

Nano-Filtration and Ultra-Filtration Ceramic Membranes for Food Processing: A Mini Review

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Abstract

This mini-review investigates the application of nano- and ultra-filtration ceramic membranes in the field of food processing. This type of application appeared recently and the number of food processing sectors that can be interested with these techniques is likely to increase. In addition, food production represents a novel niche for ceramic membranes. Selected publications reviewed the application of ceramic membranes in the field of drinking water, dietary fats, carbohydrates, proteins and fermentation broths production. Research shows that ceramic membranes are a promising alternative to more traditional methods, although there are some challenges to overcome in order to become competitive, such as the control and reduction of membrane fouling, and a deeper understanding of the relationships at the molecular level between the solutes and the membrane surface.

Keywords: Ceramic membrane; Food process; Nanofiltration; Ultrafiltration

Introduction

The development of inorganic membranes started with vycor type glass membranes initially studied around the 1940's. The first period that preceded the current generation of inorganic membranes was related to the separation of uranium isotopes by gaseous diffusion processes. The challenge was to employ membrane materials who can sustain aggressive environment and offer reliable performances. Following such developmental work, two companies in the 1973, Ceraver and Euroceral, started to produce ceramic oxide based supports used to supply the Nuclear Fission Industry of suitable propeller. The nature of the membranes still operating in Eurodif plant (France) remains classified [1]. The second period consists on the development of microfiltration (MF) and ultrafiltration (UF) inorganic membranes as a consequence of the knowledge accumulated by the companies producing gaseous diffusion plants [1]. In the 1960's, Carre (a subsidiary of DuPont) developed the concept of liquid filtration on dynamic zirconium hydroxide supported on stainless steel. In the 1970's, Union Carbide developed ceramic oxide layers coated on carbon supports [1]. The first commercial cross-flow filtration system equipment with inorganic membrane was manufactured by SFEC in the 1978. The concept of multichannel support was introduced in the 1980's from Ceraver [1] and could be considered the starting point on the development of the new generation of ceramic membranes (CM) which began to operate at lower porosity scales: UF first and nanofiltration (NF) more recently.

This mini-review includes articles and papers published within the period from 1945 to 2014 that address the topic of UF and NF with CM. A total of 78 publications were selected, using Web of Science was used as search engine, for the study of which 25 were further investigated because of their direct application to food production processing.

As shown in Figure 1, the first publication was published in 1985 indicating that CM is an emerging technology. The steady increase of yearly publications indicates that interest in UF and NF ceramic membranes is growing rapidly. The first food processing applications in the field of UF and NF with CM were published during the 1997-1999 period. According to Figure 1, the most recent development in the food processing industry is the use of NF-CM at the beginning of the 2000's [2], but it is growing at an even higher rate than the total publications

with 50% of the total publications found being released during the last three years. During the period from 2012 to 2014, 21 papers were published, thus 27% of the total publications were submitted during the last three years while the initial paper appeared during the first half of the 1985's (i.e. 30 years earlier).

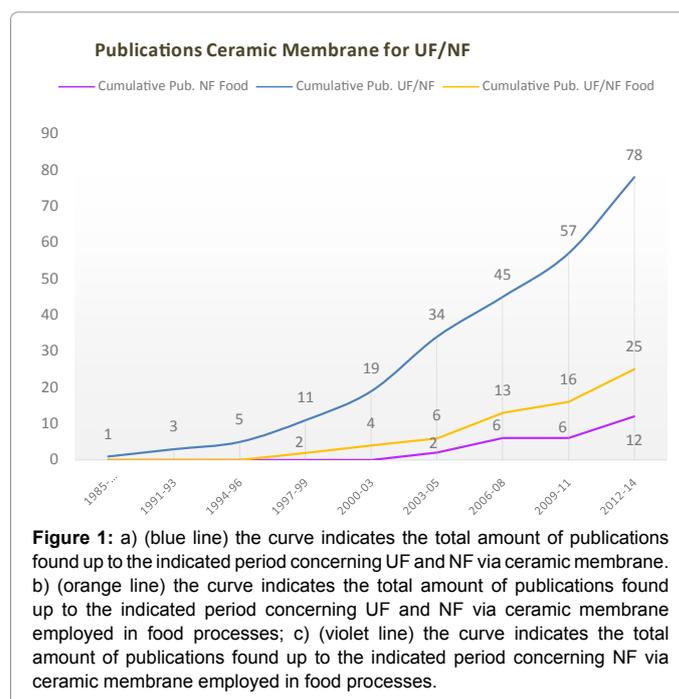


Figure 1: a) (blue line) the curve indicates the total amount of publications found up to the indicated period concerning UF and NF via ceramic membrane. b) (orange line) the curve indicates the total amount of publications found up to the indicated period concerning UF and NF via ceramic membrane employed in food processes; c) (violet line) the curve indicates the total amount of publications found up to the indicated period concerning NF via ceramic membrane employed in food processes.

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The review begins by looking at the basic principles of filtration followed by a section on ceramic membrane development and challenges in their applications. Several applications of CM in the field of drinking water, dietary fats, carbohydrates, proteins and fermentation broths production are discussed. The wide scope of this review indicates the high potential of CM in the food industry. Finally, the review includes recommendation for future works that must be addressed in order to make improvement in ceramic membrane processes.

Fundamental of Membrane Filtration

Separation mechanisms

The flux through an ideal semipermeable membrane can be described by the following equation:

$$J = Q_p / A \quad (1)$$

J indicates the flux through a membrane; calculated as volume of liquid permeating per m² of membrane surface area in an hour time period (L/hm²). Q_p indicates the permeate flow rate (in liter per hour), and A indicates the membrane surface area (m²).

In the case of MF and UF, the osmotic pressure of the permeate and retentate can be neglected while for nanofiltration (NF) and reverse osmosis (RO) this value increase to a point it becomes the dominant resistance force.

According the Hagen-Poiseuille law, the flux through an ideal membrane of an incompressible liquid can be expressed as:

$$J = \varepsilon dp^2 PT / 32 \Delta x \mu \quad (2)$$

ε indicates the porosity of the membrane, dp is the channel diameter, PT is the applied transmembrane pressure, Δx is the length of the channel, μ is the viscosity of the permeate. If a specific membrane was tested it can be assumed that for such membrane ε , dp , and Δx are constants and they can be included in a constant that can be defined as permeability coefficient A ($A = \varepsilon dp^2 / 32 \Delta x$). Therefore the equation (2) can be rewritten as:

$$J = A PT / \mu \quad (3)$$

The equation (3) shows the relationship existing between J, PT, and μ . As the pressure increases J increases. As temperature increases the viscosity of the fluid is reduced and the permeate J increases. If A/μ is defined as the reverse of membrane resistance (1/RM), equation (3) can be transformed into:

$$J = PT / RM \quad (4)$$

During the actual filtration operation, RM may become a minor resistance factor if compared to other forms of membrane resistance. In order to obtain a more representative calculation of the flux concentration polarization (RG) and fouling (RF) should be considered (equation 5):

$$J = PT / (RM + RF + RG) \quad (5)$$

RG is the resistance caused by the concentration polarization, which becomes particularly significant in case of UF, NF and RO. Concentration polarization is caused by the accumulation of solutes at the surface of the membrane. When the flux and diffusion coefficient are in the same order of magnitude the solutes tend to accumulate on the membrane surface creating a secondary filtration layer that cause a significant increase in resistance.

This type of phenomenon can be attenuated via the creation

of turbulent flow of retentate on the membrane surface: cross-flow configuration. RF represents the membrane fouling which the resistance is created by the progressive accumulation of particles on the membrane surface and within the pores of the membrane causing a decrease of permeates flux.

Ceramic membranes development

Filtration technologies based on inorganic membranes are a relatively new field that is receiving increasing interest from the industry. The CM represents a very important class of inorganic membranes [1]. The main type of ceramics currently in use for the manufacturing of filtration membranes consists of refractory oxides: alumina, zirconia or titania [3]. Nevertheless, a number of other ceramic materials such as cordierite, mullite, silicon nitride, silica and borosilicate glasses were indicated as suitable materials for inorganic membrane production [4]. One of the advantages of the application of CM over the polymeric counterparts is the capacity to withstand harsh operating conditions in terms of pH, temperature, pressure and chemical stability [5-7]. CM can be operated with liquid or gaseous media. They are manufactured within a wide range of superficial porosity and they can be employed in MF (macropores above 0.1 μ m in diameter), UF (mesopores ranging from 0.1 μ m to 10 nm of diameter) and NF (nanopores below 10 nm of diameter) [8]. Porous CM is becoming widely applied in MF and UF. Recently, they entered the NF domain and their applications are increasing.

Ceramic membranes can be produced with different geometries: flat, tubular, multichannel or monolithic geometry. Du Pont have proposed alumina hollow fibers in the microfiltration range [1]. An interesting application of a MF ceramic membrane with stamped geometric design was successfully tested for a food production process [9].

Initially the CM were of tubular shape with a low volume to surface ratio but their design has constantly evolved toward multichannel cylindrical geometries [1]. The tubular shaped channels developed into flower shaped multichannel further optimizing the surface to volume ratio and ultimately they reached a monolithic structured design with very high density of cells and thin walls. This development led to considerably larger hydraulic sections and high filtrating surface per element. All these ceramic membrane elements are currently available on the market.

All the publications examined in this mini-review concern CM used in a cross-flow configuration. The liquid feed circulates tangentially to the surface of the membrane while the permeated liquid goes through the membrane perpendicularly to the feed flow direction. The filtration driving force is generally the transmembrane pressure applied from the retentate side.

Challenges

Typically, the flow through the membrane decreases during the operation with fluids [8], one of the major causes of such loss of productivity is the fouling phenomenon. The membrane fouling was defined by Koros et al. [10] as the "process resulting in the loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surface, or within its pores". This phenomenon is complex [11] and not yet adequately described by current proposed models [12]. It influences the lifespan of a membrane, increases energy demand, maintenance and cleaning costs [13,14].

We can identify four general types of fouling:

Organic fouling [15-17]: is generated by the deposition or adsorption of dissolved organic materials [18]. Some of the organic materials typically involved in such processes can have a biological origin such as proteins or polysaccharides [19]. The hydrophobic fraction of natural organic material (NOM) present in water was found to be one of the major factors causing permeate flux reduction when processing water [20].

Colloidal fouling [21]: is generated from the accumulation of particles and colloidal matter. The materials involved in such phenomenon can be organic colloids such as aggregated NOM and proteins [22,23], or inorganic colloids such as colloidal silica, clay minerals, metal oxides (Fe, Al and Mg), suspended matter, precipitated salts and organic colloids [21].

Scaling: Typical of NF or RO where the polarization concentration of scarcely soluble salty molecules causes their precipitation on the membrane surface due to oversaturation of such compounds [24]. Examples of this type of salts could be calcium and barium sulfates, calcium carbonate and silica scales [25,26].

Biofouling: It is generated by the growth of microorganisms with accumulation of extracellular materials on the membrane surface [27-31]. Generally, more than one specific type of fouling is involved. For example, the presence of organic fouling will enhance the biofouling through accumulation of nutrients that bacteria can utilize to grow and proliferate [32,33].

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When the range of the membrane pore size reaches that of the NF scale two phenomena become of particular interest for the overall filtration performances: concentration polarization and osmotic pressure. The concentration polarization is generated from the retention of solutes on the membrane surface that causes the creation of a layer where such molecules are much more concentrated if compared to the bulk solution. Such increase in concentration can contribute to scaling, gel layer formation and other fouling types with drastic reduction of the process performances [34]. The concentration polarization also produces an increase of osmotic pressure at the membrane retentate surface side which creates a pressure force opposing the applied transmembrane pressure (TMP) thus reducing the flow of the permeate. Both phenomena can be reduced via the application of a cross-flow, which constantly reduces both the concentration polarization and the osmotic pressure generated.

The production costs of CM are still higher than the polymeric membranes (PM) and usually result in higher investment costs. However, the investment costs can be balanced by a reduction of operation costs due to several factors such as reduced need for pretreatments of the products before the UF or NF steps [3], longer membrane lifespan, more efficient cleaning to limit the fouling [35] and better sanitizing conditions [5].

The fouling control and mitigation strategies must be optimized depending on the mechanisms and factors contributing to the specific case taken into consideration. They often consist on pretreatment methods or cleaning procedures.

Examples of pretreatments methods can include:

pressure-driven methods such as pretreatment with MC or UF

prior NF process steps [36,37] or reverse osmosis [38].

Flocculation and adsorption methods [39].

Oxidating agents such as H_2O_2 or UV which showed potential for certain type of pesticides and hydrogen sulfide removal, mitigation of flux decline, and improvement in membrane cleanability [40].

The cleaning procedures of the membranes play a very significant role in the overall process performances and must be optimized based not only the surface composition but also depending of the type of feed processed [41]. Chemical cleaning exploits chemical reactions [42] such as hydrolysis, solubilization, saponification, dispersion, chelation (example using EDTA [43]), enzymatic hydrolysis [44] or variation of pH [45].

Cleaning techniques based on physical methods such as backpulsation and backflush [46,47], gas bubbling [48], ultrasounds [49,50] or the application of electric fields [51,52], can be combined with the chemical cleaning methods in an attempt to prolong the lifespan of the membranes and reverse at least partially the fouling phenomenon. The determination of the cleaning requirements and frequency is of critical importance for an efficient and robust filtration process. There is evidence that cleaning at an early fouling stage is preferable to when the fouling layer is more compacted [53]. Normally the cleaning procedures are applied when the flux decline is higher than 10-30% [12]. In some cases NF can be used with very rare cleaning steps when subcritical fluxes are used [54], this is caused by the fact the smaller pore size of the NF membranes are less subjected to pore plugging than UF and MF membranes [12].

Food application of UF and NF Ceramic Membranes

The use of membrane technologies in the food industry gives advantages such as food safety [55], ease of cleaning and sterilization, and environmental friendliness [56]. They allow for a simplification of the process flow sheets avoiding steps that are more complex or cause of chemical stress for the products [57]. They can contribute to the production of high quality foods and the creation of novel fractions that can be used for new type of dietary supplements allowing this industrial sector to satisfy more easily the evolving consumer demand coming from the markets [58]. This review considers as a food ingredient the drinkable water which is not only a fundamental component of many types of food products such as beverages but it is also a fundamental component of most of the processing steps necessary to arrive to the final products.

Drinking water

Drinking water is a fundamental component of many food products, especially beverages and a critical component of most of food production processes. Many factors are contributing to the constant increase in demand for drinking water such as population growth, personal use increase, increasing presence of pollution and contamination in the environment (especially concerning in developing countries such as India, China, and the African continent) [59], and reduced availability due to global warming effects such as desertification or glaciers melting.

The first publication testing CM operating in the UF range was released during the year 1997 [60]. The tests compared the performance of two UF ceramic membranes to filter the raw waters of the Muskan Lake (in Sweden) which contains high color content of mostly humic substances (up to 100 mg Pt/l) as well as odor and taste problems particularly during the algae blooming period. The two

CM were produced by SCT (France) and were coated with an active layer of zirconia oxide with 50 nm and 100 nm pore size respectively. The equipment was operated in cross-flow set up producing a permeate flow of 600 L/h m²Bar and stable conditions with a 50 nm pore size membrane up to a volume reduction factor of 20. The water produced with the use of the UF membranes contained between 3 and 12 mg/l of total organic carbon and a color ranging between 8 and 45 mg Pt/l. The PM, which could operate on the NF range, contained a significantly reduced amount of humic substances probably due to their lower molecular weight cut off (MWCO) with less than 1 mg/l of total organic carbon (TOC) and 1 mg Pt/l or less of color. This fact leads the researcher to conclude that the UF ceramic membranes were not a suitable option this application. Figure 2 shows the results obtained in terms of flux with ceramic membranes. It would have been interesting to test and compare how CM with MWCO in the range of the NF would have performed in comparison with a PM of comparable MWCO.

More recently, a highly integrated hybrid process was tested for the treatment of micro-polluted raw water in order to produce drinking water [59]. The superior physical and chemical stability of the CM is compared with PM. CM is integrated into one unit of the coagulation, ozonation, and filtration [59], replacing conventional sedimentation and sand filtration processes. This configuration allows for a significant reduction of the treatment time and footprint of the plant. This technique was able to achieve high performance with less land occupation and lower costs compared with the conventional processes. The results of the tests were encouraging with >99% reduction of turbidity from the raw water, and an excellent rejection performance of the CM. The filtration module was provided from Meidensha Corporation (Tokyo, Japan) with 60-70 nm average pore size.

NF polymeric membranes were initially developed as an ultra-low pressure tool for the removal of hazardous organic contaminants present in water, color or as water softeners [61-63].

The Centro de Estudios Académicos sobre Contaminación Ambiental (CEACA), Santiago de Querétaro, published the first NF application to seawater and brackish water desalination [64] that used CM. The test used seawater taken from three locations: Playa Blanca, San Jose del Cabo and Holbox. Analysis showed that the three samples had very similar parameters. They used modified ceramic NF membranes coated with TiO₂ that were impregnated with reduced Ag or Pt metals. The membranes were tubular mono channel with a contact surface of 0.0047 m² and a MWCO of approximately 5 kDa.

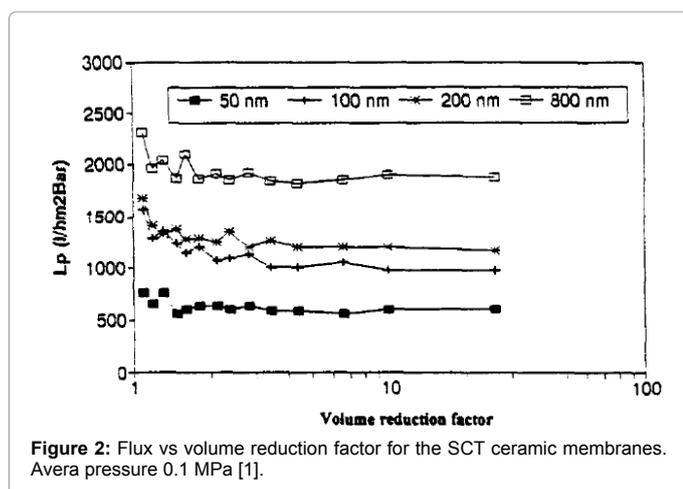
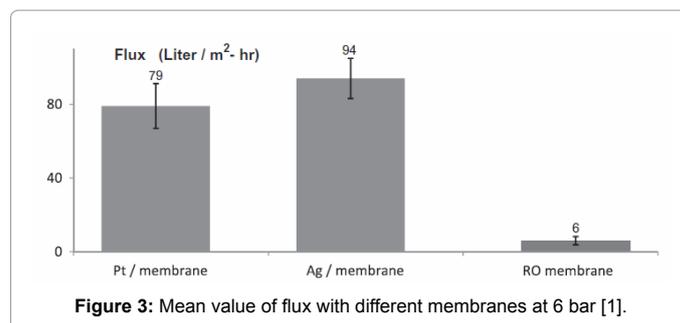


Figure 2: Flux vs volume reduction factor for the SCT ceramic membranes. Average pressure 0.1 MPa [1].



The tests were performed at 6 bars. These new membranes were tested and compared with unmodified TiO₂ ceramic membranes as a pretreatment for the traditional reverse osmosis (RO) processes. The goal was to increase the process efficiency and reduce the energy requirements. Figure 3 shows a comparison between the fluxes (J) of some of the membrane tested.

The unmodified ceramic membrane achieved a total dissolved solids rejection of about 5%, while the Pt-impregnated and the Ag-impregnated membranes had respectively a 22% and 29% total dissolved solids rejection. The rejection considering only the salt content of the seawater was respectively 17% and 24%. Their rejection was not significant with monovalent ions such as Na⁺ but it was much greater with divalent cations. The Ca²⁺ was rejected with about 60% efficiency from both modifications while in the case of Mg²⁺ the two membranes expressed significantly different rejection values with 80% rejection for the Pt-impregnated membrane and 65% rejection with the Ag-impregnated membrane. The reduction of biofouling appeared to be satisfactory due also to the fact that especially Ag⁺ has antibiotic and bacteriostatic properties [64].

Dietary fats

CM can be employed in the oil industry with potential gains in terms of both productivity as well as reduction of production steps. They can be applied directly to crude oils or to their miscella in combination with organic solvents.

In 2002, Alicieo et al. [65] investigated the use of a UF ceramic membranes with pore size of 10 nm directly on the crude soybean oil with the aim of purifying it from some undesirable components such as phospholipids, free fatty acids, pigments, sterols, carbohydrates, proteins and their degradation products. One advantage offered from the application of the CM if compared to the PM is their thermal stability, which allows for the use of higher temperatures during the process reducing considerably the viscosity of the oil. In this case, a high level of rejection was achieved for most of the mentioned components [65]. They achieved a rejection of 54, 45% for the free fatty acids, 97.91% for soaps, 99.14% for the phospholipids, and 42% reduction in color. The filtration conditions were 6 Bar pressure at 50°C in cross-flow configuration, a value of 4, 16 Kg/m²h was achieved. More details on the flux compared with time of the process are shown in Figure 4. During the study, the ceramic membrane was compared with a polysulphone hollow fiber membrane provided from AIG Technology Corporation (MWCO of 100 kDa). The results showed a higher rejection for the undesired contaminants to be removed from the soya oil in the case of the ceramic membrane but a lower flow rate when compared to the polysulphone hollow fibers. It is reasonable to attribute such differences in performances mostly to the pore size of the two membranes.

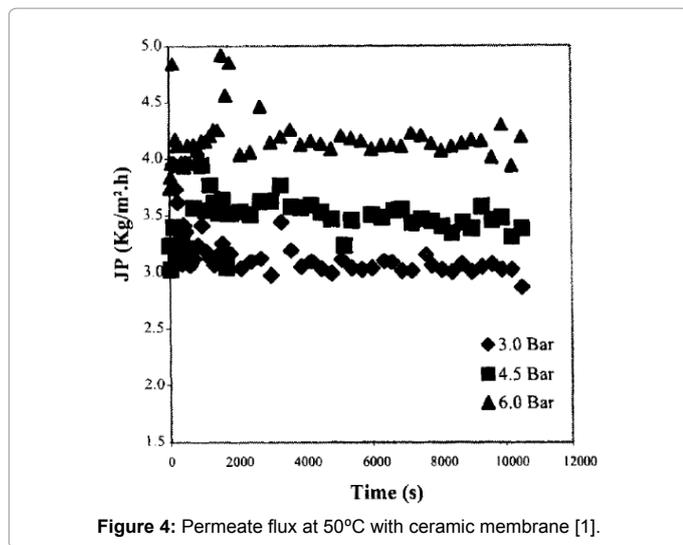


Figure 4: Permeate flux at 50°C with ceramic membrane [1].

More recently, a similar process was tested in order to degum and remove waxes from sunflower oil [66]. A ZrO₂ activated layer ceramic membrane on α -Al₂O₃ with pore size of 100 and 20 nm were tested. As predicted, the filtration with the lower pore size membrane gave better results in terms of rejection with 97% rejection of the phospholipids at 2 bar pressure. The crude oil presented a high viscosity due to the presence of various particles and a relatively high level of waxes. According to the authors [66] a multi UF step was necessary with larger porosity size as a pretreatment in order to increase the productivity of the technique so that this method could offer advantages in terms of economy and environmental friendliness of the process.

The CM could also be applied to recover the product contained in an organic solvent extract, substituting at least in part the evaporation processes necessary to remove the solvent from the non-volatiles, which is a stressful and energy consuming process. With improvement of the product quality and reduction of the energy consumption of the overall process, In 1999 a publication described an experiment concerning soybean oil extracted with hexane [67]. The goal was to test the possibility of recovering part of the solvent via UF, reducing the energy costs of its recycling through evaporation. This allows for a reduction of the total energy consumption for the process as well as a reduced stress imposed on the substrate during its production, improving the final product's characteristics [68]. The extract was directly collected from the solvent extractor without refining. It typically contained near 33 wt% of soybean oil, 0.6 wt% of phospholipids and less than 0.1 wt% of free fatty acids. The experiment performed at room temperature employed a porous alumina anodisc of 47 mm in diameter. The pore diameter of the top layer was 20 nm with a thickness of about 1 μ m. The permeate flow was recycled back to the 5 L reservoir, which was sufficient to keep a constant concentration in the recycled retentate. During the first 2 hours, the flux changed rapidly. Therefore, separation data were acquired after 2 hours of permeation when a clean membrane was used. Figure 5 shows the recorded parameters obtained during the tests.

When pure hexane was used, there was no readable transmembrane pressure even at the maximum feed rate of the pump (about 40 ml/min). This is a clear sign that the filtration via CM of non-polar solvents is strongly dependent on the liquid viscosity and there was no noticeable structural modification at the level of the pore size of the

alumina layer. This could be an interesting advantage if compared with most PM, which tend to become unstable in the presence of organic solvents or swell up sensibly and decrease their permeability. The test showed promising performances in terms of flux and process stability but the rejection was around 20% of the initial values to decrease to lower values as the concentration of the triglycerides increased. The reason of the significantly low yield obtained was the use of a too large pore size membrane. It would have been interesting to have a test of this technique utilizing a NF ceramic membrane type.

The solubilization of crude oil into organic solvent could be used to remove phospholipids (degumming), and other undesired compounds from a crude oil. In a paper from 2008 [69], a miscella of corn oil solvated into hexane was ultrafiltrated with an alumina multichannel ceramic membrane with an average pore size of 50 nm at a temperature of 40°C. The miscella contained between 25% and 35% w/w of crude oil. Such concentrations of organic solvent were not sufficient to reduce drastically the formation of heavy micelles, which did not permeate through the membrane. Surprisingly the tangential velocity had a greater influence on the permeate flux than the TMP. A higher percentage of crude oil into the miscella favored the retention of phospholipids (PL) while negatively influenced the permeate flux. In a test 35% w/w of crude corn oil was ultrafiltrated with a tangential velocity of 2,4 m/s, 40°C and 1.5 Bar TMP, achieving a 93.5% w/w rejection of the phospholipid content and a flux of 65,8 Kg/m² h which according to the comments was considered a promising result.

The CM could offer a substantial reduction of energy consumption if combined with supercritical fluid extraction. It could offer the possibility of recovering the liquid CO₂ separating it from the substrate being extracted without the decompression and recompression phase which plays a significant role in the total energy requirements of this technology. It appears that several research groups have recently started to test the feasibility of this technique. A paper published some preliminary results produced with a supercritical fluid extraction set up where the liquid CO₂ was combined with different components typically present in these type of applications, including oils composed by triglycerides [70]. The ceramic NF membrane consisted of a layer of TiO₂ deposited on a ceramic support. The MWCO of the membrane in the tested conditions was estimated to be at 800 Da, with an average pore size of 0.9 nm. In one experiment, a trimyristin oil, with a molecular weight (MW) of 723 Da, was nanofiltrated in the presence

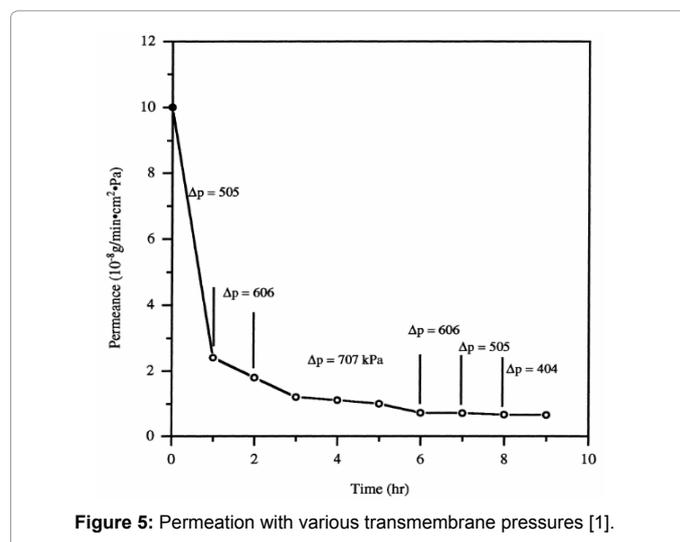


Figure 5: Permeation with various transmembrane pressures [1].

of hexane as a co-solvent at a pressure of 150 Bar and a temperature of 333 K achieving a rejection of 98%. The permeate flux decreased only of about 20% and recovered nearly completely within a few minutes after the injection of the substrate was stopped [70]. In another interesting test, oil was nanofiltrated. The triglyceride oil contained about 25 wt% of each of the following components: tricaprín (MW 554 Da), trilaurín (MW 639 Da), trimyristín (MW 723 Da) and tripalmitín (MW 807 Da). The membrane exhibited a selective permeability. The smaller molecules (in particular tricaprín) showed a greater permeability, producing a permeate fraction highly enriched in tricaprín which doubled in concentration from the initial values if compared with the feed composition as illustrated in Figure 6. This type of selectivity could play an important role in the production of high quality oils enriched with high molecular weight triglycerides, highly unsaturated with reduced content of low MW triglycerides, free fatty acids and other contaminants that would not require a winterization process.

In conclusion these initial tests illustrate how important are the specific interactions between the membrane surface and the substrates which can be adsorbed on it or flow through the nano-pores with different velocities. The pressure of 150 bar used in the set up appears to be on the lower end of the standard extractions performed in the food industry which are typically around 200-400 bar or even higher in case of co-solvent extractions [71]. It can however be regarded as a promising sign that this direction could lead to energy efficiency gains in this type of processes.

Sugar and carbohydrates

The sugar industry is emerging as another field where CM could innovate, increasing efficiencies, waste products recovery and help to develop novel food supplements.

Two publications showing the use of UF and NF ceramic membranes for the purification of oligosaccharides recovered from caprine milk that could be used for the production of infant milk formulas [72,73] were recently published. It is well documented that the goat milk has a very similar carbohydrate profile to the human milk [74]. They help protecting infants from pathogens [75] as well as helping the correct development of the bifidogenic flora typical of breastfed children [76]. The tests employed a double step filtration via CM.

The objective of the first step was to retain the protein fraction, separating it from the oligosaccharides and lactose fraction that were able to permeate. The membrane employed an INSIDE CÉRAM™ module (TAMI Industries, Lyon, France) made of ZrO_2-TiO_2 , 25 cm long, three channels and a membrane area of 94 cm². The MWCO

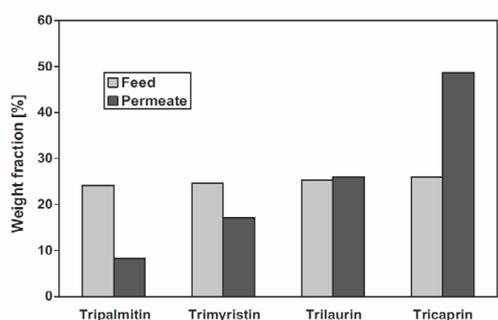


Figure 6: Comparison of triglyceride mixture composition between feed and permeate; membrane sample 5, 125 bar feed pressure, $\Delta P = 15$ bar, temperature 323 K [1].

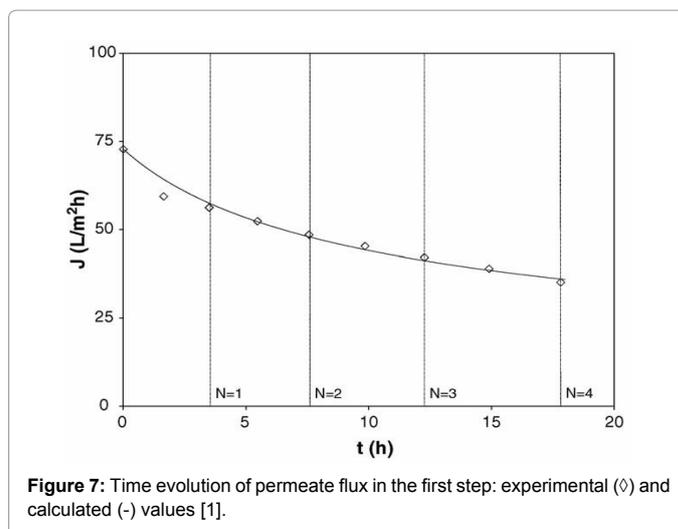


Figure 7: Time evolution of permeate flux in the first step: experimental (\diamond) and calculated (-) values [1].

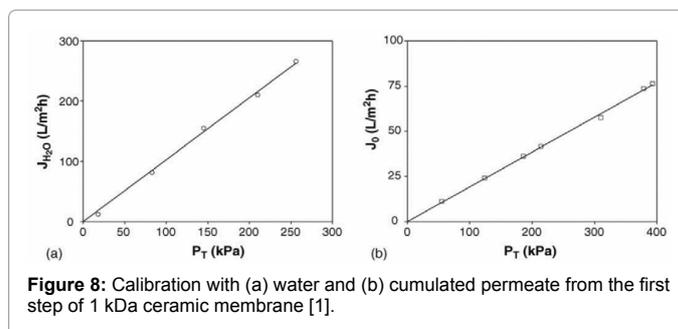


Figure 8: Calibration with (a) water and (b) cumulated permeate from the first step of 1 kDa ceramic membrane [1].

of the module was 50 kDa. More than 98% of the lactose and the oligosaccharides were eluted after 4 diavolumes, while 94% of the original protein content was retained together with 76% of the calcium which was probably linked to the large casein micelles. The flow during the UF decreased probably due to fouling as shown in Figure 7.

The second step was performed with a ceramic membrane of the same dimensions but smaller pore size and a MWCO of 1 kDa. The aim of this step was to concentrate the oligosaccharides in the retentate and reduce the concentration of lactose and salts that permeated through the membrane. The flux through the membrane with pure water and with the permeate coming from the first step demonstrated to be correlated with the pressure as shown in Figure 8.

In order to avoid an excessive compaction of the fouling layer, the transmembrane pressure was selected at 150 kPa. After the 10 h of continuous operation the flux of the permeate decreased from nearly 30 to about 20 l/m² h, then stabilized as illustrated in Figure 9, suggesting that the fouling did not affect the sieving properties of the membrane for the lactose and calcium.

The permeation of the calcium and lactose was good, after 3 diavolumes 94% of the lactose was eluted. During the second filtration step 82% of the initial oligomers were recovered while most of the lactose and calcium were removed as shown in Figure 10.

During the same year another paper was published describing a ceramic membrane set up used for the separation of non-sucrose compounds from syrup as a part of the sugar-beet processing [77]. White sugar has to satisfy rigorous demands for quality, particularly

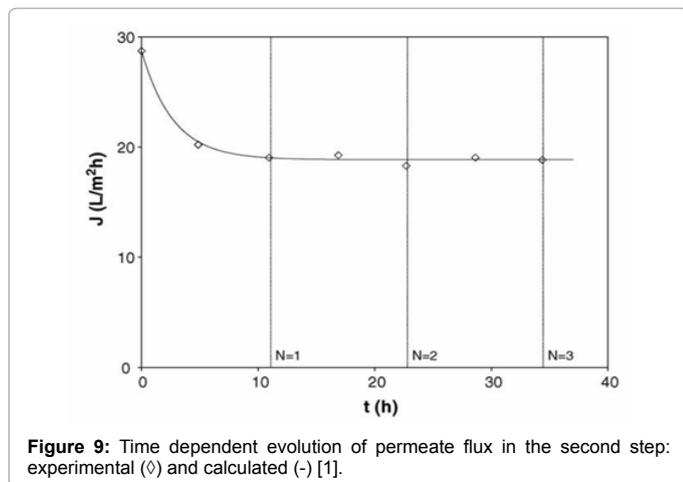


Figure 9: Time dependent evolution of permeate flux in the second step: experimental (o) and calculated (-) [1].

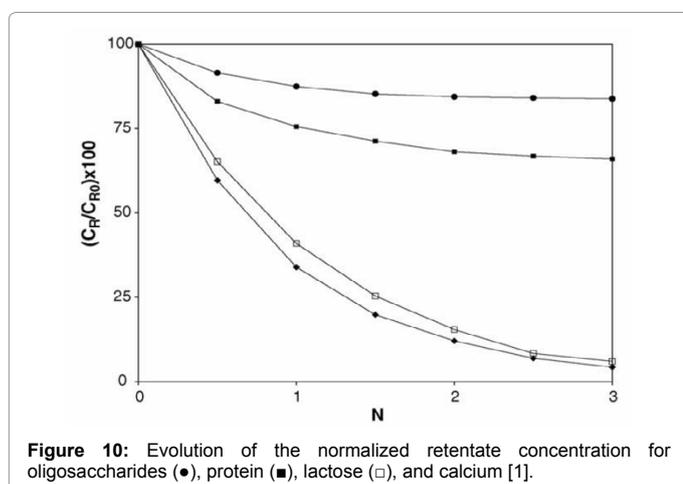


Figure 10: Evolution of the normalized retentate concentration for oligosaccharides (●), protein (■), lactose (□), and calcium [1].

those concerning its color. The non-sucrose compounds with intense color tend to be incorporated into the sucrose crystals during the purification process, especially if the purity of the beet is poor. Some of the advantages of the application of a UF step in the proper conditions and the use of a membrane with adequate characteristics are high purity and low color of the ultrafiltered syrups, absence of starch and acid substances, and drastic reduction of environmental pollution. It was also observed a faster crystallization if compared to conventionally purified syrups. The cross-flow filtration system was connected to a tubular ceramic membrane whose pore diameter was 5 nm. The membrane consisted of a titanium oxide layer coated on alumina support. The membrane was single channel, 250 mm long, with 6.8 mm inner diameter. The useful membrane surface was $4.62 \times 10^{-3} m^2$. The effect of the turbulence promotion on the filtration performances was investigated by the use of a static mixer. The tests were performed with a temperature of 70°C and 80°C but the results reported on the publication concerned only the 80°C tests.

The conclusions were that the static mixer contributed to an increase of the fluxes in most of the ultrafiltration phases. The highest flux achieved in the presence of the static mixer (SM-mode) at the beginning of the operations was approximately 35% greater than the flux in non-static-mixer mode (NSM-mode). The difference was even greater at the end of the process, when it reached a 45% increase compared to the NSM-mode UF.

In terms of color changes, the static mixer achieved a maximum of

30% greater change compared to NSM-mode configuration. At the end of the process, the difference was significantly greater when it reached a 65% improvement compared to the NSM-mode process.

Some years later another publication concerning this type of set up obtained very similar results, this type of static mixer technology was used with a 20 nm pore diameter ceramic membrane composed by a layer of zirconium oxide deposited on an aluminum oxide support [78]. A purity elimination of 80% on average compared to the feed was achieved. The static mixer appeared to have a significant impact on the permeate flux through the membrane at 80°C only when the cross-flow was below 150 L/h. At higher transmembrane pressure, the effect was less marked as illustrated from Figure 11.

The production and purification of xylo-oligosaccharides (XO) is a very expensive and complex process comprised of several steps [79], which often include HPLC purification technology, in order to reach a sufficient level of purity. The range of 75 – 95% purity is of critical importance for their use as food additives, pharmaceuticals, and nutraceuticals [80]. The possibility of employing ceramic membranes in the NF range was investigated from a paper, which tested the use of a monolithic module Kerasep Nano (from Novasep) with 1 kDa MWCO [79].

Rise husk was obtained from a local factory (Procesadora Gallega de Alimentos, Lalin, Pontevedra, Spain), air-dried, homogenized and analyzed for its content. The dry material was mixed with a ratio of 1:8 w/w with water in a Parr reactor. Applying the standard heating temperature profile, the maximum xylooligomer concentration was reached exploiting its auto-hydrolytic activity [81]. The liquors were recovered by filtration and further processed after being analyzed for their content.

The liquors were initially filtrated with a 0.45 μm membrane in order to remove particulate material. Then tested with three modules of ceramic membrane coated with TiO_2/ZrO_2 : Membralox Ti-70 1000 with 1 kDa MWCO (Pall), Membralox Ti-70 5000 with 5000 kDa MWCO (Pall), and Kerasep Nano with 1 kDa MWCO (Novasep). All experiments were carried out at room temperature. The initial composition of the liquors was about 2.55 wt% of non-volatile compounds of which about 42.47% were composed of xylo-oligosaccharides. During the tests, several PM were tested as well. The first observation was that the CM had up to three fold higher flow rates (J) even when compared with PM that had higher MWCO ranges (at least declared from the producer). Figure 12 shows the results of three tests performed with two PM (a and b) and a ceramic membrane.

The permeate flux obtained with the test of the Kerasep Nano monolithic module increased in a linear proportion up to 10 bar. The J

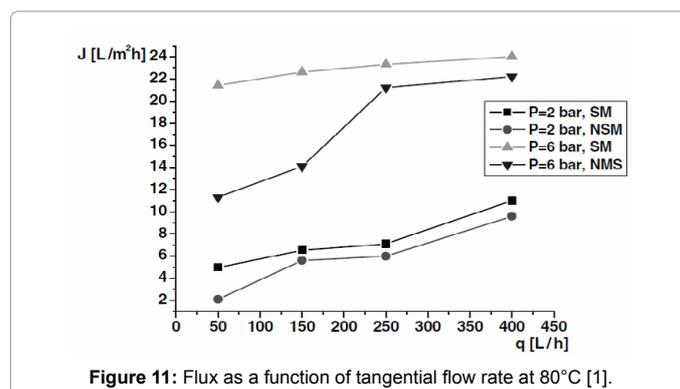


Figure 11: Flux as a function of tangential flow rate at 80°C [1].

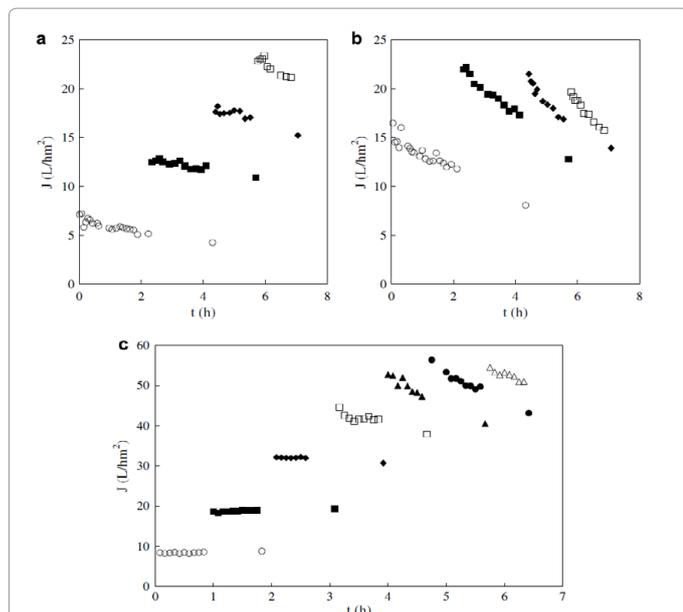


Figure 12: Time dependence of the permeate flux obtained with the (a) ESP04, (b) PU608 and (c) Kerasep Nano NF membranes, operating at selected transmembrane pressures (○ – 2 bar; ■ – 4 bar; ◆ – 6 bar; □ – 8 bar; “filled triangle” – 10 bar; ● – 12 bar; Δ – 14 bar) during the processing of raw autohydrolysis liquors. Feed velocity, 2 m/s for the UF membranes and 3 m/s for the NF membrane, $26 \pm 4^\circ\text{C}$, [1].

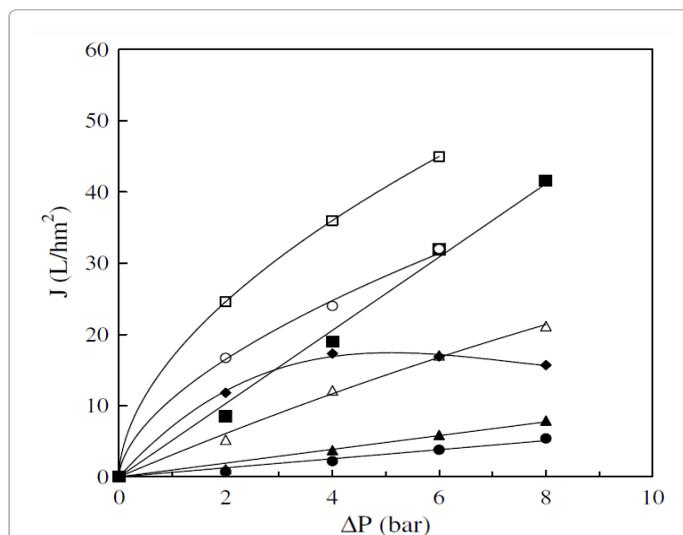


Figure 13: Effect of pressure on the permeate flux obtained during membrane processing of raw autohydrolysis liquors (feed flow velocity, 2-3 m/s; temperature, $26 \pm 4^\circ\text{C}$). ● – PCI AFC30; “filled triangle” – osmonics DL2540; Δ – PCI ESP04; ◆ – PCI PU608; ■ – Kerasep Nano; ○ – Pall membralox 1 kDa; □ – Pall membralox 5 kDa [1].

was constant and presented no reversible fouling during the utilization when the TMP was lower than 8 bar as it can be seen in Figure 12c. The results showed that the transmembrane flux limit for this membrane was $40 \text{ L m}^{-2} \text{ h}^{-1}$ (around 8 bars), higher pressures produced fouling and gradual loss of performances. In Figure 13 a comparison between tested membranes polymeric and ceramic types can be observed. Most of the membranes that demonstrate high initial J values appear to suffer also from a higher reversible fouling when the TMP increases. Table 1

gives a summary of the results of the tests performed at 8 bar pressure; the values included in the highlights are regarding the mentioned membranes.

The best performances in terms of flow and fractionation effect were obtained from Kerasep Nano and ESP04 (its surface was chemically modified via addition of metal salts to the polymeric matrix which changes the surface negatively and this can attenuate its fouling tendency). Kerasep Nano at 8 bar pressure was able to express higher fluxes about the double of the ESP04 and a better purification effect because able to reject with comparable efficacy the oligosaccharides but retaining less efficiently of the monosaccharides.

Proteins

The possibility of employing membrane technologies in the recovery of proteins discharged from several industrial processes into the environment is very attractive for such industries because it opens to the possibility of increasing the range of products that can be offered and reduces waste treatment costs.

The first publication about the use of CM for this type of food processes was found in 2003 [2]. The test was about the possibility of recovering fish proteins contained in the wastewaters of Chilean fishmeal industries.

The tests employed a Kerasep Nano01A (made in Oreilis from Rhodia) based on TiO_2 deposited on a $\text{Al}_2\text{O}_3 - \text{TiO}_2$ support. The tubular membrane had 19 channels of 2,5 mm, 856 mm length, with a total area of $0,1277 \text{ m}^2$ and a MWCO of 1 kDa. The pilot plan used for the tests was assembled by Rhodia. A sample of 30 L was collected from the wastewaters generated from a fish meal factory located in Talcahuano, Chile. It was filtrated through a battery Omnifilter MF cartridge of pore sizes 80, 20 and $5 \mu\text{m}$, then stored in a refrigerator at 4°C . It was observed that this filtration was not sufficient to produce a clear permeate liquid and it was recommended the use of a smaller pore size Omnifilter MF cartridge for future tests. The NF operations were carried out with a pressure ranging from 3 to 5 bar with a cross-flow velocity ranging from 2 to 4 m/s (at 5 bar pressure the flow velocity of 4 m/s was not reached for pump flow limitations). The permeate was circulated back into the feed tank in order to minimize concentration changes in the retentate. The permeate flux, J, was measured at the beginning of each experiment and after 15 minutes of operation. After a first testing phase the pressure of 4 bar and cross-flow of 4 m/s were chosen as optimal experimental conditions for the NF tests.

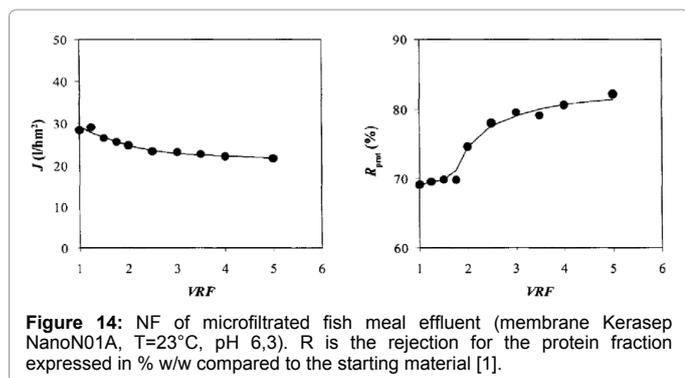
The membrane flux rapidly decreased to 21% of the pure water values of J (J_w), probably due to a strong adsorption of the proteins on the membrane surface and/or formation of a dynamic membrane layer on top of the ceramic layer. As the VRF increased, a smooth decrease to 16% of J_w was observed. After a complete washing procedure with basic and acid washing solutions, the J of the membrane was recovered to its initial values (J_w). The Figure 14 illustrates the behavior of the protein rejection in relation to the volume reduction factor (VRF) and the observed flows. It had an initial value of 69% and increased to 82% when a value of 5 in the VRF was reached. Fouling was detected and the flux could not be recovered back to the initial values until proper chemical washing was applied.

The extent of the fouling and its limitation in a continued operation set-up needed to be further investigated.

Very recently a new application for ceramic membrane was tested and published concerning protein recovery from shrimp shells [82]

Membrane	J (L/m ² h) at 8 bar	R	R	Fouling
		oligomccharides (%) xr.100	monosaccharides (%) xr.100	(% MVP)
Nanomax 95°				
AFC30	6.1	99.7	80	33
DL2540	8	99.4	76	20
Kerasep Nano	40	93	5	40
Membralox T1-70 1000n	34	78	7	60
ESPO4	21	93	10	65
Mcmbralox	47	70	4	63
TI -70 500 (rPU608)	15.7	84	5	75
Fouling was measured by percent reduction in pure water flux.				
a Data at 6 bar.				
b Data at 20 bar.				

Table 1: Comparison of membrane performance (flux, fouling and rejection) during the processing of the raw autohydrolysis liquor. The tests were performed at 8 bar. Fouling results are reported as pure water flux drop (PWF), [1].



which compose 18-42% of the shell wastes produced from the industrial processing of crustaceans and could be recovered during the process of production of chitin [83].

Shrimp shells from a seafood restaurant from the species *P. longirostris* were washed under running water in order to remove soluble organics, adherent proteins and other impurities. Then they were boiled in water for about 1 h in order to remove their soft tissues. The obtained shells were dried in an oven at 160°C for 2 h and finally crushed into a fine powder. Finally, the dried shells powder was mixed with an alkaline solution of sodium hydroxide in order to extract the removable protein fraction from the shells and create the protein-water solution to concentrate via UF [82]. The protein concentration experiments were carried out using 130 S UF pilot unit (Gamma filtration company, France) equipped with a Membralox-Ceraver module. This module was a multi-channel ceramic membrane composed of ultrafine porous ZrO₂ with 50 nm pore size coated on a porous alumina support (15 μm). Total filtration area was 0,2 m². Every test used 5 L volume of shell-proteins water which was concentrated to 2,1 L over a period of 50 minutes. The rejection coefficient of the filtration increased from the initial value of 32% to over 90% after about 30 minutes as illustrated from Figure 15a. The flow decreased to about 64 L m⁻² h⁻¹ from an initial value of 160 L m⁻² h⁻¹ as illustrated in Figure 15b.

A possible explanation for the flux reduction before stabilization after about 25 minutes from the beginning of the experiment is that

larger protein molecules accumulating on the surface of the UF membrane created a secondary filter layer that increased the rejection from the initial 30% to over 90%. If this hypothesis was confirmed it would be interesting to test the use of a NF ceramic membrane that could reject directly the majority of the proteins and maybe reduce the formation of the secondary filter layer with flow and performances benefits.

Fermentation broth products

The possibility of combing emerging technologies such as NF with other techniques can offer opportunities concerning the production of expensive but important ingredients for the food industry. For example in the production of fermentation products such as lactic acid or succinic acid, the production of lactic acid via fermentation is complex and requires many purification steps [84]. Duke et al., [85], proposed a simplification of the process for the enrichment of lactic acid. Two type of CM were prepared. One was a γ-alumina ceramic membrane with average pore size of about 4 nm, the other was composed by a support of γ-alumina coated with silica with a pore size of about 0.3 nm. The separation was performed in a pervaporation set up where the liquid contacted with the membrane was converted into vapor under vacuum as it penetrated through the membrane. The tests were performed at 25°C; a downstream vacuum pump induced the vapor phase, which permeated through the membrane. In order to simulate an actual fermentation medium a starting solution was prepared containing 15 wt% of lactic acid (LA) and 0,1 wt% of glucose.

The results of the tests showed that the γ-alumina ceramic membrane had a lower value of rejection if compared to the coated version with silica. The Figure 16a shows that the rejection of the γ-alumina ceramic membrane reduced as the concentration increased. Figure 16b shows that when the coated silica membrane was used the rejection values improved as the concentration increased.

The flux was more than one order of magnitude higher with the γ-alumina ceramic membrane though it decreased much faster than the silica-coated membrane. The scientists working on these tests produced their own theoretical models about the working mechanisms of two membranes, which might differ under some points of view; Figure 17 illustrates the proposed mechanisms.

The conclusion was that these initial studies were promising but

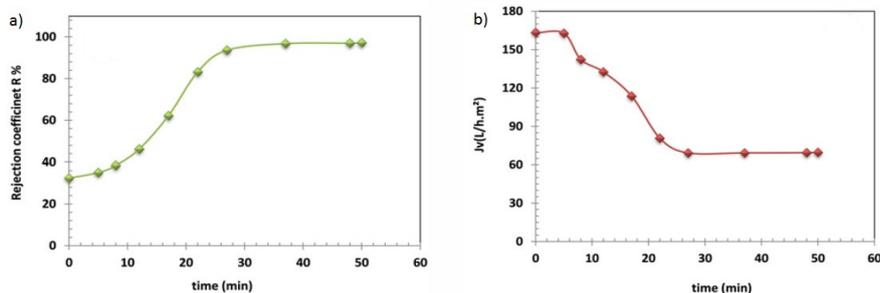


Figure 15: a) Rejection coefficient % at $U = 6$ m/s, $P = 3$ bar; b) J_v at $U = 6$ m/s, $P = 3$ bar [1].

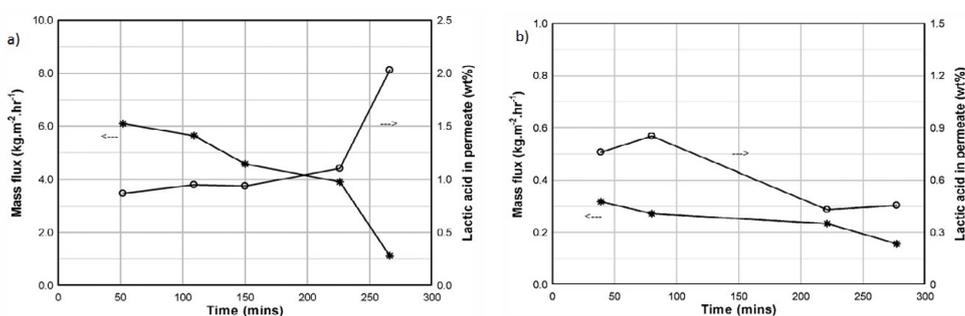


Figure 16: a) Pervaporation test performed with γ -alumina ceramic membrane at 25°C. Startup concentration of 15 wt% LA and 0.1 wt% glucose [1]; b) Pervaporation test performed with silica coated ceramic membrane at 25°C. Startup concentration of 15 wt% LA and 0.1 wt% glucose [1].

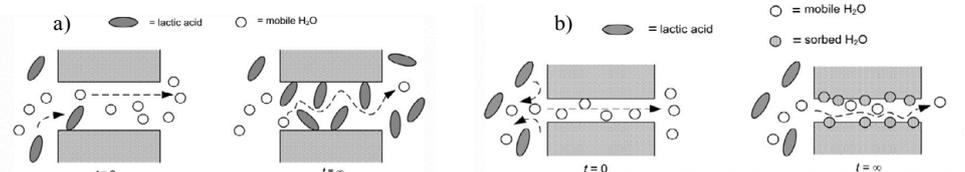


Figure 17: a) Mechanism of surface interaction and diffusion of water and LA within the pores of γ -alumina at the beginning of the permeation (left) and after steady state (right). b) Mechanism of surface interaction and diffusion of water and LA within the pores of the molecular sieve silica at the beginning (left) and after steady state (right). [1].

more tests were needed in order to improve the overall performances of the process.

Another very important fermentation product is the succinic acid, which can be produced from microbial bioconversion of the glycerol. There is growing interest in this type of technologies because the amount of waste glycerol produced from biodiesel conversion is increasing in recent years [86].

The succinic acid has important applications in the food, pharmaceutical and chemical industries (production of bioplastics). It has gained a growing interest as a renewable building block for chemical products such as 1, 4-butane-diol, tetrahydrofuran, polybutylene succinate (PBS) and other chemical compounds [87]. One of the challenges to overcome during its production is the isolation of the compound from other fermentation molecules. In case of separation of weak dicarboxylic acids such as the succinic acid, it is important to consider that also factors like pH play an important role in their separation efficiency. The capacity of the membrane to reject these compounds and the mechanisms by which such compounds are rejected are strongly influenced from the mentioned parameters:

electrostatic interaction or molecular sieving effect. NF using CM might have a useful application in this sector. The separation and concentration of succinic acid from a multicomponent aqueous solution was explored in terms of simple enrichment via NF with CM [86]. The tests were performed with a tubular ceramic mono-channel membrane coated with TiO_2 provided from TAMI Industries (France), with a MWCO of 450 Da and an effective surface of 0.0125 m^2 . All the experiments were carried out at room temperature and at a TMP in the range of 0.5-1.5 MPa. The composition of the solutions used for the NF experiments is shown in Table 2.

After the completion of a NF test the permeability of the membrane to water was tested, verifying the presence of irreversible fouling on its surface. The permeability reduction was completely removed after the washing procedure suggested from the producer. The results of the tests performed with the different solutions are illustrated in Figure 18.

The pH and the presence of other components in the solution appears to produce an effect on the performances concerning both the permeate flux as well as the retention performances. An increase of the applied pressure produced generally a reduction in the retention

Solution number	pH	Components of solution
1	<28	a) 1% Succ b) 3% Succ
2	<28	a) 1% Succ + 0.1% Cit b) 3% Succ + 0.3% Cit
3	<2.8	a) 1% Succ + 0.1% Ac
4	<28	a) 1% Succ + 0.1% Cit + 0.1% Ac b) 3% Succ + 0.3% Cit + 0.3% Ac
5	> 10	a) 1% Na ₂ Succ b) 3% Na ₂ Succ
6	>10	a) 1% Na ₂ Succ + 0.1% Na ₃ Cit b) 3% Na ₂ Succ + 0.3% Na ₃ Cit
7	>10	a) 1% Na ₂ Succ + 0.1% NaAc
8	> 10	a) 1% Na ₂ Succ + 0.1% Na ₃ Cit + 0.1% NaAc b) 3% Na ₂ Succ + 0.3% Na ₃ Cit + 0.3% NaAc

Table 2: Characterization of the solutions used for the NF tests [1].

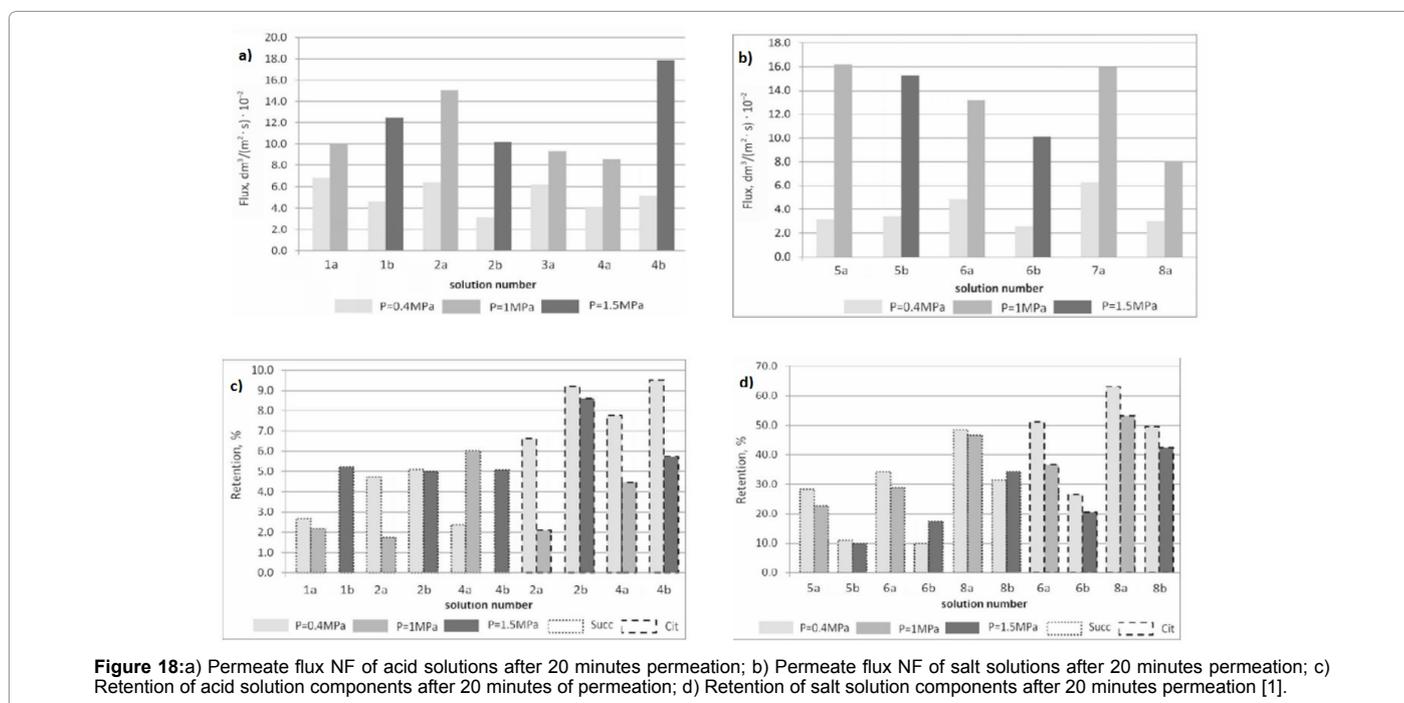


Figure 18: a) Permeate flux NF of acid solutions after 20 minutes permeation; b) Permeate flux NF of salt solutions after 20 minutes permeation; c) Retention of acid solution components after 20 minutes of permeation; d) Retention of salt solution components after 20 minutes permeation [1].

of succinic acid during the NF of the acid solutions (except in the case of the NF of the solution 4a), while in the salt solution the retention of the succinic salt didn't follow a clear trend. The best retention percentage was obtained from the NF of the solution 8a at a pressure of 0.4 MPa. It appears clear that the difference in retention between the acid and the salt solutions does not depend on the sieving effect of the membrane itself but from a polar repulsion between the membrane surface (negatively charged) and the negatively charged molecules of the Na²-succinate salt. Another possibility to consider, might be, that the Na²-succinate salts molecules organized with Na-Ac and Na-citrate salts to form larger agglomerates that were retained more efficiently.

Conclusions

This mini review is an attempt to summarize which known and potential applications CM could offer to the food processing industry in the field of UF and NF. The field started to develop recently and

its applications are gradually increasing. Nevertheless, a lot of work and development are still necessary to allow this type of application to compete with more mature technologies. Particular effort is needed on understanding and reducing the membrane-fouling issues in order to allow gains in productivity and process robustness. A limited number of scientific papers are available on industrial applications of UF or NF ceramic membranes in combination with solvent extraction or any type of solvent treatment in the food processing industry. Some of them routinely employ solvent extraction and might be interested to investigate this technology for possible integration into their processes in order to reduce their environmental impact, gain in energy efficiency, product quality, and produce novel products.

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