MATERIALS AND METHODS FOR CERAMIC MEMBRANE SYNTHESIS. SHORT REVIEW

S. Kyrii[1]

[1]National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Ukraine,

kysvit@gmail.com

This article briefly overviews the main types of raw materials used to synthesise ceramic membranes. Traditional materials such as aluminium oxide, silicon dioxide, titanium dioxide, zirconium dioxide, zeolites, and cost-effective materials like various clays and industrial waste are highlighted. Modern methods for producing high-performance ceramic membranes are discussed, including slip casting, tape casting, pressing, extrusion, solid state method etc. The general scheme for preparing a selective layer on a ceramic membrane using various methods for synthesising it is also examined. Furthermore, the cost of commercial ceramic membranes and influencing factors are analysed. Based on contemporary literature, ceramic membranes exhibit distinct advantages over polymer membranes with their potential for application under high temperature, high pressure, and aggressive environments. Additionally, their energy efficiency, compactness, and versatility make them a viable alternative for water purification, replacing more expensive methods like coagulation and adsorption. Ceramic membranes have become a competitive alternative to polymer membranes, showcasing unique material properties and excellent characteristics. Using cost-effective materials for ceramic membrane fabrication allows for utilisation in economically sensitive sectors. Such membranes demonstrate excellent mechanical properties and high permeability, while inexpensive materials can reduce costs. Current scientific research and developments focus on utilising various clays and waste materials to produce ceramic membranes, aiming to create new generations of ceramic membranes for environmentally friendly applications.

Key words: *ceramic membrane, low-cost membrane material, materials for ceramic membrane, membrane technology, selective layer, synthesis methods*

1. Introduction

Recently, membrane separation processes have gained significant importance across various industrial applications. These processes have demonstrated high efficiency in numerous separation processes, particularly in treating industrial effluent water (Issaoui et al., 2019, Issaoui et al., 2015), air purification, food industries, and other environmental applications (M.G. Buonomenna, 2013). Exploring new membrane technologies holds great potential for addressing environmental challenges.

However, a critical challenge that remains to be addressed is the cost-benefit aspect and the optimisation of membrane filtration performance. To overcome this challenge, the possibility of using different materials and methods of obtaining ceramic membranes is actively being investigated. Production porous ceramic membranes have been widely adopted in numerous industrial processes due to their distinct advantages over

polymeric membranes (Elaine Fung, 2013). These ceramic membranes offer several well-established benefits that make them preferable in industrial applications.

Compared to most polymer and inorganic membranes, ceramic membranes offer numerous advantages, including exceptional chemical, thermal, mechanical, and physical stability. Ceramic membranes exhibit remarkable durability, withstanding high temperatures, a wide pH range (0 to 14), and operating pressures up to 10 bar without compaction or swelling. This makes them suitable for applications where polymeric and other inorganic membranes are unsuitable. Ceramic membranes deliver excellent separation capabilities, have a prolonged operational life, and are often more environmentally favourable than alternative separation technologies. In addition, ceramic membranes enable highly selective filtration without phase transformation and can undergo chemical cleaning at high temperatures using caustic, chlorine, hydrogen peroxide, ozone, and inorganic solid acids. Steam sterilisation and backflushing are also possible.

Ceramic materials possess exceptional properties that make them highly suitable for demanding water purification processes, including industrial wastewater treatment, oil/water separation, and hazardous waste treatment. Initially, α-Al_2O_3 was proposed as the primary raw material for ceramic membrane preparation (DeFriend et al., 2003). However, subsequent studies have identified γ-Al_2O_3, zirconia, titania, and silica as promising materials for membrane synthesis (Yoshino et al., 2005, Sun et al., 2020). More recently, there has been a significant focus on utilising abundant natural minerals and industrial wastes that require lower firing temperatures compared to metal oxide materials. Examples of these cost-effective starting materials include kaolin, bauxite, diatomite, and dredge sediment, among others. This shift towards low-cost ceramic membranes has opened up new avenues in separation domains.

2. Materials for synthesis of ceramic membranes

Ceramic membranes can be fabricated from a wide range of materials. A precise definition of ceramics as inorganic, non-metallic materials specifies the utilization of metal oxides or zeolites. Notably, alumina and silica are frequently used as membrane precursors, exemplifying this definition (Burggraaf et al., 1996). However, the limited stability of these membranes has prompted the exploration of more stable yet expensive alternatives like titania and zirconia. Presently, a composite ceramic membrane is defined as one that incorporates at least one layer of ceramic material. This encompasses inorganic membranes supported by metal or glass substrates and hybrid membranes featuring an organic-templated top layer. Below, it is discussed several typical materials used to prepare ceramic membranes, highlighting their advantages and drawbacks.

2.1 Traditional materials
2.1.1 Aluminium oxide

Aluminium oxide (Al_2O_3) is the most widely recognized material associated with ceramic membranes. Alumina possesses abundant availability, excellent chemical and thermal stability, reasonable strength, and desirable thermal and electrical insulation properties. Typically, alumina ceramic membranes are manufactured by sintering α-

alumina and γ-alumina powders at high temperatures (>1300 °C).

The primary natural source of aluminium is bauxite ore, which consists of a mixture of minerals such as gibbsite Al(OH)$_3$, boehmite γ-AlO(OH), diaspore α-AlO(OH), Fe$_2$O$_3$, FeO, kaolinite clay, and small amounts of TiO$_2$. Heating this ore leads to the formation of various allotropes of alumina, including α-, γ-, δ-, η-, θ-, and χ-alumina. However, sintering above 1000°C transforms all these forms into α-Al$_2$O$_3$, the most thermodynamically stable allotrope. The pore sizes typically found in α-alumina membranes range from tens to hundreds of nanometers, rendering them suitable as support layers for composite membranes (Gitis, 2016).

2.1.2 Silicon dioxide

Silicon dioxide (SiO$_2$) is another prevalent inorganic material used in ceramic membranes. The Si-O bond lengths exhibit fluctuations around 1.6 Å, while the Si-O-Si angles vary between 140° in α-tridymite and up to 180° in β-tridymite (Kucera, 2013, Gitis, 2016). The flexibility of the Si-O-Si bonds and the nearly unrestricted rotation around the axis contribute to the unique properties of amorphous silica, which lacks long-range order. This property makes it suitable for preparing thin coating layers, as thin as 30 nm, used in molecular sieving applications. The coating can be achieved through methods such as chemical vapour deposition (CVD) and sol-gel.

CVD forms ultra-micropores (less than 0.7 nm) that exhibit superior separation properties but have lower fluxes. On the other hand, sol-gel coatings typically produce super-micropores (between 0.7 and 2.0 nm) that are less selective but allow for higher fluxes. Some researchers have claimed that

pore sizes of 3-4 Å can be achieved through the sol-gel method (Biesheuvel et al., 1999). Silica stands out as the only genuinely microporous material suitable for molecular sieving applications.

Sol-gel membranes are relatively easier to prepare; however, their low reproducibility limits their suitability for many industrial applications. Silica-coated membranes are widely used in various separation processes, ranging from gas separation to water desalination (Xu et al., 2013, Gitis, 2016). However, one significant drawback of amorphous silica is its hydrothermal instability. Silica-based microporous membranes typically have relatively short lifetimes, lasting only a few days at moderate temperatures (<100 °C) (Sah, 2004). Even under mild conditions, such as 200 °C, humidity and heat can significantly reduce pore volume. This occurs due to the physical sorption of water molecules on the surface silanol (Si-OH) groups, followed by a reaction with nearby siloxane (Si-O-Si) bonds. The cleavage of these bonds releases small silica "molecules" (oligomers) that migrate to small pores, recondense, and block them.

The limited hydrolytic stability of siloxane bonds imposes a natural constraint on using pure inorganic silica membranes. Presently, on an industrial scale, silica-coated membranes find extensive use, primarily in gas separation applications.

2.1.3 Titanium dioxide

Titanium dioxide (TiO$_2$) is a popular material extensively used for coating ceramic membranes due to its exceptional chemical resistance to both acidic and alkaline pH conditions (Dontsova et al., 2020). In ceramic membranes, TiO$_2$ can be used as self-standing

and coating layers. Self-standing titania membranes are typically fabricated as nanometric diameter tubes with micrometric lengths.

These membranes are produced by utilising titania nanoparticles either through synthesising titanium alkoxide compounds under alkali conditions or by subjecting TiO_2 nanoparticles to direct hydrothermal treatment under alkali conditions. The resulting titanium nanofibers, rods, and surfaces fall within the membrane category primarily because of their porous nature, allowing fluid passage through them. However, self-standing titania membranes exhibit poor structural stability (Nair et al., 1997, Gitis, 2016) and cannot be assembled into a module. In applications such as catalytic reactions, these membranes are used in a suspended particle form within the reactor.

The coating of supports with a titania layer is primarily achieved through the sol-gel method. The resulting membranes possess pore sizes below 2 nm. Certain techniques, such as physically depositing TiO_2 particles within the pores of an ultrafiltration (UF) membrane, aim to ensure the presence of TiO_2 particles on the membrane surface rather than forming a solid separation layer.

2.1.4 Zirconium dioxide

Zirconium dioxide (ZrO_2) is widely recognised as one of the most favoured ceramic coating materials due to its exceptional chemical stability, particularly in alkali solutions. However, one challenge with zirconia membranes is their tendency to crack after sintering at high temperatures, stemming from a significant volume change (approximately 9%) during the transition from tetragonal to monoclinic phases at 1173°C. To mitigate this issue, zirconia used for coating

top layers is typically fired at temperatures ranging from 500 to 600 °C or doped with Y_2O_3 in its cubic polymorph, which enhances its thermal stability.

Moreover, the thermal stability of zirconias can be further enhanced by incorporating additives such as 12-13 % CaO, 8-9 % Y_2O_3, Sc_2O_3, or 8-12 % of other rare-earth oxides (Yb_2O_3, Dy_2O_3, Gd_2O_3, Nd_2O_3, Sm_2O_3) (Bhave, 1991, Gitis 2016). Yttria-substituted zirconia is presently considered the state-of-the-art material for solid electrolyte membranes in high-temperature fuel cells, offering superior performance and reliability.

2.1.5 Zeolites

Zeolites, a group of crystalline-hydrated aluminosilicate minerals, are widely recognised as common membrane materials. However, only a select few zeolites and zeolite-like structures are suitable for membrane separations. Among these, four prominent zeolites are often used: Linde Type A (zeolite A) with eight-ring pores measuring 0.30-0.45 nm, ZSM-5 with 10-ring pores measuring 0.45-0.60 nm, zeolite Y (faujasite) with 12-ring pores measuring 0.6-0.8nm, and zeolite beta.

Zeolite membranes can be prepared in two ways: as self-standing materials or as top layers for composite membranes. A recent trend involves growing zeolite crystals during polymer membrane synthesis, resulting in metal-organic frameworks (MOFs) with adjustable separation properties and permeability (Lai et al., 2003). Self-standing zeolite crystals are typically initially grown on a support material like Teflon, which is subsequently removed after synthesis. While these membranes are valuable for model studies of ideal zeolite layers, their practical

applications are limited due to difficulties growing zeolite layers larger than a few square centimetres and their inherent fragility, hindering industrial implementation. Such membranes are prepared by crystallisation, followed by substantial growth on the support material, enabling their practical use in various applications.

One inherent limitation of zeolite membranes is the transport mechanism based on adsorption. Compounds pass through the pores via adsorption, which can make it challenging to maintain a steady-state operation as the zeolite becomes saturated with the adsorbed substance. However, this adsorption-based retention can also be advantageous since zeolites with larger pores can exhibit both high permeate fluxes and high selectivity. Furthermore, zeolites offer advantages such as thermal stability up to 400-500 °C and resistance to organic solvents, surpassing polymer membranes with similar pore sizes. These properties facilitate the practical implementation of zeolite membranes, making them well-suited for applications in gas separation and catalytic membrane reactors at elevated temperatures.

2.2 Low-cost materials

Using conventional ceramic membranes, primarily composed of costly raw materials such as alumina, zirconia, and titania, presents a challenge due to their high production costs. The energy-intensive sintering-based fabrication processes further contribute to the overall expenses. As a result, the widespread application of traditional ceramic membranes has been limited to small-scale systems, impeding their large-scale implementation (DeFriend et al., 2003, Yoshino et al., 2005).

There has been a growing interest in exploring alternative approaches by employing low-cost raw materials as precursors for ceramic membranes in recent years. This emerging trend aims to address the cost barriers associated with conventional materials. Researchers and industry experts have started focusing on developing ceramic membranes utilising these affordable raw materials, garring increasing attention (Amanmyrat et al., 2019, Nandi et al., 2008). By leveraging low-cost precursors, there is a potential to reduce production costs and enhance the scalability of ceramic membranes for a broader range of applications.

The fabrication of low-cost membranes has been explored using various materials, including natural minerals such as clays, quartz, and apatite, as well as industrial waste such as ash. Through a literature review, Fig. 1 presents a list of the materials investigated for developing affordable membranes. The figure illustrates that clays have received significant attention as the most extensively studied raw material for these applications. Additionally, fly ash has emerged as a prominent contender in this field, showcasing its potential for low-cost membrane production.
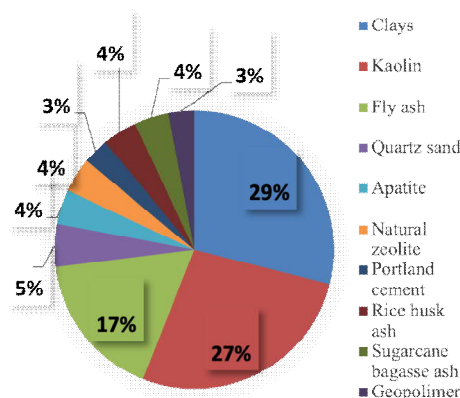
Fig. 1. *Usage of different raw materials for low-cost inorganic filtration membranes (Abdulaev et al., 2019)*

This article provides an overview of the most used materials, namely clays (including in detail kaolin), and fly ash.

2.2.1 Clays

The use of clay as a raw material for synthesizing ceramic membranes has gained recent attention as a sustainable and economical alternative to traditional ceramic materials. Clay is abundant and readily accessible, making it suitable for large-scale production of ceramic membranes. Additionally, clay exhibits good plasticity, allowing for the molding of membranes into various shapes and sizes, offering design flexibility (Abdullayev et al., 2019). Research studies have demonstrated that clay-based ceramic membranes exhibit excellent performance in wastewater treatment applications, effectively removing pathogens, organic pollutants, and heavy metals (Aloulou et al., 2020). Moreover, these membranes exhibit favorable mechanical strength and chemical stability, presenting a promising alternative to conventional ceramic membranes. The utilization of clay as a raw material for ceramic membrane synthesis holds the potential to enhance accessibility and cost-effectiveness while delivering high performance and durability in wastewater treatment applications.

Comparative analysis of clays can be challenging due to their varying composition depending on geographic origin. Clay-based support layers designed for filtration membranes generally possess a pore size ranging from 0.3 μm (Galán-Arboledas et al., 2016) to 16 μm (Lorente-Ayza et al., 2015). These support layers exhibit high porosity, reaching up to 49% (Khemakhem et al., 2006). Additionally, they have demonstrated

flexural strength ranging from 10 MPa (Saffaj et al., 2006) to 69 MPa (Zhou et al., 2011). Utilising clays as raw materials, researchers have successfully fabricated active layers for microfiltration (MF) or ultrafiltration (UF) membranes, catering to various applications such as suspended particle removal (Bouazizi et al., 2016), oil droplet separation (Eom et al., 2015), dye filtration (Foorginezhad et al., 2017), and heavy metal removal (Jana et al., 2010). The reported results strongly support the viability of clay in membrane fabrication for sustainable water filtration technology.

2.2.2 Kaolin

Kaolin, which is predominantly composed of kaolinite mineral, is the most commonly found type of clay. It exhibits favorable characteristics for membrane fabrication, primarily due to its unique pore structures and mechanical properties achievable through thermal processing. As a result, kaolin holds a pivotal position in the development of low-cost membrane technology and warrants dedicated exploration and discussion (Serhiienko et al., 2023).

Kaolin has been extensively studied in various research works as a fundamental component in developing ceramic membranes. It has been explored for different applications, including as support layers (Zhou et al, 2010, Boudaira et al., 2016), microfiltration (MF) layers (Hedfi et al., 2014), and ultrafiltration (UF) layers (Ali et al., 2018).

One of the key advantages of using kaolin is its lower thermal processing temperature compared to conventional oxide ceramics. The decomposition of kaolin results in the formation of spinel and mullite phases.

Kaolin membranes have been investigated both as composite systems and single-component structures. When processed at temperatures exceeding 1200°C, kaolin membranes without any reactive additives primarily exhibit mullite ($3Al_2O_3 \cdot 2SiO_2$) and cristobalite (SiO_2) phases. Higher temperatures promote the formation of needle-like mullite structures, leading to enhanced mechanical strength and densification of the membranes (Hedfi et al., 2014).

Different phase assemblages can be achieved by incorporating solid-state inorganic additives with a propensity to react at high temperatures. For instance, including an alumina source, such as bauxite or pure alumina, enables the reaction of cristobalite with alumina, resulting in increased mullite content.

These additives not only contribute to phase formation but can also serve as pore formers through gas evolution. For example, calcium carbonate facilitates pore formation through the production of CO_2 during decomposition. Quartz enhances the mechanical and thermal stability of the membranes, while feldspar acts as a sintering aid, creating a fluxed glassy phase at lower temperatures (Amanmyrat et al., 2019).

Kaolin particles commonly used in water purification membranes have a size range of 15 μm to 1 μm (Zhou et al., 2010, Harabi, et al., 2014) Hubadillah et al., 2019). The sintering temperatures for these membranes vary between 850°C and 1550°C, with most processes utilising temperatures higher than 1150°C. The specific temperature is selected based on the membrane's composition and desired pore size. It is worth noting that higher temperatures result in improved mechanical strength but also lead to

reduced overall porosity (Chen et al., 2015, Boudaira et al., 2016).

The mechanical strength of kaolin-based membranes is influenced by porosity and mineralogy, which are determined by the presence of additives and the sintering temperature. Higher sintering temperatures promote the formation of a glassy phase and enhance bonding between ceramic particles, resulting in more stable membranes. Typically, temperatures above 1200°C are required to obtain mullite-rich membranes with sufficient mechanical robustness for water treatment applications (Amanmyrat et al., 2019).

2.2.3 Fly ash

Waste fly ash, which is classified as hazardous industrial solid waste resulting from coal incineration in thermal power plants, poses significant environmental pollution challenges. However, one effective method of recycling fly ash is fabricating low-cost tubular mineral-based ceramic membranes for microfiltration (Dong et al., 2006). In recent developments, the substitution of industrial-grade alumina with a SiO_2-Al_2O_3-MeO system coal fly ash has been successfully realised for ceramic membrane production (Liu et al., 2016).

Some scientist have introduced a two-layered fly-ash-based ceramic membrane and assessed its permeability and anti-fouling properties for the microfiltration of particle suspensions and oil-in-water emulsions (Fang et al., 2013) . The asymmetric membrane was created by slip-casting refined fly ash onto the inner surface of a macroporous fly ash-based tube support. This fly ash-based membrane demonstrated lower membrane fouling resistance and superior performance

compared to other available inorganic membranes in both filtration processes.

Furthermore, investigated the use of fly ash to develop a ceramic microfiltration membrane composed of macroporous support and an active layer for applications in clarifying and decolourising effluents from the dyeing industry (Jedidi et al., 2011). The macroporous support was obtained by heating the original mineral coal rock at 800°C without prior grinding, resulting in an average pore diameter of approximately 4.5 μm and a porosity of 51%. The active layer was formed by depositing finely ground mineral coal powder onto the support, followed by sintering at 800°C. The authors observed that the resulting ceramic membrane is competitive compared to commercial membranes synthesised from aluminium oxide.

3. Methods for ceramic membrane synthesis

Various techniques can be employed to prepare ceramic membranes, including slip casting, extrusion, and pressing. The overall preparation procedure can be summarized as follows:

Suspension Preparation: the initial powders are mixed with a compatible binding liquid to create a suspension.

Forming: the suspension is then shaped using a predetermined method to achieve the desired membrane structure.

Heat Treatment: the formed membrane undergoes a sintering process, where high temperatures are applied to bind the particles together.

The firing step is crucial in the preparation of ceramic membranes, regardless of subsequent preparation steps. In the case of

multi-layered membranes, they can be created by applying the necessary layers (such as sol-gel, CVD, etc.) onto a membrane support prior to the firing process.

Composite membranes are manufactured by applying a coating to the membrane support and subsequently undergoing the firing process, as shown in Fig. 2.
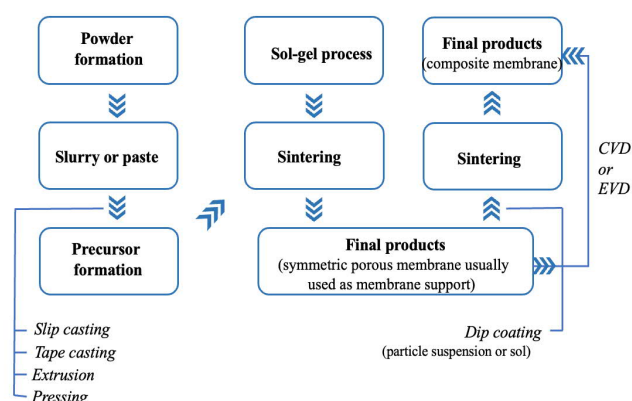
Fig. 2. *General ceramic membrane preparation procedures*

3.1 Solid state method

This method is considered the traditional and one of the earliest approaches for synthesizing ceramic compounds. The process involves mechanically blending powders of the initial materials, which can be oxides, carbonates, or salts. Subsequently, heat treatment is carried out at high temperatures, typically exceeding 1000 °C, for up to 24 hours. The prolonged heat treatment facilitates the diffusion of cations and anions within the solid state, occurring across the boundaries of the grains. This ultimately leads to the formation of the desired ceramic product (Amin et al., 2016).

The concept of solid-state reaction is commonly employed to achieve ceramic membranes with high density. However, it is possible to produce porous ceramic membranes by incorporating pore formers

during the solid-state processing of ceramic powders. This method has been successfully utilized to prepare various types of ceramic membranes. Examples of both dense and porous ceramic membranes created through this approach include alumina, mullite, silica, titania, zirconia, as well as combinations thereof (Lin et al., 2015, Amin et al., 2016).

3.2 Slip casting method

This method is widely used for membrane preparation. However, it often necessitates a lengthy casting time. Achieving precise control over the wall thickness during casting can be challenging, resulting in relatively thick walls in the final product.

The powder suspension is thoroughly blended before being poured into a porous mould. This allows the solvents to permeate through the pores, forming a gel layer as the particles precipitate on the internal surface of the mould. Subsequently, a rapid consolidation step is performed to prevent any particle penetration into the pores (Schafföner et al., 2016).

Slip casting is a method commonly used to prepare ceramic membranes, known for their exceptional permeability. This can be attributed to the presence of smaller pore sizes concentrated in a thinner region, resulting in superior permeation properties.

3.3 Tape casting method

Tape casting is used to produce ceramic membranes in flat sheet form. The process involves pouring the powder suspension into a special reservoir. Positioned behind the reservoir is a stationary casting knife that regulates the thickness of the cast layer based on the gap between its blade and the moving carrier. Subsequently, the casted layer is passed through a drying zone where solvent evaporation occurs from the membrane surface (Amin et al., 2016).

The viscosity of the powder suspension, the distance between the moving carrier and the knife blade, and the depth of the reservoir are key factors that influence the characteristics of the final product. Typically, ceramic membranes prepared using this technique have a few millimetres thickness.

3.4 Extrusion method

This method is a straightforward, significant, and highly efficient approach for manufacturing ceramic membranes. It has been widely used for producing porous ceramic tubes. The process involves forcing a uniform and firm paste through a nozzle to compact or shape it into the desired membrane. Any residual binder, solvent, and plasticizer must be evaporated to maintain the membrane's intended final shape. The die used in the process determines the shape, porosity, and distribution of pore sizes in the resulting product (Isobe et al., 2006).

3.5 Pressing method

The fabrication method is utilized for preparing disc-shaped inorganic membranes in fundamental research. A press machine is employed to apply a force exceeding 100 MPa, resulting in the formation of a sintered dense layer. This technique enables the production of ceramic membranes that exhibit selective permeability to either oxygen or hydrogen. The fired disc-shaped membrane has a thickness of approximately 0.5 mm and a diameter ranging from a few centimetres (Li, 2007).

3.6 Freeze-casting method

This innovative method represents one of the latest advancements in the fabrication

of porous ceramic membranes. It involves freezing a liquid suspension, followed by the sublimation of the frozen medium under reduced pressure. This process leads to the formation of a porous structure with relatively low mechanical properties. Subsequent thermal treatment enables the consolidation of the porous structure and the densification of its walls, thereby enhancing the overall mechanical properties (Liu et al., 2016). Depending on the initial proportion of the liquid medium in the ceramic suspension and the freezing parameters, a wide range of porosity (ranging from 30% to 99%) with diverse internal geometries can be achieved.

4. Synthesis of selective layer for ceramic membrane

The addition of a selective layer to a ceramic membrane is crucial for several reasons, especially in separation and filtration processes. This layer imparts specific properties and functionalities to the membrane that enhance its performance and suitability for various applications. The primary purpose of a selective layer is to enable the membrane to differentiate between different components in a mixture. This selectivity is critical in processes like water purification, where specific contaminants or particles need to be separated from the desired product. Also, selective layer helps improve the overall efficiency of the separation process. By allowing only certain molecules or particles to pass through while blocking others, the membrane can achieve a high separation efficiency in a single step. Moreover, selective layers can be designed to resist fouling, which is the accumulation of unwanted substances on the membrane surface. A well-designed selective layer can

minimize fouling, leading to longer membrane lifetimes and more stable performance. In addition, the selective layer can be engineered to have specific pore sizes and distributions. This customization allows for precise control over the size of particles that can pass through, optimizing the separation process for different applications (Kagramanov et al., 2001)

Certain selective layers can have functional groups that allow specific interactions with certain molecules. This is useful in processes like adsorption or ion exchange, where the membrane can selectively adsorb or exchange particular species. The selective layer can enhance the chemical and thermal stability of the membrane. It can protect the underlying ceramic material from aggressive or corrosive substances present in the feed stream (Schiffer et al., 2021).

In processes where backwashing or frequent cleaning is undesirable or not feasible, a selective layer can ensure that the membrane remains functional over extended periods without significant performance degradation.

Different applications have different requirements for selectivity, permeability, and resistance to fouling. By adjusting the composition and structure of the selective layer, ceramic membranes can be tailored to suit various industries and separation processes.

Overall, a selective layer for ceramic membranes is essential for tailoring the membrane's properties to meet specific separation requirements, improve efficiency, and ensure stable and reliable performance across various industrial applications.

The synthesis method of a selective layer for a ceramic membrane depends on the

specific application and desired properties of the membrane.

General outline of the synthesis method for a selective layer on a ceramic membrane usually are following (Ajiboye et al., 2023; Medvedkova, Nazarov, 1999, Tomina et al., 2019; Avirup, Monal, 2019):

1. *Surface preparation*. The ceramic membrane's surface needs to be properly prepared before applying the selective layer. The surface should be cleaned and, if necessary, activated to improve adhesion.

2. *Choice of approaches to fabricate a selective layer on a ceramic membrane.* One common approach to fabricate a selective layer on a ceramic membrane is the sol-gel method. It involves the hydrolysis and condensation of metal alkoxides or metal chlorides to form a colloidal suspension, called a sol. This sol can then be coated on the ceramic membrane surface through different techniques, such as dip-coating, spin-coating or spray-coating.

The dip coating technique is when the substrate is immersed and withdrawn from the coating solution and quickly dries upon exposure to the atmosphere. Subsequently, a calcination step is typically performed. This technique enables the production of very thin coatings and uniform coating (Li, 2007).

Spin-coating involves spreading the sol on the membrane surface and then spinning the membrane to obtain an even coating.

In spray-coating, a solution containing the selective material is sprayed onto the ceramic membrane using an aerosol spray. This method is relatively simple and can provide uniform coatings (Chen et al., 2018).

3. *Heat treatment*. After the selective layer is coated on the ceramic membrane, it needs to undergo a heat treatment process that helps in removing the solvent and inorganic

precursors and causes the formation of a stable and dense selective layer on the ceramic membrane.

4. *Crosslinking or modification* (optional). In some cases, additional steps may be needed to crosslink or modify the selective layer to enhance its performance or selectivity for the target separation process.

Synthesis method can vary significantly depending on the specific ceramic material, the targeted separation process, and the desired properties of the selective layer. Additionally, advanced techniques and modifications may be required for specific industrial applications of ceramic membranes.

There are several approaches to fabricate a selective layer on a ceramic membrane, each tailored to the specific application and desired properties of the membrane. Here are some common approaches:

4.1 Sol-gel method

This is a widely used technique to synthesize thin films or coatings on ceramic membranes. It involves the hydrolysis and condensation of metal alkoxides or metal chlorides to form a colloidal suspension, known as a sol. The sol is then coated onto the ceramic membrane's surface and subjected to heat treatment (calcination) to form a selective layer (Erdem, 2017).

4.2 Chemical vapour deposition (CVD) method

This technique entails depositing remarkably thin and evenly distributed layers onto a substrate. These layers can have similar or distinct compositions, enabling the modification of membrane surface properties. The deposition process is accomplished through a high-temperature gas-phase

chemical reaction. CVD involves the chemical reaction of vapor-phase precursors to form a selective layer on the ceramic membrane's surface. It offers excellent control over the film's composition and thickness, making it suitable for precise applications (Sabzi et al., 2023).

4.3 Physical Vapor Deposition (PVD)

PVD techniques like sputtering or evaporation can be used to deposit a thin film of the selective material onto the ceramic membrane. In sputtering, high-energy ions are used to eject atoms from a target material, which then deposit on the membrane surface. Evaporation involves heating the target material until it evaporates and condenses on the membrane (Kelkar, Wolden, 2016).

4.4 Anodic oxidation method and electrophoretic deposition (EPD)

Electrochemical methods involve the use of an electric potential to drive the selective material's deposition onto the ceramic membrane surface (Mavukkandy et al., 2020).

Typically, the initial material used is a highly pure aluminium foil (99.999%). To initiate the process, this foil undergoes anodization in a phosphoric acid solution under a consistent voltage, employing a lead cathode. Following anodization, the aluminium foil is immersed in a saturated $HgCl_2$ solution, where aluminium reduces Hg^{2+} ions to mercury. The anodized aluminium oxide membrane gradually separates from the foil by dissolving aluminium into mercury. Subsequently, the membrane is annealed in an oxygen-rich environment at an elevated temperature (Amin et al., 2016).

EPD is an electrophoresis-based technique where charged particles suspended in a liquid move under the influence of an electric field and deposit onto a conductive substrate, which can be the ceramic membrane (Boccaccini, Zhitomirsky, 2002).

4.5 Layer-by-Layer (LbL) Assembly

LbL assembly involves the alternate deposition of oppositely charged materials on the ceramic membrane surface. This process allows for precise control over the film's thickness and composition (Zhao et al., 2019).

4.6 In-Situ Growth

For certain applications, the selective layer can be formed in-situ during the synthesis of the ceramic membrane itself. This can be achieved by incorporating specific dopants or additives into the ceramic matrix during its fabrication (Liu et al., 2022).

4.7 Template-Assisted Methods

Templates can be used to create a porous structure on the ceramic membrane surface, and the selective layer is then deposited within the template pores. The template is subsequently removed, leaving behind the selective layer (Herregods et al., 2019).

4.8 Self-Assembly

Self-assembly techniques rely on molecular self-organization to create a selective layer on the ceramic membrane. These methods often use surfactants or block copolymers to form ordered structures (Hung et al., 2014).

The choice of approach for membrane and selective layer synthesis depends on factors like the specific separation process, the desired selectivity and permeability of the

membrane, the nature of the selective material, and the available equipment and resources.

Recently, some Advanced techniques and modifications for specific industrial applications of ceramic membranes can be tailored to meet the unique requirements of each application:

1. *Surface modification.* Surface modifications can be performed to tailor the surface properties of the ceramic membrane's selective layer for specific applications. For example, functional groups can be introduced onto the surface to enhance the membrane's affinity for certain molecules or to improve fouling resistance.

It was determined that, in addition to the conventional sol-gel and dip-coating methods, atomic layer deposition holds promise for the modification of ceramic membranes concerning the control of layer thickness and pore size tuning. Two frequently employed strategies for improving the performance of ceramic membranes in wastewater treatment involve the enhancement of surface hydrophilicity and the adjustment of surface charge. Nano-sized metal oxides such as TiO_2, ZrO_2, Fe_2O_3, and graphene oxide are regarded as potential candidates for the modification of ceramic membranes to enhance flux and alleviate fouling (Chen et al., 2021).

2. *Pore size control.* Advanced manufacturing techniques can be employed to control the pore size distribution of the ceramic membrane. This can lead to improved selectivity and performance in specific separation processes, especially in applications where precise size exclusion is crucial.

3. *Nanostructured membranes.* Utilizing nanotechnology, ceramic membranes can be engineered at the nanoscale to enhance their performance. Nanoparticles or nanofibers can be incorporated into the selective layer to improve permeability and selectivity (Bhadra, Mitra, 2013). Membranes of this kind can be prepared by incorporating internal nanopores into the matrix of conventional membranes or by nanomodifying the membrane surface (Moattari, Mohammadi, 2020).

4. *Surface coatings.* Applying thin-film coatings on the ceramic membrane's selective layer can provide additional functionalities. For example, hydrophilic or hydrophobic coatings can be used to modify the membrane's wetting properties, affecting fouling behavior.

Ceramic membranes inherently possess hydrophilic characteristics, which restrict their broader application. To devise and generate hydrophobic surfaces with specific attributes, two options are available. The first approach involves crafting a textured surface imbued with hydrophobic properties, achieved by inducing surface heterogeneity, resulting in the formation of profoundly hydrophobic surfaces through the creation of pillars and the incorporation of surface air pockets. Alternatively, the second method involves employing chemical modification through the application of grafting agent materials characterized by low surface free energy (Kujawa et al., 2017; Bico et al., 2002; Ahmad et al., 2013)

5. *3D printing.* Additive manufacturing techniques like 3D printing can be employed to fabricate complex membrane structures with precise control over pore size and distribution. This allows for customized membranes optimized for specific applications.

The outcome of 3D printing is the generation of numerous sublayered

nanofibers, compacted to form a slender membrane. This innovative approach enables the production of filtration membranes of varying shapes, sizes, and controlled porosity, surpassing the capabilities of traditional methods like electrospinning and knife casting (Dommati et al., 2019).

6. *Ion exchange modification*. Modifying the ceramic membrane surface through ion exchange can enable selective binding and separation of specific ions, making them suitable for applications like desalination and heavy metal removal.

Ceramic membranes and ion exchangers are effective at removing turbidity and ionic contaminants from water. In Choi's study, was demonstrated the performance of a hybrid ion-exchange fabric/ceramic membrane system to treat metal ions and turbidity at the same time in synthetic wastewater (Choi et al., 2020).

7. *Self-cleaning mechanisms*. Innovative techniques can be implemented to design self-cleaning ceramic membranes. These mechanisms help reduce fouling and extend the membrane's lifespan, making it more efficient in continuous operation.

Date to now, four primary approaches have been developed for the creation of self-cleaning ceramic membranes: 1) porous piezoelectric ceramic membranes; 2) photo-catalytic ceramic membranes; 3) electrochemical ceramic membranes; and 4) self-cleaning ceramic membrane surfaces. These self-cleaning ceramic membranes have the capability to autonomously eliminate and break down pollutants present on the membrane surface, leading to the restoration of water permeability. This promising attribute positions them as a highly viable solution for the treatment of industrial wastewater, eliminating the need for backwashing or other conventional methods. The self-cleaning ceramic membrane holds substantial potential to emerge as the next-generation anti-fouling ceramic membrane material, thereby revolutionizing the field of continuous water treatment (Zhou et al., 2022).

It's worth noting that each industrial application may require a different combination of these techniques or other innovative approaches. Research and development in ceramic membrane technology continue to evolve, leading to the discovery of new methods and modifications for improved performance in various industries.

5. Cost of the ceramic membranes

The cost of ceramic membranes is influenced by various factors, such as the selection of raw materials, sintering temperature, and manufacturing process. The membrane fabrication method can also significantly impact the overall cost. For instance, wet route membranes often require the addition of binders and plasticisers to achieve the desired paste consistency for extrusion. Removing these additives may involve additional energy consumption, leading to increased membrane costs (Chihi et al., 2019). Commercially available ceramic membranes typically range from $500 to $1000 per square meter (Issaoui et al., 2019). Specifically, commercial alumina ceramic membranes cost approximately $760 per square meter, as stated in the Global Alumina Ceramic Membrane Market Research Report 2020 (global alumina ceramic membrane market, 2020).

Some researchers have estimated the manufacturing cost of membranes by considering both direct and indirect manufacturing expenses. (Vinoth et al., 2016) estimated the manufacturing cost of a kaolin-based membrane with a pore size of 0.339 μm to be $69 per square meter, while (Liang et al., 2021) estimated the preparation cost of a coal fly ash-based tubular membrane to be $199 per square meter (Dong et al., 2006). These reported costs are significantly lower than those of commercially available ceramic membranes.

Moreover, studies have shown that ceramic membranes made from low-cost raw materials can be sintered at lower temperatures, such as 850°C (Chakraborty et al., 2020), compared to alumina membranes that require sintering temperatures up to 1400°C (Hu et al., 2018).

Considering the lifetime of membranes in practical applications, even though conventional polymeric membranes are available at a cost of approximately $50-200 per square meter for industrial-scale operations (Sun er al., 2020), the membrane lifespan need to be taken into account. In this regard, ceramic membranes prepared from natural minerals and industrial wastes offer a promising approach to further reduce the cost of ceramic membranes. This cost-effective solution makes ceramic membranes well-suited for demanding water purification processes.

6. Conclusion
_____

The possibility of using both traditional raw materials (aluminium oxide, silicon dioxide, titanium dioxide, and zirconium dioxide) and low-cost raw materials (clay, kaolin, fly ash) is considered. The latter is becoming increasingly popular among researchers, as they allow for producing high-quality ceramic membranes at low raw material costs. The general procedure for the production of ceramic membranes is presented, as well as a detailed review of such synthesis methods as Solid state method, Slip casting method, Tape casting method, Extrusion method, Pressing method, Dip coating method, Sol-gel method, Chemical vapour deposition (CVD) method, Anodic oxidation method, and Freeze-casting method. The advantages of using ceramic membranes in comparison with polymeric ones have been established based on modern literary data.

Acknowledgment
_____

References
_____

1. Abdullayev, A.; Bekheet, M.; Hanaor, D.; Gurlo, A. Materials and Applications for Low-Cost Ceramic Membranes. *Membranes*, **2019**, *9*, 105. https://doi.org/10.3390/membranes9090105

2. Ahmad, N.A.; Leo, C.P.; Ahmad, A.L. Superhydrophobic alumina membrane by steam impingement: Minimum resistance in microfiltration. *Sep. Purif. Technol.*, **2013**, *107*, 187–194. https://doi.org/10.1016/j.seppur.2013.01.011

3. Ajiboye, T.; Sawunyama, L; Ravele, M.; Rasheed-Adeleke, A.; Seheri, N.; Onwudiwe, D.; Mhlanga, S. Synthesis approaches to ceramic membranes, their composites, and application in the removal of tetracycline from water. *Env.Advan.,* **2023***, 12*, 100371. https://doi.org/10.1016/j.envadv.2023.100371.

4. Ali, M. B.; Hamdi, N.; Rodriguez, M.; Mahmoudi, K.; Srasra, E. Preparation and characterization of new ceramic membranes for ultrafiltration. *Ceram. Int.*, **2018**, *44*, 2328–2335. https://doi.org/10.1016/j.bsecv.2019.06.001

5. Aloulou, W.; Aloulou, H.; Khemakhem, M.; Duplay, J.; Daramola, M. O.; Amar, R. Synthesis and Characterization of Clay-Based Ultrafiltration

Membranes Supported on Natural Zeolite for Removal of Heavy Metals from Wastewater. *Environ. Technol. Innov.*, **2020**, *18*, 100794. https://doi.org/10.1016/j.eti.2020.100794

6. Amanmyrat, A.; Maged, F.B.; Dorian, A.H.; Gurlo, A. Materials and Applications for Low-Cost Ceramic Membranes. *Membr.*, **2019**, *9* (105), https://doi.org/10.3390/membranes9090105

7. Amin, Sh.; Abdallah, H.; Roushdy M.; El-Sherbiny. An Overview of Production and Development of Ceramic Membranes. *Int. J. Appl. Eng. Res.*, **2016,** *11* (12), 7708–7721.

8. Avirup, S.; Monal, D. Development and study of sandwiched layer ceramic membrane. *Desal. and Wat. Treatm.*, **2019**, *156*, 229–237. https://doi.org/10.5004/dwt.2019.23786

9. Bhadra, M.; Mitra S. Nanostructured membranes in analytical chemistry. *TrAC*, **2013**, *45*, 248–263. https://doi.org/10.1016/j.trac.2012.12.010

10. Bhave, R.R. *Inorganic Membranes: Synthesis, Characteristics, and Applications*; Van Nostrand-Reinhold: New York, 1991, 480 p.

11. Bico, J.; Thiele, U.; Quéré, D. Wetting of textured surfaces. *Colloids Surf. A Physicochem. Eng. Asp.* **2002**, *206*, 41–46. https://doi.org/10.1016/S0927-7757(02)00061-4

12. Biesheuvel, P. M.; Verweij, H. Design of ceramic membrane supports: permeability, tensile strength and stress. *J. Membr. Sci.*, **1999**, *156* (1), 141–152.

13. Boccaccini, A.; Zhitomirsky, I. Application of electrophoretic and electrolytic deposition techniques in ceramics processing. *Curr Opin Solid State Mater Sci*, **2002**, *6* (3), 251–260.

14. Bouazizi, A.; Saja, S.; Achiou, B.; Ouammou, M.; Calvo, J. I.; Aaddane, A.; Younssi, S. A. Elaboration and characterization of a new flat ceramic MF membrane made from natural Moroccan bentonite. Application to treatment of industrial wastewater. *Appl. Clay Sci.*, **2016,** *132–133*, 33–40. https://doi.org/10.1016/j.clay.2016.05.009

15. Boudaira, B.; Harabi, A.; Bouzerara, F.; Zenikheri, F.; Foughali, L.; Guechi, A. Preparation and characterization of membrane supports for microfiltration and ultrafiltration using kaolin (DD2) and CaCO$_3$. *Desalin. Water Treat.*, **2016**, *57*, 5258–5265. https://doi.org/10.1080/19443994.2015.1021998

16. Buonomenna, M. G. Membrane processes for a sustainable industrial growth. *RSC Adv.*, **2013**, *3*, 5694–5740. https://doi.org/10.1039/C2RA22580H

17. Burggraaf, A. J.; Cot, L. *Fundamentals of Inorganic Membrane Science and Technology*; Elsevier: Amsterdam, **1996**.

18. Chakraborty, S.; Uppaluri, R.; Das, C. Optimal fabrication of carbonate free kaolin based low cost ceramic membranes using mixture model response surface methodology. *Appl. Clay Sci.*, **2018**, *162*, 101–112, https://doi.org/10.1016/j. clay.2018.06.002

19. Chen, G.; Ge, X.; Wang, Y.; Xing, W.; Guo, Y. Design and preparation of high permeability porous mullite support for membranes by in-situ reaction. *Ceram. Int.*, **2015**, *41*, 8282–8287. https://doi.org/10.1016/j.ceramint.2015.02.045

20. Chen, L. et al. Preparation and mechanism analysis of high performance ceramic membrane by spray coating. *RSC Adv.*, **2018**, *8*, 39884–39892. https://doi.org/10.1039/C8RA07258B

21. Chen, M.; Heijman, S. G. J.; Rietveld, L. C. State-of-the-Art Ceramic Membranes for Oily Wastewater Treatment: Modification and Application. *Membranes*, **2021**, *11*, 888. https://doi.org/10.3390/membranes11110888

22. Chihi, R.; Blidi, I.; Trabelsi-Ayadi, M.; Ayari, F.. Elaboration and characterization of a low-cost porous ceramic support from natural Tunisian bentonite clay. *Compt. Rendus Chem.*, **2019**, *22* (2–3) 188–197. https://doi.org/10.1016/j. crci.2018.12.002

23. Choi, N.-C.; Cho, K.-H.; Kim, M.-S.; Park, S.-J.; Lee, C.-G. A Hybrid Ion-Exchange Fabric/Ceramic Membrane System to Remove As(V), Zn(II), and Turbidity from Wastewater. *Appl. Sci.,* **2020**, *10*, 2414. https://doi.org/10.3390/app10072414

24. DeFriend, K. A.; Wiesner, M. R.; Barron, A. R. Alumina and aluminate ultrafiltration membranes derived from alumina nanoparticles. J. *Membr. Sci.,* **2003**, *224*, 11–28. https://doi.org/10.1016/S0376-7388(03)00344-2

25. Dong, Y.; Chen, S.; Zhang, X.; Yang, J.; Liu, X.; Meng, G. Fabrication and characterization of low cost tubular mineral-based ceramic membranes for micro-filtration from natural zeolite. *J. Membr. Sci.,* **2006**, *281*, 592–599. https://doi.org/10.1016/j.memsci.2006.04.029

26. Dontsova, T. A et al. Enhanced Photocatalytic Activity of TiO$_2$/SnO$_2$ Binary

Nanocomposites. *J. Nanomater.*, **2020,** *2020*, 1-13. https://doi.org/10.1155/2020/8349480

27. Dommati, H.; Ray, S.; Wang, J.-C.; Chen S.-S. A comprehensive review of recent developments in 3D printing technique for ceramic membrane fabrication for water purification. *RSC Adv.*, **2019**, *9*, 16869–16883. https://doi.org/10.1039/C9RA00872A

28. Elaine Fung, Y. L.; Wang, H. Investigation of reinforcement of porous alumina by nickel aluminate spinel for its use as ceramic membrane. *J. Membr. Sci.,* **2013**, 444, 252–258. https://doi.org/10.1016/j.memsci.2013.05.025

29. Eom, J.-H.; Yeom, H.-J.; Kim, Y.-W.; Song, I.-H. Ceramic Membranes Prepared from a Silicate and Clay-mineral Mixture for Treatment of Oily Wastewater. *Clays Clay Miner.*, **2015,** *63*, 222–234. https://doi.org/10.1346/CCMN.2015.0630305

30. Erdem, I. Sol-gel applications for ceramic membrane preparation. *AIP Conference Proceedings*, **2017**, *1809*, 020011. https://doi.org/10.1063/1.4975426

31. Fang, J. Qin, Q.; Wei, W.; Zhao X.; Jiang L. Elaboration of new ceramic membrane from spherical fly ash for microfiltration of rigid particle suspension and oil-in-water emulsion. *Desalin.*, **2013**, *311*, 113–126. https://doi.org/10.1016/j.desal.2012.11.008

32. Foorginezhad, S.; Zerafat, M. M. Microfiltration of cationic dyes using nano-clay membranes. *Ceram. Int.,* **2017**, *43*, 15146–15159. https://doi.org/10.1016/j.ceramint.2017.08.045

33. Galán-Arboledas, R. J.; Cotes, T.; Martínez, C.; Bueno, S. Influence of waste addition on the porosity of clay-based ceramic membranes. *Desalin. Water Treat*., **2016,** *57*, 2633–2639. https://doi.org/10.3390/membranes9090105

34. Gitis V.; Rothenberg G. *Ceramic Membranes: New Opportunities and Practical Applications*; John Wiley & Son*s* Inc.: Hoboken, **2016**, 395 p.

35. Hamden, M.; Bouaziz, J. Preparation and characterization of tubular cermet membrane for microfiltration separation: application to the treatment of textile wastewater. *Comptes Rendus. Chimie*, **2021,** *24* (1), 135–146. https://doi.org/10.5802/crchim.69

36. Harabi, A.; Zenikheri, F.; Boudaira, B.; Bouzerara, F.; Guechi, A.; Foughali, L. A new and economic approach to fabricate resistant porous membrane supports using kaolin and CaCO₃. *J. Eur.* *Ceram. Soc.*, **2014**, *34*, 1329–1340. https://doi.org/10.1016/j.jeurceramsoc.2013.11.007

37. Hedfi, I.; Hamdi, N.; Srasra, E.; Rodríguez, M. A. The preparation of micro-porous membrane from a Tunisian kaolin. *Appl. Clay Sci.*, **2014**, *101*, 574–578. https://doi.org/10.1016/j.clay.2014.09.021

38. Herregods, S. J. F., Wyns, K., Buekenhoudt, A.; Meynen, V. The Use of Different Templates for the Synthesis of Reproducible Mesoporous Titania Thin Films and Small Pore Ultrafiltration Membranes. *Adv. Eng. Mater.*, **2019**, *21*, 1900603. https://doi.org/10.1002/adem.201900603

39. Hu, Z.; Y. Yang, Q. Chang, F. Liu, Y. Wang, J. Rao, Preparation of a high- performance porous ceramic membrane by a two-step coating method and one-step sintering, *Appl. Sci.*, **2018**, *9* (1). https://doi.org/10.3390/app9010052

40. Hubadillah, S. K.; Othman, M. H. D.; Ismail, A. F.; Rahman, M. A.; Jaafar, J. A low cost hydrophobic kaolin hollow fiber membrane (h-KHFM) for arsenic removal from aqueous solution via direct contact membrane distillation. *Sep. Purif. Technol.*, **2019**, *214*, 31–39. https://doi.org/10.1016/j.seppur.2018.04.025

41. Hung, W.-S. et al. Pressure-assisted self-assembly technique for fabricating composite membranes consisting of highly ordered selective laminate layers of amphiphilic graphene oxide. *Carbon*, **2014**, *68*, 670–677. https://doi.org/10.1016/j.carbon.2013.11.048

42. Isobe, T.; Kameshima, Y.; Nakajima, A.; Okada, K.; Hotta Y. Extrusion method using nylon 66 fibers for the preparation of porous alumina ceramics with oriented pores. *J. Europ. Ceram. Soc.*, **2006**, *26* (12), 2213–2217.

43. Issaoui, M.; Limousy, L. Low-cost ceramic membranes: Synthesis, classifications, and applications. *C. R. Chimie*, **2019**, *22*, 175–187. https://doi.org/10.1016/j.crci.2018.09.014

44. Jana, S.; Purkait, M. K.; Mohanty, K. Preparation and characterization of low-cost ceramic microfiltration membranes for the removal of chromate from aqueous solutions. *Appl. Clay Sci.*, **2010**, *47*, 317–324. https://doi.org/10.1016/j.clay.2009.11.036

45. Jedidi, S.; Saïdi, S.; Khemakhem, A.; Larbot, N.; Elloumi-Ammar, A.; Fourati, A.; Charfi, A. et al. Elaboration of new ceramic microfiltration membranes from mineral coal fly ash applied to waste

water treatment. *J. Hazard. Mater.*, **2011**, *172*, 152–158. https://doi.org/10.1016/j.jhazmat.2009.06.151

46. Kagramanov, G. G.; Nazarov, V. V. Ceramic Membranes with Selective Layers Based on SiO₂, TiO₂, and ZrO₂. *Glass and Ceramics*, **2001**, *58*, 166–168. https://doi.org/10.1023/A:1012366309705

47. Kelkar, S.; Wolden, C. Evaluation of Vapor Deposition Techniques for Membrane Pore Size Modification. *J. Membr.Sci. and Res.*, **2017**, *3*, 64–70. http://dx.doi.org/10.22079/jmsr.2016.20345

48. Khemakhem, S.; Larbot, A.; Amar, R. B. Study of performances of ceramic microfiltration membrane from Tunisian clay applied to cuttlefish effluents treatment. *Desalin.*, **2006**, *200*, 307–309.

49. Kucera, J. *Membrane materials and module development: historical perspective, Encyclopedia of Membrane Science and Technology*; John Wiley & Sons Inc.: Hoboken, **2013**. https://doi.org/10.1002/9781118522318.emst033

50. Kujawa, J.; Cerneaux, S.; Kujawski, W.; Knozowska, K. Hydrophobic Ceramic Membranes for Water Desalination. *Appl. Sci.,* **2017**, *7*, 402. https://doi.org/10.3390/app7040402

51. Kumar, V.; Monash, P.; Pugazhenthi, G. Treatment of oil-in-water emulsion using tubular ceramic membrane acquired from locally available low-cost inorganic precursors, *Desalin. Water Treat.*, **2016**, *57* (58), 28056–28070. https://doi.org/10.1080/19443994.2016.1179221

52. Lai, Z. P.; Bonilla, G.; Diaz, I.; Nery, J. G.; Sujaoti, K.; Amat, M. A. et al. Microstructural optimization of a zeolite membrane for organic vapor separation. *Sci.*, **2003**, *300* (5618), 456–460.

53. Liang, D.; Huang J.; Zhang Y. et al. Influence of dextrin content and sintering temperature on the properties of coal fly ash-based tubular ceramic membrane for flue gas moisture recovery. *J. Eur. Ceram. Soc.,* **2021,** *41*, (11), 56965710. https://doi.org/10.1016/j.jeurceramsoc.2021.04.055

54. Lin, Y.; Zou, D.; Chen X. et al. Low temperature sintering preparation of high- permeability TiO₂/Ti composite membrane via facile coating method. *Appl. Surf. Sci.*, **2015**, *349*, 8–16.

55. Liu J.; Dong, Y.; Dong, X.; S. et al. Feasible recycling of industrial waste coal fly ash for preparation of anorthite-cordierite based porous ceramic membrane supports with addition of dolomite. *J. Eur. Ceram. Soc.,* **2016**, *36*, 1059–1071. https://doi.org/10.1016/j.jeurceramsoc.2015.11.012

56. Liu, Y. et al. Alcohols assisted in-situ growth of MoS2 membrane on tubular ceramic substrate for nanofiltration. *J. Membr. Sci.*, **2022**, *659*, 120777. https://doi.org/10.1016/j.memsci.2022.120777

57. Lorente-Ayza, M.-M.; Mestre, S.; Menéndez, M.; Sánchez, E. Comparison of extruded and pressed low cost ceramic supports for microfiltration membranes. *J. Eur. Ceram. Soc.* **2015**, *35*, 3681–3691. https://doi.org/10.1016/j.jeurceramsoc.2015.06.010

58. Mavukkandy, M. et al. Thin film deposition techniques for polymeric membranes– A review. *J. Membr. Sci.*, **2020**, *610*, 118258. https://doi.org/10.1016/j.memsci.2020.118258

59. Medvedkova, N. G., Nazarov, V. V. Sol-gel preparation of selective layers of ceramic ultrafiltration membranes based on titania. *Glass. Ceram.*, **1999**, *53*, 117–119. https://doi.org/10.1007/BF01166067

60. Moattari R., Mohammadi T. Chapter 5 - Nanostructured membranes for water treatments, In Micro and Nano Technologies, Nanotechnology in the Beverage Industry, *Elsevier*, **2020**, 129–150. https://doi.org/10.1016/B978-0-12-819941-1.00005-5.

61. Nair, P., Mizukami, F., Okubo, T., Nair, J., Keizer, K.; Burggraaf, A. J. High-temperature catalyst supports and ceramics membranes: metastability and particle packing. *AIChE J.,* **1997**, *43* (11), 2710–2714.

62. Nandi, B. K., Uppaluri, R., Purkait, M. K. Preparation and characterization of low cost ceramic membranes for micro-filtration applications. *Appl. Clay Sci.,* **2008**, 42, 102–110. https://doi.org/10.1016/j.clay.2007.12.001

63. Sabzi, M.; Mousavi Anijdan, S. H.; Shamsodin, M.; Farzam, M.; Hojjati-Najafabadi, A.; Feng, P.; Park, N.; Lee, U. A Review on Sustainable Manufacturing of Ceramic-Based Thin Films by Chemical Vapor Deposition (CVD): Reactions Kinetics and the Deposition Mechanisms. *Coatings* **2023**, *13*, 188. https://doi.org/10.3390/coatings13010188

64. Saffaj, N.; Persin, M.; Younsi, S. A.; Albizane, A.; Cretin, M.; Larbot, A. Elaboration and characterization of microfiltration and ultrafiltration membranes deposited on raw support prepared from natural Moroccan clay: Application to filtration of solution containing dyes and salts. *Appl. Clay Sci.,* **2006**, *31*, 110–119. https://doi.org/10.1016/j.clay.2005.07.002

65. Sah, A., Castricum, H.L., Bliek, A., Blank, D., Elshof, J. E. Hydrophobic modification of

gamma- alumina membranes with organochlorosilanes. *J. Membr. Sci.,* **2004**, *243* (1–2), 125–132. https://doi.org/10.1016/j.memsci.2004.05.031

66. Schafföner, S.; Freitag, L.; Hubálková, J., Aneziris, C. Functional composites based on refractories produced by pressure slip casting, *J. Eur. Cer. Societ.,* **2016**, *36* (8), 2109–2117. https://doi.org/10.1016/j.jeurceramsoc.2016.02.008

67. Schiffer, S. et al. Effects of selective layer properties of ceramic multi-channel microfiltration membranes on the milk protein fractionation. *Sep. Purif. Technol.*, **2021**, *259*, 118050.

68. Serhiienko, A.; Dontsova, T.; Yanushevska, O.; Vorobyova, V.; Vasyliev, G. Characterization of ceramic membrane support based on Ukrainian kaolin, *Molec. Cryst. Liq. Cryst.*, **2023**, *752* (1), 128–141.
https://doi.org/10.1080/15421406.2022.2091279

69. Serhiienko, A. O., Dontsova, T. A., Yanushevska, O. I., Nahirniak, S. V., Ahmad, H.-B. Ceramic membranes: New trends and prospects (short review). *Wat. and Wat. Purif. Tech.. Scientif. and technic. news*, **2020**, *27* (2), 4–31. https://doi.org/10.20535/2218-93002722020208817

70. Sun, L.; Wang, Z.; Gao, B. Ceramic membranes originated from cost-effective and abundant natural minerals and industrial wastes for broad applications – a review. *Desal. and Wat.Treat.*, **2020**, 201, 121–138.
https://doi.org/10.5004/dwt.2020.25910

71. Tomina, V; Nazarchuk, G.; Melnyk, I. Modification of Ceramic Membranes by Silica Nanoparticles with Thiourea Functions, *J. Nanomater.,* **2019**, *2019*, 2534934. .
https://doi.org/10.1155/2019/2534934

72. Xu, R., Wang, J.H., Kanezashi, M., Yoshioka, T. and Tsuru, T. Reverse osmosis performance of organosilica membranes and comparison with the pervaporation and gas permeation properties. *AIChE J.,* **2013**, *59* (4), 1298–1307. https://doi.org/10.1002/aic.13885

73. Yoshino, Y., Suzuki, T., Nair, B., Taguchi, H., Itoh, N. Development of tubular substrates, silica based membranes and membrane modules for hydrogen separation at high temperature. *J. Membr. Sci.*, **2005**, *267*, 8–17. https://doi.org/10.1016/j.memsci.2005.05.020

74. Zhao, S. et al. The Future of Layer-by-Layer Assembly: A Tribute to ACS Nano Associate Editor Helmuth. *CS Nano,* **2019**, *13* (6), 6151–6169. https://doi.org/10.1021/acsnano.9b03326

75. Zhou, J.-E.; Dong, Y.; Hampshire, S.; Meng, G. Utilization of sepiolite in the synthesis of porous cordierite ceramics. *Appl. Clay Sci.*, **2011**, *52*, 328–332. https://doi.org/10.1016/j.clay.2011.02.001

76. Zhou, J.; Zhang, X.; Wang, Y.; Larbot, A.; Hu, X. Elaboration and characterization of tubular microporous ceramic support for membranes from kaolin and dolomite. *J. Porous Mater.*, **2010**, *17*, 1–9. https://doi.org/10.1007/s10934-008-9258-z

77. Zou, D.; Mao, H.; Zhong, Z. Construction strategies of self-cleaning ceramic composite membranes for water treatment. *Ceram. Internat.*, **2022**, *48* (6), 7362–7373.
https://doi.org/10.1016/j.ceramint.2021.12.086

МАТЕРІАЛИ ТА МЕТОДИ ДЛЯ СИНТЕЗУ КЕРАМІЧНИХ МЕМБРАН. КОРОТКИЙ ОГЛЯД

Кирій С. О.[1]

[1] Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», Україна, kysvit@gmail.com

Дана стаття присвячена короткому огляду основних видів сировини, що використовується для синтезу керамічних мембран. Зокрема увагу приділено як традиційним матеріалам, таким як оксид алюмінію, діоксид кремнію, діоксид титану, діоксид цирконію, цеоліти, так і недорогим матеріалам таким як різноманітні глини та відходи промисловості. Розглянуто сучасні методи виготовлення високоефективних керамічних мембран, зокрема шлікерне лиття, стрічкове лиття, пресування, екструзія тощо. Також розглянуто загальну схему підготовки синтезу селективного шару на керамічній мембрані з використанням різних методів синтезу самого селективного шару. Крім того, проаналізовано вартість комерційних керамічних мембран та чинники, які на неї впливають. На основі сучасної літератури встановлено, що керамічні мембрани з їх потенціалом для застосування при високій температурі, високому тиску та агресивному середовищі мають явні переваги над полімерними мембранами. Крім того, енергоефективність, компактність та універсальність робить їх життєздатною альтернативою для очищення води замість більш дорогих методів, таких як коагуляція та адсорбція. Керамічні мембрани стали конкурентоспроможною альтернативою полімерним мембранам, демонструючи унікальні властивості матеріалу та чудові характеристики. Використання недорогих матеріалів для виготовлення керамічної мембрани дає змогу використовувати її в економічно чутливих секторах. Такі мембрани демонструють чудові механічні властивості та високу проникність, а недорогі матеріали можуть зменшити їх вартість. Поточні наукові дослідження та розробки зосереджуються на використанні різних глин і відходів для виробництва керамічних мембран, з метою створення нових поколінь керамічних мембран для екологічного застосування.

Ключові слова: керамічні мембрани, матеріали для керамічних мембран, мембранна технологія, методи синтезу, низьковартіснімембранні матеріали, селективний шар