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Ultrafiltration with organic solvents: A review on achieved results, membrane materials and challenges to face

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ABSTRACT

Among all the available membrane processes, ultrafiltration is one of the most commonly used and industrially adapted. Apart from aqueous filtrations, the ultrafiltration of solvent-based solutions has found various applications. Some of them are the recovery of valuable compounds from agro-food industries (olive oil, wine, etc.) and the separation of solvents during edible oil production. However, the contact of the membrane (especially polymeric membranes) with an organic solvent still brings different challenges regarding permeate fluxes, rejection values and the long-term stability of the membrane. In this review, the results achieved by research works dealing with organic solvent ultrafiltration have been examined, analyzing the effects of the solvent on the process. Additionally, special attention has been paid to the pre-treatment of the membrane. All the applied strategies to pre-condition the membrane have been reported and discussed here. For the first time, all these relevant data have been formally structured and studied in-depth, aiming to gain more knowledge about organic solvent ultrafiltration.

1. Introduction

The benefits of membrane technology are undeniable nowadays. Membrane-based processes comprise a potent separation tool for a wide range of compounds and contaminants in aqueous streams and wastewater (Al Aani et al., 2020). Among their main advantages, they include a significant reduction of the energy and chemicals invested in the process, adjustable selectivity, mild requirements of applied conditions (temperature, pressure, etc.), and easy automation, escalation, and combination with other processes in line. These attributes endorse the use of membranes in a wide range of applications, such as wastewater treatment, water reclamation, medicine, chemistry, food processing, concentration of high-added value compounds, valorization of residues, etc. (Shi et al., 2022). The advantages of membrane processes to recover and concentrate target compounds have been disclosed by several authors (Álvarez-Blanco et al., 2017; Bazzarelli et al., 2016; Castro-Muñoz

et al., 2019). In particular, ultrafiltration is a powerful technology for removing impurities from a sample, separating large molecules of interest or even concentrating them (Castro-Muñoz et al., 2020; Nawaz et al., 2006; Nazir et al., 2019).

In general, the vast majority of the pressure-driven membrane processes that are in use nowadays are performed over an aqueous medium. This is also the case for ultrafiltration. However, rapid industrialization and technological development has resulted in high demand for cheap and eco-friendly separation methods applicable to organic media (Mohammed, 2022). Many applications (such as petrochemical, pharmaceutical, and fine chemical industries) unquestionably require using solvents upstream of the membrane process (Oxley and Livingston, 2022; Widodo et al., 2018). For instance, they are employed in many reactions of organic synthesis, extraction of some vegetable oils, and recovery of interesting compounds to be later applied in the industry (such as phenolic compounds, triterpenes, fatty acids, vitamins, etc.).

Abbreviations: BSA, bovine serum albumin; DCM, dichloromethane; FTIR-ATR, attenuated total reflection Fourier transform infrared spectroscopy; MCE, mixed cellulose ester; MWCO, molecular weight cut off; PAN, polyacrylonitrile; PBI, polybenzimidazole; PC, polycarbonate; PEG, polyethyleneglycol; PES, polyethersulfone; PGMEA, propylene glycol methyl ether acetate; PK, polyketone; PI, polyimide; PSF, polysulfone; PVDF, polyvinylidene fluoride; PVP, polyvinylpyrrolidone; SEM, scanning electron microscopy; SLE, solid-liquid extraction; SPEEK, poly (ether ether ketone); TPC, total phenolic content.

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Also, most processes consisting of extracting organic molecules from their original matrices include an organic solvent. Despite the plethora of advantages that solvent-based membrane processes can offer, the treatment of non-aqueous mediums through ultrafiltration is a challenge yet to be overcome. This is because the nature of a non-aqueous feed solution deeply affects some important operational aspects, such as the permeate flux, membrane stability, rejection, selectivity, or reproducibility of the procedures. Some challenges related to the use of ultrafiltration membranes with organic solvents have been summarized in Fig. 1.

Generally, researchers working on organic solvent ultrafiltration face four main problems: membrane conditioning, possible alteration of the chemical and mechanical stability of the membrane (which may compromise the polymer structure), atypical low fluxes, and variation of the membrane selectivity. Manufacturers do not usually include solvents' effect on membrane performance in the specification sheet. This fact forces researchers to investigate a repertoire of different pretreatments and strategies first to test the suitability of the membrane to work with solvents. Also, the conditioning stage aims to prepare the membrane surface and increase the low permeate flux values generally obtained in the subsequent permeance experiments. In many cases, selecting the adequate membrane for a specific application is difficult, considering that numerous factors may influence solvent permeation and solute retention. Some of these aspects are related to the structure of the active layer, the distribution of the pore size, the thickness, and the density of the membrane, etc. (Susanto and Ulbricht, 2009). Furthermore, it is unknown if the membrane will resist the solvent contact. This aspect involves an additional challenge to the inherent complexity of the process, as opposed to the filtration of aqueous solutions. Despite previous stages of membrane testing when implementing an organic solvent in the feed solution, many existing reports related to this field describe the observance of membrane disruption as a consequence of the interaction with the solvent for a considerable time (de Souza Araki et al., 2010; Torres et al., 2017). In addition, the use of organic solvents can increase membrane fouling (in comparison to aqueous filtration) and, consequently, the adequacy of the cleaning procedure gains relevance (Oxley and Livingston, 2022). Even when the filtration process is carried out in an aqueous medium, fouling is the major disadvantage of membrane-based processes. This phenomenon reduces the permeation rate and causes higher operational and maintenance costs (Tanis-Kanbur et al., 2022). However, membrane fouling can be even more severe when organic solvents are used. The characteristics of the organic solvents, such as polarity and viscosity, and their impact on membrane permeability, affect the tendency of foulants to deposit onto the membrane surface (Ma et al., 2021; Tanis-Kanbur et al., 2022). In addition, due to the characteristics of the organic solvents, the foulants could present different physical behaviors in organic solvents in comparison to aqueous mediums. The chemical interactions between the membrane and the foulants can also be altered in an organic medium. This affects

parameters like zeta potential or settling capacity, among others, which can directly alter the membrane fouling behavior (Lay and Chew, 2020). In this way, Yin et al. (2020a) reported that solvents with higher polarity present better anti-fouling properties due to the higher repulsive foulant-membrane interfacial interactions.

Overcoming the mentioned experimental obstacles is of high interest, but the combination of solvents and ultrafiltration still remains underinvestigated. Authors working in this scene have made essential discussions in their research articles, but, as stated by some researchers before (Ji et al., 2019), there is a critical lack of a systematic study that collects and discusses the relevant data to make progress in this area. Organic-solvent nanofiltration, which has been more often practiced, was excellently covered by Van der Bruggen et al. (2008). However, despite the obvious similarities between organic-solvent nanofiltration and organic-solvent ultrafiltration, there are several aspects that are not shared by both techniques. Among the main differences between organic-solvent nanofiltration and organic-solvent ultrafiltration, it is possible to find the membrane type (in terms of material, pore size, etc.), the organic solvents more commonly used, and the final application of the process. Whereas nanofiltration membranes can offer much higher purification efficiency, an ultrafiltration process requires lower energy consumption and provides higher values of permeate flux. In addition, the membrane material conditions the permitted organic solvent to be used, as will be thoroughly discussed in this work. For all these reasons, the area of application of organic-solvent nanofiltration and organic-solvent ultrafiltration is different. The main applications for organic-solvent nanofiltration rely on the petrochemical industry, food industry and byproducts, bulk industry, fine chemistry, and pharmaceutical industry (Priske et al., 2016). Organic-solvent ultrafiltration, as will be exposed in Section 2, has been mostly proposed in the food industry sector, specially for the recovery of beneficial compounds from industrial wastes, and in the edible oil industry. Some applications in biorefineries have also been proposed (Álvarez-Blanco et al., 2017; Lipnizki et al., 2019; Ochoa et al., 2001; Ramesh et al., 2021).

More recently, Merlet et al. (2020) examined hybrid ceramic membranes whose surfaces were submitted to organic functionalization to be applied in organic-solvent nanofiltration. Additionally, Ren et al. (2021) published a remarkable review about new advances in solvent-resistant materials and their implementation in different membrane processes. However, to the best of our knowledge, a critical review specifically dedicated to organic solvent ultrafiltration processes is not yet available in the literature. Taking into account the existing gap within the written knowledge on this topic and the procedures that are mainly performed in membrane technology, the present contribution will discuss the reported performance of several types of membranes during the ultrafiltration of solvent-based solutions. Additionally, the industrial interest in organic solvent ultrafiltration and the future directions of this field will be discussed. Although the intention of this review was not to restrict the study to only polymeric membranes, the use of ceramic membranes (made of alumina, titania, zirconia, or hafnia) for this application is hardly available in the literature. This fact can be attributed to the observed values of permeate flux, which have been reported to be low, due to the highly hydrophilic character of ceramic membranes, in comparison with less polar solvents, such as hexane, for instance (García et al., 2005). In consequence, details about inorganic membranes are less abundant (but not absent) in this review. Furthermore, polymeric materials have lower fabrication costs, higher flexibility, and ease of processing compared to inorganic materials (Alhweij et al., 2022). In addition, the structure of polymeric membranes is more sensitive to being altered by the solvent than ceramic ones.

The most common alterations of membrane morphology and the observed effects on permeate flux will also be described. Additionally, a specific section will be devoted to the different conditioning strategies, which are a crucial stage to ultrafilter non-aqueous mediums. Finally, some of the most solvent-resistant polymer materials to be applied in this area will be described in detail. Although not exclusively, the focus

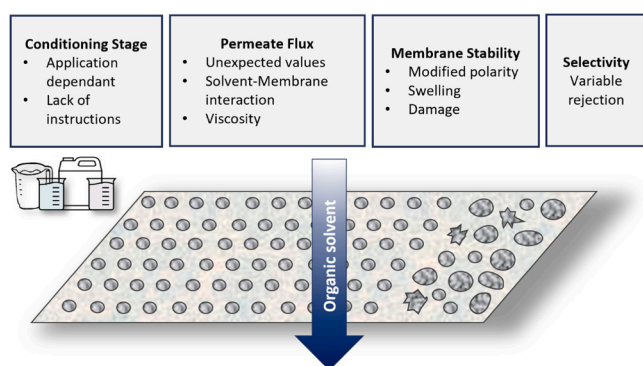


Fig. 1. Characteristics of an ultrafiltration process dealing with organic solvents.

will be placed on alcohols. Especially, the effect of ethanol on the membrane performance will be commented, because it is one of the main and more widely used extractant agents in laboratories and industries. The main findings and methodologies of this promising research area will be provided.

2. Areas of application for organic solvent ultrafiltration

Annual use of organic solvents across the world is calculated to be around 30 million tons (Savaş-Alkan and Çulfaz-Emecen, 2022). As commented before, many industries applying organic solvents in their process can benefit from implementing organic solvent ultrafiltration. The following sub-sections include those industrial applications that have been more widely supported by research studies. Mainly, these applications include the recovery of interesting compounds from industrial waste (such as olive pomace, olive mill wastewater, winery sludge, grape seeds, bark, and lignocellulosic residues), the recovery of solvents, the degumming stage in the edible oil industry and several separations in biorefineries.

2.1. Recovery of valuable compounds from industrial waste

The fabrication of many commercial products implies the generation of vast amounts of residues during the production process. In many cases, those industrial by-products still contain valuable compounds. These compounds can be of interest due to their nutritional value or because of their bioactive and functional properties (Álvarez-Blanco et al., 2017). In order to extract the valuable compounds from the sample that contains them, a solvent-mediated extraction is the most preferred methodology. In fact, ethanol as a solvent is commonly selected. According to the Registration, Evaluation, Authorisation, and Restriction of Chemicals regulation (REACH), under the European Regulation (EC) N° 1907/2006, the ethanolic extraction of organic molecules is a highly preferred option, due to the biocompatible character of ethanol, its low toxicity and easy handling (Baptista et al., 2015; Crespo and Brazinha, 2010; Koncsag and Kirwan, 2012; Loginov et al., 2013; Nawaz et al., 2006; Tovar-Sánchez et al., 2022). This has been regulated by the European Chemicals Agency (ECHA), which is the agency responsible for the implementation of the European Union's chemicals legislation to protect the environment and human health. Apart from the consistently employed alcohols (especially ethanol, as mentioned), there is a growing tendency towards the implementation of the denominated green solvents (cyrene, methyltetrahydrofuran, ethyl lactate, etc.), both in academia and at the industrial level (Chang, 2020; Szekeley et al., 2014). These are less toxic solvents, sometimes biodegradable and renewable, and ultimately safer than conventional solvents for the operators and for the environment (Naziri Mehrabani et al., 2022).

In this way, interesting molecules can be extracted from the residues generated by industries such as winery, olive oil production, and pulp and paper fabrication. Once this solvent-based extract is generated, the target compounds must be purified. Traditionally, the extracted compounds have been separated from the co-extracted solutes by chromatographic techniques, e.g., adsorption chromatography (Crespo and Brazinha, 2010). Nevertheless, chromatography requires large volumes of eluents and solvents to condition the stationary phase. In this context, organic solvent ultrafiltration appears as a more effective alternative to be implemented in the circular economy of the previously mentioned industries.

2.1.1. Winery industry

The winery sludge, which is the solid by-product obtained after the decanting stage, contains a high concentration of phenolic compounds (up to 19 g·kg⁻¹) (Bustamante et al., 2008). These molecules can be extracted with ethanol, and they can be further purified by organic solvent ultrafiltration. This technique allows the separation of

polyphenols and pectins, which are also extracted along with the bio-phenols (Galanakis et al., 2013). Grape seeds are another fruitful source of phenolic compounds. After an extraction with ethanol at 50% (v/v), the polyphenols can be concentrated by an organic solvent ultrafiltration process (Nawaz et al., 2006).

2.1.2. Olive oil industry

The by-products generated by the olive oil industry are concerning because of their high organic load. However, membrane technology has been demonstrated to contribute greatly to their valorization. A mixture of ethanol at 50% (v/v) allows the extraction of a plethora of phenolic compounds with interesting bioactivities (Tapia-Quirós et al., 2020). These molecules can be later purified by organic solvent ultrafiltration (Sánchez-Arévalo et al., 2022). Olive leaves are another interesting residue from the olive oil industry. They can be employed as a source of oleuropein, which is a powerful antioxidant (Jemai et al., 2009). After an extraction with a hydroalcoholic mixture, the olive leaves extract can be treated by organic solvent ultrafiltration in order to remove suspended solids and reduce the fouling of a subsequent organic solvent nanofiltration process to assess the concentration of this valuable molecule (Erragued et al., 2022).

2.1.3. Pulp and paper industry

Bark is a lignocellulosic residue generated by the pulp industry. Apart from lignin, cellulose, and hemicellulose, bark contains phenolic compounds of interest (Pinto et al., 2013). The phenolic content of bark can be extracted with hydroalcoholic mixtures and later concentrated by organic solvent ultrafiltration, generating a natural product rich in polyphenols (Baptista et al., 2015; Pinto et al., 2014, 2017). Furthermore, the molecules released during the degradation of polymeric lignin, such as dilignols and trilignols, can be recovered by means of an ethanolic extraction, followed by organic solvent ultrafiltration (as a pre-treatment of the extract to remove suspended solids) and organic solvent nanofiltration (Koncsag and Kirwan, 2012).

2.2. Applications in the edible oil industry

Organic solvent ultrafiltration also finds its application in the separation of vegetable oils from the solvents employed for their extraction from seeds or fruits. This mixture of solvent and extracted oil is known as miscella. Traditionally, oil purification from the extractant solvents has been performed by distillation, generating significant energy costs (Johnson and Lusas, 1983). Another disadvantage of distillation is the potential alteration of the oil quality and nutritional properties due to the high temperatures applied during this process (Reverchon and De Marco, 2006). This could be hugely reduced with its substitution by a membrane process, replacing a thermal separation process with a non-thermal process (Ramesh et al., 2021). Organic solvent ultrafiltration offers the possibility to recycle the solvent and reuse it in a following round of the process. In fact, this technology has been proposed in the literature to perform the separation of mixtures of soybean oil and hexane (Badan Ribeiro et al., 2006; de Melo et al., 2015; Tres et al., 2012). Vegetable oil degumming is also an appropriate field for the application of organic solvent ultrafiltration. After the extraction of edible oils, entailing organic solvents, and the separation of the oil and the solvent, vegetable oils undergo a degumming stage (Abdellah et al., 2020). The aim of this process is to remove the phospholipid content, as they affect the organoleptic properties of the final product (García et al., 2006). In this case, a membrane process is a more eco-friendly solution than traditional methods such as filtering, settling or centrifugal action, since these conventional techniques generate large amounts of wastewater and require high energy consumption (García et al., 2006). For example, Ochoa et al. (2001) studied the membrane degumming of crude soybean oil with four polymeric (made of PVDF, PES, and PSf) ultrafiltration membranes. Results demonstrated that PVDF membranes were stable in contact with hexane and phospholipid retention values

were over 98%.

Thus, it is evident that the implementation of membrane processing exhibits enormous potential in several lines of work, but more efforts are required to improve the current limitations and insufficient chemical resistance of most of the available ultrafiltration membranes. In addition, only a few organic solvent ultrafiltration membranes are commercially available. These membranes must have long-term chemical and physical stability to resist the contact with the solvent during the operation time (Oxley et al., 2022). An important manufacturer in this field is SolSep BV (Apeldoorn, The Netherlands), also known for the fabrication of organic solvent nanofiltration membranes. Also, several commercial membranes from Microdyn Nadir (Wiesbaden, Germany) and Alfa Laval (Lund, Sweden) have demonstrated to resist the contact with ethanol and mixtures of ethanol and water, even though these membranes are, in principle, conceived for aqueous separations (Johnson and Lusas, 1983; Machado et al., 2000; Oxley et al., 2022; Ramesh et al., 2021). Thus, solvent-resistant membranes are not abundant in the market. Similarly, accurate information about their properties and pre-treatment guidelines is not abundant in the literature (Argyle et al., 2015; Badan Ribeiro et al., 2006; Susanto and Ulbricht, 2009).

2.3. Applications in biorefineries

Separation and purification processes, such as membrane separations, have paramount importance in biorefineries (Ramaswamy et al., 2013). In particular, microfiltration and ultrafiltration are the pressure-driven membrane processes most used in this field (Kiss et al., 2016), considered as a white biotechnology. Conventional refineries include biofuel production, biochemicals production, and water and wastewater treatment. In the case of lignocellulosic biorefineries, agricultural residues and woods are used as raw materials. In both cases, membrane separation processes can be applied before and after the fermentation stage. In the case of organic-solvent ultrafiltration, it finds an application during the production of bioethanol. Aqueous microfiltration and ultrafiltration techniques can be used as pretreatment, in combination with a decanter, to purify the raw material after the hydrolysis process and before the fermentation step. However, if the combined hydrolysis and fermentation is preferred, an organic-solvent ultrafiltration can be employed to remove the biofuel from the fermenter (Chadni et al., 2023; Lipnizki et al., 2019). This avoids the inhibition of the yeast activity by the ethanol molecules and improves the productivity of the process.

3. Possible effects of organic solvents on membrane structure

Organic solvents are carbon-based compounds capable of dispersing or dissolving one or more substances. Generally, organic solvents can be divided into non-polar and polar solvents. The molecules of non-polar solvents (e.g., toluene, hexane, and benzene) present atoms with very similar electronegativities, and the charge is distributed symmetrically around the molecule. By contrast, polar organic solvents (e.g., acetonitrile, methanol, and ethanol) present higher dipole moments due to the different electronegativities of their atoms (Richez et al., 2013; Yin et al., 2020a). In addition to polarity, there are other physical properties of the organic solvents that should be considered in order to select the most suitable one. These include surface tension and viscosity (Haghighbakhsh et al., 2020; Wongsawa et al., 2018). Surface tension is a phenomenon at the surface of a liquid medium caused by intermolecular forces. It is related to the tendency of a fluid to occupy the lowest possible area. Therefore, liquids with strong intermolecular forces present a high surface tension. Takeuchi et al. (1987) explained that, for the membrane to be properly wetted by the solvent, the surface tension of the organic solvent should be lower than the critical surface tension of the membrane material. On the other hand, viscosity reflects the flow resistance of the liquid, and it is related to the forces of intermolecular attraction. In the following section, the relation between viscosity and permeate

flux will be discussed. Fig. 2 contains a classification of the main organic solvents used in ultrafiltration, in terms of polarity, surface tension, and viscosity, since these are the most important solvent characteristics to consider for organic solvent ultrafiltration.

Regarding the membrane materials, polyimide (PI), polycarbonate (PC), polysulfone (PSf), cellulose acetate, polyethersulfone (PES), polyvinyl chloride, and polyvinylidene fluoride (PVDF) are the most common synthetic polymers for the manufacturing of ultrafiltration organic membranes (Naziri Mehrabani et al., 2022). However, there are other membrane materials with good solvent-resistant properties, such as polyketone (PK), polybenzimidazole (PBI), and sulfonated poly(ether ether ketone) (SPEEK) (Chen et al., 2019; Yee et al., 2013; Zhang et al., 2019). In order to use these membranes at an industrial scale, the mentioned materials should have high selectivity and rejection, high permeability, good mechanical and thermal stability, low fabrication cost, and high surface area (Nasrollahi et al., 2022). One of the key challenges of organic solvent ultrafiltration is that polymer membranes tend to swell or dissolve in organic solvents, and the pressure and temperature applied can also affect the membrane's long-term stability (Abdulhamid and Szekely, 2022). Therefore, the study and selection of the correct material are of paramount importance in order to minimize the possible effect of the organic solvent.

A considerable percentage of the organic solvents involved in ultrafiltration experiments are alcohols, primarily ethanol. The exact mechanisms underlying their observed effects on ultrafiltration membranes are still unknown, but some theories have emerged up to date. The chemical structure of alcohols, $(\text{CH}_3)_n\text{-OH}$, may explain the uncommon permeate fluxes that have been observed by some authors (references in this regard will be given in the following sections of the present review). It has been suggested that the solvent molecules will adopt one disposition or another depending on the relative polarity between the membrane and the solvent. Thus, the hydrophilic section of the solvent molecules will approach the most polar sector, and the hydrophobic tail will be headed to the section with lower polarity. In the study performed by de Melo et al. (2015), the conditioning of α -alumina oxide/zirconium ceramic membranes with n-butanol ensured a notable improvement in hexane permeate flux. As the membrane of this study was inorganic, any change in the ceramic structure can be excluded. However, the modulation of the properties of the active layer is plausible and was supported by the results of these authors. A possible explanation was related to the interaction of the hydroxyl radical of n-butanol with the membrane surface, whereas the carbon tail would be oriented toward the bulk solution, then reducing the high hydrophilicity of the membrane and making its polarity more similar to that of hexane. Additionally, Van der Bruggen and co-workers reported the modulation of the top layer polarity of polymeric membranes due to a clustering phenomenon occurring on the membrane's active layer. Their findings suggested that, after an immersion in ethanol, the original polarity of the membrane could be modified upwards for less polar, hydrophobic membranes. Alternatively, the polarity of hydrophilic, polar membranes could be reduced as a result of the solvent contact (Van der Bruggen et al., 2002).

Regarding the study of Argyle et al. (2015), they employed ethanol to condition PSf membranes. It was suggested a possible preferential adhesion to the membrane pores of the polar hydroxyl radical of the molecules of ethanol, while the hydrophobic part would be oriented to the pore space. Thus, the membrane's charge and polarity decrease, lowering the adhesion of water to the pore wall. Charge reduction was confirmed by zeta potential measurements. Consequently, these authors reported a larger water flux through the membranes after ethanol conditioning.

Solvents might also affect the chemical nature of the polymer that entitles the membrane, causing a phenomenon of swelling (Ren et al., 2021). The expansion of the membrane material is a recurrent event when working with organic solvents and has been reported since the first papers dealing with this topic were published (Nguyen et al., 1979).

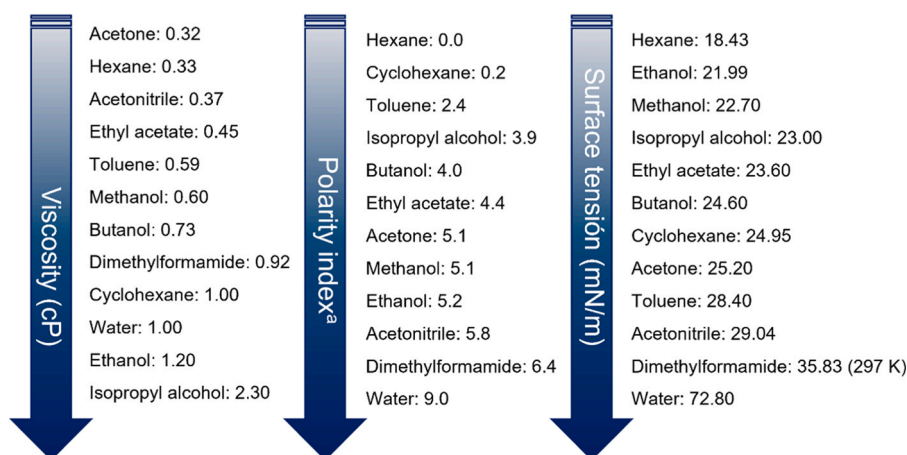


Fig. 2. Viscosity (293 K), polarity and surface tension (293 K) of the main organic solvents (and water) used in ultrafiltration (DDB, 2001; Sadek, 2002; STD, 2017). ^a: according to (Sadek, 2002).

It consists of a dissolution of the polymer and modification of its morphology because of the alteration (by the solvent molecules) of the forces that enable the crosslinking of the membrane. This is commonly traduced in a thickening of membrane pores, which can affect both the active layer's micropores and the support layer's macropores. In consequence, expansion and distension of the structure and lowering of the rejection performance of the membrane are possible. It is possible that only one of these situations can be observed, but also both cases may occur simultaneously. The nature of the membrane polymeric material plays an important role in the degree of swelling. Hydrophilic polymers are more vulnerable to swelling during solvent exposure. By contrast, hydrophobic polymers have a higher solvent resistance, but a relevant disadvantage is that, due to their insolubility in most of solvents, they cannot be manufactured applying phase inversion techniques (Gungormus and Alsoy Altinkaya, 2023). Several authors have reported some findings related to the observance of the swelling phenomenon during the use of polymeric membranes for organic solvent applications. Krupková et al. (2023) studied the performance of commercial cellulose membranes with a MWCO between 1 and 5 kDa, treating organic markers dissolved in methanol and dichloromethane (DCM). Methanol has a polar character, whereas DCM is nonpolar. Their results confirmed that, in the case of DCM, due to its nonpolar character, swelling was more pronounced. However, due to the robustness of the membrane support layer (made with PP) swelling was not significant. Depending on the percentage of rupture of polymer-polymer forces and the type of pores affected, different scenarios can be favored, leading to the different results observed by some authors. Even though the expansion of membrane pores may lead to higher permeate fluxes, swelling should be taken cautiously, because a great drop of the rejection is possible too, affecting membrane selectivity (Argyle et al., 2015; Ji et al., 2019; Zeidler et al., 2013).

Additionally, the eventual bonds established between the polymer and the solvent molecules may result in membrane rupture, as the microstructure of the polymer is chemically altered. Even small fissures in the polymer chain are possible and, logically, they are able to impact the performance of the membrane (Ji et al., 2019). As reported in the literature, when membranes are disrupted by solvents, their tensile resistance is modified and they are more sensitive to pressure increments (de Souza Araki et al., 2010). As a result, when certain pressure values are achieved, the linear relation between pressure and flux is no longer applicable and membrane deformations, such as swelling or shrinking, are possible. This repertoire of effects varies depending on polymer composition, type of solvent, range of applied pressure, etc.

The variety of events that can take place at the membrane surface underlines the importance of performing a visual analysis of the

membrane itself. Microscopic/spectroscopic technologies can bring a lot of benefits to evaluate differences in polymer structure before and after membrane conditioning or ultrafiltration experiments. García et al. (2005) provided a very valuable set of Scanning Electron Microscopy (SEM) images during their study about the preparation of oil-in-water emulsions. They employed 10 kDa and 50 kDa polyamide membranes and reported the effect of iso-propanol and isooctane, used as conditioning solvents. SEM images of the membrane cross-section revealed detailed information about the pores. Swelling and structural modification were noticeable, although the ultrafiltration performance was, in the end, stable and reproducible. Argyle et al. (2017) studied the effect of an ethanol-based pre-treatment on the mechanical structure and surface modification of PSf ultrafiltration membranes (with polypropylene support) with a MWCO of 50 kDa. After Fourier Transform Infrared (FTIR) analysis, they observed slight differences between both spectra (before and after treatment) and reported the disappearance of some spectral bands (at 920 and 1040 cm^{-1}) after the pre-treatment. According to Belfer et al. (2000), these bands can be attributed to membrane preservatives. Weis et al. (2003) described that the band at 1040 cm^{-1} may correspond to an aliphatic alcohol, such as glycerol. Therefore, the FTIR analysis performed by Argyle et al. (2017) revealed that a simple treatment of PSf membranes with ethanol can remove preservatives and modify the characteristics of the active layer. Microscopy observations are included in other articles, with the aim of studying possible membrane structure modifications after the use of organic solvents. This is the case of de Souza-Araki et al. (2010), who studied the membrane structural stability after hexane filtration with several commercial ultrafiltration polymeric membranes: 30 kDa and 50 kDa PVDF, 10 kDa PES, 0.05 μm PC, and 0.05 μm and 0.025 μm mixed cellulose esters (CME). SEM images confirmed that there were no apparent visual morphological changes before and after the treatment with hexane. Some other research works included a visual interpretation of microscopy data (Ji et al., 2019; Torres et al., 2017; Yin et al., 2020a). As stated, image confirmation of solvent effects over the membrane is highly recommended, in order not to attribute to the solvent some abnormal results that may come from other experimental aspects. In many cases, potential morphological alterations, such as swelling, clustering, wrinkling, or fracture, can be visually detected and used to complete the data of the study.

4. Permeate flux of organic solvents in ultrafiltration

As it was commented before, organic solvents have a fundamental role in many industries. The use of these solvents implies a further separation, recovery, or disposal. Recently, membrane processes have

become one of the most promising and emerging technologies for this purpose (Savaş-Alkan and Çulfaz-Emecen, 2022).

Ultrafiltration membranes are porous mediums, with pore sizes in the range of 0.02–0.05 μm . In consequence, the corresponding permeate flux (J) through the membrane is described by the Darcy's law (Eqs. 1 and 2):

$$J = \frac{\Delta P}{\mu \cdot R} \quad (1)$$

or

$$J = \frac{L \cdot \Delta P}{\mu} \quad (2)$$

where ΔP corresponds to the transmembrane pressure, R is the membrane resistance, L is the membrane permeability, and μ is the viscosity of the fluid permeating across the membrane pores. As it is obvious in (1) and (2), the viscosity of any solvent other than water will influence the value of the permeate flux. In this way, Jaffrin, Charrier (1994) already reported in 1994 that the viscosity of ethanol was mainly responsible for the flux reduction that they observed during the ultrafiltration of ethanol/water solutions of albumin, using PSf (with a molecular weight cut-off (MWCO) of 10 kDa) and cellulose acetate (with a MWCO of 20 kDa) membranes. As reflected in Fig. 2, some alcohols display higher viscosity than water (Huber and Harvey, 2018), but the differences in this parameter are not enough to justify the values of permeate flux that have been reported by other authors (de Souza Araki et al., 2010; Pinto et al., 2017), because some findings are substantially distant from the observed water flux using the same membranes. Baptista et al. (2015) found that hydraulic permeability was always higher (even more than twice) than the permeability of an ethanol-based feed. As an example, a PVDF membrane with a MWCO of 30 kDa displayed a hydraulic permeability of $91.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, whereas the permeability of an 80% (v/v) ethanol solution was $35.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. This variation could be expected according to the differences in the medium viscosity, as water viscosity is half of the viscosity of the hydroalcoholic solution. Interestingly, Pinto et al. (2014) also studied the same membrane and observed a decrease in permeability (from $50 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ to approximately $36 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) when increasing the ethanol percentage from 52% to 80% (v/v). At 35°C, the viscosity of ethanol 80% (v/v) is lower than that of ethanol 52% (v/v) (Khattab et al., 2012). If viscosity was the only parameter affecting the process, an increase in permeability would be expected, but the opposite effect was observed. Thus, these results demonstrated that solvent viscosity was not the only variable involved and other factors, like the polarity of the solution or membrane-solvent interactions, should be considered too. In fact, it is possible to find membranes with similar MWCO and very different permeabilities to a given solvent, depending on the material of the polymer and its affinity regarding the ultrafiltration feed.

To better understand the results that have been reported when using organic solvents during ultrafiltration experiments, it is convenient to distinguish between processes dealing only with solvent solutions and those with solutes dissolved in the samples.

4.1. Permeate flux when only solvent solutions are treated

Some authors have performed the ultrafiltration of feeds containing only the solvent or mixtures of water and solvent, at different percentages. These works allow the study of the modifications in the permeate flux that are only attributed to the effect of the solvent, and not to other molecules present in the feed solution.

de Souza-Araki et al. (2010) performed a complete study in which they tested six flat sheet polymeric membranes, composed of materials such as mixed cellulose esters (MCE), PC, PVDF, and PES. The permeate flux of water, ethanol, and hexane was studied for each membrane. The most noteworthy results were obtained for the PVDF and MCE

membranes. In the case of PVDF, the water flux was significantly higher than for the MCE membrane. Both solvents displayed almost half of the flux obtained with water. MCE membranes did not resist the contact with ethanol above 3 bar. For this material, they observed that the permeate flux of hexane was higher than the water flux, suggesting a better affinity of hexane for the membrane material due to its hydrophobic character. However, when a membrane of the same material and larger pore size was evaluated, the permeate flux did not increase. The authors then proposed a possible solvent immobilization on the membrane surface, derived from a strong interaction. In such event, a contraction of the pores can occur, thus blocking the migration of solvent molecules into them and across the membrane (Paul and Ebra-Lima, 1971). Oxley et al. (2022) recently published an interesting work about the preparation of crosslinked (with two grafting agents, elastamine and 2-methoxyethylamine), organic-solvent-resistant PBI ultrafiltration membranes. Acetonitrile was the solvent with the highest permeate flux values (in the range of $33\text{--}68 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), whereas toluene provided the lowest values, around $10 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. The MWCO of the membranes was between $2000\text{--}20,000 \text{ g}\cdot\text{mol}^{-1}$, therefore being in the limit between an ultrafiltration and a nanofiltration membrane. Savaş-Alkan et al. (2022) also studied the preparation of solvent-resistant ultrafiltration membranes in order to recover the solvent, which was propylene glycol methyl ether acetate (PGMEA). They fabricated cellulose acetate UF membranes by alkaline hydrolysis, varying the precursor solution (dimethyl sulfoxide (DMS), acetone and polyethyleneglycol (PEG)). When the organic solvent (dimethylformamide (DMF), DMSO, methanol and PGMEA) permeability was measured, the two tested membranes (membrane C20P10, made with 20 and 70 wt % of CA and DMS, respectively and, membrane C25P10A10-AN, made with 25 and 55 wt% of CA and DMS, respectively) obtained the highest permeability with methanol (values of $32 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and $2.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, respectively). These two membranes were also tested with PGMEA, whose molar volume is $137 \text{ cm}^3/\text{mol}$, and the permeability using this solvent were much lower for both membranes, with values of 0.5 and $0.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ for the C20P10 and C25P10A10-AN membranes, respectively.

In addition to polymeric membranes, the solvent flux behavior of ceramic ultrafiltration membranes was studied by Buekenhoudt et al. (2013). In this work, three ceramic ultrafiltration membranes (with a pore diameter of 3, 5, and 100 nm) were evaluated in terms of pure water and organic solvent (methanol, dimethylformamide, tetrahydrofuran, toluene, and hexane) permeability. Results demonstrated that pure water flux was higher than any organic solvent flux, for all the membranes. According to their results, lower values of permeate flux were obtained for solvents with lower polarity, being toluene and hexane the solvents leading to the lowest flux for the tested three membranes.

4.2. Permeate flux when solutes are present in the feed solution

If the feed contains solutes, they can be involved in the concentration polarization phenomenon and contribute to the fouling of the membrane. Thus, the obtained results can be influenced not only by the organic solvent, but also by the presence of these dissolved compounds in the feed solution. In organic-solvent membrane filtration, physico-chemical membrane properties, such as polarity and functional groups, have a great impact on the interaction between the membrane and the solutes and, logically, on the solute rejection (Ignacz and Szekely, 2022). If an unexpected permeate flux is obtained, it should not be directly attributed solely to the solvent. The combined effect of the solutes (if present) should be observed too. In this context, Ma et al. (2021) applied molecular dynamics simulations to understand the adsorption process of dextran onto a polyacrylonitrile (PAN) membrane. They studied it in an aqueous medium, but also in formamide. The authors found that the solvent-solute and solvent-membrane interactions were different in each case. In water, the dextran-membrane interaction was more relevant,

leading to more severe fouling and a higher rejection of the dextran molecules. On the contrary, the dextran-solvent interaction was higher in formamide, which generated a solvation phenomenon that reduced membrane fouling and procured lower rejection values. Fig. 3 illustrates the importance of the solute-solvent-membrane interaction and its possible influence on membrane fouling.

A different solvent, in contact with the same solute and the same membrane, determined a specific fouling tendency and permeate flux, which underlines the importance of the solvent environment during ultrafiltration. Yin et al. (2020b) also studied PAN ultrafiltration membranes to check the membrane fouling after a series of experiments with three colloidal foulants (SiO_2 , TiO_2 , and Al) dissolved in methanol, ethyl acetate, and acetonitrile. When only the pure organic solvent was present in the feed solution, methanol exhibited the greatest permeate flux, followed by ethyl acetate. For the three foulants dissolved in organic mediums, aluminum was the one causing the lowest fouling. The behavior of the other two foulants suggested a higher resistance of the cake layer that varied with the different solvents. Jaffrin et al. (1997) published an interesting work on the ultrafiltration of ethanol-based albumin solutions. PSf hollow-fiber membranes with a MWCO of 30 kDa were employed. As it was reported, ethanol contributed, not only to the medium viscosity, but also to a progressive membrane fouling that continued increasing for many hours and was partly responsible for the low permeate flux. Albumin diffusivity was reduced in the ethanolic medium. Consequently, its transport to the bulk solution was disfavoured and its accumulation at the membrane surface enhanced the fouling.

As these results suggest, there are many aspects, not excluding viscosity, that influence the flux through the ultrafiltration membranes. Some of the events (e.g. pore modification, swelling, etc.) that have been explained in the previous section may participate in flux modification. Thus, the prediction of ultrafiltration flux when working with organic solvents must take into account other mechanisms apart from the simple permeation, especially when polymeric membranes are involved (Guizard et al., 2002). The degree of compatibility between the polarity of the solvent and the membrane surface can influence the tendency of the solvent to permeate. In the case of water and hydrophilic membranes, the permeance is enhanced by the hydrogen bonds that are formed between the molecules of water and the polymer (Guizard et al., 2002; Pinto et al., 2014). However, if water is substituted by an organic solvent (even if it is a mixture of miscible solvent and water), the capacity to establish these bonds will be different and generally lower (Ballal and Chapman, 2013), which considerably affects the transport through the

membrane. In the case of ethanol, the transport through a hydrophilic membrane would be less favored than water transport, due to the lower polarity of this alcohol (see Fig. 2).

Nevertheless, it should not be concluded that the higher the hydrophobicity of the membrane, the higher the permeate flux of an organic solvent, because potential hydrophobic interactions and adsorption issues are possible too and must be considered. Each case should be studied carefully in order to reach a compromise solution between the polarities of both mediums and the overall process efficiency.

5. Conditioning of ultrafiltration membranes

During the ultrafiltration of organic solvents, unexpected low fluxes may be obtained. Thus, prior to apply a solvent-based ultrafiltration, it is recommended to condition the membranes to achieve an effective process (Razali et al., 2017). The conditioning procedure consists of a previous contact between the membrane polymer and the organic solvent to ensure the membrane stability during organic solvent ultrafiltration and to prepare it to operate without any interference from the organic solvent (Fraga et al., 2012). Fig. 4 shows a proposed workflow for solvent-based UF process.

As shown in Fig. 4, it is essential to first condition the membrane, not only to enhance its resistance to the solvent and extend its lifetime, but also to ensure an adequate performance. Possibly, this operation is the most important step of the whole procedure, as the success of the ultrafiltration depends to a large extent on an optimal design of the pre-treatment of the membrane. For ceramic membranes, conditioning plays a crucial role in regulating their high hydrophilicity. Similarly, polymeric membranes strongly depend on the conditioning methodology to maintain their integrity and display proper operation performance (Shukla and Cheryan, 2002). In this section, an analytical description of the conditioning strategies that have been preferentially adopted by researchers is exposed. No similar examination has been

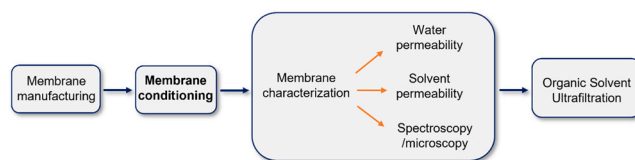


Fig. 4. Proposed workflow during solvent-based UF process.

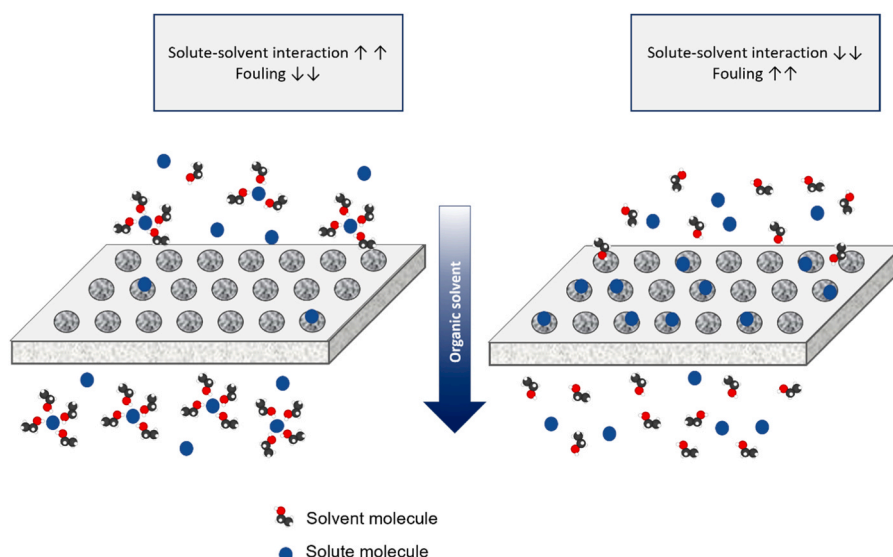


Fig. 3. Potential effect of solute-solvent-membrane interaction on membrane fouling.

done before in the literature, but the importance of this topic makes it greatly interesting to be discussed. Table 1 can be helpful to explore the information contained in this review. The table includes data about the membrane material of each study, conditioning strategy (or strategies) and derived results about permeate flux of the tested solvent or any other corresponding feed solution, as well as the observed rejection values. Every article described in this section has been included and carefully detailed in Table 1.

5.1. Organic solvent applied as pre-treatment and permeation solvent

As already stressed, membrane conditioning is unavoidable when the solvent is intended to be present in the feed solution. Immediately after the conditioning, there is a common practice of testing the hydraulic permeability of the membrane (Koncsag and Kirwan, 2012). Indeed, it seems very accurate to compare the membrane performance just after the conditioning and at the end of the ultrafiltration experiment, in order to study possible changes in membrane performance due to the pressure variation, temperature, etc., and, consequently, the suitability of the conditioning step. Similarly, it is advised to check water and solvent permeability after each experiment of organic solvent ultrafiltration, to gather information related to fouling, membrane-solvent interactions, and overall process efficiency.

Three experimental approaches have been proposed up to date: membrane immersion in the same solvent as in the feed solution, membrane immersion in solutions of increasing percentage of the same solvent, and membrane immersion in different solvents. Some authors (Argyle et al., 2015; Shukla and Cheryan, 2002; Tsui and Cheryan, 2007, 2004) have performed the conditioning directly in the ultrafiltration equipment, circulating the solvent and applying pressure. Those cases have been indicated in the corresponding sub-section.

5.1.1. Membrane immersion in the same solvent as in the feed solution

One of the first proposed methodologies to prepare ultrafiltration membranes to work with organic solvents replicates the general protocol followed when treating aqueous mediums. Membranes were immersed in the same solvent as would be found in the feed tank (Lencki and Williams, 1995). Torres et al. (2017) let a PSf membrane in contact with pure ethanol during 24 h. After that, they proceeded to measure the ethanol permeate flux and they observed a low permeability ($5.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), which was attributed to a shrinkage of the dense layer, leading to a structural alteration of the pore size. A similar approach was implemented by Koncsag and Kirwan (2012). These authors tested the SelRO™ MPS-U20S 20 kDa composite membrane from Koch Separations (Germany). The material of this membrane is crosslinked PAN (Vandezande et al., 2008) and the polymer was reported to be hydrophilic and solvent-stable. After an overnight immersion in water, they soaked the membrane in an ethanol/water (75:25 (v/v)) solution during 24 h. Afterwards, the membrane was again flushed with the fresh solvent mixture and employed to ultrafilter an alcoholic extract of straw, obtained with the same proportion of ethanol and water mixture. Water flux at the selected operating conditions (8 bar and 22 °C) was $343 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, while the flux of the ethanol/water mixture was $332 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. When the straw extract was treated, permeate fluxes were in the range of $35\text{--}87 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, varying according to the organic load of the sample. These authors did not find a significant decrease in permeate flux at the beginning of the process, which suggests that the cake layer was not formed or, conversely, the nature of the ethanolic feed prompted a pore blocking at the beginning of the operation. After performing a cleaning stage consisting of two cycles of rinsing with the working solvent, the membrane permeability (both to water and to the hydroalcoholic pure solvent) was restored, indicating that the fouling was reversible. As detailed in Section 4.2, Ma et al. (2021) also observed a low fouling tendency of a formamide solution of dextran during an ultrafiltration process with a 20 kDa PAN membrane from the company SolSep BV. They obtained permeate fluxes of $180\text{--}160 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$

and indicated the importance of the interactions occurring within the trio PAN-formamide-dextran.

5.1.2. Membrane immersion in solutions of increasing percentage of the same solvent

In this section, several studies in which the conditioning procedure includes a gradual exposure to organic solvents are presented. Shukla & Cheryan published in 2002 an outstanding paper in which several conditioning alternatives were discussed (Shukla and Cheryan, 2002). In order to condition different types of polymeric membranes for a posterior ultrafiltration of a 70% ethanolic extract, several possibilities were studied. They tested three different pre-treatments: a conditioning with 70% ethanol solution, a transition from 100% ethanol to 70% ethanol and a gradual change from 10% to 70% ethanol, increasing the ethanol proportion by 10% each time. This last approach proved to be the most respectful with the membrane, whereas direct exposure to a high percentage of ethanol resulted in membrane damage. Thus, they demonstrated that abrupt changes in the polarity of the solvent were not advisable. The long-term stability of polymeric membranes in the presence of ethanol was checked in a posterior contribution of the same authors (Shukla and Cheryan, 2003), providing useful data about the most resistant materials. The optimal conditions in terms of pre-treatment and membrane selection were reflected in successive works (Tsui and Cheryan, 2007, 2004), in which the conditioning always consisted of setting the membrane in the ultrafiltration device, application of pressure to remove any remaining chemicals from the pores and posterior treatment with different solutions, increasing the percentage of ethanol by a 10% until reaching the ethanol proportion of the feed solution. This strategy has been adopted by other authors, who were able to suitably employ the membranes conditioned with this methodology (Baptista et al., 2015; Pinto et al., 2014). See Table 1 (and Section 4) for more details about these contributions.

5.1.3. Membrane immersion in different solvents

A similar concept underlies the soaking of the membrane in different solvents before its contact with the solvent of the feed. The intention is to gradually modify the polarity of the medium and slowly adapt the membrane. Instead of increasing the ratio of solvent/water (as presented before), the whole solvent is substituted by another one with higher or lower polarity, depending on the final objective. Following this strategy, Savaş-Alkan and Çulfaz-Emecen (2022) proposed a simple immersion of polymeric membranes in ethanol/water 20:80 (v/v) until use. This article was widely commented in Section 4.1. de Souza Araki et al. (2010) soaked their membranes in water, ethanol, and, finally, hexane, which was the solvent aimed to be ultrafiltered. More details about their work can be found in Section 4.2 and in Table 1. García and co-workers (2005a) also investigated the effect of the pre-treatment in the hexane permeate flux. They conditioned some organic (PES, 4 kDa) and ceramic (ZrO_2 ; 1 and 5 kDa) membranes by successive immersion in solutions of water/iso-propanol 50:50 (v/v), iso-propanol/hexane 50:50 (v/v) and, finally, pure hexane. Each immersion lasted 24 h. This strategy was compared to a different pre-treatment, consisting of direct immersion in hexane (as in Section 5.1.1). For the organic membranes, the sequential modification of the solvent polarity gave satisfactory results. Hexane permeate flux reached $120 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 1.2 MPa in this case, whereas the flux was almost zero when the conditioning consisted only of an immersion in hexane. On the contrary, ceramic membranes did not benefit from any of the strategies and always displayed a downwards flux, as if hexane fouled the membrane. Badan Ribeiro et al. conditioned a ceramic membrane with mixtures of water/ethanol and ethanol/hexane (Badan Ribeiro et al., 2008) and achieved an evident improvement in hexane permeate flux. First, they moderately increased the proportion of ethanol until 70% was reached, and then, they slowly changed hexane abundance in the medium until the membrane was in contact with pure hexane. Before the membrane preparation, hexane permeate flux was nearly negligible, but after the conditioning, it reached values of

Table 1

Detailed description of each work described in this review, including the employed membranes, conditioning solvent, and procedure. Derived results of permeability and rejection are provided too.

Ref.	Membranes	Feed solution	Feed solvent	Conditioning procedure	Before conditioning	After conditioning			Rejection
					Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Solvent permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Permeate flux (feed solution) (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	
(Oxley et al., 2022)	PBI-M0 ^a	PEG solution	Acetonitrile, MeOH ^b , DMF ^c , toluene	-	n.s.	n.s.	68 (acetonitrile) 39 (MeOH) 32 (dimethylformamide) 10 (toluene)	n.s.	Rejection of PEG 2000 g·mol ⁻¹ 32% (acetonitrile) 58% (MeOH) 68% (dimethylformamide) 56% (toluene)
	PBI-M90 ^a						65 (acetonitrile) 29 (MeOH) 18 (dimethylformamide) 10 (toluene)		Rejection of PEG 2000 g·mol ⁻¹ 50% (acetonitrile) 62% (MeOH) 75% (dimethylformamide) 56% (toluene)
	PBI-M97.5 ^a						42 (acetonitrile) 25 (MeOH) 12 (dimethylformamide) 9.5 (toluene)		Rejection of PEG 2000 g·mol ⁻¹ 65% (acetonitrile) 76% (MeOH) 95% (dimethylformamide) 58% (toluene)
	PBI-M100 ^a						33 (acetonitrile) 18 (MeOH) 10 (dimethylformamide) 10 (toluene)		Rejection of PEG 2000 g·mol ⁻¹ 90% (acetonitrile) 90% (MeOH) 96% (dimethylformamide) 58% (toluene)
(Savaş-Alkan and Çulfaz-Emecen, 2022)	Cellulose C20 (15 kDa) ^d	DMF, DMSO ^e , MeOH, PGMEA ^f		Storing in EtOH 20% until use	n.s.	18	n.s.	-	n.s.
	Cellulose C20P10 (14 kDa) ^d					24	14 (DMF), 1 (DMSO), 32 (MeOH), 0.5 (PGMEA)		Rejection of SU-8 42%
	Cellulose C25P10 (13 kDa)					7	n.s.		n.s.
	Cellulose C25P10-AN (13.5 kDa) ^d					8	n.s.		n.s.
	Cellulose C25P10A10 (5.8 kDa) ^d					3.5	n.s.		Rejection of SU-8 82%
	Cellulose C25P10A10-AN (3.5 kDa) ^d					3	1.2 (DMF), 0.2 (DMSO), 2.4 (MeOH), 0.1 (PGMEA)		Rejection of SU-8 84% Rejection of PEG

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Table 1 (continued)

Ref.	Membranes	Feed solution	Feed solvent	Conditioning procedure	Before conditioning	After conditioning				
					Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Solvent permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Permeate flux (feed solution) (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Rejection	
	Cellulose C30P10A10 (4 kDa) ^d					1	n.s.			1000 Da 90% (DMSO), 20% (MeOH), 40% (water) Rejection of SU-8 82%
(Ma et al., 2021)	PAN (20 kDa)	Dextran solution (0.2 g·L ⁻¹) (Water, formamide)	Water, formamide	n.s.	n.s.	n.s.	n.s.	Water: 750–433 Formamide: 180–160		~65% (water), 0% (formamide)
(Abdellah et al., 2020)	Ceramic: Al ₂ O ₃ /ZrO ₂ (5 kDa)	Canola oil/solvent mixtures	<i>p</i> -cymene, EtOH, limonene, hexane	1. 3 h immersion in EtOH (pressurization) 2. Overnight immersion in EtOH (pressurization)	-	-	16.7 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (EtOH); 20 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (<i>p</i> -cymene); 35 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (hexane); 18 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (limonene); 12 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (pinene);	Hexane/oil 90:10 (v/v): 13 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ <i>p</i> -Cymene/oil 90:10 (v/v): 11 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ ; Limonene/oil 90:10 (v/v): 10 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ Pinene/oil 90:10 (v/v): 7 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹		Rejection of phospholipids hexane/oil 90:10 (v/v): 95% <i>p</i> -cymene/oil 90:10 (v/v): 97%; limonene/oil 90:10 (v/v): 92%; pinene/oil 90:10 (v/v): 92%
	PES (10 kDa)						33 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (EtOH); 27 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (<i>p</i> -cymene); 67 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (hexane); 8 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (limonene); 3 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (pinene)	Hexane/oil 90:10 (v/v): 25 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ <i>p</i> -Cymene/oil 90:10 (v/v): 7 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ Limonene/oil 90:10 (v/v): 3 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ Pinene/oil 90:10 (v/v): 9 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹		n.s.
	PSf (90 kDa)						55 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (EtOH); 38 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (<i>p</i> -cymene); 82 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (hexane); 23 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (limonene); 8 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ (pinene)	Hexane/oil 90:10 (v/v): 19 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ <i>p</i> -Cymene/oil 90:10 (v/v): 21 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ Limonene/oil 90:10 (v/v): 9 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ Pinene/oil 90:10 (v/v): 3 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹		n.s.
(Ji et al., 2019)	PSf (100 kDa)	Dextran solution (1 g·L ⁻¹), BSA solution (1 g·L ⁻¹), pepsin	Water	Immersion in hot water (70°C), afterwards: <u>Studied strategies</u> A. EtOH ⁸ 60%: 35°C, 75 min, 130 rpm	110	After treatment A: 600 After treatment B: ~840 After treatment C: 205–250	-	<u>After treatment B</u> Dextran: 600–750 BSA: 150–350 Pepsin: 225–350		Rejections after treatment B Dextran 70 kDa: 0.84%; 100 kDa: 2.31%; 229 kDa: 11.62%; 2000 kDa: 49.32%

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Table 1 (continued)

Ref.	Membranes	Feed solution	Feed solvent	Conditioning procedure	Before conditioning	After conditioning			
					Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Solvent permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Permeate flux (feed solution) (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Rejection
		solution (1 g·L ⁻¹)		B. EtOH 100%: 50°C, 120 min, 130 rpm C. NaOH treatment (0.55 M and 1 M)					BSA: ~20% Pepsin: ~75%
(Torres et al., 2017)	PVDF (7 kDa)	Biodiesel	EtOH	Overnight immersion in feed solvent	12.4	-	24.1	1.9	Rejection of total glycerol 23.7%
	PSf (5 kDa)				9	-	1.7	0.38	13.7%
(Argyle et al., 2015)	PSf (50 kDa)	Black tea liquor	Water	1. Immersion in hot water (temperature n.s.) 2. Overnight immersion in EtOH 50% or 100% (pressurization)	<u>Relative water flux</u> 1	<u>Relative increase of water flux</u> 1.32 ± 0.01 (EtOH 50%), 2.32 ± 0.02 (EtOH 100%)	-	<u>Relative filtration flux</u> 0.7–0.4 (EtOH 50%); 0.6–0.25 (EtOH 100%)	Rejection of TPC ~0.4 (EtOH 50% and EtOH 100%)
	PSf (100 kDa)				1	3.75 ± 0.11 (EtOH 50%), 3.8 ± 0.06 (EtOH 100%)	-	0.4–0.2 (EtOH 50%); 0.3–0.15 (EtOH 100%)	~0.3 (EtOH 50% and EtOH 100%)
	PSf (0.1 µm)				1	2.09 ± 0.04 (EtOH 50%), 2.13 ± 0.04 (EtOH 100%)	-	0.35–0.15 (EtOH 50%); 0.32–0.12 (EtOH 100%)	~0.28 (EtOH 50% and EtOH 100%)
(Baptista et al., 2015)	Polyamide composite (1 kDa)	<i>Eucalyptus globulus</i> bark extract (EtOH 80%)	EtOH/water 80%	Increasing EtOH proportion by 10% until 80%	3.9	-	1.7	1.67	Rejection of TPC 49.4%
	PES (5 kDa)				72.4	-	25	2	49.4%
	PVDF (30 kDa)				91.2	-	35.5	3.33	61.1%
	PSf (60 kDa)				191.3	-	57.2	13.33	13.9%
(de Melo et al., 2015)	Ceramic: Single channel, ZrO ₂ /Al ₂ O ₃ active layer (20 kDa)	Synthetic and real soybean oil/solvent mixtures (EtOH, propanol, hexane)	Hexane	1. Overnight immersion in EtOH 2. Overnight immersion in n-propanol 3. Overnight immersion in iso-propanol 4. Overnight immersion in butanol	192.5	After 1: 120.5 After 2: 76.1 After 3: 70.4 After 4: 60.6	After 1: 9.2 After 2: 4.8 After 3: 172.4 After 4: 313.8	<u>Real soybean oil/hexane mixture</u> 14 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹	Rejection of soybean oil 4–8% ^h
(Pinto et al., 2014)	Polyamide composite (1 kDa)	<i>Eucalyptus globulus</i> bark extract (EtOH 52% and EtOH 80%)	EtOH/water 52%, EtOH/water 80%	Increasing EtOH proportion by 10% until 52% or 80%	4	-	< 2.5	n.s.	15–20% (gallic acid); 20–25% (maltose); 45–50% (tannic acid)
	PES (5 kDa)				70	-	25–40	1.5	n.s.

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Table 1 (continued)

Ref.	Membranes	Feed solution	Feed solvent	Conditioning procedure	Before conditioning	After conditioning			
					Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Solvent permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Permeate flux (feed solution) (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Rejection
(Buekenhoudt et al., 2013)	PVDF (30 kDa)				90	-	35–50	3	n.s.
	PSf (60 kDa)				190	-	40–60	n.s.	n.s.
	3 nm ZrO ₂	MeOH, DMF, THF ⁱ , toluene, hexane		n.s.	50	-	38.2 (MeOH), 21.6 (DMF), 28 (THF), 9.6 (toluene)	-	-
	5 nm TiO ₂				120	-	70 (MeOH), 46 (DMF), 53 (THF), 14.8 (toluene)	-	-
	100 nm TiO ₂				700	-	225 (MeOH), 159 (DMF), 220 (THF), 420 (hexane)	-	-
(Koncsag and Kirwan, 2012)	SelRO™ MPS-U20S (20 kDa)	Degraded straw extract (EtOH 75%)	EtOH/water 75%	1. Overnight immersion in water 2. Overnight immersion in feed solvent	42.88	-	41.50	4–11	n.s.
(Tres et al., 2012)	PES/PVP (50 kDa)	Refined soybean oil/n-hexane mixtures	Hexane	1. Overnight immersion in EtOH 2. Overnight immersion in n-propanol 3. Overnight immersion in butanol	120	-	After 1: 0.02 g·m ⁻² ·h ⁻¹ ·bar ⁻¹ After 2: 36 g·m ⁻² ·h ⁻¹ ·bar ⁻¹ After 3: < 26 g·m ⁻² ·h ⁻¹ ·bar ⁻¹	13–60 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ ^h	Rejection of soybean oil 10–30% ^h
(de Souza Araki et al., 2010)	PC (0.05 μm), MCE (0.5 μm)	Water, EtOH, hexane		30 min immersion in hexane	40	35	50 (EtOH), 40 (hexane)		-
	MCE (0.025 μm)				-	95	210 (hexane); flux for EtOH n.s.		-
	PVDF (30 kDa)				90 ^j	30	30 (EtOH), 200 (hexane)		-
	PVDF (50 kDa)				-	150	150 (EtOH), 1700 (hexane)		-
	PES (10 kDa)				-	45–65 ^k	25–35 (EtOH), 17–32 (hexane)		-
					-	20	35 (EtOH), 1.7–4 (hexane)		-
(Kochan et al., 2009)	PES (MWCO n.s.)	Water	Acetone, EtOH, iso-propanol	2 h immersion in feed solvent	1055	2853 (acetone), 2211 (EtOH), 2192 (iso-propanol)	-	-	-
		Sludge supernatant			-	-	-	Data for EtOH n.s., 2000–10 (iso-propanol), 1350–5 (virgin)	-
		Water			339 (EtOH), 339 (iso-propanol).	1170 (EtOH), 1004 (iso-propanol)	-	-	-

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Table 1 (continued)

Ref.	Membranes	Feed solution	Feed solvent	Conditioning procedure	Before conditioning	After conditioning				
					Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Solvent permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Permeate flux (feed solution) (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Rejection	
					Data for acetone n.s.					
		Sludge supernatant			-	-	-	1100–86 (EtOH), 1050–82 (iso-propanol), 350–58 (virgin)	-	
		BSA solution			-	-	-	1100–90 (EtOH), 1000–90 (iso-propanol), 340–140 (virgin)	-	
		Dextran solution			-	-	-	1100–50 (EtOH) 1000–60 (iso-propanol) 350–40 (virgin)	-	
(Badan Ribeiro et al., 2008)	Ceramic: 19-channels, Al ₂ O ₃ active layer (0.1 μm)	Miscella: Soybean oil in hexane (32% m/m)	Water, EtOH, hexane	1. Increasing EtOH proportion (30%, 50%, 70% and 100%). 2. Increasing hexane proportion 30%, 50%, 70% and 100%)	-	225	EtOH: 198 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹ Hexane: 215 kg·m ⁻² ·h ⁻¹ ·bar ⁻¹	28	Rejection of phosphorous content 99.7%	
(Tsui and Cheryan, 2007)	SelRO™ MPS-U20T (20 kDa) RTM-PX (n.s.)	SLE of corn xantophiles (EtOH 85%)	EtOH/water 85%	Increasing EtOH proportion by 10% until 85%	-	-	2.54 3.7	0.32 0.05	74% 91.4%	
García et al. (2006)	PES-ES404 (4 kDa) PES-ES209 (9 kDa)	Crude oil	Hexane	-	n.s. n.s.	14.1 47.6	9.7 17	8 13.8	Rejection of phospholipids 94.6% 96.5%	
(García et al., 2005)	PES (4 kDa) Ceramic membranes (ZrO ₂ ; 1 kDa) Ceramic membranes (ZrO ₂ ; 5 kDa)	Hexane		Studied strategies A. Immersion in iso-propanol 50% (24 h), iso-propanol/hexane 50:50 (24 h), hexane (24 h) B. Overnight immersion in hexane	n.s. n.s. 29.1	After treatment A 14.1 n.s.	9.7 2.5–1.5 5		- - -	
(Giorno et al., 2005)	Polyamide (10 kDa) Polyamide (50 kDa)	Isooctane		Studied strategies A. Water (4 h), iso-propanol 50% (3 h), isooctane (12 h) B. Water (4 h), iso-propanol 80%	180 320	After Treatment C 600 700–525 Rest of pre-treatments: n.s.			- -	

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Table 1 (continued)

Ref.	Membranes	Feed solution	Feed solvent	Conditioning procedure	Before conditioning	After conditioning			Rejection
					Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Solvent permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Permeate flux (feed solution) (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	
				(12 h), iso-propanol:isooctane 50:50 (12 h), iso-propanol:isooctane 20:80 (12 h), isooctane (12 h) C. Water (4 h), iso-propanol 80% (12 h), isooctane: isooctane 50:50 (3 h), iso-propanol: isooctane 20% (12 h), isooctane (3 h) D. Water (4 h), iso-propanol:isooctane 50:50 (1.5 h), isooctane (3 h)					
(Shukla and Cheryan, 2002)	Cellulose acetate (10 kDa)	Zein ethanolic solution	EtOH/water (0–70%)	Studied strategies	-	Results for EtOH 70%, after Treatment A			After Treatment A
				A. Increasing EtOH proportion by 10% until 70%	49.5	-	18.2	n.s.	94
	Cellulose ester (10 kDa)			B. First treatment with water. Second one with EtOH 70%	8.7	-	8		97
	Regenerated cellulose (10 kDa)			C. Direct treatment with EtOH 70%	107.1 ¹	-	0.014		95
	Prop. Composite (5 kDa)			D. First treatment with EtOH 100%. Second one with EtOH 70%	8.2	-	8.5		86
	PAN (25 kDa)				57.5	-	27.9		99
	PES (10 kDa) – UFC				24	-	10.9		n.s.
	PES (10 kDa) – PES4H				8.2	-	2.3		95
	Modified PES (10 kDa) – Omega				54.5	-	19.8		98
	Modified PES (10 kDa) – Alpha				138.2	-	54.5		78
	PSf (10 kDa)				32.7	-	16.1		n.s.
	PSf (30 kDa)				167.3	-	33		n.s.
	PVDF (25 kDa)				n.s.	-	0.011		51

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Table 1 (continued)

Ref.	Membranes	Feed solution	Feed solvent	Conditioning procedure	Before conditioning	After conditioning			
					Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Water permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Solvent permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Permeate flux (feed solution) (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Rejection
	SelRO™ MPS-U20S (20 kDa)				See (Koncsag and Kirwan, 2012)	-	3.6		93
	SelRO™ MPS-U20T (20 kDa)				n.s.	-	9.1		n.s.
(Ochoa et al. (2001))	PVDF 15%-AM 1 (22 kDa)	Crude soybean oil	Hexane	-	n.s.	660.9	95.9		Rejection of phospholipids
	PES 17%-AM 2 (10 kDa)			-	n.s.	291.6	55.4		98.8%
	PVDF 17%-AM 3 (6 kDa)			-	n.s.	180.8	110.3		83.6%
	PSf 17%-AM 4 (10 kDa)			-	n.s.	374.4	222.3		99.3%
									60%

For the conditioning description, the capital letters (A, B, C...) indicate the different strategies evaluated; the numbers (1, 2, 3...) denote the order of the stages within a single treatment. When several treatments were applied, the results for the optimum conditioning have been reported here. As the values reported here have been retrieved from variable sources (graphs, tables, paper plain text...), some decimals may vary. The units of those values which are different from those specified in the Table heading have been detailed in the corresponding cell of the Table. When not specified, all solvent percentages are expressed on a v/v basis.

^aPBI-based membranes prepared with different grafting conditions; ^bMeOH: methanol; ^cDMF: dimethylformamide; ^d: cellulose membranes prepared with different casting solutions; ^eDMSO: dimethyl sulfoxide; ^fPGMEA: propylene glycol methyl ether acetate; ^gEtOH: ethanol; ^hDepending on the mass ratio of the mixture oil/solvent; ⁱTHF: tetrahydrofuran; ^jData retrieved directly from the manufacturer; ^kdepending on the feed temperature.

215 kg·m⁻²·h⁻¹·bar⁻¹ (around 328 L·m⁻²·h⁻¹·bar⁻¹). In a later work, de Melo et al. (2015), whose work has been already introduced in previous sections, tested several solvents (water, ethanol, n-propanol, iso-propanol, and n-butanol) to pre-condition a 20 kDa ceramic membrane (α -Al₂O₃/ZrO₂) before the ultrafiltration of an hexane solution. When the membrane was not pretreated, they found an extremely low permeability for hexane, lower than 0.25 L·m⁻²·h⁻¹·bar⁻¹. It was reported to be higher for water, because its polarity is more similar to that of the membrane, supporting the influence of the solvent/membrane hydrophobicity or hydrophilicity that was commented in Section 3. They obtained a large difference in solvent permeability after the conditioning. In the best case, hexane permeability was converted into 313.8 L·m⁻²·h⁻¹·bar⁻¹. N-butanol, whose polarity was the most similar to hexane, was chosen as the best medium to treat the membrane. Also, n-butanol molecules have the longest carbon chains, which is in accordance with the theory of the molecular organization already described in Section 3. In a similar study, the same range of solvents was examined to condition a 50 kDa polyethersulfone/polyvinylpyrrolidone (PES/PVP) organic membrane. In contrast, n-butanol was not the best option to improve the permeate flux, but n-propanol (Tres et al., 2012). These results again remark the complexity of the polymer-solvent interactions and the need to adapt the pre-treatment stage to the own characteristics of the membrane and solvent considered.

5.2. Organic solvent applied only as a pre-treatment agent

There are studies in which ethanol (or other organic solvent) has been used to condition the membrane prior to the permeance of aqueous mediums. They show a certain increase in water flux. Normally, this is due to the enlargement of pores and membrane layers, which facilitates the crossing of water molecules from one side to another of the membrane. Again, this pre-treatment could improve the accomplishment of the ultrafiltration, but also, it could negatively impact the results if the obtained rejections are not satisfactory.

In this context, a two-fold increment in pure water permeability was reported by Kochan and co-workers, who treated a PSf membrane with 80% ethanol solution as a wetting agent (Kochan et al., 2009). When they ultrafiltered protein and dextran solutions, alcoholic pre-treatment was reported to not affect the final permeability. However, the membranes wetted with 80% ethanol suffered a faster decline in the permeate flux during the filtration of the feed solutions. This may be attributed to the enlargement of the polymer pores, as a result of the solvent contact. Thicker pores could be susceptible of being blocked by larger molecules, which normally would remain in the cake layer, but in this case, the pores would be big enough to accommodate them. Argyle et al. (2015) also conditioned several PSf membranes with ethanolic solutions (Section 3). The feed solution in this study was black tea liquor, whose ultrafiltration was favored in terms of permeate flux. The authors observed increases in the relative flux that ranged between 1.32 and 2.13, depending on the membrane MWCO. An impressive 600% increment in water permeability was found by Ji et al. (2019) after an ethanolic pre-conditioning of PSf membranes. However, the expansion of pores had some disadvantages too. It reduced rejection values and promoted the adsorption of proteins coming from the feed (pepsin and BSA solutions) on the membrane surface. As commented by these authors, the contact with the organic solvent may favor the adsorption of larger molecules from the feed inside the pores, thus, fouling should always be considered.

6. Most resistant membrane materials to work with organic solvents

At this point, it seems pertinent to study the most suitable membrane materials when ultrafiltrating organic solvents. The selection of the appropriate polymer can be crucial in the success of the process. During the careful optimization that is required to find the adequate membrane,

it is also reasonable to consider the polymer stability and break strength in the presence of the organic solvent. In-advance knowledge of potential interactions between solvent molecules and the membrane polymer could prevent some undesired phenomena, such as membrane damage, fouling, or insufficient separation efficiency in terms of solute rejection and permeate flux.

This task is not effortless, because the membrane material is not the only variable able to influence the results available in the literature. In contrast, other specific characteristics of each study (feed solvent, viscosity, operation time, applied pressure, etc.) may be considered. All of these aspects have already been disclosed above.

However, previous results obtained in this area are very useful information to rely on. In this section, the results obtained with the most common membrane materials have been summarized and classified according to the organic solvent of choice. Such classification aims to provide a guide about the polymer selection once the solvent to use has been determined. The use of ethanol and hexane (two of the organic solvents most commonly considered in the literature) for membrane filtration has been detailed. Ethanol is a colorless liquid, volatile, and flammable organic compound that belongs to the group of alcohols. It is used in the industry as raw material for the production of alcoholic drinks. Besides, it is present in pharmaceutical preparations and in the chemical industry (for cosmetics or perfume production). In addition, as it was mentioned in Section 2, ethanol is one of the most eco-friendly organic solvents due to its biocompatible character, its low toxicity, and easy handling (Baptista et al., 2015; Crespo and Brazinha, 2010; Koncsag and Kirwan, 2012; Loginov et al., 2013; Nawaz et al., 2006; Tovar-Sánchez et al., 2022). Hexane is an organic compound, colorless and volatile, with six carbon atoms forming a straight-chain alkane. Despite its toxicity (Morrow, 2014), this organic solvent is broadly employed in many industries, such as chemical industries and edible oil industries.

6.1. Organic solvent: ethanol

In order to compare the results from different research works dealing with ethanol and the same membrane material but different MWCO, Table 2 has been provided. This table contains information about those references that included the water and the solvent permeability of the employed membranes. These data (included in Table 1) allowed the calculation of the deviation of the solvent permeability with respect to the water permeability of each membrane. This parameter was calculated following Eq. 3:

$$\text{Solvent to water permeability ratio} = \frac{\text{Solvent permeability}}{\text{Water permeability}} \quad (3)$$

It should be noted that, for this calculation, the water permeability of the membranes without any conditioning or contact with an organic solvent has been considered. These water permeability values can be consulted in the sixth column of Table 1. Therefore, the reported ratio allows the comparison of the membrane performance in an aqueous environment and an organic medium.

As can be inferred from Table 1 and Table 2, PSf is one of the most used materials in membrane technology. Many PSf membranes are currently available for aqueous ultrafiltration. For that reason, there is a high interest in the design of a strategy that allows its application with organic solvents. PSf membranes of a wide range of MWCO have been tested with this objective. According to Table 2, the solvent-to-water permeability ratio for PSf membranes was 0.2–0.5 when they are used with ethanol. Shukla and Cheryan compared PSf membranes of different MWCOs (10 and 30 kDa) and configurations (flat sheet or hollow fiber) and obtained solvent permeabilities (ethanol/water 70:30 (v/v)) of 20 L·m⁻²·h⁻¹·bar⁻¹ and 33 L·m⁻²·h⁻¹·bar⁻¹, respectively, with flat sheet membranes (Shukla and Cheryan, 2002). Apart from PSf, Shukla and Cheryan studied cellulose-based membranes, PAN, PES, and PVDF polymers. The PAN (25 kDa) membrane was also a good alternative

Table 2

Ratio between ethanol and water permeability of the membranes described in this review and employed to treat hydroalcoholic solutions.

Membrane material	Proportion (ethanol/water) ^a	Ratio ethanol/water permeability	Reference
PVDF	100:0	1.94	(Torres et al., 2017)
PSf	100:0	0.19	(Torres et al., 2017)
Polyamide	80:20	0.44	(Baptista et al., 2015)
PES	80:20	0.35	
PVDF	80:20	0.39	
PSf	80:20	0.3	
Polyamide	52:48	0.63	(Pinto et al., 2014)
	80:20	0.40	
PES	52:48	0.36	
	80:20	0.57	
PVDF	52:48	0.39	
	80:20	0.56	
PSf	52:48	0.21	
	80:20	0.32	
SelRO™ MPS-U2OS	75:25	0.97	(Koncsag and Kirwan, 2012)
PC	100:0	1.32	(de Souza Araki et al., 2010)
MCE	100:0	0.33	(Shukla and Cheryan, 2002)
Cellulose acetate	70:30	0.37	
Cellulose ester	70:30	0.92	
Regenerated cellulose	70:30	0	
Prop. Composite	70:30	1.04	
PAN	70:30	0.49	
PES	70:30	0.45	
PES	70:30	0.28	
Modified PES	70:30	0.36	
Modified PES	70:30	0.39	
PSf	70:30	0.49	
PSf	70:30	0.20	

^a : ethanol proportion is expressed in a v/v basis.

(with a solvent permeability of $27.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), despite an observed ratio between solvent and water permeability of 0.49. When PES membranes were tested (with a MWCO of 10 kDa), permeability values of $2\text{--}11 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ were obtained for ethanol at 70% (v/v) (Shukla and Cheryan, 2002). In those cases, the rejection values to zein protein were high, above 78% at 1.38 bar. Among all the tested membranes, which were equally conditioned (Section 5.1.2), these authors found the highest values of permeability for a modified-PES membrane (purchased from Pall Filtron) with the same MWCO of 10 kDa and subjected to the same pre-treatment ($55 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$). In this work, a ratio between solvent and water permeability of 0.39 was obtained for the same membrane. These results suggest that the modified PES polymer displayed a lower tendency to get fouled by the solvent molecules, in comparison with the PSf membranes evaluated. The swelling phenomenon cannot be used here to explain the higher permeabilities of this PES membrane, because the corresponding rejection value was 78% when a zein protein (whose molecular weight is around 22–27 kDa (Elzoghby et al., 2015)) solution was ultrafiltered with this set of membranes. PSf and PES polymers also yielded significant permeabilities in the study of Kochan et al., but the largest values were obtained for PES again (Kochan et al., 2009).

Membranes of PVDF, which is a solvent-resistant polymer (Ebnesajjad, 2011), have been another common alternative. In Table 2, the highest ratio between solvent and water permeability (1.94) was observed for a PVDF membrane after the filtration of pure ethanol. It indicates a considerably higher solvent flux than the water flux of the membrane. This fact can be attributed to a high affinity between the organic solvent and the PVDF material, which are both hydrophilic (Torres et al., 2017). Furthermore, this membrane was prepared using a casting solution of low viscosity, which led to a finger-like substructure under the top layer that may have improved the solvent permeate flux.

The works of Pinto and Baptista also dealt with PVDF membranes. For a 30 kDa MWCO membrane, they obtained similar permeabilities to ethanol at 52% (v/v), around $35.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, corresponding to a ratio between solvent and water permeability of 0.39 (Baptista et al., 2015; Pinto et al., 2014). The same polymer, with equal MWCO, was tested by De Souza Araki and co-workers. As they performed a different conditioning and selected pure ethanol as the feed solution, their results are not comparable, but the high permeability that they obtained (more than $150 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) is very promising and sets PVDF as an interesting polymer in this area.

Among those works in which the membrane was pretreated by overnight immersion in the feed solvent (such as ethanol or mixtures of ethanol/water), Koncsag and Kirwan (2012) obtained a high permeability ($343 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and $332 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ when they used water or mixture ethanol/water 75:25 (v/v), respectively) with the composite membrane MPS-U2OS, from Koch (Koncsag and Kirwan, 2012), already introduced in Section 5.1.1. Torres and co-workers also applied this conditioning strategy to membranes made of different materials (Torres et al., 2017). They reported higher permeability values for the membrane of PVDF versus the PSf membrane (see Table 1). The PVDF membrane had a slightly higher MWCO (7 kDa with respect of 5 kDa), however, the rejection of total glycerol was higher for this membrane than in the case of the PSf membrane.

6.2. Organic solvent: hexane

When the solvent to be processed was hexane, PES membranes were employed in several studies. Tres et al. employed a 50 kDa PES/PVP membrane to perform the separation of mixtures of soybean oil and hexane. To enhance the flux of hexane, several solvents were tested to condition the membranes. An overnight immersion in n-propanol gave the best results in this case, leading to a hexane permeability of $36 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ (Tres et al., 2012), which corresponds to $0.055 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, considering that hexane density is $654.8 \text{ kg}\cdot\text{m}^{-3}$. De Souza-Araki also evaluated the permeability of hexane with a PES membrane (after a progressive conditioning with water, ethanol, and hexane (Section 5.1.3) (de Souza Araki et al., 2010), nevertheless, the contrasting of the results should be done carefully here, because the MWCO of the membrane was 10 kDa and so the differences in the permeate flux were expected. Still, the hexane permeability found in this work was around $3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, which is larger than the value reported by Tres et al., despite working with a tighter membrane. These results underline the importance of a correct pre-conditioning of the membrane, especially when solvents of low polarity are employed.

In the study of De Souza-Araki, other polymers, such as MCE, PC, and PVDF were tested, with the latter being the most permeable to hexane. The major values of permeate flux registered were $25\text{--}30 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (at 1.5 bar). This data was achieved with a 30 kDa PVDF membrane, whereas a 50 kDa PVDF provided a permeate flux of $13 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (at 1.5 bar) approximately. The authors explained these results by a different morphology of the pores, according to their SEM analysis. For the membranes whose water permeability was reported, the ratio between solvent and water permeability (calculated according to Eq. 3) has been detailed in Table 3. As can be seen, solvent flux was not lower

Table 3

Ratio between hexane and water permeability of the membranes described in this review and employed to treat pure hexane.

Membrane material	Ratio hexane and water permeability	Reference
PC	1.05	(de Souza Araki et al., 2010)
MCE	2.22	(Buekenhoudt et al., 2013)
100 nm TiO ₂	0.6	

than the flux obtained with water for polymeric membranes (ratios higher than 1), suggesting that PC and MCE are also valid materials to work with hexane. By contrast, for ceramic membranes, in the study published by Buekenhoudt et al. (2013), hexane permeability was lower than water permeability (ratio lower than 1), which can be attributed to the high hydrophilic character of the membrane surface and low polarity of the solvent.

Several authors selected ceramic membranes to deal with hexane, and their works have been discussed in Section 5.1.3. Badan Ribeiro et al. (2008); de Melo et al. (2015) found satisfactory values of permeate flux after a proper conditioning of the membranes. Despite their higher price and a lower ratio of membrane area with respect to the module volume, the high chemical stability of inorganic membranes makes them a suitable option to work with organic solvents.

6.3. Other organic solvents

Even though the most prevalent organic solvents regarding membrane technology are ethanol (and its corresponding mixtures with water) and hexane, some applications require the use of other solvents less extended in the literature, such as acetone, heptane, isooctane, and iso-propanol. One of these applications is membrane emulsification (Piacentini et al., 2014). According to this technique, the membrane acts as a barrier between the phase that will form the drops (dispersed phase) and the phase that will contain those droplets. By applying pressure, the dispersed phase will be forced through the membrane, creating drops when entering in contact with the continuous phase. One of the challenges of this procedure relies on the achievement of an adequate flow of the dispersed phase. Thus, the compatibility of the membrane and the organic solvent that may act as this dispersed phase is essential to overcome this limitation. To investigate this, Giorno et al. (2005) tested the flow of isooctane (a potential dispersion phase in membrane emulsification) with polyamide membranes. After a treatment with water, iso-propanol at 80%, iso-propanol at 20%, and, finally, isooctane, they obtained isooctane permeate fluxes of $600 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and $700 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ for a 10 kDa membrane and 50 kDa membrane, respectively. Then, the applied conditioning allowed the obtention of high fluxes to form oil-in-water emulsions with polymeric membranes.

7. Conclusions and future perspectives

Ultrafiltration is a commonly practiced technique, both at the industrial level and within research laboratories. It finds many applications in the food industry, for protein concentration, lactose concentration, separation of nutrients, etc. Wastewater treatment is also one of the main uses of this technology, including oil removal, reduction of the organic load, etc. Even the pharmaceutical industry has benefited from ultrafiltration, performing blood plasma purification, for instance. All these uses disclose the versatility and advantages of this membrane process. However, the implementation of ultrafiltration membranes to treat solvent-based solutions is a less explored area, despite all the advantages that are derived from this technique. Among the applications of solvent-based ultrafiltration, it is possible to mention the recovery of valuable compounds from the agri-food and the pulp and paper industry, and the applications in the edible oil industry (during the step of recovering the solvent and the degumming process), and biorefineries.

Other membrane technologies, such as organic-solvent nanofiltration, have a well-established research community (from the academic and industry fields) aiming to advance in the knowledge and application of the process. In contrast, the investigation of solvent-based ultrafiltration still finds some room for growth. Researchers on the topic and membrane manufacturers have some work ahead to improve the performance of this procedure. The most commonly employed solvents in this area are ethanol (and mixtures of ethanol and water), and hexane. As reported in many studies, these solvents may interfere with the membrane structure, causing swelling and even membrane rupture.

Therefore, investigating the interactions between the solvent and the polymer is still a pending task that will for sure allow the development of better, more resistant polymers. Furthermore, it is necessary to gain more knowledge regarding the solute-solvent, solute-membrane, and solvent-membrane interactions in organic media, because these three pairs of interactions may influence the fouling tendency and the transport of solutes during the ultrafiltration process.

To contribute to this effort, this review presents an overview of relevant data, regarding available values of permeate flux, rejection and selectivity, and variations of polymer morphology after the contact with the solvent. The importance of membrane pre-conditioning has also been highlighted. According to the literature, the main strategies to condition an ultrafiltration membrane prior to its utilization in organic media are, on one side, its immersion in the same solvent as will be later employed in the feed stream, and, on the other side, the application of solvent solutions with increasing concentrations. Alternatively, the combination of different solvents with decreasing polarity has also been proposed.

As has been commented, some of the most preferred materials for organic solvent ultrafiltration are PA, PVDF, PES, PSf, PC, and cellulose derivatives. The values of permeability and permeate flux that have been presented here may imply a double interpretation when deciding if a given polymer is adequate or not for a specific application. This aspect has been highlighted during the whole extension of this review. In some scenarios, the highest permeate flux can be desirable, to enhance the productivity of the process. However, if the rejection of solutes is a priority, membranes which had displayed a lower permeability after the conditioning could be preferable. In those cases, the organic solvent could generate swelling events and, even if satisfactory permeate fluxes are obtained, the solutes of interest may not be retained. Then, the conditioning of the membrane polymer should be optimized, and adjusted to each application, because its impact on the membrane performance is not trivial. With a correct proceeding, the pre-treatment of the membrane may allow the tuning of its properties, then tailoring the polymer according to the application. The MWCO should be carefully selected in those contexts and, even in some cases, a lower MWCO could be worthy of testing, in order to anticipate the potential swelling of the membrane and reduce its impact on the rejection.

The literature gap regarding solvent-based ultrafiltration indicates the challenges of this topic. However, the possibilities of this technique are an excellent incentive to increase the research efforts, improve the current understanding of the process and broaden its applications.

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Declaration of Competing Interest

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