration of any particles into the pores. The following figure illustrates that technique [Benito et al., 2005; Schafföner et al., 2016].

Examples of porous ceramic membranes prepared by slip-casting method include $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ [Zhang et al., 2015], alumina [Barmala et al., 2009], zirconia [Bouzerara et al., 2015], and perovskite [Athayde et al., 2016]. Ceramic membranes prepared by slip casting are known for their high permeability, which is attributed to the presence of smaller pore size over a thinner region, thereby giving superior permeation properties.

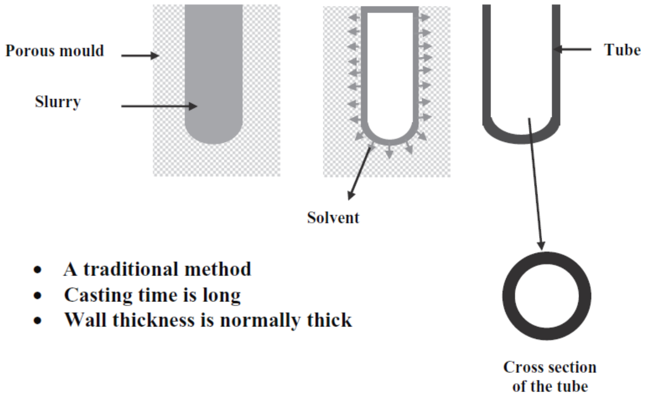
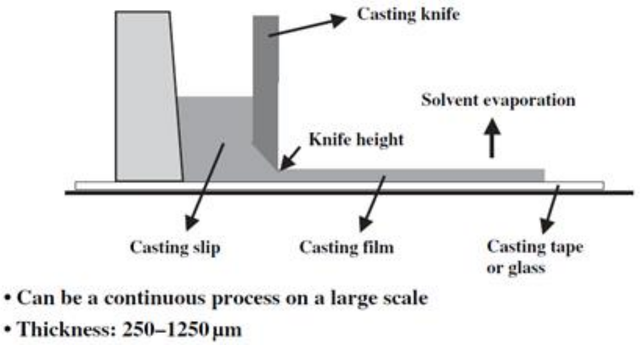


Figure 6: Slip casting method

Tape casting method

Tape casting is used in flat sheet ceramic membranes production. Fig (7) shows the presence of a reservoir in which the powder suspension is poured; behind this reservoir is a stationary casting knife which controls the thickness of the cast layer by the gap between its blade and the moving carrier. The produced casted layer is then passed through a drying zone at which the solvent evaporation from the membrane surface takes place [Burgraaf and Cot, 1996; Etchegoyen et al., 2006].

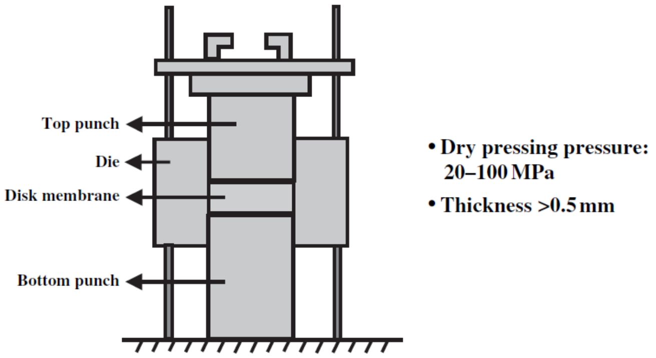
Powder suspension viscosity, the gap between moving carrier and the knife blade, and the reservoir depth are the factors that affect the product specification. The ceramic membranes prepared by this technique are usually few millimeters thick.
Examples of tape casted membranes include $La_{1-x}Sr_xFe_{1-y}Ga_yO_3$ [Geffroy et al., 2010], $La_{0.5}A_{0.5}Fe_{0.7}Co_{0.3}O_3^-$(A = Ca, Sr, and Ba) [Reichmann et al., 2014], and $La_{0.5}Ba_{0.5}Fe_{0.7}B_{0.3}O_3^-$(B = Al, Co, Cu, Mg, Mn, Ni, Sn, Ti, and Zn) [Reichmann et al., 2015].



- Can be a continuous process on a large scale
- Thickness: 250–1250 µm

Figure 7: Tape casting method

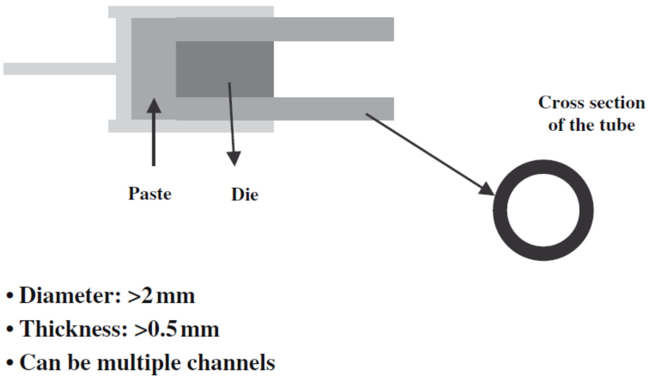
Pressing method
Disc inorganic membranes for fundamental research are prepared using this fabrication method (Fig. 8). An applied force is used to produce a sintered dense layer using a press machine which applies pressure higher than 100 MPa. Ceramic membranes that are only permeable to oxygen or hydrogen can be produced using this technique. The formed disc after firing has a thickness of about 0.5 mm and diameter in the range of few centimeters [Li, 2007].



- Dry pressing pressure: 20–100 MPa
- Thickness >0.5 mm

Figure 8: Pressing method

Extrusion method
This is a simple, important, and mass productive method of producing ceramic membranes. It has been extensively used for the fabrication of porous ceramic tubes. In this method, a homogeneous stiff paste is forced through a nozzle to be compacted or shaped to form the final green membrane, as shown in Fig (9). To keep the membrane in its desired final shape, any remaining binder, solvent, and plasticizer should be evaporated. The die dictates the shape, porosity, and pore size distribution of the final product [Isobe et al., 2006].



- Diameter: >2 mm
- Thickness: >0.5 mm
- Can be multiple channels

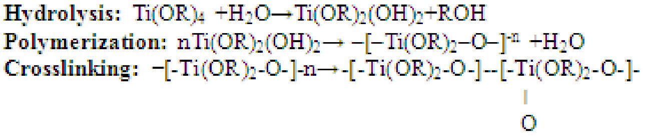
Figure 9: Extrusion method

Sol-gel method [Buggraaf and Cot, 1996; Li, 2007; PENG, 2008; Nath, 2008]
Sol-gel is an important synthesis route for the production of ceramic membranes. It has the merit of allowing tight control of pore size and pore size distribution. The sol-gel technique consists of two main routes as shown in Fig (10):

1) The colloidal route, in which the metal alkoxide that is dissolved in an alcohol is hydrolyzed by adding excess acid or water. A stable colloidal solution of dense oxide particles is formed when the resulted precipitate is maintained as a hot solution for an extended time. The resulted colloidal solution is cooled down then coated on the surface of a support membrane. This results in the formation of a metal oxide layer that is sintered at a temperature ranging from 500 to 800 ºC. The following equations show the colloidal route for γ-alumina membrane preparation.

Precipitation: $Al(OR)_3 + H_2O \rightarrow Al(OH)_2$
Peptisation: $Al(OH)_2 \rightarrow \gamma\text{-}Al2O_3 \cdot H_2O$ (Boehmite)
Sintering: $\gamma\text{-}Al2O_3 \cdot H_2O \rightarrow Al_2O_3 + H_2O$

2) The polymer route, in which the metal alkoxide that is dissolved in an alcohol is partially hydrolyzed when a low amount of water, is added. The inorganic polymer molecule is formed by the reaction of the active hydroxyl groups on the alkoxides and the formed polymer layer is coated on the surface of membrane supports. A metal oxide film forms on drying and sintering. The following chemical equations show the polymeric route for the preparation of titania membrane:



Hydrolysis: $Ti(OR)_4 + H_2O \rightarrow Ti(OR)_2(OH)_2 + ROH$
Polymerization: $nTi(OR)_2(OH)_2 \rightarrow -[-Ti(OR)_2-O-]^{-n} + H_2O$
Crosslinking: $-[-Ti(OR)_2\text{-}O\text{-}]\text{-}n \rightarrow \text{-}[\text{-}Ti(OR)_2\text{-}O\text{-}]\text{--}[\text{-}\underset{\underset{O}{|}}{Ti}(OR)_2\text{-}O\text{-}]\text{-}$

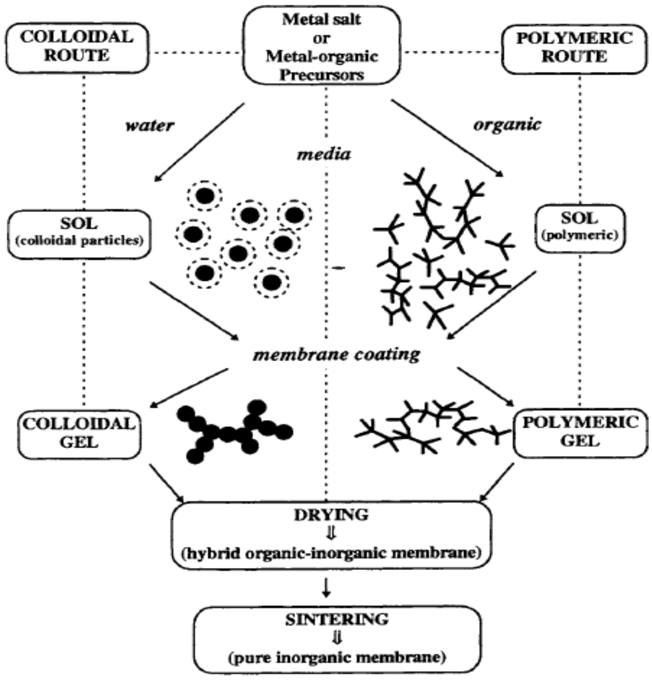


Figure 10: The sol-gel method for ceramic membrane preparation

Dip coating method [Li, 2007; CSEM-UAE Innovation Center LLC, 2012]

The following figure illustrates the dip coating technique. As the dip coated substrate enters in contact with atmosphere it rapidly dries off. A calcination step usually follows. Very thin coatings can be obtained by this technique.

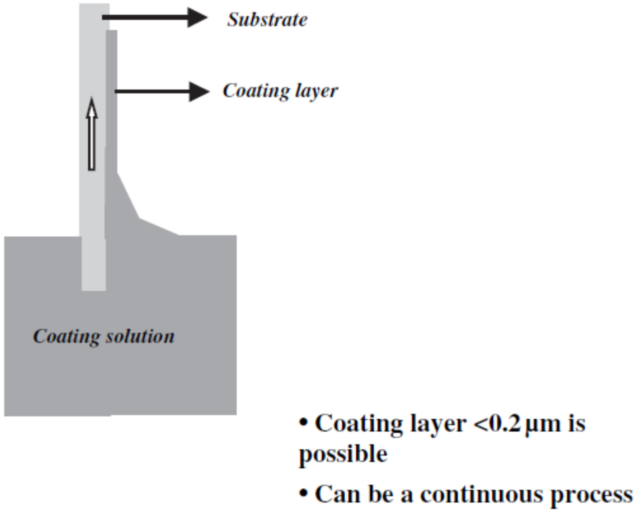


Figure 11: Dip coating method

Chemical vapour deposition (CVD) method

This method involves the deposition of extremely thin and uniform layers on a substrate. These layers can be of similar or different compositions which can lead to modification of the membrane surfaces properties. This deposition can be done using a gas phase chemical reaction at high temperature. A CVD system is shown in the following figure.

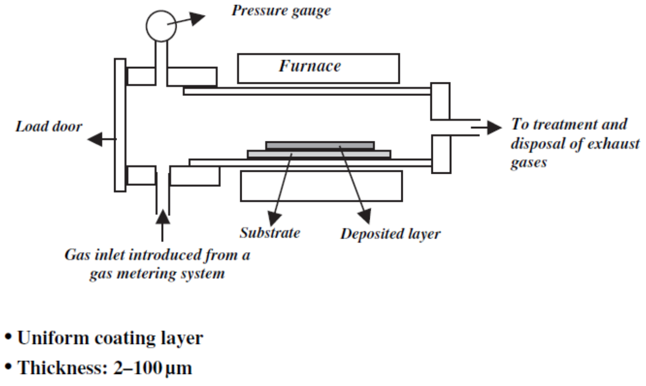


Figure 12: Chemical vapour deposition (CVD) method

The following table displays some CVD reactions.

Table 2: Chemical reactions in CVD

Reaction	Equation
Thermal Deposition	$2Al(OC_3H_7)_2 \longrightarrow Al_2O_3 + 6C_3H_6 + 3H_2O$
Oxidation	$SiH_4 + O_2 \longrightarrow SiO_2 + 2H_2$ (at 420°C)
Hydrolysis	$2AlCl_3 + 3H_2O \longrightarrow Al_2O_3 + 6HCl$

Anodic oxidation method

The starting material is usually a pure aluminum foil (99.999 %). This foil is anodized in phosphoric acid solution under a constant voltage, using a lead cathode. The anodized aluminum foil is then immersed into saturated $HgCl_2$ solution where by Hg^{2+} ions are reduced to mercury by aluminum. The anodized aluminum oxide (AAO) membrane can be separated gradually from the oil by aluminum solving into mercury. The membrane is then annealed at an elevated temperature in air [Zeng-Fu et al., 2003].

Freeze-casting method

This is one of the most recent and novel methods for the preparation of porous ceramic membranes. In this method, a liquid suspension is frozen, followed by sublimation of the frozen liquid medium under reduced pressure. This step results in the formation of porous green structure with low mechanical properties. Upon thermal treatment, the porous structure consolidates and its walls are densified, hence the overall mechanical properties are improved [Liu et al., 2016]. Depending on the initial proportion of the liquid medium in the ceramic suspension and the freezing process parameters, a wide range of porosity (30-99) % with various internal geometries can be achieved.

PRODUCTION OF CERAMIC MEMBRANES USING TRADITIONAL RAW MATERIALS

Gamma-alumina membranes were the first and most investigated mesoporous membranes prepared by the sol-gel process, based on the method developed by Yoldas as early as 1975. Since then, γ-alumina membranes have been very popular with a multitude of researches involved in their characterization and application [Gislmann et al., 1988; Hsieh et al., 1988; Cini et al., 1991; Okubo et al., 1992; Agoudjil, 2008]. However, these membranes suffer from poor chemical stability at high pH and structural evolution under thermal conditions, which is why they have not been much applied at the industrial level despite being commercially available at reasonable prices.

They are prepared by the hydrolysis of aluminum alkoxide to form aluminum hydroxide (AlOOH) sols through the sol-gel process. A well-defined pore structure of γ-Al_2O_3 phase is produced by heating the obtained AlOOH at 400 °C. The main disadvantage of this process is the formation of cracks during drying of the gel. Some organic binders like polyvinyl alcohol (PVA), polyethylene glycol (PEG) are often added to the sol to prevent crack formation in the initial drying process. These are burned off during the heat treatment [Cheong et al., 1999; Lambert and Gonzalez, 1999; Hao et al., 2004].

Leenaars et al. [1984; 1985] reported the characteristics of unsupported and supported γ-aluminum membranes using flat supports. Tubular supports were further used by Labort et al. [1987] to prepare γ-aluminum membranes with almost the same characteristics. On the other hand, Falamaki et al. [2006] proved that the characterization and preparation of flat functionally graded alumina micro-filters can be done using different preparation routes utilizing a similar slip of highly dispersed γ-alumina particles processed under different rates and by using centrifugal casting.

Benito et al. [2005] prepared multilayer membranes for the treatment of oily water. They prepared α-Al_2O_3 intermediate layers, alumina and cordierite supports. The sol-gel method was used to prepare high porous γ-Al_2O_3 top layers and due to the importance of this filtration layer, a detailed study has been performed. They also studied the effect of the calcination temperature and the sol concentration on the final structure. They also investigated the possibility of preparing membranes having no defects by adjusting the added amount of binder or plasticizer like PVA.

Jiansheng et al. [2006] used a new technique for the reparation of alumina membranes from aluminum chloride. Boehmite sols were produced on the inner surface of hollow fiber supports by its deposition using a filtration technique. Pore size distribution, phase transformation and thermal evolution were determined for the produced γ-alumina membranes. SEM imaging revealed that the produced γ-alumina membranes were defect free. Gas permeability and its separation factor for H_2 / N_2 and H_2 / CH_4 were 3.31 and 2.25 at 0.1 MPa, respectively. The main pore diameter, pore volume, and specific surface area of the unsupported membrane calcined at 600 °C, were 3.7 nm, 0.18 ml/g, and 176.9 m^2/g respectively.

Toshihiro et al. [2007] utilized nylon fibers in an extrusion method in order to obtain unidirectionally aligned cylindrical pores that resulted after firing of the prepared porous alumina ceramics. The porous ceramic which was fabricated using a traditional method and characterized by randomly distributed pores was compared to the product obtained by the previous extrusion method. The mechanical properties and gas permeability of the prepared porous alumina ceramics were investigated. The prepared porous alumina ceramics has 156 MPa bending strength and 39 % porosity with cylindrical pores showing excellent orientation. The alumina ceramics fabricated by the traditional process showed lower mechanical properties and gas permeability than the extruded one.

Ahmad et al. [2008] prepared porous γ-alumina with a bimodal pore size distribution by adding nano-sized polystyrene beads to boehmite sol as templating units. The primary pore diameter was in the range of 4-6 nm and secondary pore diameter was 50 nm with minor pore shrinkage. The membrane showed a reduced transport resistance compared with α-alumina with uni-modal porous structure in the dye adsorption test as well as in the water permeability study.

Kamal and Khalil [2007] used a novel gel mixing method to fabricate meso-porous CeO_2 and Al_2O_3 composites by using a mixture contains 10, 20 and 30 % weight per weight percent CeO_2. The hydrolysis of $(NH_4)_2Ce(NO_3)_6$ (ammonium cerium (IV) nitrate) with aqueous $(NH_4)_2CO_3$ (ammonium carbonate solution) yielded a CeO_2 gel while the controlled hydrolysis of aluminum tri-iso-prop-oxide produced an alumina gel. The mixture of CeO_2 and Al_2O_3 gel was dried then calcined at different temperatures ranging from 400 °C to 1000 °C for 3 hours to produce a meso-porous thermally stable structure.

Ylker [2006] used the dip-coating of alumina powder with zirconia solution to prepare ceramic supports. The resulted ceramic support has 40 % porosity and can be used in protein lactose separation produce 40 l/m^2.h permeate flux. He proved that separation of any components with high yield can be done by using ceramic composite membranes.

Highly ordered $Mg(OH)_2$ nano-tube arrays inside the pores of porous anodic alumina membranes (AAM) were prepared by Zhang et al. [2006] using simple chemical deposition method. Removal of nickel ions from wastewater with high removal efficiency could be performed using the obtained $Mg(OH)_2$ / Al_2O_3 composite membranes.

Zhu et al. [2016] fabricated TiO_2 / ZrO_2 ceramic nano-filtration membranes through the polymeric sol-gel route followed by the dip-coating technique. Disk type α-alumina supported meso-porous γ-alumina (pore size: 5-6 nm) was employed as the support in dip-coating. The unsupported and supported composite ceramic membranes were systematically characterized and evaluated in terms of phase composition, chemical stability, gas adsorption, molecular weight cut-off (MWCO), membrane pore size, water flux and salt rejection. It was found that the TiO_2 / ZrO_2 ceramic membranes have an amorphous phase at 400 °C and 500 °C, suggesting a high thermal stability. The fabricated membranes have a molecular weight cut-off (MWCO) of 620-860 Da, corresponding to the membrane pore size of 1.2-1.5 nm. Relatively low water permeability can be attributed to the low micro-porosity of the membrane.

Wang et al. [2016] fabricated hollow fiber nano-filtration (NF) composite membranes from γ-Al_2O_3 / α-Al_2O_3 having a different MWCOs. These were produced using dip-coating γ-AlOOH sol on the surface of the ceramic membrane. Scanning electron microscopy, membrane performance, and dynamic contact angle were determined. The resulting NF membrane showed a good stability and excellent solvent resistance.

Medjemem et al. [2016] produced multi-layer membranes used for the sterilization of nutrient medium. Flat and tubular ceramic supports were prepared then sintered on the temperature range 1200 °C to 1250 °C. Two layers were deposited on the ceramic support using a slip casting method. The intermediate layer was made of anorthite while the top layer consisted of zirconia. These layers were sintered at 1500 °C for the intermediate layer and 1100 °C for the top layer. The resulted membranes show excellent performance.

PRODUCTION OF LOW-COST CERAMIC MEMBRANES FROM RECYCLED WASTE

General

Commercial ceramic membranes are usually manufactured from expensive raw materials such as titania, zirconia or alumina. Besides, their manufacturing cost is usually elevated such that the cost of some commercial ceramic membranes is approximately five times that of polymeric membrane modules. Prices range from $100-200 per piece to reach up to $1000-2000 per square meter for special ceramic membranes operating under extremely harsh conditions. However, their operating life is much longer than that of polymeric membrane. It can reach up to 23 years without a need for a change.

On the other hand, the industrial and economic growth witnessed in recent decades has brought about a qualitative as well as a quantitative increase in the generation of different types of waste (urban, industrial, construction, etc.) despite waste management policies adopted nationally and internationally. The practice of dumping and/or the inadequate management of waste from the various manufacturing sectors have had a notable impact on the receiving environment, leading to water, soil, air and noise pollution, amongst other complications, and adding to existing environmental problems. At the same time, these practices usually come at an economic cost [Medina et al., 2011].

However, if waste is managed correctly it can be converted into a resource which contributes to savings in raw materials, conservation of natural resources and the climate, and promotes sustainable development. Recycling of solid wastes is another major productive area in which considerable quantity can be utilized for manufacturing new products.

In this respect, producing a low cost stable ceramic membrane from available low cost materials or industrial wastes will greatly reduce the membrane price while maintaining its superior properties and performance [Nandi et al., 2008].

The manufacture of low-cost ceramic membranes was investigated by many researchers using a diversity of waste types.

Fly ash wastes

Jo et al. [1996] used fly ash produced from coal-fired power stations to prepare ceramic membrane filters. Fly ash waste contains several oxides with a wide particle size distribution. Experimental work revealed that the prepared membrane can be used in gas particulate separation at high temperature. Glassy material fusion in the fly ash was responsible for imparting a high mechanical strength to the membrane.

Jedidi et al. [2009 a] used mineral coal fly ash to fabricate a new mineral porous tubular membrane by an extrusion technique. Crushed mineral coal was calcined at 800 °C to yield a coal fly ash paste that was used in the preparation of the porous tubular support. The fabricated support had an average pore diameter of about 4.5 μm and porosity of 51 % when heated at 1125 °C. The permeate flux obtained was comparable to that of a commercial alumina microfiltration membrane.

On the other hand, the same authors used a mineral coal fly ash to fabricate a new mineral porous tubular membrane [Jedidi et al., 2009 b]. A suspension consisting of a mixture of flyash powder, polyvinyl alcohol (PVA) and water was slip-casted to fabricate the mesoporous layer. Here also, the permeate flux obtained was comparable to that of a commercial alumina microfiltration membrane. They also prepared a microfiltration membrane for use in industrial wastewater treatment application from mineral coal fly ash [Jedidi et al., 2009 c].

Jedidi et al. [2011] also prepared a membrane support using fly ash mixed with organic additives and water. The resulting mix was shaped and fired at 1125 °C to produce a membrane with good mechanical properties that can be used in micro and ultra filtration processes. The obtained membrane with average pore size of 0.25 μm was used for the treatment of the dying effluents generated by the washing baths in the textile industry. It showed a substantial decrease of turbidity (< 1 NTU), of chemical oxygen demand (COD) values (retention rate of about 75 %) and a total color removal.

Dong et al. [2009] mixed bauxite with industrial waste fly ash to prepare bulk porous mullite supports for ceramic membranes. The gas permeation flux increased owing to increased porosity. At elevated temperatures, the average flexural strength increased despite an increase in porosity. This abnormal increase in mechanical strength was ascribed to the precipitation and growth of more mullite crystals, as well as the increase of bonding area between large sintered particles. In another work they used a bauxite variety containing titania. The presence of this latter oxide promoted sintering at 1450 °C causing an increase in bending strength [Dong et al., 2010].

Fang et al. [2011] used refined fly ash to prepare crack-free tubular supported ceramic for use in micro-filtration membranes through a slip-casting technique. The properties of the prepared membrane were affected by withdrawal speed, slip concentration and contact time. The pure water permeability of the fabricated membranes was higher than other commercial membranes. Fang et al. [2013] also produced a low cost spherical-fly-ash-based membrane to be used in micro-filtration processes. It also exhibited a low fouling resistance when compared to other inorganic membranes.

Cao et al. [2014] fabricated low-cost porous mullite ceramic membrane supports from a blend of recycled coal fly ash and natural bauxite. V_2O_5 and AlF_3 were used as additives to cause the growth of mullite crystals with various morphologies via an in situ reaction sintering. The fabricated membrane supports showed high porosity without mechanical strength degradation, possibly owing to the formation of mullite whiskers.

Liu et al. [2016] fabricated anorthite-cordierite-based porous ceramic membrane supports from coal fly ash by adding dolomite mineral to the waste with high-temperature sintering. It was found that the level of dolomite addition had an inhibiting effect on the sintering behavior of coal fly ash.

Guo et al. [2016] removed efficiently oil droplets from oil-in-water emulsion by fabrication of a hollow fiber, low-cost and multi-layer-structured mullite-titania composite ceramic using coal fly ash recycled waste. The surface and mechanical properties, crystalline phase, and morphology were determined. The prepared membrane showed high separation efficiency for oil-in-water emulsion separation process.

Other wastes

Norliza et al. [2009] used the rejected waste powder from sanitary ware production to prepare ceramic membranes of 40 % porosity thus positively contributing to solve an environmental problem. Prince et al. [2011] produced low cost glass membranes for filtration purposes utilizing recycled waste glass that displayed shorter sintering periods and temperatures. One advantage of glass membranes was the possibility to achieve a porosity of at least 75 % with uniform pore size distribution despite the resulting high tortuosity. Thses membranes also displayed high flux rates.

Khemakhem et al. [2011] used the mud originating from the hydro cyclone laundries of phosphate to prepare a new support to be used in ultra-filtration membranes by the slip-casting method. The porous tubular support produced had an average pore diameter of about 1 μm and a porosity of 39 %. The heating treatment at 700 °C leads to an average pore size of 5 nm. The results show that this membrane can be used in water treatment as it decreases the turbidity of the cuttlefish effluent and provides good performances with respect to pollution retention and permeate flux. Its properties were comparable to those of alumina membranes used in ultra-filtration.

Saffaj et al. [2013] produced porous ceramic supports for micro-filtration and ultra-filtration membrane from cortical animal bone. The support was prepared by extrusion of the paste and sintering at 1300 °C. This work proved that the animal bone based material is appropriate for the development of low cost supports for micro-filtration membranes which could find application in industrial wastewater. The structural properties of animal bone support were satisfactory in terms of porosity and pore diameter.

Lü et al. [2014] sintered a mixture of bauxite and coal gangue at temperatures in the range 1100 °C to 1500 °C adding pore forming agent like corn starch. They studied mechanical properties, gas permeation flux, shrinkage, dynamic sintering behavior, porosity and pore size distribution, phase evolution and microstructure. The average pore size and porosity of the mullite ceramic membrane supports were improved by adding corn starch.

Baláz et al. [2014] produced eggshell membranes (ESM) using a biomaterial that is generally considered as waste. These membranes could find use on both laboratory and industrial scales.

Wan et al. [2015] used a low-toxic aqueous gel-casting method to produce bulk mesoporous silica ceramics having homogeneous microstructure from industrial waste. It was found that the addition of glutinous rice flour increased both pore size and porosity while maintaining nano-scale uniform pore size. It was proposed that these membranes can be used in applications such as filter industries and catalyst industries.

Bose and Das [2015] produced ceramic membranes from sawdust which is a wood waste as pore-former. The particle size of saw dust used played a major role in assessing the mechanical strength of the membranes and controlling the porosity and pore size.

Tolba et al. [2015] prepared an effective adsorptive membrane based on amorphous nano-silica nano-particles obtained from rice husk, which is known to cause environmental problems. It is worth mentioning that using rice husk in such membrane helps in minimizing environmental pollution and reduces the membrane production cost. The obtained membrane was used in dye removal due to the high silica content in rice husk.

Hua et al. [2016] used Al_2O_3 powders and construction waste to produce anorthite-mullite-corundum porous ceramics membrane. MoO_3 and AlF_3 were added as crystallization catalyst and mineralizer, respectively. Mechanical properties, microstructure, pore size distribution and phase composition were determined. The produced membranes showed an average pore size of 1.32 μm, a bending strength of (23.8 ± 0.9) MPa, and an open porosity of (66.1 ± 0.7) %.

Roller kilns used in the production of ceramic tiles are routinely ground to remove traces of contamination. The fine ground powder is usually discarded as a useless waste. Amin et al. [2016] used the kiln rollers grind waste as a raw material in the production of stable, highly active nano-size ceramic membranes for use in water treatment. The support ceramic membrane samples were formed into disks using an organic binder (PVA) and subsequently pressed at 25 MPa, and fired at temperatures ranging from 1100 °C to 1300 °C for different soaking times. Results showed that the highest porosity necessary for membrane operation was obtained by soaking for one hour at 1150 °C. Preliminary trials undergone for water desalination suggested that the prepared membrane offered a promising cheap and effective alternative.

CONCLUSION

This article presents an overview on ceramic membrane production and development, based on an extensive literature review. Many successful attempts were performed to use traditional raw materials with modified techniques and to incorporate different types of waste into the production of low-cost ceramic membranes including fly ash wastes, glass waste and mud from hydro cyclone laundries, cortical bone animal, coal gangue, sawdust, and rice husk. Utilization of solid wastes is encouraged as a cost-effective alternative to be used in ceramic membranes manufacturing.

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