Low-cost ceramic membranes: a research opportunity for industrial application

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SUMMARY

Obtaining low-cost ceramic membranes has attracted great interest in the scientific community in last years, as it allows to preserve the advantages of ceramic materials while significantly reduce their manufacturing costs. This type of membranes is mainly based on the use of raw materials and manufacturing processes typical of traditional ceramic materials, i.e silicate-based ceramics. This work exhaustively reviews the raw materials, ceramic compositions and variables of the manufacturing processes used in the development of these membranes, with special emphasis on their numerous potential industrial applications.

1 Introduction

In practice, a membrane is a barrier that moderates the permeation of species in contact with it. This semipermeable interface can be homogeneous or heterogeneous, dense or porous, organic or inorganic, liquid or solid, etc. The mass transport from one phase to another occurs when a driving force is applied (normally a difference in pressure or concentration). Currently, processes in which

membrane technology can be used are expanding. The most developed industrial separation processes that make use of membrane technology are microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis. It is also being applied in other industrial processes, such as gas separation, pervaporation, membrane reactors, as well as medical applications. According to the material of construction, the main types of membranes are polymeric and ceramic membranes. These latter are manufactured from inorganic materials such as aluminium oxides, zirconia and titania. Ceramic membranes are usually more costly than polymeric ones for the reason that their raw materials are expensive as well as the manufacture complexity. However, ceramic membranes are characterized by a series of advantages such as long-term durability, high mechanical strength, resistance to chemicals and solvents and thermal stability [1-5].

Porous ceramic membranes usually comprise several layers of one or more ceramic materials. They generally consist of a macroporous support, one or more mesoporous intermediate layers and a microporous top layer. Normally, the support provides mechanical strength, while the intermediate layers bridge between the support and the top layer, with the aim of gradually reducing the pore size. The top layer is the selective layer, where the separation process of the membrane takes place (Figure 1).

These asymmetric configurations of porous multilayers are combined to provide ceramic membranes with a wide range of separation performance as set out in Table 1.

The porous support is usually obtained by conventional ceramic shaping methods and its only function is to support and give mechanical strength to the whole. On this support, one or more intermediate layers are usually deposited, whose missions are to prevent the infiltration of the selective layer in the support, minimize surface roughness and inherent defects in support and provide a smooth and flawless surface for good deposition of the selective layer. The most common methods of layer deposition are dip-coating and casting. Finally, the selective layer is deposited, from which it is necessary to exhaustively control the pore size, because it will determine what will pass through the membrane and what will be retained [2,5].

The quality of the support is critical, since the defects and irregularities of the support usually produce defects in the layers applied on it; in this way, the supports must be smooth, present a constant and homogeneous surface characteristics (as wettability) as well as a narrow pore size distribution and enough mechanical strength. The porous support can be obtained by different techniques, using powders or suspensions as precursors. The methods usually used for shaping the support are mainly extrusion and pressing, among others, and the choice of one of them is mainly based on the final configuration of the membrane (extrusion for tubular membranes, pressing for flat membranes). The pore sizes usually obtained are greater than 0.1 μm. In this process, in order to obtain defect-free supports, the adequacy of the powders, especially the granule size (usually between 0.2 and 20 μm) and the incorporation of additives that improve powder processing (deflocculants, plasticizers, binders and lubricants) are of great importance. After shaping the support, the drying and subsequently the sintering are carried out. Drying should be made at a rate that minimizes the appearance of cracks and defects. Finally, the ceramic is thermally treated for sintering; the structure of the firing cycle must ensure the correct elimination of the added organic additives to improve the processing (first part of the firing), together with achieving the desired final properties by sintering (second part of the firing). The density, total pore volume, pore diameter and mechanical strength depend on the maximum sintering temperature (lower than the melting temperature of the material) and residence time at that temperature. Due to the nature of the materials used to obtain the support, the sintering temperatures must be quite high (> 1000 ℃) [3,4].

Depending on the desired pore size in the selective layer, the required precursors are different, as detailed in Table 2. Ceramic oxide suspensions are used for the preparation of microfiltration and ultrafiltration layers with relatively large pore size. However, it is necessary to apply the sol-gel technology to synthesize layers of smaller pore size: preparation of colloidal sols for ultrafiltration layers of reduced pore size and polymeric sols for obtaining nanofiltration layers.

As set out above, ceramic membranes offer unique advantages in membrane processes due to their excellent properties, such as mechanical strength, thermal stability and chemical resistance under severe conditions (extreme pH, oxidizing agents, etc.), as well as their reduced tendency to

fouling [2,6]. However, its high price has limited its use in cost-sensitive processes such as environmental applications [3-5]. Ceramic membranes are usually made up of high purity refractory oxides whereas for many applications the benefits provided by these oxides are not necessary, such as, for example, in the treatment of domestic or industrial wastewater, in which the required quality of the treated effluent can be obtained with membranes synthesized with more conventional materials, namely low-cost ceramic membranes. This would imply a significant reduction in raw materials and processing costs, considerably reducing the price of the obtained ceramic membranes.

Low-cost ceramic membranes base their composition on lower-priced raw materials, usually related to traditional ceramic products (tile, sanitaryware, earthenware, porcelain, etc.). Processing of the substrates is also based on the traditional ceramic industry, with pressing and extrusion being the most commonly used forming processes; on the other hand, the sintering temperatures applied are lower than those employed in commercial ceramic membranes, thus reducing processing cost.

Taking as a reference that the prices of ceramic membranes based on alumina and zirconia can lie between 500 and 3000 $\cdot m^{-2}$ [7] and those of polymeric membranes between 20 and 200 $\cdot m^{-2}$ [8-10], there is a wide margin in which low-cost ceramic membranes can be marketed. The approximate price of a commercial alumina membrane is about 500 $\cdot m^{-2}$ [8,9,11], which doubles that of a membrane based on a kaolin-quartz-feldspar composition of 250 $\cdot m^{-2}$ [12]. This price difference is mainly due to the raw materials used and the different conditions along manufacturing process, especially during sintering. The price of alumina is approximately 100 times higher than that of kaolin; moreover, the energy required for sintering an alumina membrane is much higher than that of a kaolin one, due to the difference in temperature that needs to be reached (approximately 1600 °C for alumina, as opposed to 1200 °C for kaolin-based compositions). Moreover, kaolin membranes display a lower apparent density (2.7 $g \cdot cm^{-3}$) than alumina membranes (3.98 $g \cdot cm^{-3}$), therefore the amount of material needed per unit area decreases, reducing the cost of raw materials [13].

Thus, the interest in low-cost ceramic membranes has increased in recent years, as they combine the high performance of ceramics with economy. For this reason, great efforts have been made in recent years in the field of membrane technology to develop new porous ceramic materials based on locally available low-cost raw materials such as clay, kaolin, bauxite, diatomaceous earth, andalusite, etc.., [14-23]. These materials are available in abundance and require significantly lower sintering temperatures than those used in commercial oxide membranes. Thus, the mixture kaolin and dolomite was explored as raw material in [16] and [20]. This research emphasized the multiple role of dolomite in the ceramic composition as, on the one hand, it provides adequate porosity and, on the other hand, it acts as a sintering inhibitor. Similar approach was followed in [7,8] but replacing dolomite by calcite as pore former and sintering inhibitor. Also, diatomaceous earth can be used with this same objective as demonstrated by Akhtar et al. [15]. Weir et al. addressed the use of sepiolite clay mineral and showed the benefits of including this high-plasticity mineral in the starting composition [19]. Crystalline phases from aluminosilicate raw materials have been also commonly explored in many works such as cordierite ceramics in [13] and mullite ceramics in [14]. Findings showed the good performance of these ceramics for membrane application. Finally, zeolites have been also considered in low-cost ceramic membrane literature [17,18]. When using zeolites, micropores associated to these materials are accessible to diffusing molecules therefore applications related with gases can be also contemplated.

The compositions employed in this type of membranes largely depend on the raw materials available in the areas of study, the application for which it is intended, etc. Broadly speaking, there could be two different branches: those compositions based on advanced ceramics (e.g. those containing alumina) with potential applications in very aggressive media and compositions exclusively based on traditional ceramics for applications with lower demanding performance.

Although research activity on low-cost membranes has been intense in recent years, due to the numerous potential applications in the industry, very few studies have attempted to correlate the microstructural characteristics of sintered substrates with their functional properties, due to the fact that the use of natural minerals (clay, kaolin, etc.) as raw materials makes it difficult to model the intricate microstructure of these membranes [1,24]. For example, Li et al. [24] applied the

equations of Carman-Kozeny and Hagen-Poiseuille to relate the membrane permeability and its microstructural parameters, obtaining a good correspondence with the experimental data. Marchese et al. calculated the characteristic parameters of the membranes (hydraulic radius) based on water permeability, as well as different structural characteristics of the membranes (topography, roughness and friction) measured by Atomic Force Microscopy (AFM) [1].

Recently Lorente-Ayza et al. have reported a complete research on the effect of starch on the microstructure of low-cost ceramic membranes [25-27]. The research includes the effect of the nature, amount and particle size of the starch on the microstructure and permeability of different low-cost ceramic membrane compositions. Thus, starch content influences membrane characteristics as porosity, pore size distribution and permeability. In their work, Lorente-Ayza et al. [25] determined that the experimental data of water permeability fit the Hagen-Poiseuille equation confirming the significant contribution of coarse pores generated by starch to membrane permeability. In addition, the effect of starch particle size as well as the influence of fluxing elements present in the starch ashes were also showed by Lorente-Ayza et al. in [26] and [27] respectively.

The development of ceramic membranes based on conventional, naturally occurring minerals could trigger a technological revolution that would provide greater economic value to many natural minerals (widely available throughout the world), as well as to the ceramic companies that process these raw materials. From the above, it can easily be understood the growing interest among the scientific community in research into conventional ceramic raw materials that would allow the design of cheaper ceramic compositions for the manufacture of low-cost ceramic membranes, evaluating the incorporation of numerous raw materials, additives and even residues, both at laboratory and pilot scales.

This review aims to analyze and discuss the research developed in recent years on the raw materials, processes and applications of low-cost ceramic membranes, highlighting the interest of this line of research in the field of membrane separation processes.

2 Low-cost ceramic membranes synthesis

Low-cost ceramic membranes addressed in the literature usually consist of a symmetrical support, directly applied as a microfiltration membrane. In some cases, the support serves as a substrate on which one or more layers are applied, the composition of which can be also based on low-cost raw materials (clays, feldspars, etc., or even some waste) or on raw materials typically used to obtain selective layers (alumina, titania, zirconia, etc.).

2.1 Raw materials

The properties of low-cost ceramic membranes are determined by their composition (nature and proportion of raw materials and additives), the content and type of pore-forming materials and the firing cycle (sintering temperature and dwell time). However, the forming method defines the geometry of the final product, and the ceramic composition must be adapted to it [13,28].

Literature reports great variety of raw materials for this type of compositions. For economic reasons, all these raw materials have in common their proximity to the research center, being very diverse their origin: Algeria, India, Argentina, Cameroon, Malaysia, Tunisia, Iran, etc. Clays and kaolins are the most commonly used raw materials due to its optimum characteristics for ceramic processing. As an example, the following tables 3 and 4 show a compendium of some works carried out with clays and mixtures of kaolin+clay.

Mullite-based ceramic membranes represent one of the best alternatives to alumina due to their excellent properties such as low thermal expansion and conductivity, excellent thermal shock resistance and high thermal, chemical and mechanical stability [39,40]. Clay minerals must be included in the initial composition to produce the necessary amount of mullite phase. However, membranes prepared with clayey raw materials present disadvantages, such as low porosity, small pore size or high sintering shrinkage, as a result of the high densification rate of clays due to the existence of minor fluxing minerals or impurities in their composition. Thus, N. Saffaj et al. reported the sintering behavior of a filtration support prepared from natural Moroccan clay [41]. The authors emphasized that at certain high temperature the formation of a vitreous mass by silica and some impurities present in the clay lead to porosity and pore size decrease. In the same way,

J. Zhou et al. stated that it is difficult to get the required properties for membranes based on clay minerals since these minerals can be easily sintered by the action of various existing impurities [18]. P. Belibi et al. also pointed out the marked sintering effect associated to clay-minerals when a local Cameroonian kaolinitic-illitic clay was used to make microfiltration ceramic membranes [32]. According to these authors, the phenomenon is also attributed to the formation of glassy phase from illite mineral which gives rise to a progressive reduction of porosity.

A commonly used strategy to increase porosity and pore size consists in the introduction of different pore forming organic materials, which are named in the tables above and defined in detail in later sections. On the other hand, the addition to the initial composition of minerals containing alkaline earth metals (mainly Mg and Ca), such as wollastonite, calcite or dolomite, may contribute to the reduction of sintering temperature and time, as well as increasing the membrane mechanical strength. Since alkaline earth carbonates are also used as pore formers, their influence on the composition is detailed in later sections. Furthermore, there are different ceramic raw materials, such as feldspars, quartz, bentonites, talcs, etc., which can be added to clays and kaolins to improve membrane processing and properties.

Finally, in recent years there has been an increase in the number of studies valuing wastes in the production of low-cost ceramic membranes, as a main ingredient with diverse functionality or as a pore forming material, depending on the nature of the waste used. Fly ashes from coal-fired power plants, coal gangue and bauxite and diverse phosphate industry sub-products have been reported as ingredients in low-cost ceramic membrane compositions [42].

2.2 Pore former materials

Ceramic membranes must have an adequate porosity and pore size, so that their permeability and selectivity are suitable for the separation process for which they are intended. The addition of a temperature-sensitive compound to create porosity is applied both in the manufacture of ceramic membranes based on pure oxides (alumina, titania, zirconia, etc.) and in low-cost membranes. This compound disappears totally or partially during the sintering heat treatment by decomposition, evaporation, liquid phase formation or combustion [43], generating an additional

porous network that modifies the pore size distribution that could be obtained with the ceramic composition by itself and increasing the permeability of the membrane.

There is a large number of materials that can be used as pore generators, ranging from chemically pure substances as urea [44], processed substances such as starch [45], flour [46], polymethylmethacrylate [47], polystyrene and other materials as coal and their derivatives [48], activated carbon [37,49], natural products such as poppy seeds [50], rice bran [51], millet or corn [48] or even wastes as sawdust [12, 32,52]. Recently the use of olive stone as pore former material to make low-cost ceramic membranes for a membrane biological reactor (MBR) was reported [53]. The composition of the ceramic membranes was based on agricultural and industrial wastes, such as olive stones (from olive oil production), marble waste powder (from quarrying and processing of marble) and chamotte (from fired tile scrap) together with high-plasticity clay.

Starches and carbonates are the most widely used pore formers. Starch is a natural biopolymer that easily oxidizes (at temperatures close to 500ºC), is inexpensive and ecological. However, this substance comes from natural sources (potato, pea, corn, wheat, etc.) and therefore is subject to different extraction and conditioning processes which may affect membrane characteristics. Despite this variability, the nature and properties of starch are not usually considered in low-cost membrane research. Thus, in a study with five different starches Gregorová et al. showed that the mean particle size varied considerably from one starch to another, in values between 4 and 50 µm, even modifying the amplitude and shape of the particle size distribution curve (monomodal or bimodal) [45]. Lorente et al. confirmed the variability in starch particle size as well as its effect on membrane microstructure and permeability by comparing six samples of different starches in a clay-based low-cost ceramic membrane composition [26]. As observed in Figure 2, a starch of large particle size (average diameter of 50 µm) is required to significantly increase the permeability of membranes. As the most frequent average size of commercial starches lies between 20 and 50 µm it is necessary to carefully select the particle size of the starch in order to induce significant changes in membrane permeability. Also, the influence of starch ash from different starches (corn, potatoes, wheats and pea) on membrane characteristics has been recently reported as displayed in Figure 3. This figure shows the variation of air permeability with sintering

(dwelling) time for a clay-based low-cost ceramic membrane composition prepared from the same amount of starch but of different nature. As observed, the figure highlights that there is a non-negligible effect of the starch ash on the sintering behavior and consequently on membrane microstructure and permeability [27].

Nevertheless, the parameter with the greatest influence on permeability and pore size is the proportion of starch added to the composition. In order to reach the optimum level of permeability, the proportion added usually varies between 2 and 20 wt.%. Thus, by adjusting the amount of starch added, a wide range of pore size and permeabilities can be obtained. For example, the average pore size of alumina membranes varies from 1 to 2 µm and porosity increases from 23 to 44 % as the amount of starch grows from 0 to 15 wt.% [54], while in clay membranes porosity increases from 9 to 32 % as the proportion of starch augments from 0 to 35 wt.% [55]. As shown in Figure 4a and 4b, Lorente-Ayza et al. reported the effect of the amount of corn starch on the microstructure of alumina-kaolin low-cost ceramic membranes [25]. On the one hand, porosity significantly increases, and pore size distribution broadens by introducing starch in the membrane composition as revealed by the marked arrow in the mercury pore size distributions (Figure 4a). On the other hand, Figure 4b displays the relation between membrane air permeability and the amount of starch added for two sintering temperatures (1200 ºC and 1400 ºC). Thus, based on a percolation model, the authors estimated that a threshold amount of starch around 10 wt.% was necessary for an effective interconnection of the pore network created by the pore former, in terms of permeability increase.

These same authors explain the mechanism of pore formation from starch addition. Thus, the membrane without starch exhibits a bimodal pore size distribution, as a result of its composition: small pores (around 0.1 µm) mainly caused by the porosity of the matrix made up of decomposed kaolin particles and large pores (around 0.45 µm), generated between the decomposed kaolin and alumina particles. The pore size grows (around 0.7 µm) and the pore size distribution becomes wider when reduced amounts of starch are added to the composition (less than 10 wt.%). Nevertheless, the bimodal distribution becomes trimodal as well as the pore size dramatically increases when starch is added to the composition in high proportions (more than 10 wt.%). This

is because over this percentage of starch the large pores generated by starch burning out start to create a connected network accessible to fluids. Similar findings concerning a 10 wt.% starch content threshold was reported by G.C.C. Yang et al. with alumina-bentonite membranes [54]. According to these authors, the packing of alumina particles in the green specimens were disrupted by the larger starch agglomerates. As the starch content increased over 10 wt.% a greater number and degree of contacts among the individual alumina-starch shells resulted in a larger nominal pore size and porosity. In a recent paper D.O. Obada et al. have confirmed the pore interconnection mechanism associated with pore former addition [56], by using powdery high density polyethelene (PHDPE) as porogen agent. Thus, the authors showed that the addition of sufficient amount of PHDPE (20 wt.% was considered optimum) increases porosity and pore size as well as pore connectivity, owed to the increase of interconnected pores created by pore former burnout which gave rise to an increase of permeability.

Sánchez et al. also confirmed the effect of the amount of pore former on membrane permeability in the aforementioned research on low-cost ceramic membrane based on olive stone recycling [53]. Hence, as observed in Figure 5, the amount of recycled material as well as the sintering temperature largely affected the water permeability of the obtained membranes.

Alkaline earth carbonates (calcite, magnesite and dolomite) are also commonly used as pore-forming materials. The decomposition temperatures of calcite and magnesite are, respectively, 920 and 630 ℃; dolomite decomposes in two stages, at 730 and 930 ℃ [57]. However, the decomposition of calcium or calcium-magnesium carbonates can produce a double effect, since at low temperatures (< 1000 ℃) large pores form, which are reduced at higher temperatures (> 1300 ℃) as a consequence of the sintering mechanism in the presence of liquid phase induced by alkaline earth oxides content [58-60]. Recently, studies by Harabi et al. and Boudaira et al. showed that the addition of calcium carbonate to a kaolin-based composition allowed to obtain ceramic materials based on mullite, without the appearance of the cristobalite phase, undesirable due to its high coefficient of thermal expansion [13,61]. However, the effect of carbonates on the properties of membranes depends on their nature, proportion and membrane composition. Thus, for example, in a kaolin-based composition, the addition of calcium carbonate in proportions of

5 to 20 wt.% produces an increase in porosity from 51 to 55 % and in pore size from 5.2 to 8.6 µm. For higher additions, there is a minimum porosity of 50 % at 25 wt.% content; however, the pore size continues to increase, reaching values of 17.6 µm for 30 wt.% content [13]. Nevertheless, the use of these pore-forming materials whether organic or inorganic in nature that decompose during membrane sintering implies the need to design very slow firing cycles to prevent cracks and defects, which has a negative effect on processing cost.

2.3 Support fabrication

The composition of the ceramic membrane is the main factor conditioning the sintering cycle, as well as its microstructure and price. However, the method of fabrication of the substrate determines the final geometry of the product, also having a great impact on the microstructure and, consequently, on the properties and performance of the final product [62-64]. Thus, recently Lorente et al. have compared the microstructure and characteristics of clay-based, low-cost ceramic membranes compositions formed by uniaxial pressing and extrusion [65]. In this research, the authors analyzed the impact of the shaping method in compositions with starch and variable amount of clay ranging from 40 to 85 wt.%. Figure 5a shows the sintered microstructure of pressed and extruded pieces for the composition with the highest amount of clay. As it can be observed, the microstructure of the extruded specimen clearly differs from that of the pressed counterpart. Hence, the extruded microstructure shows an orientated pore distribution, which follows a helical profile because of the movement of the colloidal clay particles travelling through the extruder auger. In addition, pores display lower connectivity when compared with pressed microstructure. Consequently, fluid transport properties of membranes were also influenced by the shaping method. As displayed in Figure 3b, permeability dramatically decreases as the clay content in the starting composition grows. However, for any clay content, extruded pieces are always less permeable than pressed specimens, while this difference is amplified as the clay content in the starting composition increases.

Ceramic membranes usually present different configurations, establishing two main groups: flat discs and tubular membranes [66,67]. There are other more complicated configurations, such as multichannel monoliths (honeycombs) and hollow fiber modules, which can be considered

variations of tubular forms. Powder pressing and extrusion (for tubular geometries) represent the common forming methods reported, with a minority of studies using slip casting [32,37,38,49,68], and very rarely the phase inversion technique [69].

The following figure illustrates the stages of the pressing and extrusion processes used for obtaining low-cost ceramic membranes. After dry homogenization of the raw materials, the composition is conditioned to accomplish with the selected forming process. After forming, the obtained support is dried and then sintered.

i.   Dry uniaxial pressing

Uniaxial pressing is used to obtain simple geometries such as flat membranes and circular supports. It is an inexpensive technique and suitable for large production volumes [67]. After mixing the raw materials, the composition must be conditioned for subsequent forming. This includes the possible addition of water and/or organic binders (polyvinyl alcohol, polyacrylic acid, polyethylene glycol or methylcellulose) in appropriate proportions [6,9,67], which increase the mechanical strength of the unfired support. The binder must be completely removed during sintering without leaving residues or ashes on the final support. The material is then compacted by uniaxial pressure applied by a plunger or piston; the pressure used depends on the composition, the compacted area and the final characteristics of the substrate and, according to the literature, ranges from 20 to 200 MPa. As the applied pressure increases, there is an enhancement in the unfired mechanical strength of the substrate, as well as a reduction in pore size; however, a maximum pressure exists beyond which an increase in the applied pressure does not produce further microstructural changes [67,70]. In pressing, the internal friction forces are high, as the particles rub against each other, therefore the energy needed to form the part is greater than that in extrusion process [66].

ii.   Extrusion

Compositions containing clay present better characteristics for extrusion forming, due to the plasticity of this material, which allows to obtain a paste that can be shaped with relatively low extrusion pressure. However, different additives are usually added to extruding compositions, such as binders, plasticizers and lubricants which give the pastes the suitable rheological behavior

for extrusion, minimizing the appearance of defects and cracks. Normally, cellulose derivatives as binders (methylcellulose, carboxymethylcellulose, etc.) and organic polymers as plasticizers or lubricants (polyvinyl alcohol, polyethylene glycol, etc.) are commonly employed [5,14,67]. There are also starch products that are used in numerous works as binders (e.g., amijel Cplus 12072, Cerestar) [13,14,23,61,71].

After mixing the composition with appropriate additives and water, it is kneaded until a highly viscous paste is obtained. After kneading, a homogenization or ageing stage should be carried out [5]. Finally, shaping of the support takes place, normally, in an auger extruder, usually under vacuum conditions in order to reduce the amount of air contained in the paste. In extrusion, the ceramic paste is forced to pass through a die by applying a force with the help of an endless screw. The geometry of the die determines the final configuration of the support (flat, multichannel tubular, honeycomb structure, etc.). The dough is transported against the internal friction forces (between the particles and the wall) and against the friction forces with the die walls. Extrusion pressure and rate are the main variables to control the process. Nature (plasticity) of the material, particle size and water content are the key compositional characteristics for the extrusion process [5,66,67].

iii.   Other forming methods.

In addition to the shaping methods described previously, some alternative forming procedures has been proposed for membrane manufacture as slip casting, freeze casting or tape casting (figure10). The slip-casting technique is one of the more traditional ceramic shaping processes and is well established for preparing ceramic samples with complex shape and high homogeneity. The slip is poured into a porous mold, usually made of plaster of Paris. Water from the slip is absorbed by the mold, leading to the formation of a solid layer on the mold walls. The thickness of this solid layer is related to the time in which the slip is kept in the mold. When the desired wall thickness is reached, the excess slip is removed, and then the piece demolded, dried and sintered [72].

The freeze-casting (also known as ice templating), is a technique that consists of freezing a liquid suspension, followed by sublimation of the frozen solvent under reduced pressure. This allows controlling size, shape, local distribution and orientation of pores [73]. Concretely, the porous

structure is almost a direct replica of the frozen solvent crystals. During freezing, the dispersed particles are redistributed by the moving solidification front. Thus, the final morphology of the porous ceramics and the structure of the solidification front are directly related to the interaction between the dispersed particles and the solvent. In addition, the final porosity can be tuned by varying the solids loading of particles in the suspension, and the size of the pores is influenced by the freezing kinetics. Due to the directional solidification of the solvent, the porous channels of the resulting ceramics can run directionally from the bottom of the sample to the top [74].

Tape casting is a standard shaping technique used to produce flat ceramic sheets. This method consists of a wet-shaping process based on casting of a tape from a slip with pseudoplastic behavior. The slip is composed of an inorganic powder dispersed in a liquid (water or organic), which acts as a solvent for organic additives (dispersants, plasticizers, and binders) and as a dispersion medium for the ceramic particles. The prepared slurry is poured into a container and after casting, the tape is formed onto a moving polymer tape, where a leveling blade, commonly named "doctor blade", controls the thickness of the green tape. The green tape is dried and cut into parts, then sintered to remove organics and promote the desired densification [75].

iv.   Drying and sintering

After the shaping of the substrate, it is dried and sintered to provide the desired final properties. Drying is usually carried out in two stages. In the first stage, the supports remain at room temperature for a certain period (usually 24 hours); they are then placed in a stove at a higher temperature (between 100 and 200 ºC) for a time ranging from 24 to 48 hours. The first stage corresponds to the elimination of the interstitial water that fills the space between the particles, and the greatest contraction occurs during drying. In the second stage, the adsorbed water is eliminated, and the drying contraction attributed to it is reduced. This procedure is carried out with the substrates formed both by pressing and extrusion, in order to guarantee that the substrates are free of cracks and defects, although in the case of pressing forming it can be simplified, as a result of the much lower amount of water in the starting powder. In some cases, as tubular supports, drying is carried out inside rotating rollers to avoid curvatures and warps [5,57].

Firing represents the final step in the manufacture of low-cost ceramic membranes, giving rise to a material with the desired final properties. The thermal cycle is defined by the maximum firing temperature and the dwell time at that temperature, as well as by the heating rate; furthermore, constant temperature dwellings can be introduced at lower temperatures for a given time. The firing cycle must be defined in such a way as to allow the elimination of additives and pore formers introduced into the composition, as well as to favor the reactions that take place between raw materials. Normally, the cycles used are divided into two stages: the first corresponds to the combustion of organic materials (with a low heating rate, between 1 and 5 ºC·min^{-1}, to minimize the appearance of cracks or defects due to rapid combustion), and the second allows sintering of the ceramic by densification and grain growth. The maximum temperature and residence time used condition the properties of fired substrates: apparent density, porosity, pore size distribution, mechanical resistance, permeability, etc. [5,57].

When modifying the maximum temperature of the thermal cycle, the properties of the ceramic membranes vary. Usually, as the temperature increases, the porosity decreases and the pore size distribution shifts to larger sizes. However, the amplitude in the variation of properties when modifying the firing temperature depends to a large extent on the composition of the membrane. Membranes with clay-based compositions show a reduction in porosity from 19 to 16 % when the sintering temperature increases from 1000 to 1300 ºC [76]. Other membranes with compositions based on mixtures of kaolin, quartz and carbonates show a similar trend: porosity decreases from 40 to 22 % as sintering temperature increases from 900 to 1000 ºC, while pore size augments from 2.6 to 5.5 µm [8]. Similar trends have been found in more complex membranes, based on mixtures of kaolin, pyrophyllite, feldspar, clay, quartz and calcite, in which porosity shows a maximum between 41 and 46 % when firing temperature increases from 850 to 1000 ºC, while the mean pore diameter grows from 0.87 to 1.1 µm [9].

2.4 Deposition of selective layers

As mentioned above, low-cost ceramic substrates can be used directly as microfiltration membranes. However, selective layers can also be applied to them, which reduce the effective pore size of the membranes and allow them to be used in other separation processes. The

composition of these layers may be based on ceramic oxides such as alumina, zirconia or titania [30,37,77-79], on zeolites [38,80], or also on low-cost ceramic materials.

The composition of low-cost selective layers is usually similar to that of the substrate on which they are applied; in this way, the probability of cracks and fissures forming during sintering of the asymmetric membrane minimizes. Thus, layers have been obtained from Tunisia clay [31,81], kaolin from Algeria [71], lime loams [82], apatite [83], anorthite [84], diatomaceous earth [85], phosphates [86] and even compositions with different raw materials (clay, bentonite, alumina and quartz) [34] or residues from the phosphate industry [87].

Layer composition particle size is one of the main factors which controls porosity and pore size of selective layers. The grinding of raw materials is usually carried out in ball mills, in an aqueous medium, with milling times ranging from 2 to 48 hours, obtaining particle sizes lower than 10 µm [34]. In order to improve the rheological properties of the suspensions and obtain layers with homogeneous properties, it is necessary to incorporate additives such as deflocculants (sodium silicate, sodium carbonate, etc.) and dispersants (carboxylic acids); on the other hand, the addition of binders (usually polyvinyl alcohol, PVA, which also acts as a plasticizer) improves the adhesion and finish of the obtained layers. In many of the reported studies, the prepared suspensions usually consist of between 5 and 15 wt.% of raw materials, 28 and 40 wt.% of a 12 wt.% aqueous solution of PVA, to which the necessary additives have been added [31,71,82-84,86]. Thus, Khemakhem et al. prepared an ultrafiltration layer using the following formulation: 1.5 wt.% illite, 62.5 wt.% hydroxyethylcellulose suspension at 2 wt.%, 4 wt.% polyethylene glycol and 32 wt.% of an aqueous solution of a 0.1 wt.% dispersant agent [31].

The layers are applied by dip-coating; the flat supports are introduced into the precursor suspension, removing them after a certain contact time, as shown in Figure 11 [88]. In tubular supports, the layer can be applied inside the tube (usual arrangement) or outside. If it is applied to the outside, the procedure to be followed is similar to that of flat supports, after sealing both openings of the tubular support. For the application of the layer on the inner surface, these are vertically arranged, and the lower opening of the tube is sealed; the support is then filled with the suspension, which remains in contact for a certain time after which the suspension is drained from

the lower part of the tube [86]. The contact time between the suspension and the support can range from few seconds to ten minutes. However, because the thickness of the layer obtained depends on the solids content of the suspension and the deposition time, these parameters are related; Almandoz et al. reduced the contact time to 13 seconds by increasing the solids content to 50 wt.% [34]. Other factors influencing the thickness and morphology of the resulting layer are the viscosity and density of the suspension, as well as the speed of substrate extraction.

After deposition, the as-deposited layer is dried at room temperature for a long period (between 12 and 24 hours). The layer is then sintered. Some reported characteristics of the firing cycles for selective layer sintering are as follows: slow heating rate (1-4 ºC·min^{-1}) to avoid cracking, maximum sintering temperature lower than that of the substrate and dwell time between 1-2 hours. In addition, the firing cycle must include a long dwell time (1-2 hours) at 250 ºC to eliminate the added additives (polyvinyl alcohol). The maximum sintering temperature of the layer determines the properties of the membrane, as well as improves the adhesion between the substrate and the layer. Finally, when making a multilayer membrane, each layer must be sintered after application; in this case, the sintering temperature of a given layer must be higher than the sintering temperature of the subsequent layer.

3 Characteristics of low-cost ceramic membrane supports

Despite the fact that a ceramic membrane is based on a multilayer assembly, most of the low-cost ceramic membrane literature has focused on the characteristics and properties of the ceramic supports due to their potential application as microfiltration membranes. Besides, it is also of special interest to evaluate the properties of low-cost ceramic substrates, as they condition some of the final properties of the membrane, such as permeability and mechanical strength. The following tables summarize the main characteristics of some of the low-cost ceramic substrates developed in the literature from clay minerals or kaolin and formed by pressing (Table 5) and extrusion (Table 6): pore size, porosity, water permeability and mechanical strength.

Pore size and porosity vary over a wide range of values, due to their dependence on the particle size of the starting raw material, the percentage of pore-forming materials added, the forming

process and the sintering cycle, especially the maximum temperature. Likewise, water permeability fluctuates between very different values, due to its close relationship with porosity and pore size. Finally, the mechanical strength of low-cost ceramic membranes is in the same range as microfiltration ceramic membranes based on alumina, which usually have values higher than 50 MPa [69].

Although many works only focus on the composition design and membrane characterization, many other emphasize the relationship between microstructure features and filtration performance. Thus, M. Rawat et al. optimized a ceramic composition mainly comprising kaolin and fly ash [89]. The selected membrane resulted in a good combination of pore size (0.885 µm), porosity (42.7 %), mechanical strength (43.6 MPa) and chemical stability (<3 wt.% loss in acid and 0.02 % in alkali). This membrane was successfully applied in the separation of humic acid from water while high flux recovery was also reported. In a recent research, S. Saja et al. designed low-cost ceramic microfiltration membranes based on natural perlite and corn starch [90]. Some characteristics of the membrane were: 52.1 % porosity, an average pore size of 1.7 µm, 1433 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ water permeability and a mechanical strength of 21.7 MPa. Good chemical resistance both in acidic and alkaline medium was also reported. With this membrane, the authors obtained a retention of turbidity of 97 % and 96 % for agro-food and tannery effluents respectively by frontal microfiltration mode. M. Issaoui et al. developed low-cost tubular microporous supports for ceramic membranes by extrusion from a powdery mixture containing kaolin, starch and sand [91]. Results confirmed that tubular supports for membrane elaborated from a paste containing 87 wt.% kaolin + 10 wt.% starch + 3 wt.% sand presented the best performance by featuring a permeability of 221 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$. In these conditions, membrane was found to be suitable for algal separation as well as easily cleaned by water. Ceramic microfiltration membranes from a kaolin-quartz-calcium carbonate mixture were developed by D. Vasanth et al. [8]. The membrane sintered at 900 ºC (porosity of 30 %, average pore size of 1.3 µm and flexure strength of 34 MPa) was inferred as an optimum membrane for microfiltration applications. Filtration results showed a maximum rejection of 85 % and 99 % for oil (feed oil concentration of 250 $mg \cdot L^{-1}$) and bacteria (feed bacteria concentration of $6 \cdot 10^5$ $CFU \cdot mL^{-1}$) respectively. Emani et al. addressed the

preparation of microfiltration membranes from mixtures of kaolin, quartz and calcium carbonate [6]. The prepared membranes possessed porosity ranging from 35.4 % to 39.4 %, average pore size varying from 0.9 to 1.85 µm and flexure strength ranging from 7.8 to 11 MPa. The optimum membrane provided a transmembrane flux of 90 to $44 \cdot 10^{-6}$ $m^3 \cdot m^{-2} \cdot s^{-1}$ at 206.7 kPa with an enzyme-treated centrifuged juice, and a negligible alcohol-insoluble solids content in the permeate. Alumino-silicate compositions were also used by M. C. Almandoz et al. [92]. Their results indicated that an appropriate election of the particle size of the raw materials as well as of the sintering temperatures allows to obtain membranes with mean pore sizes within the range from 0.1 to 1 µm that make them suitable for microfiltration. Tests with synthetic aqueous solution containing microbial charge revealed good membrane selectivity with a microorganism rejection higher than 90 %.

4 Comparison between properties of commercial ceramic membranes and those based on low-cost raw materials incorporating selective layers

Low-cost ceramic membranes possess the characteristics of ceramic materials: chemical stability, high mechanical resistance, brittleness, thermal and electrical insulation, etc. However, due to the difference in raw materials and manufacturing processes, the properties of low-cost ceramic membranes differ from those of commercial ceramic membranes based on pure oxides. As already indicated, commercial membranes usually consist of substrates and selective layers, their pore size being at least lower than 10 µm, and most of them lower than 1 µm, as set out in Table 7. On the other hand, as set out above most of the low-cost ceramic membrane literature has focused on the characteristics and properties of the ceramic support due to the potential application as microfiltration membrane. Nevertheless, as shown in Table 8 many other works have addressed to develop multi-layer assemblies by depositing some low-cost selective layers on the microfiltration support to enhance microfiltration performance or, more interestingly, to reach ultrafiltration range. As observed in these tables (7 and 8), properties of commercial and low-cost ceramic membranes display similar variability ranges. Porosities of commercial membranes, 30-

40 %, are slightly lower than those of low-cost membranes (40-50 %) while water permeability values lie at similar intervals, all below 1000 L·h^{-1}·m^{-2}·bar^{-1}.

Thus, Khemakhem et al. developed defect-free illite ultrafiltration membranes by slip-casting [31]. The most concentrative pore diameter of composite membranes was about 15 nm. Moreover, the illite-based membranes possessed high thermal stability. These ultrafiltration membranes can be used as support materials for a nanofiltration layer or directly for solution purification. The average permeability was about 88 L·h^{-1}·m^{-2} bar^{-1}. The molecular weight of the dextran whose retention reached 90 % was taken as the molecular weight cut-off, obtaining a value of 185 kDa. This value agreed with the pore size measured by nitrogen adsorption–desorption experiments. B. Ghouil et al developed multilayer (3-layers) microfiltration membranes from alumino-silicates (kaolin and calcium carbonates mixtures) [71]. A ceramic support featured by a porosity of 47 % and an average pore size of 8 µm with an intermediate layer of about 0.5 µm of average pore size was coated by an alumino-silicate selective layer of 40 µm thickness and an average pore size of 0.2 µm. The intermediate layer had also the role of preventing the infiltration of suspensions into the support, allowing a reduction of the thickness of the top layer and eliminating the defects of the support (surface roughness reduction). The water permeability of the multilayer assembly was about 550 L·h^{-1}·m^{-2}·bar^{-1}, whereas the microfiltration performance of the membrane with dextran solution was demonstrated.

In another work, Khemakhem et al. designed a multilayer microfiltration membrane from Tunisian natural materials [81]. The support showed mean pore diameter and porosity of about 6.3 µm and 49 %, respectively. The pore diameters measured for the microfiltration layer were centred near 0.18 µm. A defect-free membrane was only obtained for selective layer thickness less than 10 µm. Results proved well the efficiency of these microfiltration membranes. Nevertheless, these membranes can also be used as a support for an ultrafiltration layer. In [83] Masmoudi et al. developed a hydroxyapatite-based multilayer membrane with the following characteristics: average pore diameter of 0.50 µm; average apatite layer thickness of 32.5 µm and a porous volume of 48 %. A stabilized flux of 120 L·h^{-1}·m^{-2}·bar^{-1} was obtained with a cuttlefish effluent in microfiltration mode. Besides, the regeneration of the membrane can be performed

using a thermal treatment at 450 °C during 3 h. Harabi et al. reported the development of supports and MF membranes manufactured from local kaolin and calcium oxide mixtures [84]. The MF layer, deposited on the supports, was obtained by the slip-casting technique using suspensions of anorthite $(CaO \cdot Al_2O_3 \cdot 2SiO_2)$ powder. The membrane may be used for MF and also as a support for UF and nanofiltration (NF) membranes.

Ha et al. prepared sintered diatomite supports for microfiltration by using a sacrificial polymer template [85]. The largest pore sizes of the sintered diatomite remained at around 1 µm. Furthermore, these largest pore sizes of the supports could be controlled by depositing a diatomite separation layer. Findings showed the feasibility of using sintered diatomite as a porous ceramic membrane for microfiltration. Barrouk et al. prepared and characterised low-cost ceramic MF membranes, with tubular configuration based on Moroccan phosphate [86]. The membrane support was prepared by the extrusion of a ceramic paste made with lixiviated phosphate powder. The MF layer made also from the same material was deposited on the support by slip casting. In consequence, this selective layer presents the advantage of having the same composition as that of its support. The membrane displays interesting retention properties regarding the suspended matter, turbidity, total phosphorus, and pathogens. Filtration tests conducted using effluent water produced by the washing phosphate process, suspensions of lime or alumina hydroxide and water wells clearly revealed the performance of the MF membrane elaborated, which was similar to that of a commercial α-alumina membrane. Again, the ceramic MF membranes elaborated in this work can also be used as a support for diverse ultrafiltration layers.

As can be deduced from the above, the literature provides abundant evidence of the characteristics of low-cost membranes as well as their potentially good performance in microfiltration and even ultrafiltration applications. Comparison with the characteristics of commercial ceramic membranes based on pure ceramic oxides also allows us to deduce the numerous industrial applications that could be expected. However, in most of the reviewed research, the performance of the membranes developed is based on laboratory or pilot scale tests with relatively short experimental times compared to industrial practice. Consequently, it is necessary to advance in the study of this type of ceramic membranes accessing to a research phase where the designed

membranes are tested in real environments for enough time to estimate, in a more precise way, the advantages of these new ceramic membranes.

5 Applications

The potential applications of low-cost ceramic membranes cover virtually all applications of commercial ceramic membranes obtained with pure oxides. Thus, the range of applications of low-cost ceramic membranes includes oil removal, toxic heavy metal removal, wastewater treatment of various industries, etc. They have also been tested in several production processes, especially in food industry.

5.1 Food industry: manufacturing processes

In the processing of fruit juices, ceramic membranes make it possible to obtain high quality, additive-free juices with a fresh, natural taste that lasts during storage. Considering that many varieties of fruit juices are acidic, with pH between 3 and 5, low-cost ceramic membranes are a good alternative, due to their high chemical and thermal stability (in some varieties of juice high temperatures are used to increase the permeate flow) and their low price. Emani et al. prepared ceramic membranes for filtration of mosambi (sweet lime) juice with mixtures of kaolin, quartz and calcium carbonate by uniaxial pressing [6]. Qin et al. made ceramic membranes using fly ash particles, which were applied in the microfiltration of centrifuged kiwi juice [97].

In the dairy industry, ceramic membranes can be used for both milk pasteurization and whey valorization. The microfiltration of milk has the advantage of reducing the number of bacteria and spores without affecting the taste, extending the life of the milk, compared to other pasteurization processes such as the UHT process. Almandoz et al. used ceramic membranes whose composition was based on a mixture of low-cost raw materials (clay, bentonite, feldspar, quartz and alumina) in the microfiltration of goat milk from local dairy farms [34]. The tests were carried out at a transmembrane pressure of 72 kPa and a temperature of 30 ºC, obtaining a high degree of pasteurization of the milk, with high efficiency in bacteria removal, maintaining practically constant the other physicochemical properties of the original milk. On the other hand, the dairy

industry produces a large amount of whey that can be recovered for use in various industries. It is normally processed for food use in the form of whey powder and other high-quality protein-rich products. In addition, its value increases if it is demineralized, an operation that can be carried out by means of membranes. However, when whey is not valued, especially in emerging countries, it is discharged into rivers near the production site. Over time, the whey acidifies, and bacteria are generated that contaminate the drinking water pumped from the river. In this case, the whey becomes a contaminant of the river, making it impossible to use the water for human consumption. Thus, the use of low-cost ceramic membranes for the recovery of whey has a twofold advantage: increase the profits of the farmer and reduce pollution of river water. To this end, Khider et al. synthesized ceramic membranes based on Algerian clay for use in the treatment of whey from a dairy plant in the region of Boudouaou (Algeria) [30].

Another case described is the refining of raw rice bran oil, which is obtained from the rice husk, and is used in food processing and cosmetics manufacture. This oil is mainly composed of triglycerides; however, it also contains minority compounds, such as phospholipids, β-carotene, chlorophyll, free fatty acids, particulate matter, sterols, pigments, proteins, etc., which reduce oil quality and processing efficiency. The presence and quantity of these minority compounds depend on the nature and origin of the rice husk. Roy et al. evaluated the pilot-scale efficacy of a low-cost alumina and clay-based membrane to remove polymers, waxes and acids from rice bran oil micelles [98].

5.2 Food industry: wastewater treatments

The canning industry of marine products produces a large amount of wastewater, which is generally discharged into the coast and is responsible for a large pollution, increasing the phenomenon of eutrophication (increase of nutrients in fresh water, which causes an excess of phytoplankton (Anon n.d.)) and the proliferation of unwanted algae. As an example, prior to freezing, cuttlefish should be cleaned to remove the black color caused by its ink, generating a highly colored wastewater. Khemakhem et al. developed microfiltration ceramic membranes based on Tunisian clay for the treatment and discoloration of wastewater generated in the cuttlefish conditioning process [31].

Slaughterhouse wastewater treatment plants must be designed to reduce the levels of certain parameters, such as chemical oxygen demand (COD), oils and fats, suspended solids, and pathogens, among others. Normally, pretreatment is carried out using grids and collectors to retain solids and grease. Next, a primary treatment is applied to eliminate a significant amount of suspended solids by means of physicochemical processes (addition of flocculants). Finally, the effluent undergoes secondary biological treatment. Almandoz et al. used ceramic membranes based on low-cost compositions (clay, bentonite, feldspar, quartz and alumina) in the microfiltration of the pre-treated effluent from the wastewater of this process, operating at a pressure of 100 kPa and a temperature of 25 ℃; obtaining promising results, with a high retention of bacteria and reduction of COD [34].

5.3 Textile industry: wastewater treatments

Textile manufacturing processes include the wet chemical processing operations required to prepare, purify, dye or finish the product, which generate wastewater whose pollutant load includes both the impurities of the raw materials used and the remains of the chemical reagents employed during the aforementioned operations. This industry generates high volumes of effluents, with a very variable composition and concentration of contaminants, including COD, biological oxygen demand (BOD), oils and fats, pigments, phenols, heavy metals, etc. Conventional treatment for wastewater from the textile industry mainly includes biological treatment, precipitation, coagulation/flocculation, flotation, oxidation and adsorption. However, the main problem comes from residual pigments, as many are not biodegradable, which makes difficult to treat this wastewaters using conventional systems [99]. Palacio et al. developed membranes from Moroccan clays and phosphates to carry out an initial clarification of wastewater from the Moroccan textile industry, reducing the concentration of pigments such as murexide (ammonium purpurate), methyl orange and potassium chromate [33]. Khemakhem et al. prepared ceramic membranes based on residues from the phosphate industry for the treatment of wastewater from the textile industry, obtaining effluents with reduced turbidity (99% reduction), color (removal greater than 96%) and COD (90% decrease) [87].

Tannery industry involves the transformation of animal skins into leather, producing both liquid and solid contaminants. The entire tanning process can be divided into 3 main stages: beamhouse (section of the tanning where the skins are prepared for pickling (Anon n.d.)), tanning and finishing. Beamhouse stage generates the greatest volume of wastewater (around 40%). The effluents from the tanning industry are characterized by high concentrations of pollutants and a wide variety of compositions, such as suspended solids, sulphur and chromium salts, etc. Consequently, physical, physicochemical and biological treatments can be applied. Majouli et al. developed a microfiltration membrane, with cordierite support and selective zirconia layer, for the treatment of wastewater from the preparation stage of the tanning industry [100].

5.4 Metallurgy industry: chromium plating baths

Chromium electrolytic coatings are used in industry to protect metals from corrosion, improve their appearance and performance. Chromium coatings are applied for both technical and decorative purposes in numerous industries, in the manufacture of automobiles, household appliances, furniture, taps, electronics, etc.

Chromium plating baths, which consist mainly of concentrated solutions of Cr (VI) in sulphuric medium, are used to coat objects with metallic chromium by means of electrochemical procedures. With this method, the chromium plating layer is obtained by reducing the Cr(VI) to Cr metal on the object to be coated. However, during the process there is also the partial reduction of Cr(VI) to Cr(III), which can no longer be reduced to metal under normal operating conditions in chrome plating cells. In consequence, when the concentration of Cr(III) reaches a certain limit, chrome plating cannot be carried out properly, and the bath is considered to be exhausted. However, these baths still contain a high concentration of Cr(VI), making them a highly polluting residue, given their very acidic and oxidizing character.

Sánchez et al. developed a ceramic membrane based on a kaolin-alumina mixture for the regeneration of exhausted baths in an electrochemical reactor [101-103]. This membrane separates the two cells of the reactor, allowing the passage of the electric current through the migration of ions, but preventing the diffusion of Cr(III) and CrO_4^{2-}. In this way, Cr(III) is

oxidized to Cr(VI) by an electrochemical procedure, and the membrane prevents the formed CrO_4^{2-} from returning to the exhausted bath cell.

5.5 Separation of oil-water emulsions

Oil-water emulsions are one of the major pollutants in aquatic environments. Industries such as metallurgy, petrochemistry, transport, textiles, food, etc., generate wastewater containing oils in concentrations between 50-1000 $mg \cdot L^{-1}$, which must be treated before discharge, as the maximum allowed concentration is around 10-15 $mg \cdot L^{-1}$. Among all the available separation technologies, membrane filtration is one of the most promising methods for the separation of water-oil emulsions, due to its advantages: no chemical additives are needed to break the emulsions, it has high efficiency in the elimination of COD and the installations are compact and automated.

To apply filtration through membranes in the separation of oil-water emulsions at an industrial level, ceramic membranes have advantages over polymeric ones, due to their greater stability against polar and chlorinated solvents, extreme pH, high concentrations of oils present in industrial wastewater, as well as their much better thermal and mechanical stability. This has favored the publication of abundant literature related to the separation of these emulsions by means of low-cost ceramic membranes. There are numerous studies from different groups that asses the efficiency of kaolin-based membranes for the separation of oil-water emulsions, analyzing process parameters as well as fouling mechanisms (Vasanth et al. [104,105], Nandi et al. [106], Eom et al. [107]). In the study by Abbasi et al. the suitability of mullite ceramic membranes for the treatment of oil-water emulsions was analyzed, obtaining promising results [108].

5.6 Treatment of groundwater and surface water for human consumption

Several studies have appeared using ceramic filters based on local low-cost raw materials for water purification in areas with scarce economic and water resources. The treated water was intended for human consumption, and the elimination of viruses, bacteria and other microorganisms was carried out through a simple gravitational filtration process [109-111]. One example is the work of Hasan et al., which applied a ceramic membrane based on local clay in a

membrane biological reactor (MBR) for the removal of arsenic from groundwater in Bangladesh [51]. The iron oxide flocs adsorb the arsenic from the water and are then separated by a low-cost membrane inserted into the MBR.

The use of low-cost ceramic membranes made from waste materials for a membrane biological reactor (MBR) was recently reported as set out above [112]. The ceramic composition was formulated to valorize waste products from different agricultural and industrial processes. Ceramic supports were coated with selective, low-cost ceramic layers as well. An immersed reactor comprising membrane modules with 50 flat hollow membranes was designed as seen in Figure 10A. Water conditioning trials showed good permeability in the industrial assembly (Figure 10B). Moreover, preliminary tests with real wastewater containing between 8-10 $g \cdot L^{-1}$ of activated sludge displayed a promising performance of the reactor.

5.7 Emerging applications

An incipient application of low-cost ceramic membranes deals with supports for the deposition of active substances, which transform them into basic components for more sophisticated processes than those of the different levels of filtration.

One possible application is ion exchange ceramic membranes, which allow the substitution of organic membranes in the electrodialysis treatment of very acid or corrosive effluents. Ion exchange membranes (cationic and anionic, Figure 13) are the key components of an electrodialysis reactor. Although these membranes are usually organic, they are not compatible with certain effluents (such as residual chromium plating baths, very acidic and oxidizing). Therefore, low-cost ceramic membranes in whose porous network an ion exchanger, also inorganic, has been fixed represent an interesting alternative. In this way, a ceramic microporous support was manufactured from kaolin, alumina and starch by the traditional ceramic method and the ion exchangers were deposited into its porous network. The cation exchanger was hydrated zirconium phosphate [113], and the anion exchanger hydrated zirconium oxide [114], or hydrated cerium dioxide [115], which were deposited as layers of nanometric particles (Figure 14). The electrochemical behavior of the ceramic membranes resembled that of the organic ion-exchanger membranes under certain conditions.

Another application is to use the low-cost membrane as a support for catalysts, so that the catalytic membrane obtained becomes a component of catalytic reactors. A specific case is the synthesis of membranes for the elimination of nitrate ion in waters from aquifers, the high concentration of which is a public health problem in many areas. Pérez-Fernández et al. developed a catalytic membrane based on a low-cost ceramic support, in whose porous network they deposited Pd and Cu as catalysts [116]. This membrane allowed the reduction of the nitrate ion to N_2, passing through it the water previously saturated with H_2. In laboratory conditions, 60 % nitrate conversions were achieved.

Finally, the digital printing revolution has also reached low-cost ceramic membranes. Although it is in the early stages of development, some work has already been done to deposit the intermediate and selective layers using inkjet printing on a low-cost ceramic substrate [117]. The possibility of controlling the type and quantity of material deposited in each point of the surface of the support, will allow in the future to control the microstructure of the different layers, and to include active substances, as catalysts, in specific points of the layers. Therefore, it can be expected that in the coming years the variety of available low-cost ceramic membranes will increase, as well as the range of potential applications for them.

6 Conclusions

In recent years, intense research activity has taken place in the field of ceramic membranes with the aim of designing new materials based on ceramic raw materials typical of the most traditional ceramics (silicate ceramics), often incorporating residues in the initial composition. The driving force of this research activity has been the clear possibility of lowering the cost of current ceramic membranes, based on ceramic oxides, maintaining, as far as possible, their performance.

Broadly speaking, regarding the starting compositions employed, there are two main different branches: compositions based on advanced ceramics (e.g. those containing alumina) with potential applications in very aggressive media and compositions exclusively based on traditional ceramics with applications with lower demanding performance. Regardless the branch adopted, clay minerals are commonly used to provide the composition with enough plasticity for the

subsequent shaping step. Very commonly, pore former materials are indispensable for the ceramic membrane to obtain the necessary pore size and porosity for the intended application. Starch as organic and calcite/dolomite as inorganic represent typical porogen substances but many other raw materials and wastes have been tested. The paper has also discussed the pore formation mechanism attributed to these pore former materials. Basically, a minimum amount of pore former is necessary so as to create an interconnected porosity which enhances membrane permeability.

Membrane fabrication processes for low-cost ceramic membranes follow the same steps and use the same shaping processes as their commercial ceramic membrane counterparts. The most common manufacturing methods are extrusion and pressing, being slip casting, tape casting and freeze casting less frequent. The choice of a given method depends on the application requirements, the intended membrane structure and the available materials. Low-cost ceramic substrates can be used directly as microfiltration membranes. However, selective layers can also be applied to them, which reduce the effective pore size of the membranes and allow them to be used in other separation processes. Dip-coating is the main deposition method for selective layers where conventional compositions are used to follow the low-cost philosophy by means of a higher intensity milling.

Low-cost ceramic membranes generally possess the characteristics of ceramic materials: chemical stability, high mechanical resistance, brittleness, thermal and electrical insulation, etc. Characteristics of commercial and low-cost ceramic membranes display similar variability ranges. Porosities of commercial membranes, 30-40 %, are slightly lower than those of low-cost membranes (40-50 %) while water permeability values lie at similar intervals, all below 1000 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$. However, due to the difference in raw materials and manufacturing processes, the properties of low-cost ceramic membranes differ, in some extent, from those of commercial ceramic membranes based on pure oxides.

The potential applications of low-cost ceramic membranes cover virtually all applications of commercial ceramic membranes obtained with pure oxides. Thus, the range of applications of low-cost ceramic membranes includes oil removal, toxic heavy metal removal, wastewater

treatment of various industries, etc. They have also been tested in several production processes, especially in food industry. However, most of the research is based on laboratory or small pilot plants, therefore much more industrial research is necessary to validate the performance of this new type of membranes in real application environments for long time.

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Table 1 Common configurations in porous ceramic membranes for different applications.

Application	Configuration	Pore diameter (nm)	Selective layer
Microfiltration	1 layer	5000	Macroporous
	2 layers	250	Macroporous
	3 layers	100	Macroporous
Ultrafiltration	4 layers	5	Mesoporous
Nanofiltration/Gas separation/Pervaporation	5 layers	1	Microporous

Table 2. Precursors to be used as a function of the desired filtration range.

Filtration mode	Pore size (nm)	Precursor material
Microfiltration	>60	Particle suspension
Ultrafiltration	20-50	Particle suspension
	3-20	Colloidal sol
Nanofiltration	<2	Polymeric sol

Table 3: Compositions mainly based on clays.

Particle size (µm)	Other raw materials	Pore former	Origin	Ref.
--	--	$CaCO_3$ (21 %); Starch (2-10 %)	Algeria	[23,29,30]
--	--	--	Tunisia	[31]
0.3-30	--	Sawdust (25 %)	Cameroon (Adamawa)	[32]
--	Phosphates	Starch (5-35 %)	Morocco	[33]
0.2-50	Bentonite; Alumina; Quartz; Feldspar	$CaCO_3$ (10-17 %)	Argentina (Piedra Grande)	[34]

Table 4: Compositions based on kaolin-clay mixtures.

Main raw materials	Particle size (µm)	Other raw materials	Pore former	Origin	Ref.
Kaolin (9 %) Clay (82 %)	0.2-70	--	Corn starch (9 %)	Tunisia (Oueslatia)	[35]
Kaolinite (56-59 %) Clay (37 %)	--	--	Sawdust (2.5 %)	Indonesia (Sukabumi)	[36]
Kaolin Clay	1-40	Feldspar Sand	Active coal (1 %)	Algeria (Ghazaouet)	[37]
Kaolin (10-15 %) Clay (13-18 %)	5-10	Feldspar Quartz Pyrophyllite	$CaCO_3$ (17-23 %)	India	[9,38]

Table 5: Membranes based on kaolin and/or clay and formed by pressing.

Support material	Porogen substance	Max. Temp. (°C)	Pore size (μm)	Porosity (%)	Mechanical strength (MPa)	Water permeability (L·h^{-1}·m^{-2}·bar^{-1})	Ref.
Kaolin	Dolomite(0-15 %)	1000-1300	0.7-24	37-42	6-19	--	[14]
	CaCO$_3$ (10-28 %)	1100-1300	5-18	50-55	--	--	[13]
Kaolin; Quartz	CaCO$_3$ (25 %)	900-1000	1-3	20-30	35-46	14,400-50,400	[8]
Kaolin; Alumina	Lignite (20 %)	1100-1200	0.4-1.8	18-41	13-38	900-3,800	[93]
Kaolin; Quartz Boric acid	CaCO$_3$	900	0.7-1.7	35-40	7-11	1,600	[6]
Clay	Starch (5-35 %)	950	0.3-1.7	--	--	18,000-50,400	[33]
Clay; phosphates	Starch (5-35 %)	950	--	--	--	18,000-57,600	[33]
Kaolin; Clay; Feldspar; Quartz,	CaCO$_3$ (17 %)	850-1000	~1	41-46	25-32	700-1,800	[9]

Table 6: Membranes based on kaolin and/or clay and formed by extrusión.

Support material	Porogen Substance	Max. Temp. (°C)	Pore size (µm)	Porosity (%)	Mechanical strength (MPa)	Water permeability ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$)	Ref.
Kaolinite	$MgCO_3$	1380	18	41	29	--	[94]
	$CaCO_3$ (10-28 %)	800-1100	0.5-8	40-50	--	--	[84]
Kaolin		1100-1300	1-7	45-53	28-87	--	[13,61,95]
	Dolomite (0-30 %)	1000-1300	2-49	8-55	20-80	1,000-18,000	[14,18]
Kaolin; Cordierite	$MgCO_3$; Wheat starch	1300-1400	8.6-9.5	17-46	13-50	--	[97]
Kaolin; Alumina	--	1100-1300	--	22-40	--	--	[40]
Kaolin; Alumina	Lignite (20 %)	1100-1200	0.7	36	39	410	[93]
	--	1090-1100	6.3	48	--	--	[31]
	$CaCO_3$	1150-1250	1-4	49-52	25	1,700-19,000	[23]
Clay	Starch (10 %)	950	1.2	48	--	--	[30]
	$CaCO_3$ (21 %) Starch derivative (2.5 %)	1150-1300	1-5	51-56	--	--	[29]

Table 7: Properties of ceramic membranes based on pure oxides (commercial membranes).

Industrial membrane	Pore size (μm)	Porosity (%)	Water permeability (L·h⁻¹·m⁻²·bar⁻¹)	Ref.
Jiawu High-Tech Co.	0.2-0.5	--	523-891	
Carbosep	0.45	--	177	[34]
CeRAM Tami Industries	0.1	--	342	
α-alumina (different suppliers)	0.1-0.5	40	--	
	1-10	30-40	--	
α-alumina (Netzsch and Membralox)	0.01-0.05	--	--	[67]
γ-alumina (US Filters)	0.005	--		
Titania (TAMI industries)	1.7	32	--	

Table 8: Properties of selective ceramic membranes based on low-cost raw materials

Material	Max. temperature (ºC)	Dwell time (h)	Pore size (μm)	Water permeability (L·h⁻¹·m⁻²·bar⁻¹)	Ref.
Lime loams	1000	2	0.4	870	[82]
Apatite	600	3	0.5	--	[83]
Tunisia clay	900	2	0.18	--	[31,81]
Illite	800	2	0.015	88	[31]
Anortite	850	2	0.5	--	[84]
Diatomaceous earth	1200	1	--	--	[85]
Algerian kaolin	1050-1150	1	0.2	550	[71]
Phosphate	800	2	0.35	700	[86]
Clay; Bentonite; Alumina; Quartz	1200	0.5	0.09-0.55	500-1000	[34]
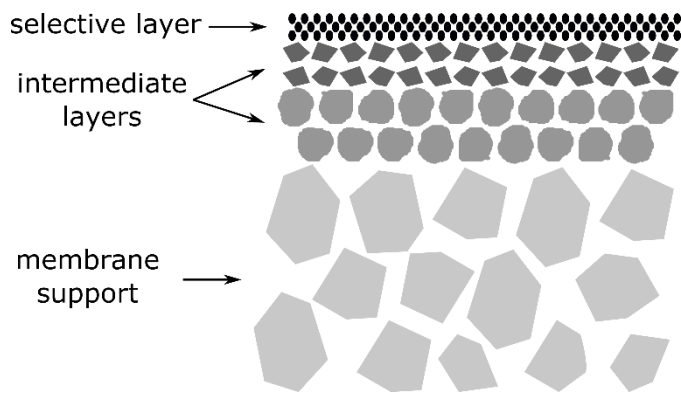
Figure 1: Diagram of an asymmetric membrane.
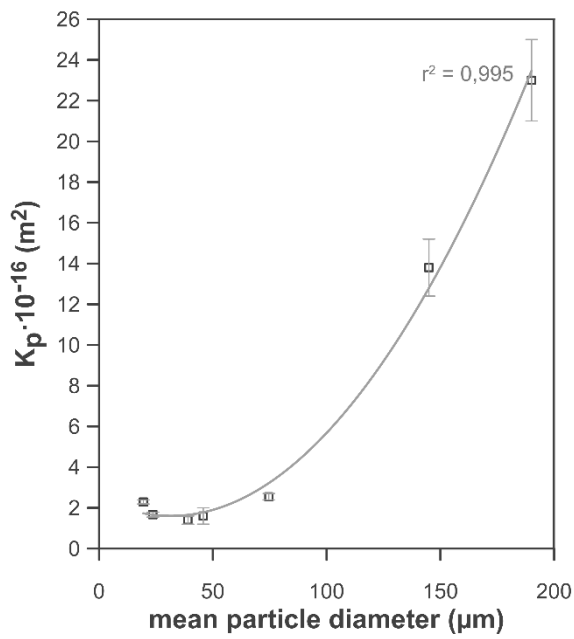
Figure 2: Relation between the water permeability (K_P) of a clay-based low-cost ceramic membrane and the mean particle diameter of used starch (data from [26]).
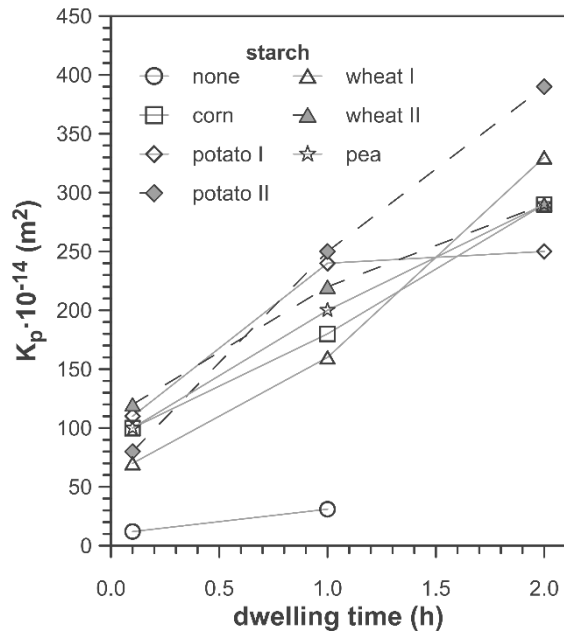
Figure 3: Variation of air permeability (K_p) with sintering (dwelling) time for a clay-based low-cost ceramic membrane composition prepared from the same amount of starch but of different nature (corn, potatoes, wheats and pea) (data from [27]).
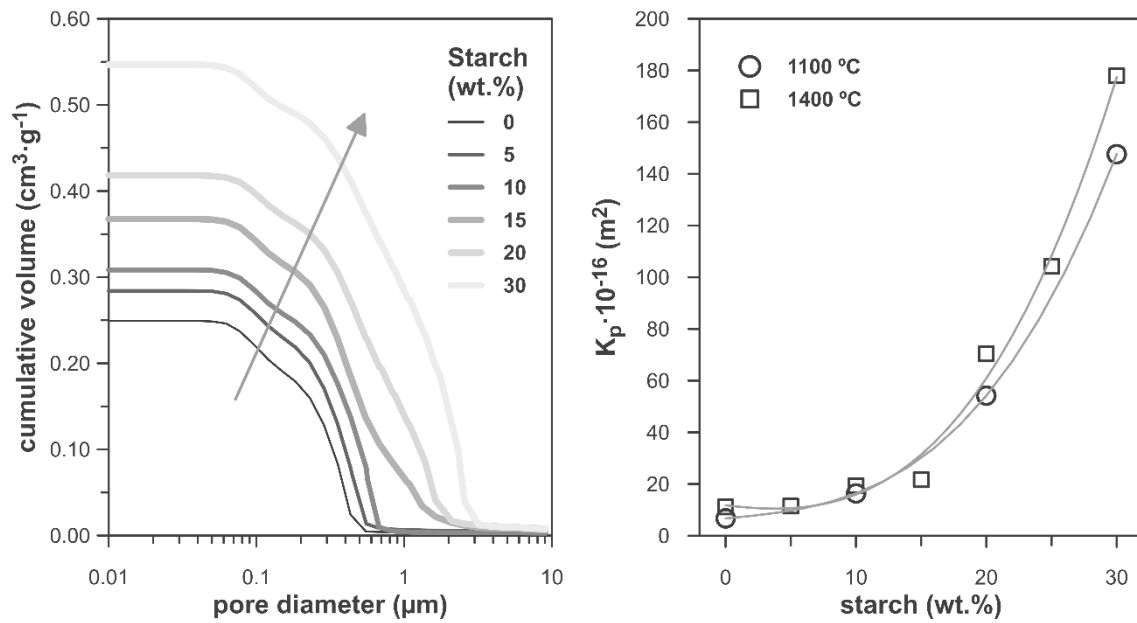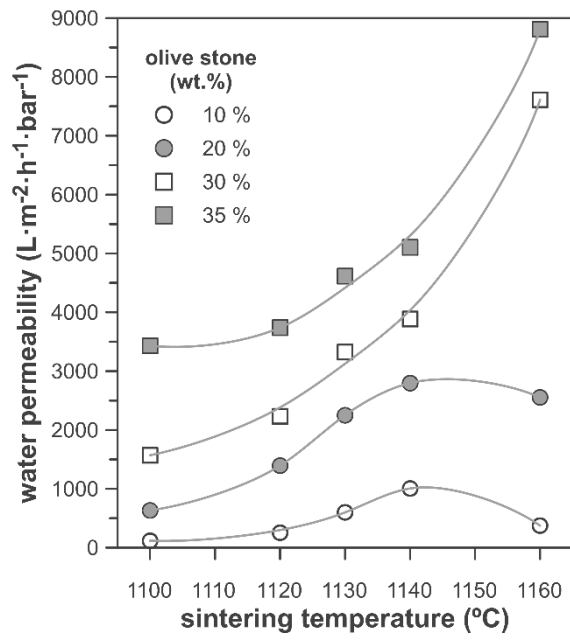

Figure 4: Effect of the amount of starch content in a kaolin-alumina based low-cost ceramic composition on a) accumulate pore size distribution of membranes sintered at 1400 ºC and b) air permeability (K_p) of the membranes sintered at 1100 ºC and 1400 ºC (data from [25]).

Figure 5: Influence of olive stone content and sintering temperature on water permeability of low-cost ceramic membrane containing olive stone as pore former (data from [53])
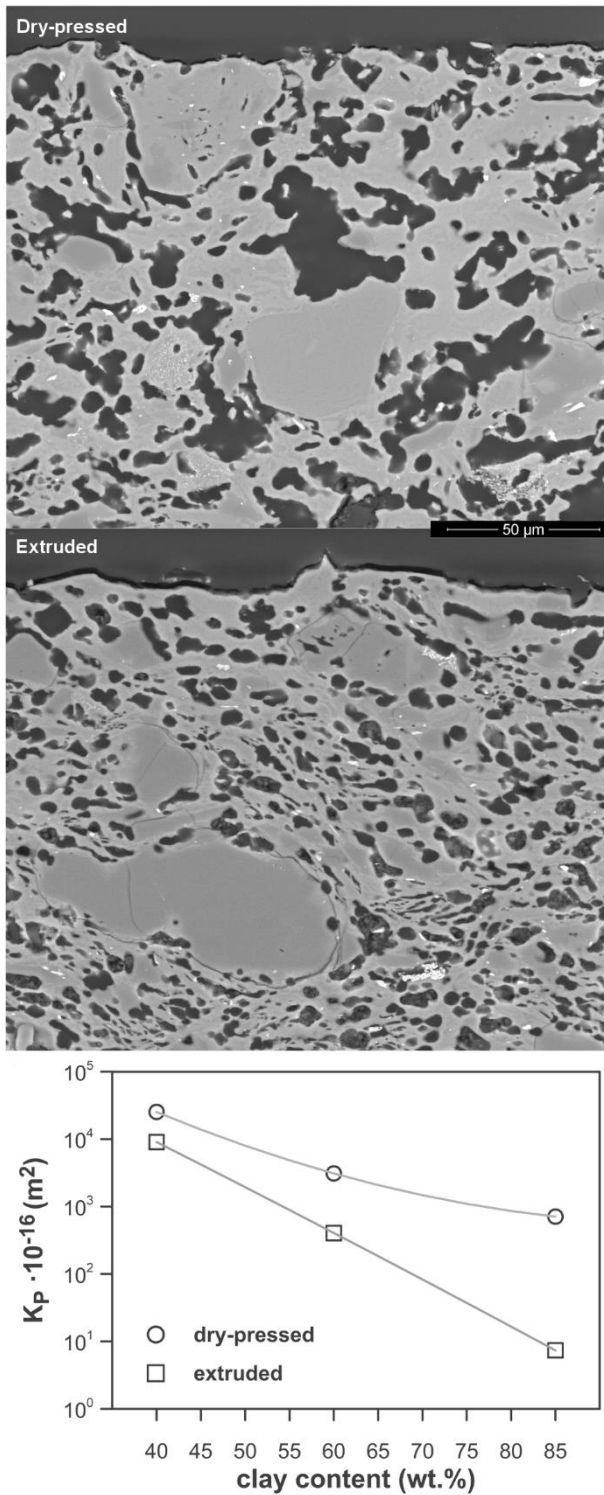
Figure 6: Effect of the shaping method (pressing and extrusion) in clay-based, low-cost ceramic compositions containing three different amounts of clay: 40, 60 and 85 wt.%. a) micrographs of pressed and extruded sintered specimens with 85 wt.% of clay content and b) variation of air permeability (K_P) for the pressed and extruded sintered specimens of the three compositions (data from [65]).
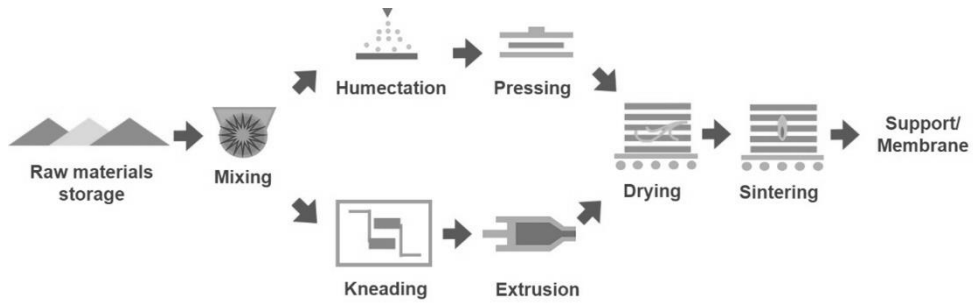
Figure 7: Processes for obtaining low-cost ceramic membranes.
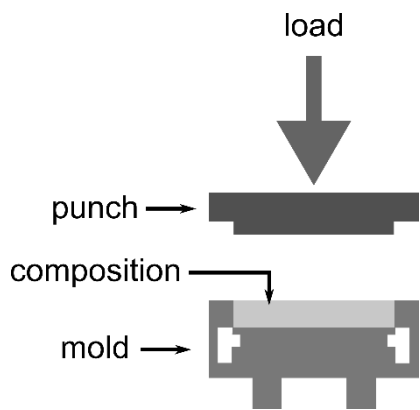
Figure 8: Scheme of uniaxial pressing shaping.
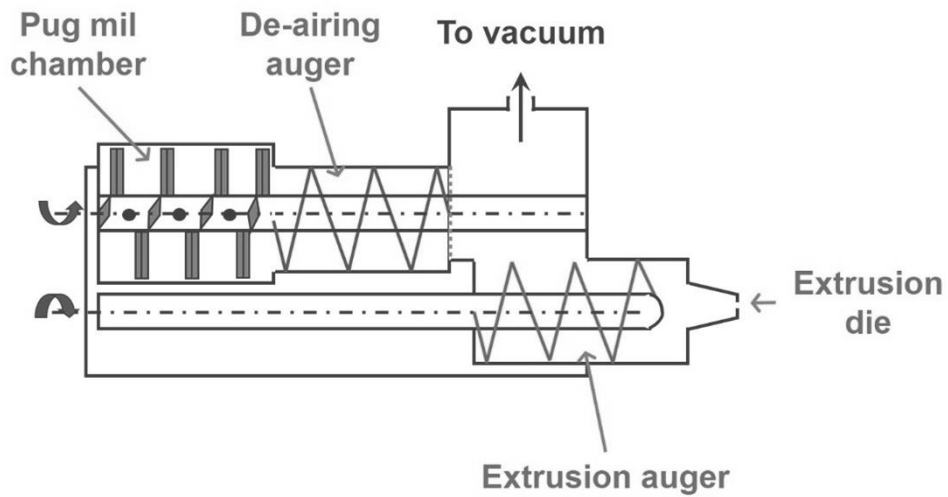
Figure 9: Diagram of an auger extruder with vacuum system.
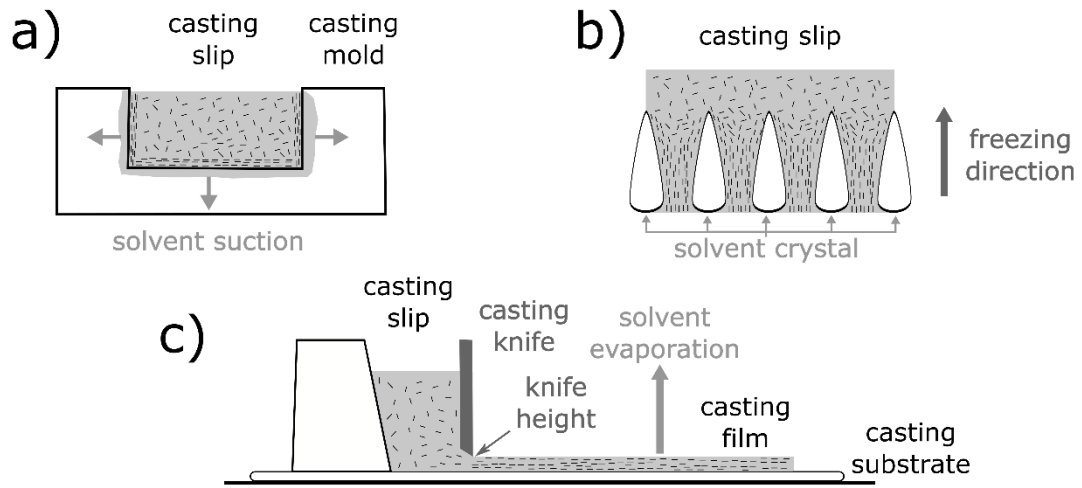
Figure 10: Schematic description of the other forming methods: a) slip casting; b) freeze-casting; c) tape casting.
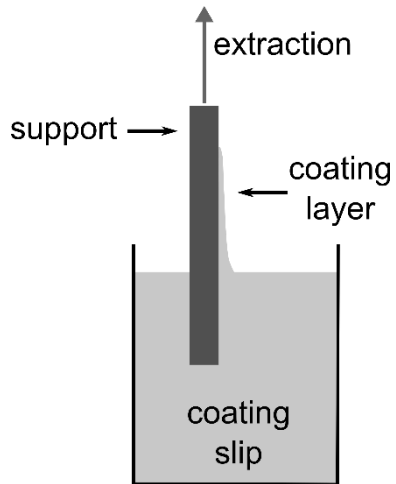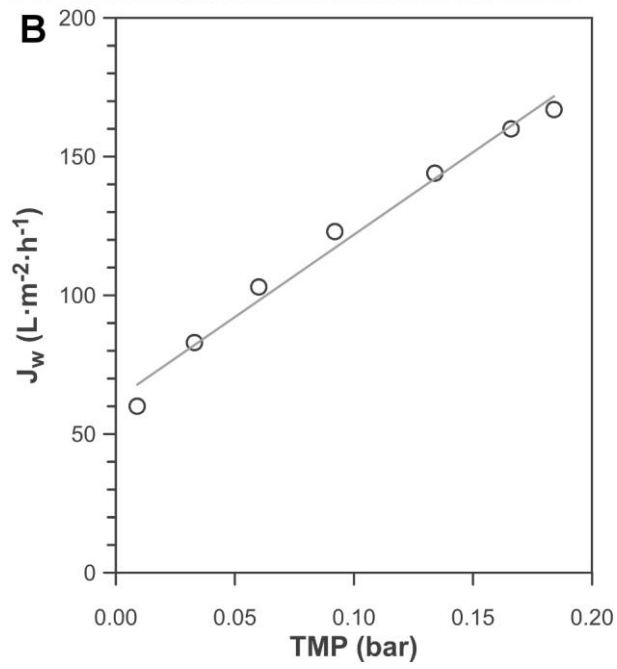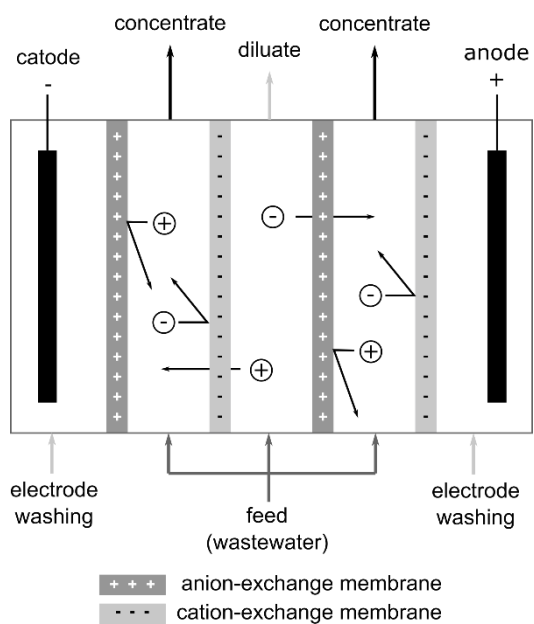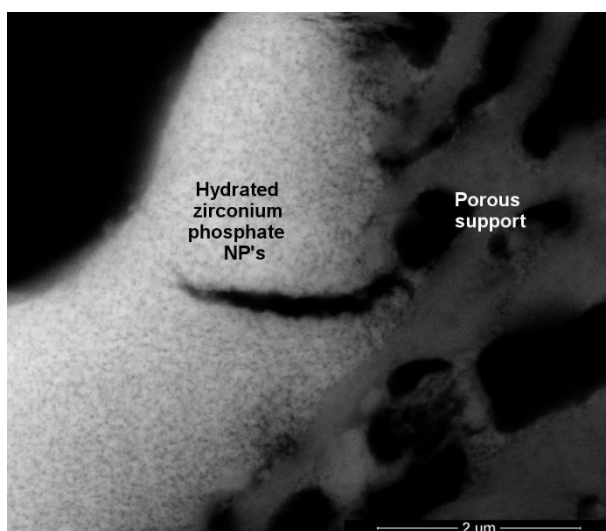

Figure 11: Process for membrane (flat) support dipping.

Figure 12: Use of low-cost ceramic membranes for membrane biological reactor (MBR): A) view of the ceramic membrane modules inside the tank and B) plot of water flow (J_w) versus transmembrane pressure (TMP) in water conditioning tests of the membranes in the reactor.

Figure 13: Scheme of an electrodialysis unit.

Figure 14: SEM image of a layer of nanoparticles of hydrated zirconium phosphate deposited over the surface

of a pore inside the porous support.