23 A Critical View on Separation Processes by Membrane Technology Applied in Vegetable Oil Refining

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23.1 INTRODUCTION
Membranes are among the most important industrial applications today, and every year, the use of this technology in processes such as water purification, industrial wastewater treatment, dehydration solvent recovery of volatile organic compounds, and protein concentration is increasing [1].

A membrane is phase permeable or semipermeable, consisting of polymer, ceramic, or metal, which restricts the mobility of certain compounds. The membrane (barrier) controls the relative rate of mass transport of various compounds through it and then, as in all separations, leads to a free product of certain compounds and a second concentrated product in these compounds. The performance of a membrane is defined in terms of two factors: flow and retention or selectivity. Flow or permeation rate is the volume of fluid passing through the membrane per unit membrane area per unit time. Selectivity is the measure of the relative permeation rate of different compounds through the membrane. Retention is the fraction of solute in power retained by the membrane. Ideally, a membrane with high selectivity or retention and high flow or permeability is desirable. Normally, however, procedures to maximize one factor are compromised by the reduction of the other [1].

Membranes are used in several separations, such as mixtures of gases and vapors, liquids miscible, dispersions, solid/liquid and liquid/liquid, dissolved solids, and solutes of liquids. The main feature that distinguishes membrane
23.2 INTRODUCTION TO MEMBRANE PROCESSES

The evolution and expansion of the use of ultrafiltration (UF) on an industrial scale became possible after the development of asymmetric polymeric membranes, especially of cellulose acetate and aromatic polysulfones (PSs). These membranes were initially developed for desalination of seawater by reverse osmosis and then were used in various applications from other polymeric materials. Until the development of asymmetric membranes, considered as second generation, were available symmetric polymeric membranes, so-called first generation, thicker to obtain mechanical strength and hence poor performance. The so-called third-generation membranes, mineral or inorganic asymmetric membranes that are homogeneous or composite, were developed to meet the needs of high mechanical resistance to pressure, high chemical resistance, and high thermal resistance.

The processes of membrane separation most importantly controlled by mechanical energy, hydrostatic pressure, are listed in Table 23.1, while the characteristics of membrane processes in terms of the substances distributed between retentate compounds, retained by the membrane, and permeate, compounds that permeate the membrane or are filtered, are listed in Table 23.2.

The main processes of membrane separation include microfiltration (MF), UF, nanofiltration (NF), reverse osmosis, pervaporation, and gas separation. These processes can be distinguished by the size of the particles or molecules which the membrane is able to retain or let permeate. This property is related to the size of the pores of the membrane (Figure 23.1). Obviously, all the particles or molecules with a large pore diameter will be retained [2].

Nakao (1994), cited by Snape and Nakajima [3], summarized the classification of membrane processes based on the pressure applied and the particle size or molecular weight. MF uses pressure less than 0.2 MPa and is applied primarily to separate particles of a size in the range of 0.025–10 μm. UF uses pressure above 1 MPa and separates particles of molecular weight between 1 and 300 kDa. NF uses pressure between 1 and 4 MPa and separates solutes of molecular weight between 350 and 1000 Da, while reverse osmosis uses pressure between 4 and 10 MPa and is used to concentrate solutes with molecular weight less than 350 Da (Figure 23.2).

The distinction between processes of NF and reverse osmosis is not always clear, and sometimes, manufacturers membranes classified as reverse osmosis, while the above classification, could be NF. Therefore, in many cases, we adopt the nomenclature of RO/NF to the membrane [3].

In some cases, refer to the pore size of the membrane molar weight cutoff (MWCO), which represents the molecular weight of a less retained component in at least 95% of cases.

---

**TABLE 23.1**

<table>
<thead>
<tr>
<th>Membrane Separations by Application of Hydrostatic Pressure</th>
<th>Major Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF micropore symmetric or asymmetric</td>
<td>Clarification, sterile filtration</td>
</tr>
<tr>
<td>UF micropore asymmetric</td>
<td>Separation of macromolecular solutions</td>
</tr>
<tr>
<td>NF asymmetric</td>
<td>Separation of organic compounds of low molecular weight</td>
</tr>
<tr>
<td>Reverse osmosis asymmetric</td>
<td>Separation of salt solutions</td>
</tr>
</tbody>
</table>


**TABLE 23.2**

<table>
<thead>
<tr>
<th>Process</th>
<th>Driving Force</th>
<th>Retentate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osmosis</td>
<td>Chemical potential</td>
<td>Solutes, water</td>
<td>Water</td>
</tr>
<tr>
<td>Dialysis</td>
<td>Difference of concentration</td>
<td>Macromolecules, water</td>
<td>Small molecules, water</td>
</tr>
<tr>
<td>MF</td>
<td>Pressure</td>
<td>Suspended particles, water</td>
<td>Dissolved solutes, water</td>
</tr>
<tr>
<td>UF</td>
<td>Pressure</td>
<td>Macromolecules, water</td>
<td>Small molecules, water</td>
</tr>
<tr>
<td>NF</td>
<td>Pressure</td>
<td>Small molecules, divalent salts, dissociated acids, water</td>
<td>Monovalent ions, nondissociated acids, water</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Pressure</td>
<td>All solutes, water</td>
<td>Water</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>Electric potential</td>
<td>Nonionic solutes, water</td>
<td>Ionized solutes, water</td>
</tr>
<tr>
<td>Pervaporation</td>
<td>Pressure</td>
<td>Nonvolatile molecules, water</td>
<td>Small volatile molecules, water</td>
</tr>
</tbody>
</table>

In membranes, the mechanism of separation is more complex than the retention or flux of particles or molecules determined by the diameter of the pores of the membrane. Many other variables such as membrane composition, manufacturing method, 3D configuration or morphology of molecules, their interactions with each other and the membrane surface, the dynamics of fluid in the filtration unit, pressure, and temperature influence the process of separation [4].

Membranes for commercial use in large-scale separation processes had not been developed until the invention of asymmetric membranes in the late 1950s. With this type of membrane, a high flow of permeate, essential for commercial applications, has been established [5].

The microstructure of asymmetric membrane is heterogeneous, determining different behaviors of the membrane, depending on the side in contact with the feed solution [6].

The membrane’s benefit in the food industry was first realized when reverse osmosis membranes were developed for the purification of water, a process known as desalination. After this application, membranes were introduced in various conventional processes, such as concentration by UF instead of evaporation. Membranes allow the development of processes and entirely new products. Among the main benefits of using membranes in the food industry are the separation of molecules and microorganisms, the absence of thermal damage to the products and microorganisms, and low power consumption [5].

The examples of applications of membrane technology in food processing are shown in Table 23.3.

In principle, almost all separation processes commonly applied in food processing can be achieved using conventional unit operations. For example, sterilization is traditionally achieved by heat treatment. In cold sterilization, MF is
TABLE 23.3
Examples of Applications of Membranes in Food Processing

<table>
<thead>
<tr>
<th>Process or Application</th>
<th>Typical Product</th>
<th>Membrane Process</th>
<th>Industry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold sterilization</td>
<td>Beer, wine, milk</td>
<td>MF</td>
<td>Dairy, beverages</td>
</tr>
<tr>
<td>Clarification</td>
<td>Beer, wine, fruit juice</td>
<td>MF, UF</td>
<td>Beverages</td>
</tr>
<tr>
<td>Concentration/clarification</td>
<td>Protein (whey), fruit juice</td>
<td>UF, reverse osmosis</td>
<td>Beverages, dairy</td>
</tr>
<tr>
<td>Removal of alcohol</td>
<td>Beer, wine</td>
<td>Pervaporation</td>
<td>Beverages</td>
</tr>
<tr>
<td>Fractionation</td>
<td>Proteins (egg, whey, blood), carbohydrates</td>
<td>UF, electrodialysis</td>
<td>Dairy, meat, eggs, sugar</td>
</tr>
<tr>
<td>Recovery</td>
<td>Citric acid, lactic acid</td>
<td>Pervaporation, reverse osmosis</td>
<td>Biotechnology</td>
</tr>
<tr>
<td>Sensorial improve</td>
<td>Flavors</td>
<td>Reverse osmosis, electro dialysis, NF</td>
<td>Beverages, dairy</td>
</tr>
<tr>
<td>Desalination</td>
<td>Drinking water, reduced hardness water, unsalted cheese</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


used to remove bacteria contamination at low temperature. The introduction of cold sterilization by the membrane process began with products of high added value in the pharmaceutical industry to prevent irreversible damage caused by heat treatment. Cold sterilization has become commonplace in the food industry, since it preserves the quality of the product and, at the same time, avoids the appearance of off-flavors [5].

According to Cheryan [6], one of the advantages of membrane technology compared with traditional methods of water removal is the absence of phase change or state solvent during the process. Evaporation and concentration by freezing are two techniques commonly used in liquid foods.

Evaporation requires energy equivalent to 540 kcal kg⁻¹ of water evaporated while the freeze requires 80 kcal kg⁻¹ of frozen water only to effect change in the state of water from liquid to vapor and liquid to solid, respectively. Separations by membranes require no change of state for the concentration, resulting in considerable savings, 65% less energy than traditional methods. Another advantage is the reduced need for heat transfer or heat generation equipment.

Membrane processes require only electricity to pump, as well as the facilities may be located far from the main unit's power plant. Additionally, membrane processes can operate at room temperature; low temperature, to prevent problems with the growth of microorganisms or degradation of heat-sensitive compounds; and high temperature, to minimize microbial growth, reducing the viscosity of the retentate to reduce pumping costs and increase the mass transfer and flow. The problems of thermal degradation and oxidative processes common to evaporation can be avoided.

Finally, since small molecules pass freely through membranes of MF and UF, the concentration on each side of the membrane will be the same at trial and equal to the original feed solution. Therefore, there is little change in the micro-environment processes during MF and UF, without causing changes in pH or ionic strength, a particular advantage when isolating and purifying proteins.

There are some limitations in membrane processes. None of them can be applied to the total drying of a product. In reverse osmosis, often the osmotic pressure of concentrated solutions that limit its. In the case of MF and UF, osmotic pressure of the macromolecules retained is negligible, but the low rate of mass transfer is obtained with macromolecules concentrated and high viscosity that makes it difficult to pump the retentate and thereby limits the process. Other problems are plugging of membranes, poor cleaning, and restricted conditions of operation. However, the development of superior materials and better designs of filter modules has minimized these problems [6].

One can also cite high costs in general, as referred to membranes, facilities, modules or operational units, and technical support. However, due to the advantages represented by membrane technology compared with conventional processes in the food industry, these costs have been minimized consistently.

According to Cuperus and Nijhuis [5], NF, UF, and MF involve separation mechanisms in porous membranes, while reverse osmosis and pervaporation make use of dense membranes. Membrane UF and MF effect the separation by a simple mechanism of exclusion by molecular size. In such cases, the particle size in relation to the average size of the pores of the membrane determines which particles can permeate through the membrane.

In UF membranes, the spatial configuration of molecules and electrical charges represent only a minor role in the mechanisms of separation. The effects are small, and the osmotic pressure applied to the filtration process, on the order of 1–7 bar, acts primarily to overcome the resistance caused by the viscosity of the fluid supply through the porous membrane network [1].

Reverse osmosis and pervaporation are able to separate molecules of similar size, such as sodium chloride and water. In such cases, the affinity between the membrane and the target component is important, as the speed of permeation through the membrane. Components that have a greater affinity for the membrane material dissolve in the membrane more easily than other components, causing the membrane material acts as an extraction phase. Differences in diffusion coefficients of components through the membrane allow the separation. According to the theory of solution–diffusion, solubility and diffusivity together will control the membrane selectivity. The mechanism by which NF membranes act is
not entirely clear. Probably, both the mechanism’s: size exclusion and the effect of solution–diffusion, both work together in the separation of components [5].

23.3 TERMS COMMONLY USED IN MEMBRANE TECHNOLOGY

The following terms or parameters are essential for the control of the filtration process mediated by membranes [2,6,7]:

1. Permeate flow rate ($F$) or ($J$): It measures the volume (liters) of permeate obtained during the process per area ($m^2$) of membrane as a function of time (hours), the equation being $F = J/A \cdot t$. A correlation exists between the pore size and the experimental flow rate of water. The flow of solvent through the pores of a membrane is represented as a function of the mean pore diameter ($dp$), number of pores ($N$), porosity ($\varepsilon$), pressure applied ($PT$), solvent viscosity ($\mu$), and the membrane thickness ($\Delta x$). The model most frequently used to describe the flow through the pores of a membrane is based on the Hagen–Poiseuille model for laminar flow through channels, the equation being $J = \frac{(edp\mu PT)}{32\Delta x}$. In this equation, the flow rate ($J$) is given in terms of the velocity ($g \cdot cm^{-2} \cdot s^{-1}$), which can be converted into $L \cdot h^{-1} \cdot m^{-2}$, since the density of water is $1 \ g \cdot cm^{-3}$. This model assumes that all the membrane pores are perfect cylinders, and thus, in some cases, the discrepancy between the estimated flow rate and the experimental flow rate can be attributed to a crookedness factor related to the true configuration of the membrane pores.

2. Concentration factor ($FC$): It measures the decrease in the mass of the feed fluid during the process, that is, the ratio between the feed mass ($MA$) at the start of filtration and the mass of retentate ($MR$) at the end of the process, governed by the following equation:

$$FC = \frac{MA}{MR}.$$

3. Coefficient of retention ($R$): It measures the retention rate (%) of a determined solute by the membrane during filtration. Retention ($R$) can be defined by the following equation: $R = 100 \left(1 - \frac{CP}{CR} \right)$, where $CP$ is the solute concentration in permeate, and $CR$ is the concentration of the solute in the retentate.

4. Membrane permeability ($JV$): This is represented by the following equation: $JV = \frac{V}{A \cdot t \cdot P}$, where $V$ is the permeate volume, $A$ is the membrane permeation area, $t$ is the filtration time, and $P$ is the operational pressure.

5. Transmembrane pressure ($PTM$): This represents the mean between the entrance pressure ($PE$) (exerted by the feed flow on the side of the retentate) and the exit pressure ($PS$) (on the permeate side, usually atmospheric pressure), that is, $P = \frac{(PE + PS)}{2}$.

23.4 CHARACTERISTICS AND TYPES OF MEMBRANES

Depth filters consist of an array of fibers oriented randomly, and the filters retain particles inside the filter material. Depth filters are constructed of materials such as cotton, fiberglass, sintered metals, and diatomaceous earth. Insoluble or colloidial particles are removed from the fluid by attraction and capture or adsorption to the filter matrix. Particles of $0.01 \mu m$ can be retained by these filters. Frequently, materials of various stages are combined in one filter, where the feed comes into contact with the matrix initially more open. Depth filters are operated in perpendicular mode [6].

In contrast, membrane filters effect the separation of compounds by retaining particles on its surface. Usually, the structure is more rigid, uniform, and continuous, with pore size more precisely controlled during manufacture. Unlike depth filters, membranes are rigid, with little risk of material migration, and the growth of microorganisms is often not a problem. Because membranes are filters with defined pore size, this feature allows for their classification. The advantage of this type of filters is that the particles retained are not lost on the inside, and a high recovery of the material removed is possible. This can be important if the target of the process is to maximize the recovery of solid retentate [6].

In relation to its microstructure, membranes can be classified as symmetric (microporous) or asymmetric (Figure 23.3), also referred to as membranes with skin filter.

Microporous membranes are sometimes classified as isotropic, with uniform pore size through the body of membrane, or anisotropic, where pores are changing in size of a membrane surface to another. In microporous membranes, occur despite retention of all particles larger than the pore size of the membrane, the particles of the same pore size can pass through them and block them, irreversibly sealing the membrane [6].

Asymmetric membranes, on the other hand, are characterized by the presence of a thin skin filter on its surface. The layers situated below the skin filter are used to support it. Rejection occurs only on the surface, but due to its unique microstructure, particles or macromolecules retained above

![FIGURE 23.3](image-url) A cross-sectional view of an asymmetric membrane, which shows porous structure. Source: Personal archive.
the molar weight cutoff rating do not enter the body of the membrane. Asymmetric membranes are rarely blocked the way it occurs in microporous membranes, although, like all filters, asymmetric membranes are susceptible to falling of phenomena such as flow concentration polarization and/or fouling. Most membranes used in UF, NF, and reverse osmosis are asymmetric, while the majority of polymeric MF membranes are microporous [6].

According to Porter [2], membranes that presenting an asymmetric structure, which are currently the most used in separation processes, the two basic properties required for any membrane, that is, high rates of mass transport for certain components and mechanical strength are physically separated. An asymmetric membrane consists of a very thin layer of skin selective filter, 0.1–1.0 µm, prepared on a thick highly porous substructure, 100–200 µm.

The skin membrane filter is the real membrane, and their separation characteristics are determined by the nature of the polymer and the pore size, while the rate of mass transport is determined by the thickness of the membrane, since the mass transport rate is inversely proportional to the thickness of the actual filter, the skin. The subporous layer acts only as a support for thin skin filter, having little effect on the separation characteristics and the rate of mass transfer of the membrane. Asymmetric membranes are primarily used in membrane processes controlled by pressure, such as reverse osmosis and UF, where the unique properties of high rates of mass transfer and good mechanical stability can best be used [2].

In addition to high rates of filtration, asymmetric membranes are more resistant to fouling. Membranes act as conventional symmetrical filters and traps particles deep within its internal structure. These particles trapped blocked the pores of the membrane, and thus, the transmembrane flow decreases during the process. Asymmetric membranes behave as filters for surface and retain all rejected particles on the surface, where they can be removed by shearing forces applied by the feed solution during its passage parallel to the membrane surface, the tangential filtration mode [2].

Membranes can be natural or synthetic. Regarding the type of material, synthetic membranes can be divided into organic, made of various polymers (Figure 23.4), and inorganic, composed of ceramic or metal (Figure 23.5).

The literature shows that over 130 different materials have been used in the manufacture of membranes; however, few have achieved commercial importance, and fewer still have passed for regular use in food products [6].

Commercial synthetic membranes are made of two distinct materials: polymers, made up of organic material, such as cellulose acetate, polyamides (PAs), PSs, and polyvinylidene fluoride (PVDF), among others (Table 23.4), and the inorganic material, such as metals and ceramics [5].

According to the technological evolution, membranes can be classified into four distinct classes:

- **First generation**: Membranes derived from cellulose acetate, which had been originally developed for desalination of seawater. They are sensitive to pH (3–8) and temperature (maximum 50°C), and they are susceptible to microorganisms and disinfectants [6].
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TABLE 23.4
Examples of Some Commercial Polymeric Membranes Used in UF Processes

<table>
<thead>
<tr>
<th>Identification</th>
<th>Composition</th>
<th>Pore Average Diameter of MWCO</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 CME</td>
<td>Mixed cellulose esters</td>
<td>0.025 µm</td>
<td>Millipore®</td>
</tr>
<tr>
<td>0.05 CME</td>
<td>Mixed cellulose esters</td>
<td>0.05 µm</td>
<td>Millipore®</td>
</tr>
<tr>
<td>0.05 PC</td>
<td>Aromatic polycarbonate</td>
<td>0.05 µm</td>
<td>Millipore®</td>
</tr>
<tr>
<td>30 PVDF</td>
<td>PVDF</td>
<td>30 kDa</td>
<td>Osmonic®</td>
</tr>
<tr>
<td>50 PVDF</td>
<td>PVDF</td>
<td>50 kDa</td>
<td>DBD Filters®</td>
</tr>
<tr>
<td>10 PES</td>
<td>Polyethersulfone</td>
<td>10 kDa</td>
<td>DBD Filters®</td>
</tr>
</tbody>
</table>


- **Second generation**: Membranes made of polymers, mainly derived from polyolefins or polyethersulfone. They were introduced in 1975, with different chemical compositions and functional properties, such as PA and PS membranes. They are resistant to hydrolysis (cleavage of internal links of the polymer) and strong acids and bases and high temperature. However, they have a low resistance to mechanical compaction. These membranes are commonly used today.

- **Third generation**: Membranes consisting of ceramic material based on zirconium oxide or alumina deposited on a surface of graphite or other support materials. They have great mechanical strength, supporting high pressure. Moreover, they tolerate all pH range (0–14) and temperature above 400°C and are chemically inert but of much higher cost [5].

- **Fourth generation**: Representing a combined process recently developed and consists in an association of conventional electrodialysis and several pore sizes membranes to MF, UF, and NF [7]. This combination is called continuous electrophoresis with porous membranes (CEPM) and can be defined as an electrochemical process for the separation of charged organic molecules. In this process, the separation driving force is based on the direct application of an electric field. By the effect of an electric potential, ions are transported from one solution to another through one or more semipermeable porous membranes [9,10]. In UF, for example, the majority of the membranes are polymeric; however, ceramic membranes also have an important role. Typical polymers for the manufacture of membranes are PVDF, PS, polyethersulfone, polyacrylonitrile (PAN), aliphatic PA, polyimide (PI), and cellulose acetate, while typical inorganic materials are alumina, zirconia, and stainless steel sintered [1].

According to Cheryan [6], inorganic ceramic membranes are extremely versatile, since they do not have the disadvantages of common polymeric membranes. However, one should consider that although ceramic membranes are very resistant to extreme operating parameters, the organic materials of filtration modules are the components that limit the performance of the process such as seals, gaskets, and o-rings.

The properties of ceramic membranes are as follows: Inert to most solvents and chemical agents, have high heat resistance, and can easily withstand steam sterilization, 125°C; some membranes can operate up to 350°C; use in a wide range pH, 0.5–13 for most of the membranes, and many can operate at pH 0–14; long operating life, with some filtration systems for ceramic membranes can operate for more than 10 years after installation with the same set of membranes. Unlike polymeric membranes, whose life is affected primarily by the nature and frequency of cleaning, inorganic membranes are able to tolerate a regime of frequent aggressive cleaning, in some cases above 2000 mg kg⁻¹ of chlorine in alkaline solution. Regarding the resistance to pressure, surprisingly, many manufacturers recommend the use of ceramic membranes in static pressure up to 100 bar. This is mainly due to the limitations of seals and the configuration of the housing (membrane case) and not due to membranes [6].

Some limitations of inorganic ceramic membranes are its sensitivity to mechanical impact, vibration, temperature, and pressure variations; pore size, which is limited only to UF and MF applications; need of high-capacity pump to obtain the recommended speed flow of 2–6 m s⁻¹; and finally, high cost, which probably represents the main limitation to the application of inorganic membranes [6].

According to Scott [1], in organic or polymeric membranes, mechanical properties, chemical, thermal, and permeation, are influenced by the state of the molecular structure of polymer. Important parameters that directly influence the performance of a polymer membrane are the degree of crystallization and glass transition temperature, Tg. A polymer splits into two states: the glassy state and the gummy state (flexible). In the glassy state, the mobility of polymer chains is very restricted. In the gummy state, there is a high mobility of polymer chains. The degree of crystallization of a polymer has a great influence on the polymer’s mechanical properties and transport phenomena. Generally, it is desirable to use a polymer that is chemically and thermally stable. Materials with high glass transition temperature, high melting point, and high degree of crystallization are desirable. Crystalline polymers exhibit high thermal and chemical stability and are generally used in MF membranes. Noncrystalline polymers, amorphous, with high glass transition temperature are usually recommended to UF membranes such as PS and polyethersulfone (PES).

According to Cheryan [6], polyethersulfone is a polymer widely used in membrane MF and UF, due to several favorable characteristics, such as high heat resistance, up to 125°C; in some cases, polyethersulfone is tolerant to pH of 1–13, and this is a great advantage for cleaning purposes, good resistance
to chlorine, and some manufacturers provide solutions up to 200 mg kg\(^{-1}\) of chlorine for cleaning and 50 mg kg\(^{-1}\) for the storage of the membrane; the versatility of polymer for the manufacture of membranes in a variety of settings and modules; wide range of pore sizes available for use in MF and UF, ranging from 1 kDa to 0.2 \(\mu\)m in commercial membranes, good resistance to hydrocarbons, alcohols and acids.

### 23.5 Characteristic Aspects of Membrane Processes

In the first minutes of an UF process occurs a very sharp initial drop in the permeate flux, which is mainly due to the polarization of concentration. This polarization, which is basically a function of hydrodynamic conditions of the process, grows fairly rapidly to the subsequent formation of the gel layer polarization. In the second stage, which occurs more slowly, the flow rate continues to decrease due to the effect of interactions between the material making up the membrane and the solute, a process known as fouling. In the third stage, when the process has reached an almost stationary state, a phase occurs where the flow rate decreases very slowly, remaining almost constant, due to particle deposition and the consolidation of fouling. There is a phase where the flow decreases quite slowly due to particle deposition and consolidation of the fouling.

The polarization of concentration occurs when hydrocolloids, macromolecules (proteins), or other large particles, compared with the pore membrane, are rejected and they begin to accumulate on the surface thereof. This buildup can cause an increase in resistance to the solvent permeation and lead to higher local osmotic pressure. If transmembrane pressure and solute concentration in the feed stream are large enough, the particle concentration can increase to form a layer of gel, known as the gel polarization layer, which will act as a second membrane. The flow of solute to the membrane surface due to convection is balanced by the flow of solute passing through the same plus the diffusive flow originating on the surface due to concentration gradient formed with the current supply. Steady-state conditions are reached when the convective transport of solute to the membrane is equal to the sum of the permeate flow over the diffusive transport of solute in the opposite direction to the permeate flux. Many attempts to explain the mass transfer phenomena in the gel layer polarization were made, the most popular based on the theory of film, which assumes the presence of a boundary layer of certain thickness, which is the diffusion of solute from the membrane surface for the supply current [2,6,11].

Fouling is a phenomenon in which the membrane adsorbs or interacts in some way with the solute of the supply current, resulting in decreased flow and/or increased rejection of solute by the membrane. Unlike the polarized gel layer, fouling is generally not reversible or time dependent. As a result of the interaction between the membrane and various solutes in the solution, or even between solutes adsorbed on the membrane and solutes present in the feed stream, the fouling can result from three main factors or interaction between them: the properties of the constituent material of the membrane, the properties of the solute, and operational parameters [6].

The polarization of concentration can facilitate the irreversible membrane fouling by altering interactions between the solvent and the solute. The key to understanding the phenomenon of fouling is in the chemical composition of the membrane structure, in the interaction between solute and membrane, and in the interaction between the molecules of solute present. In particular, the interaction between membrane and solute will determine the fouling formed by the adsorption of solute molecules on the membrane surface.

The ways in which pores are blocked are presented as a function of the size and shape of the solute and dispersion of the membrane pore size. The complete blockage of pores occurs when particles deposited on the membrane surface are larger than the pore size of the membrane, completely blocking the pores, and the effect on mass transfer due to reduced area of membrane permeation depends on the tangential velocity of flow that can lead to increased transmembrane pressure applied. The partial blockage of pores occurs when macromolecules alone or grouped partially seal the pores and then form a layer (cake) on the membrane surface, increasing the resistance to permeation. The internal pore blocking occurs when chemical species are adsorbed or deposited inside the pores of the membrane, reducing the amount available to the passage of permeate.

Concentration polarization occurs when hydrocolloids, macromolecules (proteins), or other particles with larger dimensions as compared with the diameter of the membrane pore are rejected and accumulate on the surface of the membrane. This accumulation can cause an increase in resistance to solvent passage and lead to a greater local osmotic pressure. If transmembrane pressure and solute concentration in the feed flow are sufficiently large, the particle concentration can increase to the point of precipitation, forming a gel layer known as a polarized gel layer, which functions as a second membrane. Many attempts have been made to explain mass transference through the polarized gel layer, the most accepted being based on the theory of films, where one assumes the presence of a limiting layer of a determined thickness, where solute diffuses from the membrane surface to the feed flow [2,6,11].

Fouling is the result of the interaction between the membrane and diverse solutes present in the solution, or even between solutes adsorbed onto the membrane and solutes present in the feed flow. This phenomenon can be the result of three main factors or interaction between them: the properties of the material constituting the membrane, the properties of the solute, and operational parameters [6].

The different ways in which pores become blocked are a function of the size and form of the solute in relation to the pore size distribution of the membrane. The complete blockage of pores occurs when particles that deposit on the membrane surface are larger than the pores, completely...
obstructing them. The partial blockage of pores occurs when isolated macromolecules or groups of them partially seal the pores, with the possibility of forming cake on the membrane surface, increasing the resistance to permeation. The internal blockage of pores occurs when chemical species are deposited or adsorbed on the inside of the pores, reducing the volume available for the passage of the permeate.

23.6 PHYSICAL OPERATIONAL PARAMETERS IN MEMBRANE PROCESSES

The main physical operational parameters that affect the permeate flow rate are as follows: pressure, temperature, viscosity and density of the feed fluid, and the tangential velocity [13].

The permeate flow rate is directly proportional to the pressure applied and inversely proportional to the viscosity. The viscosity can be controlled by two factors: solids concentration in the feed and temperature.

An increase in feed concentration alters the viscosity, density, and diffusivity of the feed solution, causing a decrease in permeate flow rate [7]. An increase in temperature results in a decrease in fluid viscosity and increase in molecular mobility, that is, in diffusivity. For its part, an increase in tangential velocity increases the permeate flow rate by provoking greater turbulence, causing a dispersion in the solute molecules concentrated on the membrane surface, reducing the thickness of the gel layer. This is one of the simplest and most effective methods to control the effect of concentration polarization [6,14,15].

In membrane processes, an increase in pressure results in a greater convective rate for the transport of solute to the membrane surface, increasing its concentration at the interface, causing an increase in the diffusivity of the solute in the opposite direction to that of the process pressure, and thus decreasing the permeate flow rate [2,16].

There is a linear relationship between flow rate and the inverse of the solvent viscosity for NF and UF membranes, indicating that the main mass transport mechanism in these systems is convection. In the majority of UF membranes, this linear relationship between flow rate and the inverse of the solvent viscosity remains independent of the concentrations of organic solvents miscible with aqueous solutions [17].

The configuration (flat sheet, tubular modules, hollow fibers, plates units, and spiral wound) also affects membrane performance. Good membrane performance with respect to permeate flow rate and the retention of the desired solute should be balanced with respect to its characteristics such as propensity for fouling, cost, ease of cleaning, and substitution [2,6].

23.6.1 MAIN PHYSICAL PARAMETERS THAT AFFECT PERMEATE FLUX IN MEMBRANES

The main operating physical parameters that affect permeate flux are as follows: pressure, temperature, viscosity, and density (related to the concentration of solutes) of the feed, tangential velocity, and filtration mode (perpendicular/tangential).

For pure water or other solvents, there is a linear relationship between permeate flux and transmembrane pressure up to a certain limit. With a solvent-solute model as feed, there is the tendency of the flow curve reach an asymptotic behavior with increasing pressure. This is due to several phenomena, including the concentration polarization, gel layer formation, fouling, and osmotic effects. Flow values are also dependent on temperature; that is, these values generally increase with increasing temperature as a result of the decrease in the viscosity and diffusivity of the fluid supply [1].

The permeate flux is directly proportional to the applied pressure and inversely proportional to the viscosity of the fluid supply. Viscosity is controlled primarily by two factors: concentration of solids from the feed solution and temperature. The increase in temperature or pressure increases the permeate flux. However, the use of high pressure can cause compression of the gel layer, increasing the pore plugging of the membrane. This is partially true and depends on certain conditions, such as low pressure, low concentration of solids in the fluid feed, and high permeation speed. When the process deviates from any of these conditions, the flow becomes independent of the applied pressure. The increase in the concentration of solutes affects the viscosity, density, and diffusivity of the feed solution, causing a decrease in the permeate flux. In general, higher temperatures provide higher permeate flux in regions where there is pressure control and mass transfer. The effect of temperature is caused due to the reduction in fluid viscosity and the mobility of molecules, that is, the diffusivity. The increase in tangential velocity increases the rate of permeation to cause more turbulence. The turbulence from agitation or pumping flow causes a disruption in the concentration of solutes on the membrane surface, reducing the thickness of the boundary layer. This is one of the most simple and effective methods to control the effect of concentration polarization [14].

There is a linear relationship between flow and the inverse of the viscosity of the solvent. In membranes for NF and UF, the main mechanism of mass transport in these systems is by convection. In NF membranes, the differences in concentration of organic solvents in aqueous solutions (water miscible such as ethanol) could be influencing the primary mechanism of mass transport, and concentrations of ethanol up to 50%, the viscosity was the main factor, while above this percentage, other physical properties such as molar volume of solvent and surface tension, ruled the behavior of permeation. In contrast, In most of the UF membranes, the linear relationship between the flow of solvent and the inverse of viscosity remains independent of the concentrations of organic solvents miscible in aqueous solutions [17].

Similarly, Shukla and Cheryan [18], studying the behavior of the permeation of 18 UF membranes, found that 15 of these membranes agree with the Darcy model, in which the permeate flux decreased in linear correlation with the increasing viscosity of the permeation solvent, indicating that in these 15 UF membranes, the transport phenomenon of the solvent was affected by viscosity.
The setting also affects the performance of membranes. The high performance of a membrane on the permeate flux and solute retention desired must be balanced on the characteristics of it, likely pore plugging behavior, low cost, easy cleaning and replacement [2].

Assuming that fouling does not occur in the passage of fluid through the membrane, among other factors due to precipitation of salts, starch gelatinization or proteins denaturation, increased temperature leads to increased permeate flux through the membrane due to the effect this factor on the density and viscosity of the fluid, and increases the diffusivity of the same through the membrane [6].

The increase in the concentration of the solution leads to increased osmotic pressure, resulting in a decrease in the flow of solvent permeate through the membrane. In addition, high solute concentration causes an increase in the viscosity of solution, which leads to a decrease in the flow through the membrane. Solute size and very low molecular weight, when present in a highly concentrated solution, may plug the pores of the membrane, thereby decreasing the flow through the same [13].

An increased pressure in membrane processes results in a higher rate of convective transport of solute to the membrane surface and an increase in the concentration of the interface, which leads to increased diffusivity of solvent in the opposite direction to which the process pressure acts by decreasing the permeate flux [2].

In a pressure regime high enough, the permeate flux becomes independent of the applied pressure, which is the critical flow of the process. The presence of a layer of particles trapped and compressed on the surface of the membrane leads to the maintenance of a constant pressure drop in the gel layer polarization, and this pressure is the critical pressure of the system. Considering that the thickness of the layer retained on the membrane surface is very small, relative to the diameter of the pore channel, we can neglect its effect in relation to the hydraulic conditions of flow, and thus, the flow on the surface can be given as zero, thus characterizing the critical flow.

When applying pressure that results in a flow less than the critical flux, the transmembrane pressure quickly stabilized at a new level, and the flow rate increased or decreased. On the other hand, an equilibration is achieved when in a flow greater than the critical, the transmembrane pressure decreases quite slow when the flow is decreased again. Even when the flow is reduced to critical levels, transmembrane pressure does not restabilize. This behavior of transmembrane pressure with the flow shows that the gel polarization layer formed on values above the critical flow begins to be consolidated into a structure resistant to redispersion.

The time required for the UF process reaches a steady state, which decreases with increasing flow rate, while the permeate flux, with the process already in steady state increases with increasing fluid velocity. The increase in tangential velocity may also decrease the accumulation of solute on the membrane surface and thereby increase the permeate flux [15].

A process of membrane filtration can be conducted for a long time without a significant change being observed in the permeate flux, provided that it is performed at a low pressure so as not to reach the critical flow. By increasing the pressure of work can the formation of fouling be increased, causing a rapid decline in permeate flux.

The asymptotic relationship between pressure and flow is due to the effect of the concentration polarization. At low pressure, low solute concentration of the feed, and high fluid velocity, the effects of the concentration polarization are minimal and the permeate flux is affected by transmembrane pressure. Deviations from the linear relationship between flow and pressure are observed at high pressures, independent of other operating parameters, due to the consolidation of the polarized gel layer of the solute.

The gel layer is dynamic, thus changing operating conditions, such as reducing the pressure or the concentration of feed solutes or increasing the speed of the feed; you can revert the system to an operating system controlled by pressure. If, however, the fouling is consolidated, the permeate flux does not return to original levels, except after the cleaning procedures of the membrane.

The flow in the region regardless of the pressure can be controlled by the efficiency in reducing the thickness of the boundary layer and increasing the rate of the transfer of polarized molecules back to the center of feed, transport by diffusion, which opposes the flow of solutes by convection toward the surface of the membrane [6]. Regarding the effects of temperature in increasing flux, the rate of permeation is inversely proportional to the viscosity of the fluid, and since the viscosity of the solvent decreases with increasing temperature, have been found experimentally in many cases filtration membranes that permeate flux increases 3% on average, per °C increase in temperature, in aqueous systems [2]. The initial applications in filtration by membranes were performed by a designed mode in which the fluid permeated perpendicular to the membrane (dead-end mode). This classic mode of filtration is marked by the concentration polarization, fouling, and formation of cake on the membrane surface, leading to a sharp decline in the flow and hence the inefficiency of the process (Figure 23.6).

While this mode of filtration is very simple, in virtually all cases, the principle of cross-flow filtration has been used (cross-flow mode). In this technique, the fluid is pumped in parallel to the membrane surface, thus reducing the hydraulic stagnant layer, where there is turbulence, and reducing the intensity of the concentration polarization and fouling (Figure 23.7).

The cross-flow filtration is often used in combination with the procedure known as backflushing, whereby the filtration flow is reversed for a short period of time so that particles or molecules very attached are removed from the membrane surface. The speed of cross-flow filtration, transmembrane pressure, and the frequency of backflushing are important process parameters, which are optimized to obtain low fouling, high permeate flux, and low energy costs. In many such
while low pressure is used to avoid the compression of the gels on the surface [2].

However, although the permeate flux can be increased by the increase in tangential velocity, the pressure drop in the supply channel can become very high and result in large reduction in transmembrane pressure, causing the process failure. It is necessary to optimize the speed and configuration of the membrane to obtain higher filtration efficiency [1].

### 23.7 PHENOMENA THAT AFFECT THE PERMEATE FLUX

The main factors extrinsic to the membrane, that is, that occurs or acts independent of their type and that cause interference with the permeate flux, leading to its decline during the process are: the phenomenon of polarization near the surface of the membrane, gel layer formation—polarized and/or phenomenon of impregnation in the membrane (fouling).

In principle, all the membranes can be considered as selective filters, which are more permeable to certain compounds than others. This means that, at the molecular level, there is an increase in the concentration of retained molecules toward the membrane surface. This phenomenon is known as the concentration polarization. Molecules retained on the membrane surface, but also dissolved, form an additional resistance to permeation of the solvent, leading to a decline in the flow. However, the concentration of solutes near the membrane interface can reach such high values that promote the formation of a gel layer, this phenomenon occurring with great intensity in proteins. The formation of the gel layer is often referred to as fouling of the membrane and is irreversible or, at best, only partially reversible. The fouling of the membrane can also be caused by other phenomena, such as the adsorption of molecules and occlusion or closing of the pores of the membrane. In adsorption, molecules are smaller than the diameter of pores, but instead of moving freely, molecules get stuck to the wall thereof, while in occlusion, molecules are of the size close to the pores of the membrane. These molecules are forced to pass through the pores, by applying pressure during the process, thus leading to blockage of the pores. An immediate and reversible decline in the flow through the membrane can be due to the concentration polarization, while a long-term decline is due to irreversible fouling in the membrane, which in turn is attributed to the formation of gel layer by the evolution of the concentration polarization, adsorption, and occlusion of its pores. Both the concentration polarization and the fouling usually occur in all the processes of filtration membranes, but their effects are more important in MF, UF, and reverse osmosis [5].

If the fouling is present in the membrane as a result of the filtration process, the deposited material can, in some cases, be removed by aggressive cleaning agents such as detergents, acids, bases, or organic solvents. The advantage of using a chemically resistant membrane is that powerful cleaning
agents can be used. However, even with regular cleaning, the permeate flux do not can be always restored to initial levels, resulting in fouling in the long-term [2]. This phenomenon is a residual fouling, limiting the operational life of the membrane.

23.8 MEMBRANE–SOLVENT–SOLUTE MOLECULAR PHYSICOCHEMICAL INTERACTIONS

The mechanisms of separation by membrane processes are complex. Many variables such as composition of membrane, method of membrane manufacturing, shape and configuration of the molecules, their interactions with each other and the membrane surface, fluid dynamics of the membrane unit, and pressure, temperature, and velocity of the mixture influence the separation process [4].

Two important factors that control the efficiency of membrane separations are size exclusion and chemical interaction between membrane surfaces and bulk species. Adsorption of bulk species to membrane surfaces is frequently cited as the primary cause of fouling, which results in pore plugging [19].

It is discussed that fouling is initiated by solute–membrane material interactions. Chemical binding, van der Waals forces, and electrostatic and Lewis acid–base interactions are the main phenomena involved in the interactions occurring between surfaces and solutes on a molecular level. In consequence, physicochemical properties of membrane surfaces are changed, and this facilitates the deposition of other molecules and aggregates [20]. Also, membrane–solvent interactions can be expected to vary with changes in the solvent properties, such as viscosity, molecular size, surface tension, and dielectric constant [21].

The particles brought into the surface of the membrane by convection can interact with the membrane by adsorption, by physically blocking the pores, or by acting on a surface or inside the pores and then stay connected to other particles in the gel layer polarization. At sufficiently high concentrations, these particles can form a cake on the membrane surface. If repulsive forces are weak and/or convective forces are strong, the particles can bind to a layer structure in a reversible or irreversible state.

The MF process is used to reject particles in the range of 0.05–10 µm, while UF rejects the particles on the order of 1–50 nm. The transport of solvent, carried out by convection, is directly proportional to the applied transmembrane pressure, which can be described, among other models, by the Hagen–Poiseuille model.

Adsorption occurs as soon as the membrane surface is in contact with the solution (macromolecular), when solute molecules adsorb on the membrane surface due to chemical and physical interactions, for example, hydrophobic interactions (dispersion forces) and polar interactions (dipole–dipole and induced dipole). The nature of the membrane material, the type of solute, the solute concentration, ionic strength, and pH are parameters that determine the extent of adsorption [11].

The relationship between the type of solvent, polar or non-polar, and the type of membrane, hydrophilic or hydrophobic, used in separation processes must be carefully analyzed. Polar solvents have significantly higher flow (8–10 times) than nonpolar solvents in processes carried out in hydrophilic membranes. In turn, nonpolar solvents have a flow of 2–4 times greater than polar solvents in hydrophobic membranes. As examples can be cited the flux values obtained for the permeation of methanol (polar) and hexane (non-polar); in a pressure of 13 bar, through a hydrophilic membrane, resulting in flows, respectively, 18 and 2.52 L m⁻² h⁻¹. On the other hand was observed an opposite tendency in flux for the same compound and same pressure, when the process is conducted in a hydrophobic membrane, the flows obtained were, respectively, 21.6 and 10.8 L m⁻² h⁻¹ to methanol and hexane [22].

In the membrane separation processes, the importance of the effect of possible associations between the solute and solvent and the membrane material is quite clear. This behavior resulting in differential permeation rates of solutes due to these phenomena of interactions can be observed in the case of retention of Sudan IV, an organic compound of molecular weight equal to 384; in this molecule are present four aromatic rings, and its rejection by a hydrophobic membrane was 25% and 10%, respectively, when dissolved in n-hexane, at a pressure of 15 bar, and methanol, 20 bar. Under the same conditions, a crossing of two solutions in a hydrophilic membrane was performed, resulting in the values of the retention of 86% for the compound in the solution of methanol and 43% for the same compound in the solution of n-hexane [23].

The interaction between the factors of molecular weight and solute rejection by the membrane can be observed by the results obtained in the analysis of the rejection of triacylglycerols present in a solution of n-hexane, where for higher molecular weights higher percentage of rejection is obtained. As examples of these findings, in the same pressure and temperature, the values of retention were 92% and 72%, respectively, for molar weight equal to 807 and 554 [23].

In a study of the interaction of three different membranes, two synthetic polymers and cellulose, and solutions containing different concentrations of dextrose, was evaluated the relative reduction of water flow, given in percentage, the difference between the flow before and after solute adsorption divided by flow prior to adsorption. In SG-PES and PES-GR polymeric membranes, water flux declined of about 4%–12% and 11%–15% respectively, while for the cellulose membrane was not observed a significant reduction in the flow, indicating a significant adsorption of dextrose on the surface of membranes made of synthetic polymers (more hydrophobic). The significant difference in the reduction of the flow in the membranes of synthetic polymers is due to differences in the characteristics of the membrane surface [12].

In the process of membrane separation performed in the mixture of soybean oil and hexane, it can be observed that the decrease in pore diameter of the membrane leads to greater efficiency. Hexane having a lower viscosity, a lower molecular
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According to Guizard et al. [28], different approaches like the models proposed by Machado et al. [26] and Bhanushali et al. [22] stress the complexity of mechanisms involved in organic solvent permeation through polymer membranes. A simple permeation model comparable to Darcy’s law ($J = L \Delta P/\eta$) or Fick’s law widely used for aqueous systems still remains to be found for organic solvents.

### 23.8.1 Transport Phenomena in Membrane Processes

In membrane processing, the basic relationship between applied pressure, osmotic pressure, and flow of solvent through a membrane is expressed in terms of the flux and the driving force and resistance. For an ideal semipermeable membrane,

$$J = A x (P T - \pi F)$$

where

- $J$ is the flux
- $A$ is a membrane permeability coefficient (the reciprocal of resistance flow)
- $PT$ is the membrane pressure
- $\pi F$ is the osmotic pressure of the feed solution

Thus, there has to be a positive driving force; that is, $PT$ must be always greater than $\pi F$. Since MF and UF are design to retain only the larger dissolved solutes, it is assumed that the prevailing osmotic pressures in UF and MF are usually low enough to ignore, and thus, the operating strategy will be maximizing mass transfer effects and control viscosity. In RO and NF, osmotic pressure effects are likely to be the dominant resistance [6].

All membranes can be regarded as selective sieves that are more permeable for certain compounds than others. This means that on a molecular level, in the direct proximity of the membrane, a buildup in the concentration of the retained molecules occurs. Convective transport of solute to the membrane will cause a steep concentration gradient within the boundary layer and causes a back transport of the solute into the bulk because of diffusion. No more solute molecules can be accommodated because of the close-packed arrangement and restricted mobility of solute molecules. This phenomenon is called concentration polarization and could cause the solute to precipitate out and foul the membrane. Membrane fouling can also be caused by other phenomena, such as the adsorption of molecules on pore wall and plugging of pores. Hence, a reversible and direct decline in flux across the membrane might be defined as concentration polarization, whereas irreversible and long-term decline in flux termed membrane fouling generally occurs in every membrane processes [5, 21].

UF and MF membranes separate on the basis of a simple sieving mechanism. The particle relation dimensions or pore size distribution of the membrane determines whether a particle can pass through the membrane. Reverse osmosis and pervaporation are able to separate molecules that have comparable sizes. In such cases, the affinity between the membrane and the target component is important, as well as the velocity of the molecule permeating the membrane. Molecules that have greater affinity for the membrane...
material dissolve more easily in the membrane than other molecules, and the membrane plays as an extraction phase. Differences related to diffusion coefficients of the molecules across the membrane causes separation. According to the solution–diffusion theory, solubility and diffusivity together determine the membrane selectivity [2,6,11,13].

According to Cuperus and Nijhuis [5], the mechanisms in which NF membrane works are not completely clear. Possibly both size exclusion and solution–diffusion mechanisms play a role. This is in agreement with the work of Subramanian et al. [29]. These authors observed that solution–diffusion is the predominant mechanism of the transport of vegetable oil constituents through nonporous (dense) membranes. The effect of viscosity (temperature) on permeation suggests that transport by convective flow exists in these membranes but the extent observed is not significant.

Cheryan [6] reported two models to explain the mass transport through membranes.

### 23.8.1.1 Pressure Controlled Region

In an ideal situation, for example, with uniformly distributed and evenly sized pores in the membrane, with no fouling, negligible concentration polarization, etc., it is generally believed that the best description of fluid flow through micro-porous membranes is given by the Hagen–Poiseuille law for streamline flow through channels. This model relates pressure drop, viscosity, density, and channel dimensions (such as diameter of a tube) to flow rate through the channel. One form of the model useful in membrane processing is as follows:

\[
J = \frac{q_d d_p^2 PT}{32 \Delta \chi \mu}
\]

where

- \( J \) is the flow rate through the membrane
- \( d_p \) is the channel diameter (in this case, the mean pore diameter)
- \( PT \) is the applied transmembrane pressure
- \( \mu \) is the viscosity of the fluid permeating the membrane
- \( \Delta x \) is the length of the channel (the membrane skin thickness)
- \( \phi \) is the surface porosity of the membrane

To assume these statements, several assumptions have been made in deriving the model shown: laminar flow, that is, \( Re < 2100 \); constant density, that is, incompressible liquid; steady-state conditions; newtonian fluid; and, finally, negligible end effect.

According to the model, flux is directly proportional to the applied pressure and inversely proportional to the viscosity. For Newtonian fluids, viscosity is primarily controlled by two factors: solids concentration (or feed composition) and temperature. Thus, increasing the temperature or increasing the pressure should increase the flux. This happens only under low pressure, low feed concentration, and high feed velocity. When the process deviates from any of these conditions, flux becomes independent of pressure, sometimes even at quite low pressure.

### 23.8.1.2 Mass Transfer Model

One of the simplest and widely used theories for modeling flux in pressure-independent mass transfer controlled systems is the film theory. As solution is ultrafiltered, solute is brought onto the membrane surface by convective transport at a rate, \( J_s \), defined as follows:

\[
J_s = JC_B
\]

where

- \( J \) is the permeate flux (volume/time)
- \( C_B \) is the bulk concentration of the rejected solute

The resulting concentration gradients cause the solute to be transported back into the bulk of the solution due to diffusional effects. Neglecting axial concentration gradients, the rate of back transport of solute will be given by the following:

\[
J_s = D \frac{dC}{dx}
\]

where

- \( D \) is the diffusion coefficient
- \( dC/dx \) is the concentration gradient over a differential element in the boundary layer

At steady state, the two mechanisms will balance each other, and permeate flux can be equated and integrated over the boundary layer to give:

\[
J = \frac{D}{\delta} \ln \frac{C_G}{C_B} = k \ln \frac{C_G}{C_B}
\]

where

- \( C_G \) is the solute concentration at the membrane surface
- \( \delta \) is the thickness of the boundary layer over the concentration gradient
- \( k \) (\( D/\delta \)) is the mass transfer coefficient

According to Cheryan [6], neither of the two models discussed the entire pressure flux behavior observed during typical UF and MF. A better approach that describes the entire pressure flux behavior observed during typical UF or MF is the resistance in the series concept. For an ideal membrane and feed solution, flow rate through the membrane can be rewritten as follows:

\[
J = A \frac{PT}{\mu}
\]

where

- \( A \) is a membrane permeability, which includes the terms characteristic of the membrane itself
- \( \mu \) is the viscosity of the permeate
For a particular feed solution at a given temperature, viscosity is usually included with the A value and can be written as 1/Rₘ, where Rₘ is the intrinsic membrane resistance:

$$J = \frac{PT}{R_m}$$

In actual operation with a real feed, the membrane resistance may be only a small part of the total resistance. Other resistances can be added to the intrinsic membrane resistance:

$$J = \frac{PT}{R_m + R_f + R_g}$$

where

- Rₗ is the fouling resistance
- R₇ is the additional resistance caused by concentration polarization and the boundary layer

Kim et al. [21] reported that several operating parameters can affect the mass transport through membrane (micellar permeation rate). In general, higher temperature will lead to higher flux in both the pressure-controlled region and the mass transfer-controlled region. In the pressure-controlled region, the effect of temperature on flux is due to its effect on fluid density and viscosity. Diffusivity also increases with temperature. As a natural result, with increasing micelle concentration, the flux decreases due to the increase in viscosity, higher osmotic pressure of the gel layer, and thicker concentration polarization layer. Another factor, turbulence, has a large effect on flux in the mass transfer-controlled region. The turbulence of the fluid near the membrane surface sweeps away the accumulated solute, reducing the hydraulic resistance of the cake and the thickness of the boundary layer and controlling the effects of concentration polarization by reducing the thickness of the gel layer.

23.9 ASPECTS OF PHYSICAL CHEMISTRY AND PROCEDURES IN MEMBRANE CONDITIONING TO IMPROVE PERMEATE FLUX, STABILITY TO SOLVENTS, AND SOLUTE RETENTION

The extraction of vegetable oil is usually carried out by hexane. The miscella formed in this process is evaporated to separate the oil from this solvent. This practice requires considerable amount of energy (around 530 kJ per kg of oil), since it involves the phase change of the solvent. Additionally, the explosive vapors generated in the industrial plant represent a security problem. These limitations can be partly solved by membrane technology; that is, miscella can be pumped through a suitable membrane, which is permeable to solvent and holds the oil. Permeate (containing essentially pure solvent) would be recycled, while the retentate passes through successive stages of membrane units to maximize the recovery of solvent and minimize the amount of solvent to be evaporated. Both reverse osmosis membranes and NF membranes are suitable for separating the oil (triacylglycerols) of the solvent. However, few commercially available membranes are stable to hexane [30].

Parameters of flux behavior, performance and chemical stability of the compounds polymeric are critical in membranes resistant to organic solvents. Many commercially available membranes have low stability to nonpolar hydrocarbons, as hexane. Several membranes composed of PVDF are also destroyed by hexane, possibly due to the incompatibility of the membrane composite support material to this solvent [31].

Polymeric membranes are resistant to solvents but do not cover all potential applications. According Van der Bruggen et al. [32], chemical stability of polymeric membranes can be improved through various factors: polymeric superficial layer (top layer) cross-linking degree increase; alternative materials for membranes, such as polyorganophosphazene making cross link with polyurethane; adding polydimethylsiloxane and PI or improvements of common materials such as PAN.

Experimental observations and semiempirical models have shown that the permeation of organic solvents through polymeric membranes is not only based on the viscosity or molecular diffusion but also depends on additional parameters caused by the phenomena of interaction between the solvent and the membrane (surface tension, sorption, hydrophilicity, or hydrophobicity interface). According to Araki et al. [31], typical polymeric membranes are manufactured as aromatic PA, PS, and cellulose acetate, among other polymers. These compounds have both hydrophilic and hydrophobic sites in their structures. In dense membranes (nonporous), the water permeation process is, typically, a diffusion activated through numerous hydrophilic sites. Residual charged groups in polymeric chains (e.g., carbonyl) facilitate water transportation by increasing the sorption capability of this solute. However, in most nonaqueous systems, the permeate flux through such membranes containing hydrophilic sites would be considerably lower than the water flux.

Ceramic membranes, on the other hand, present some differences, the rigidity of the porous network and the absence of the phenomenon of sorption, in addition to being resistant to organic solvents. However, the modeling of the permeation of organic solvents in porous ceramic membranes is very incipient [28].

Typical membranes are made of polymers such as aromatic PAs, PS, of methyl cellulose acetate, among others. These materials have both hydrophilic and hydrophobic sites in their structures. In dense membranes (nonporous), the process of permeation of water is typically activated by a diffusion of many hydrophilic sites. Charged residual groups present in polymer chains (e.g., carbonyl) facilitate the transport of water by increasing the sorption capacity of solute. Hence, the presence of other solutes, the water is preferentially transported through these hydrophilic sites, then leading to high rates of permeation. However, in most nonaqueous systems, the permeate flux through such membranes containing hydrophilic sites would be considerably less than
that of water, because of links type hydrogen bond, which are limited in alcohol and absent in hydrocarbons [22].

Hydrophilic membranes have a higher difference in the flow due to pure solvent polarity when compared with hydrophobic membranes. According to Bhanushali et al. [22], the permeation of pure solvents in hydrophilic membrane (composed of aromatic PA) shows that polar solvents (methanol, ethanol, and isopropanol) have significantly higher flow (8–10 times) than nonpolar solvents (pentane, hexane, and octane). In contrast, the flow of nonpolar solvents was two to four times greater than the flow of polar solvents on hydrophilic membranes (consisting of dimethyl silicone).

The permeation of binary mixture of ethanol/hexane showed that transport through dense membranes (solvent stable) occurs by couple diffusion, while for porous membranes transport has a convective nature. It was shown that permeation through dense membranes is more affected by mutual affinities of membrane and solvent, whereas viscosity is the major transport parameter for porous membranes [33].

Not only the flow but also the stability of polymeric membranes used in organic solvents is critical. Many commercially available membranes have low stability in nonpolar hydrocarbons such as hexane. Some membranes composed of PVDF are also destroyed by hexane, probably due to the incompatibility of the material used for membrane support in this solvent. The understanding of interactions between membrane material and solvent is then essential to the development of materials and the optimization of filtration [22].

According to Van der Bruggen et al. [23], the surface layer structure of a membrane can be modified upon exposure to organic solvents. Consequently, flux and rejection are modified in the function of the time that the membrane is exposed to solvents. Because these modifications in polymeric chain structures are dependent on the interaction between solvent and time exposure, the concept of membrane stability toward organic solvents becomes ambiguous.

In a study of conditioning of polymeric membranes in organic solvents, Van der Bruggen et al. [23] submitted hydrophilic membranes (composed of polyethersulfone) and hydrophobic membranes (polymeric composition not reported) at a pretreatment consisting of 24 h of the immersion of membranes in ethanol (for flows with ethanol) or hexane (for flows with hexane). These authors found that the pretreatment of the membranes with ethanol increased the flow of solvent in the hydrophilic membrane and decreased the flow to the membrane hydrophobic. In the first case, this effect is explained by the decrease in the difference in surface energy between the solvent and the membrane, whereas in the latter case, the resistance to permeation of ethanol increases by increasing the difference in surface energy between the solvent and the membrane. This is achieved by reorganizing the structure of the membrane; that is, immersion in ethanol causes an effect of clustering in hydrophobic and hydrophilic groups in the surface layer of the membrane; thus, hydrophilic membranes become more hydrophobic (in addition to increased pore size), while hydrophobic membranes become more hydrophilic. These statements were supported by the images of scanning electron microscopy (SEM).

In previous conditioning with hexane, the hydrophilic membrane showed no flow of hexane when untreated, have become permeable to this solvent. This shows that the membrane structure changed to a less hydrophilic conformation, allowing the passage of hexane (reduced resistance to mass transport). These changes were not uniform and showed differences between samples due to the small membrane area (0.00024 m²) used in the experiments, leading to variability in the pattern of hexane flux in these membranes after pretreatment with this solvent [23]. According to Van der Bruggen et al. [23], parameters that reflect on hydrophilicity/hydrophobicity can also have a considerable influence on the rejection of solutes. Components in aqueous solution can be wrapped with a layer of water (hydration), which increases the effective size of this component, as this effect does not occur for components in organic solutions, the effective size of the particle will be smaller, reducing the rejection or retention of solute. Additionally, there is an increased mobility of polymer chains due to contact with organic solvents, increasing the average size of pores and, thus, further decreasing the rejection of the components. So, the concept of pore size is ambiguous in organic solvents, considering that polymer chains and, consequently, pores are not rigid. The rejection can drop dramatically due to this phenomenon. Therefore, the molar weight cutoff, determined in aqueous solutions, is not fully applicable in determining rejection properties of organic solvents. Consequently, the flow of solvents through polymeric membranes is highly dependent on the solvent properties. Among them, the most important is the polarity; an increase in solvent polarity decreases the flow in hydrophobic membranes and increases the flow in hydrophilic membranes, due to the fact that the polarity of organic solvents is strongly related to surface tension. These findings confirm the experimental observations obtained by Yang et al. [34] under which both the viscosity and surface tension are the main parameters that influence the flow of solvents in NF membranes.

For the retention of solutes, even when rejection in aqueous solution is high, the rejection of the same compound in organic solvents can be very low due to the absence of the formation of hydration shell around the solute (resulting in a smaller size) in the latter case. Finally, the structure of the surface layer of a membrane can be altered by exposure to organic solvents. As a result, flows (and rejection) are modified as a function of the time of exposure to solvents. Because these changes in the structure of polymer chains are dependent on the interaction between solvent and exposure time, the concept of stability to organic solvents becomes ambiguous [23].

According to Yang et al. [34], the molar weight cutoff (MWCO) rating specified by the manufacturer in polymeric membranes is only valid for predicting rejection in aqueous solutions, and the retention of solutes in organic solvents, molecules of the same molecular weight, or even for the same molecule is unpredictable and dependent on a specific solvent.
Despite the viscosity and polarity being the main parameters to influence the flow of solvents in polymer membranes (the latter related to surface tension), in addition, there is an interaction between membrane and solvent, which influences the mechanism of mass transport that depends on the type of membrane material and of the specific properties of the solvents and is thus important in determining the flow of the solvent. However, this is another mechanism of mass transport in organic solvents that has not yet been elucidated and needs a better understanding of the complex mechanisms of the specific interaction between solvent–solute and polymer [34].

The stability of membranes in organic solvents depends on the physicochemical characteristics of solvents and membranes. The interactions of solvents with membranes can result in dilation (swelling), plasticization, or dissolution of the membrane material, and subsequent change of membrane structure, leading to changes in the properties of separation and loss of mechanical resistance to pressure. The characteristics of solvents such as molar volume, solubility, viscosity, surface tension and dielectric constant, and properties of membranes as hydrophilicity/hydrophobicity and solubility play an important role in determining the stability of membranes [17].

Several experimental tests can be performed to determine the membrane resistance or chemical stability of polymeric membranes to organic solvents like hexane, such as test of area variation after hexane exposure (Table 23.5), permeation test with organic solvents along time (Figure 23.8), and SEM (Figures 23.9 and 23.10).

In Figure 23.8, it is seen that hexane flux along time remains constant in the six polymeric membranes studied, indicating that these membranes are resistant or showed chemical stability to this organic solvent and, thus, are suitable for applications in permeation processes with nonaqueous media such as oil-solvent micelle.

SEM is a technique that allows detecting more precisely polymeric degradation/integrity in membranes due to the attack of organic solvents, which can modify its micro- or ultrastructure. In Figure 23.9, it is clearly seen that the degradation of the polymeric matrix on solvent exposure occurs. In Figure 23.10, it is shown that in contrast, no visual modifications occur in polymer structure, indicating that this PA membrane was resistant (chemically stable) to hexane in the performed experimental conditions.

The intense solvent–polymer interaction can cause solvent immobilization in the polymeric matrix (intumescence), leading to the contraction of membrane pores.

Consequently, the permeate flux declines, as also observed in the compaction resulting from the physical compression of the membrane [35].

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Area of Intact Membrane (mm²)</th>
<th>Area after Treatment (mm²)</th>
<th>Area Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 CME</td>
<td>96.92a</td>
<td>96.92b</td>
<td>0.25</td>
</tr>
<tr>
<td>0.050 CME</td>
<td>91.62c</td>
<td>90.91c</td>
<td>0.00</td>
</tr>
<tr>
<td>0.050 PC</td>
<td>91.38d</td>
<td>90.69d</td>
<td>−0.02</td>
</tr>
<tr>
<td>30 PVDF</td>
<td>92.90e</td>
<td>92.90e</td>
<td>0.25</td>
</tr>
<tr>
<td>50 PVDF</td>
<td>94.68f</td>
<td>94.45f</td>
<td>0.27</td>
</tr>
<tr>
<td>10 PES</td>
<td>96.95g</td>
<td>96.71g</td>
<td>0.24</td>
</tr>
</tbody>
</table>

* Means followed by the same letter do not significantly differ, at 1% of probability, by the significance test for paired comparisons (Student’s t-test).

Among the factors that determine the permeation of organic solvents, Bhanushali et al. [22] included the solvent molar volume, surface energy, and sorption.

In the analysis of membrane-selective permeability, solvent characteristics are important parameters to be considered, among others [31]. According to Machado et al. [26], the specific permeability of a solvent depends mostly on its physical and chemical properties. Water, with 18 cm$^3$ mol$^{-1}$ molar volume, could penetrate polymer more easily than ethanol, with 58.5 cm$^3$ mol$^{-1}$, which would have a preference over hexane, with 131 cm$^3$ mol$^{-1}$ [26]. In addition, water permeation is favored by hydrophilic groups and charged sites present in polymers, helping in the convective flux that is determinant in this case. Therefore, the flux in nonaqueous systems would be considerably smaller since the formation of hydrogen bonds is low in the presence of alcohols, and the organic solvents do not form hydrogen bonds.

The polymeric membrane application in an organic medium should consider developing new materials or additives resistant to organic solvents so that they could contribute with hydrophobic characteristics that enable higher permeate flux. Moreover, Machado et al. [25] found no correlation between flow and molecular volume of organic solvents, and only the viscosity and surface tension (polarity) determined the permeation of the solvent.

There is a linear relationship between the flow and the inverse of the viscosity of the solvent in membranes for NF and UF, indicating that the main mechanism of mass transport in these systems is through convection. In NF membranes, differences in the concentration of organic solvents dissolved in aqueous solutions (water miscible such as ethanol) is most to represent the primary mechanism of mass transport and concentrations of ethanol up to 50%, the viscosity was the main factor while above this threshold, other physical properties such as molar volume of solvent and surface tension, ruled the behavior of permeation. In contrast, in most of the UF membranes, the linear relationship between the flow of solvent and the inverse of viscosity remains independent of the solvent concentrations in aqueous solutions [17]. Membrane manufacturers usually provide them semidry or immersed in water. It is an important condition in most polymeric membranes before use with organic solvents. Conditioning comprises rinsing the membrane and permeation of solvent under appropriate pressure in order to remove impurities and wetting the surface membrane and inside of the pores. Conditioning ensures complete contact of the membrane with the solvent, facilitating the permeation and increasing the performance of the membrane.

The method of conditioning has a marked effect on the flow and structural integrity of the membrane and improves the levels of work pressure in polymeric membranes [17].

According to Vandezande et al. [36], thin-film composite (TFC) membranes’ performance can be increased through an adequate postpolymerization treatment (conditioning). Different techniques have been described, including heat treatment, ultraviolet, and chemical treatment. For example, the membrane’s active-layer treatment with ammonia or certain alkylamines under high temperature has been tested in order to increase permeate flux without solute’s rejection. Similarly, additives usage may allow an initially polar media projected membrane’s application in an apolar media. For instance, polydimethylsiloxane can be added in the intermediate layer of a PA membrane to the polymerization. The resultant membrane from polymer (PA) and the additive (silicon) presents high permeability to hexane. To improve separation performance in an asymmetric membrane and promote its stability in the long term, many posttreatment or conditioning procedures can take place, such as promoting an annealing or structural strengthening, form cross molecular bindings, drying through solvent change and conditioning agents treatment.

According to Shukla and Cheryan [18], in many cases, there were breaks in the polymeric matrix of UF membranes that were not properly conditioned. Conditioning promotes a gradual change in the membrane, minimizing the degradation of pores. Shukla and Cheryan [18] studied the effect of conditioning on the performance of UF polymeric membranes in solutions with various concentrations of ethanol in water. These authors analyzed membranes made of materials such as PS, polyether-sulfone, PAN, PVDF and methyl cellulose acetate. Methods of conditioning consisted of gradual change in the levels of ethanol in aqueous solution at 0%–70%, with the increase of 10%–10% (method 1), a direct change of 0%–70% ethanol (method 2), exposure to direct solution of 70% ethanol (method 3), and reduction from 100% to 70% ethanol (method 4). After each conditioning method, the membranes were tested for flow and rejection of zein (protein present in corn, soluble in ethanol,

![SEM of a single polymeric (PA) membrane. (a) Intact membrane before treatment. (b) Membrane after 48 h of immersion in hexane. Magnification: 15,000×. (From Author’s personal collection.)](image-url)
and with a molecular weight of 22,000 Da, approximately. The conditioning data were expressed in terms of a model of mass transport by convection \(J = LPPT/\mu\), where \(J\) is the flow, \(PT\) the transmembrane pressure, \(\mu\) the viscosity of permeate, and \(LP\) represents the coefficient of permeability of the membrane. Membranes which were not affected by the solvent shows a linear relationship between the flow and the inverse of viscosity, especially when a significant effect of solvent on the membrane, leading to swelling of the polymer and pore dilation, this relationship was not linear. Since the viscosity of solutions of ethanol is maximum at 50% concentration of this solvent in water, the flow should show a corresponding minimum at this concentration of ethanol, assuming that the membrane is not affected by the solvent in any other way. This phenomenon is governed by Darcy’s law and Hagen–Poiseuille law, according to the equation mentioned earlier. From 18 UF membranes tested, 15 were submitted to the Darcy model, in which the flow decreased in linear correlation with the increased viscosity of the permeation solvent. These results indicated that in these 15 UF membranes, the transport phenomenon of solvent was affected by the viscosity parameter. Regarding the effect of conditioning methods on the permeability and on the rejection of protein, the results indicated that in some cases (combination of method/membrane), where the solvent flows were high (as in the membrane composed of PVDF, conditioned by methods 2 through 4), the probable reason was attributed to an expansion of pores, which thus resulted in the low rejection of protein (zein). Membranes conditioned by method 1 (gradual change of 0%–70% of ethanol solution in water) maintained its integrity (as shown by the increased flow of solvent in relation to pressure) and had high rejection of zein. Membranes conditioned by other methods resulted in low rejection of protein, in almost all cases. Some membranes that showed high rejection of zein at low pressure (138 kPa) have become permeable to this protein at high pressure (>275 kPa). This occurred because solvents tend to decrease the glass transition temperature of polymers, acting as plasticizers, which in turn reduces the ability of polymer to withstand high pressure. Solvents that are capable of forming hydrogen bonds are usually much less destructive to the polymer matrix that highly nonpolar solvents such as hexane. Therefore, under exposure to organic solvents, the full working pressure was significantly reduced in many cases, except when membranes were conditioned gradually, using method 1.

The efficiency of the aforementioned membrane conditioning done gradually with different concentrations of miscible solvents enters into an agreement with the results obtained by Giorno et al. [37], which studied the effects of organic solvents on UF membranes of PA with the molar weight cutoffs of 10 and 50 kDa, in order to prepare emulsions of oil in water by an emulsification technique and using tangential filtration. These authors reported that the permeation of polar solvent isooctane through polar membranes (hydrophilic) was possible by the pretreatment (conditioning) of the membranes in a miscible solvent gradient of decreasing polarity, with the purpose of removing water from the pores and fill them with isooctane.

Four different procedures were evaluated based on the percentage of solvents and the time of contact with membranes. The influence of solvents on PA membranes was studied by the analysis of SEM, which showed a pronounced change in the structure and morphology of the thin surface layer (selective) of the membranes. When the membranes were subjected to pretreatment with solvents, there was an inverse relationship between the molecular weight of the original cut and the final size of the pores.

For example, the original membrane of 10 kDa presented the average pore size of 0.038 \(\mu\)m, and after pretreatment, the size was 0.075 \(\mu\)m, while the original membrane of 50 kDa was 0.02–0.04 \(\mu\)m of medium pore size. This effect was probably due to different properties of mass transfer and the swelling capacity of the structure of the thin surface layer on the membrane of 10 (dense) and 50 kDa (porous). Isopropanol promotes by the swelling effect, leading to a more open of the pores, as a spongy structure.

Additionally, in the membrane of 10 kDa, isooctane led to partial melting of the dense layer of polymer surface, with the formation of tortuous pore channels. In general, increasing the contact time of membranes with solvents (isooctane and isopropanol) caused an increase in average pore diameters and the range of size distribution. These related effects were significant in both membranes, despite more pronounced in the 10 kDa membrane.

The authors concluded that although pretreatments have caused the changes in the structure and morphology of the membranes as described earlier, it was possible to obtain stable and reproducible performance in terms of permeate flux of isooctane and the formation of emulsions of oil in water, which were stable for at least 3 months. Then the methodology of pretreatment allowed obtains high permeate flux (up to 70 L h\(^{-1}\) m\(^{-2}\) in the membrane of 50 kDa) and low transmembrane pressure (0.5 bar).

García et al. [38] studied the effect of pretreatment on the flux of hexane through polymeric and ceramic membranes. The pretreatment consisted of immersing the membranes in solvent mixtures of decreasing polarity, starting with 50% water/isopropanol for 24 h, 50% isopropanol/hexane for 24 h, and finally 100% hexane for 24 h. The flow of hexane in the membrane (polieterssulfone—PES) was virtually “0,” which was attributed to low surface tension of this solvent (18 mN m\(^{-1}\) at 25°C) compared with water (73 mN m\(^{-1}\) at 25°C), considering that the membranes of PES are slightly hydrophilic.

According to Van der Bruggen et al. [23], cited by García et al. [38], PES membranes that had zero flow in hexane were permeable to this solvent, after pretreatment which consisted of immersing the membranes in hexane for 24 h. Occurs a change in the membrane structure to a conformation less hydrophilic, which allowed permeation of hexane was performed.

According to Araki et al. [31], constant flux solvent throughout time was a clear indication of the mechanic stability, the purity of the solvent, and its low interaction with the membrane material.
Using the pretreatment recommended by García et al. [38], the flow of hexane obtained in the membranes of PES was high and stable over time in each transmembrane pressure used. These authors reported then that the pretreatment used was highly effective for these polymeric membranes. Two explanations have been suggested for this behavior. The pretreatment may have helped to remove the pore water, initially by replacement with isopropanol and, after, with hexane. Moreover, the pretreatment also promotes a gradual change in the polarity of the membrane, facilitating the permeation of hexane.

In ceramic membranes (zirconia), however, the pretreatment was ineffective. In these membranes, the permeate flux (hexane) decreased over time and between successive tests, indicating a possible interaction between the solvent and the membrane material, or adsorption of solvent on the membrane surface.

This effect of adsorption between hexane and the surface of zirconia may decrease the effective size of the pores and, consequently, lead to a decrease in the flow of hexane. Additionally, the surface of zirconia may be able to catalyze the isomerization of cyclohexane and decomposition reactions, which could also explain the reduction in permeate flux observed. These authors concluded then that the membranes of polyethersulfone submitted to pretreatment showed high flow with hexane, was stable over time, and increased linearly with pressure, following the usual behavior for pure solvents. The stability of these membranes pretreated to hexane allows a full potential of applications in edible oils. In ceramic membranes, however, the decline in the flow of hexane observed as a function of time indicated that the solvent interacted with the membrane, being adsorbed on its surface. As a result, the flow of hexane through ceramic membranes was much lower than those obtained with polyethersulfone membrane with similar values of molar weight cutoff. The results are not explained by simple models used to predict conventional solvent flow, as the equation of Hagen–Poiseuille; therefore, parameters other than viscosity must be taken into account, such as surface tension and hydrophilicity of the membrane.

**23.10 MEMBRANE TECHNOLOGY APPLIED TO VEGETABLE OILS**

Membrane technology is still developing, with more and more applications being found in food processing. Applications of conventional membranes, such as MF, UF, and reverse osmosis, can currently be considered standard unit operations, which are being implemented in many cases. Currently, the focus of this technology for the food industry is to produce membranes more suitable to a particular process and product or even to improve the quality of existing products [5].

Recent research on the application of membrane technology in vegetable oils aimed mainly at desolventization and acidification [39]; degumming [40]; synthesis and purification of structured lipids [41,42]; separation of compounds present in small quantities in oil, as antioxidants; and clarification or bleaching. Figure 23.11 shows the conventional oil refining system and that proposed using membrane technology.

**FIGURE 23.11 Conventional refining process and the model proposed for refining by membrane technology. (Adapted from Snape, J.B. and Nakajima, M., J. Food Eng., 30, 1, 1996.)**

23.10.1 **GENERAL ASPECTS ON THE REFINING OF VEGETABLE OILS BY MEMBRANE TECHNOLOGY**

Typically, in the refining of vegetable oils, seeds are first cleaned and, depending on the type of seed on the oil content, can be processed in two different ways. Seeds containing high oil content are initially subjected to prepressing process, before extraction by solvent. Moreover, seeds containing low oil are processed to flakes or expanded and subjected to direct extraction by an organic solvent (hexane). The resulting mixture of oil and solvent, which is named micelle, leaves the extractor with 70%–75% solvent by weight, and sequentially, the solvent is recovered by distillation. Triacylglycerols make up over 95% of the composition of crude vegetable oils, and the minor components consist of phospholipids, free fatty acids, pigments, sterols, carbohydrates, proteins, and their degradation products. These substances can give the oil modified color and taste and shorten its shelf life. Therefore, crude vegetable oils need to be subjected to refining processes to achieve the desired quality. Because this process consists of several stages, a large amount of energy is consumed [43].

Engineering processes and designing of equipment for refining have improved considerably in recent years, mainly by reducing the energy requirements and losses of neutral oil. However, the basic principles of the processing of edible oils have remained virtually unchanged for nearly 60 years [4].

Membrane technology can be applied to the oil industry to simplify the process of refining, reducing energy consumption and waste water [44].

Membranes are semipermeable barriers that separate different compounds in a solution, by the restriction or not of the passage of components of the mixture [6].
Theoretically, triacylglycerols and phospholipids have similar molecular weight, about 900 Da, which makes it difficult to separate them by a membrane. However, phospholipids are surfactants molecules; that is, they have hydrophilic and hydrophobic regions, forming reverse micelles with globular structure, in a nonaqueous system. The micelles formed have the molecular weight of 20,000 Da or more. Thus, phospholipids can be separated from triglycerides, by using appropriate membranes. Most of the pigments and some of the free fatty acids and other impurities are adsorbed on the micelles of phospholipids and removed [44].

Until the mid-1990s, the literature did not contain sufficient information on membrane degumming and for problems with their stability, fouling, and cleaning, and most of the membranes evaluated did not have reasonable selectivity and satisfactory permeate flux necessary to make this technology commercially viable. This situation began to change with the appearance of stable membranes to hexane, creating great opportunities for the application of membrane technology in the refining of crude vegetable oils [44]. In degumming by membranes, typically permeate flux is inversely proportional to the retention of phospholipids and is desirable in a practical application to obtain greater flow and maximum retention possible.

Two important factors controlling the efficiency of membrane separations are molecular size exclusion and chemical interaction between the membrane surface and the components of the fluid feed. The formation of micelles of phospholipids influences the separation in a positive way since monomers pass through the pores of the membrane more easily than micelles. Moreover, the adsorption of compounds on the membrane surface is often cited as the primary cause of fouling, resulting in blocking of pores. This phenomenon of adsorption is influenced by the polarity of the membrane surface and the polarity of the liquid medium in which are dissolved solutes to be separated. In nonpolar medium, as miscella of soybean oil dissolved in hexane, these authors reported that hydrophobic membranes showed greater tendency to adsorption of phospholipids and triacylglycerols of that hydrophilic membranes.

In the traditional process of degumming, using water, phospholipids are precipitated by hydration, and then agitation and centrifugation. The phosphorus content of soybean oil is reduced to a range of 60–200 mg kg\(^{-1}\) due to hydratable phospholipids. The remaining nonhydratable phospholipids need not be removed through acidification and clarification. In the process of degumming mediated by membranes, the almost total removal of phospholipids occurs in one step, indicating that membranes are able to reject both phospholipids hydratable and nonhydratable. In the degumming of soybean oil by polymer membranes, more than 99% of the content of phospholipids present in the crude oil decreased in the permeate [45].

The main dynamic phenomena limiting the use of membrane technology in the oil industry, as well as other applications in food, are represented by the polarization of concentration, formation of gel layer, and fouling.

Fouling is described as the result of complex mechanisms that occur during the processes of filtration, that is, adsorption of substances of low molecular weight on the walls of pores, cake formation on the membrane surface, and mechanical seal of pores. Molecules such as proteins, polysaccharides, and fatty acids are known to cause drastic reduction in the permeate flow during the filtration process, despite its size, often much smaller than the diameter of pores. This fouling is attributed to the internal adsorption of these compounds on the surface of membranes. It is postulated that fouling is initiated by interactions between solutes and the membrane material. Chemical bonds, forces of van der Waals, and electrostatic and acid–base interactions are the main phenomena involved in the interactions that occur between surfaces and solutes on a molecular level. Consequently, the physicochemical properties of the surfaces of membranes are altered, and this facilitates the deposition of other molecules and aggregates, leading to a dramatic fouling, which added to the permeate low flow due to high fluids viscosity, limiting, in some cases, the industrial application of membrane technology in large scale [20].

Studies suggest that fouling appears mainly due to the adsorption of phospholipids on the surface of membranes, and, therefore, this is more relevant at the stage of degumming of crude oil.

In a study on fouling by adsorption on inorganic membranes for the filtration of vegetable oils, Hafidi et al. [20] reported that there is a drastic decline in permeate flux during the filtration of crude sunflower oil in different membranes composed of alumina. Purified sunflower oil, with or without free fatty acids, did not show fouling relevant during cross-flow filtration, indicating that both triglycerides and free fatty acids are not involved in this phenomenon to a large extent. In contrast, the presence of phospholipids caused a drastic drop in the permeate flux. The main reason for the occurrence of this phenomenon was attributed to rapid adsorption of phospholipids on the surface of membranes, which occurred in the first moments during the filtration process. These authors concluded that the phospholipids formed supramolecular structures on the surface of membrane, causing fouling.

Prior to the consolidation of fouling, which represents the penetration of the solute molecules of the feed fluid in the pores of the membrane, blocking them, there is an increased concentration of solutes on the membrane surface due to the concentration of solutes in solution, resulting from transport by convection, which is known as concentration polarization. This polarization leads to the precipitation of solute molecules on the surface of the membrane, a phenomenon known as the formation of gel layer. Later, the adsorption of small molecules on the inner wall of pores, and a complete occlusion by the molecules of solute leads to consolidated fouling. These phenomena determine a rapid reduction in the permeate flux.

According to Wu and Lee [24], in an experiment using the UF of miscella of crude soybean oil by a porous ceramic membrane, it was found that the polarization of concentration
profoundly influences the efficiency of UF, and solute deposition occurs on the membrane surface during the filtration process.

The main operational parameters that influence the performance of a process mediated by membrane separation are tangential velocity, solute concentration in the feed fluid, pressure, and temperature.

Concentration polarization can be minimized by increasing the turbulence of the fluid, tangentially to the membrane. Turbulence in the retentate side is an effective way to reduce the concentration polarization and thus increase the efficiency of separation [24].

According to Kim et al. [21], agitation in the retentate side causes an increase in the rate of permeate flux. Turbulence in the feed fluid derived both for pumping and agitation has a great effect on the flow in the region controlled by mass transfer. Turbulent regime of fluid near the membrane surface dissolves the accumulated solutes and reduces the hydraulic resistance of the cake, reducing the boundary layer thickness. It is also believed that high shear force obtained by intense agitation in the fluid effectively reduces the thickness of the gel. Anyway, this is one of the most simple and efficient methods of controlling the effects of concentration polarization. However, when the system is in the region controlled by the pressure, the effect of turbulence is negligible. This occurs because the concentration of solutes in the fluid supply is not high enough, the pressure is very low, and the speed is high enough to minimize the formation of boundary layer or gel. When these conditions do not prevail, the effect of speed or turbulence becomes significant.

Pioch et al. [46] evaluated the effect of tangential velocity on the permeate flux in the filtration of crude sunflower oil by a polymeric membrane. The speed of 3.5 m s⁻¹ gets a significant increase on the permeate flux, compared to the speed of 2.5 m s⁻¹. However, at 4.5 m s⁻¹, the flow curve showed no increase compared to the intermediate speed. These authors attributed these results to the fact that the polarized layer of solutes has reached a threshold thickness at 3.5 m s⁻¹. In their study, it is demonstrated that a limited increase in the flow can be obtained by increasing the tangential velocity.

Wu and Lee [24] reported the effects of transmembrane pressure and stirring rate on the retention of phospholipids in the UF of crude soybean oil, by a ceramic membrane. The rejection decreased with increasing transmembrane pressure without agitation. However, the influence of transmembrane pressure decreased with agitation, particularly at high speeds. The rejection was significantly increased with the agitation. The permeate flux also increased with increasing agitation speed. According to these authors, of course, the agitation facilitated the minimization of the concentration polarization, thus increasing the rejection and permeation.

After the fall of permeate flux during the first 2 h of filtration, the increase in transmembrane pressure did not affect the permeate flux, indicating that there was an accumulation of solutes, triacylglycerols, and phospholipids of soybean oil, which formed a gel layer on the membrane surface. These authors concluded that the polarization of concentration is an important phenomenon in the process of UF and can be reduced by agitation on the retentate side. The results also showed that smaller pore size, down 0.02 µm, is essential for an efficient separation of phospholipids in UF by ceramic membranes. However, the permeate flux becomes lower when the size of pores is reduced, implying that a larger area surface of membrane is needed.

The effect of pressure on rise of the permeate flux, decreases after a certain time of filtration previously reported by Wu and Lee [24] enter into agreement with the results obtained by Kim et al. [21] in degumming of crude soybean oil by a PI UF membrane. According to these authors, the gel layer represented by the precipitation of solute on the membrane surface makes the permeate flux independent of pressure, and an increase in pressure resulted in a layer of solute denser and thicker. Initially, with the increase in the work pressure, the rate of permeation of oil miscella in hexane increased. However, up to 3 kg cm⁻², the rate of permeation of miscella tended to become constant, which is a behavior usually observed in UF membranes. This trend was observed in three concentrations of miscella analyzed (20%, 30%, and 40%, m m⁻³). This is attributed to the fact that the phospholipid layer due to the polarization of concentration retained on the membrane surface can control the permeation rate above the critical pressure. From this stage, therefore, the permeation rate is not more related to a function of the pressure.

Considering the effects of the parameters, solute concentration in the fluid supply and temperature, a higher concentration of solutes leads to high viscosity of the fluid, reducing the permeate flux. On the other hand, increased temperature reduces the viscosity, thus leading to an increase in the permeate flux.

Kim et al. [21] reported that the increase in the concentration of miscella leads to a drop in permeate flux. These authors attributed this result to the fact that higher concentrations of solutes promote fouling. The transport of solutes to the membrane by convection causes a steep concentration gradient within the boundary layer, leading to the transport of solutes back into the interior due to diffusion phenomena. No more solute molecules can be accommodated due to the close arrangement and increased mobility of smaller molecules. This increase in concentration leads to precipitation and, therefore, the plugging or fouling in the membrane.

According to Kim et al. [21], generally, high temperatures lead to higher permeate flux, both in the region controlled by the pressure and in the region controlled by mass transfer. One can assume from this statement that other unusual effects do not occur simultaneously, such as fouling of the membrane due to the polarization of insoluble salts and denaturing or gelatinization of solids at high temperatures. In the region controlled by the pressure, the effect of temperature on the flow is due to its effects on the density and viscosity of the fluid supply. The diffusivity also increases with increasing temperature. Therefore, the temperature determines a significant effect on the increased flow.

Pioch et al. [46] studied the effect of temperature on the permeate flux and retention of phosphorus in the cross-flow
filtration of crude sunflower oil, by a ceramic membrane. These authors reported that an increase of 20°C in the oil temperature, of 25°C–45°C, allowed a small increase in the rate of permeate flux, from 230 to 280 L h⁻¹ m⁻². However, the efficiency of the process regarding the retention of phosphorus had a sharp decline, from 88% to 24%, with 70 mg kg⁻¹ of phosphorus in the permeate at 45°C instead of 11 mg kg⁻¹ to 25°C. Due to the size of the molecules to be retained and disposed of oil, compared to the size of the pores, it is assumed that this stage of filtration is based on the retention of the micelles. In this case, the loss of efficiency in the retention due to increase in temperature can be attributed to the well-known tendency of the solutes in rather than join together with the increase in temperature, increasing diffusivity and by a change in the interactions between oil components and the membrane. For that reason, despite the limitation in the rate of flow, more low work temperatures would be more appropriate for edible oils due to the preservation of minor components.

Stafie et al. [47] investigated the filtration of refined miscella of sunflower oil, in hexane, by PAN composite membranes as a support and polydimethylsiloxane as a selective layer, with 30 and 50 kDa molar weight cutoff. These authors reported that with increasing pressure, the increase in the flow of hexane was much larger than the relative increase in the flow of oil, leading to an increased retention at high pressures. Both the flow and retention of the solute (oil) were dependent on the applied transmembrane pressure and feed concentration. Increased pressure was favorable in terms of flow and retention. Regarding the effect of the concentration of the feed, besides the higher flows obtained at low concentrations, the oil retention ranged from 80% (30% sunflower oil/hexane miscella), to 90% retention, in 8% concentration of oil in the feed, of which 19% of oil concentration, the retention of the same stood at intermediate values between 80% and 90%.

The magnitude of the effects of different filtration parameters (temperature, pressure, tangential velocity, and solute concentration in the fluid supply) varies according to the type of membrane used in the permeation of vegetable oils, namely, at the level of UF porous membranes or the level of nonporous or dense NF membranes. Subramanian et al. [37] investigated the effect of temperature on the permeate flux during the filtration of oil (high oleic sunflower oil) for nonporous polymeric membranes. The results showed that the increase in temperature led to increase in the total flow of permeate due to the cumulative effect of the increase in solubility and diffusivity. However, the change in the viscosity of the fluid due to increased temperature did not have a significant effect on the permeate flow. These authors concluded that the behavior observed in these filtration systems suggests that solution–diffusion is the predominant mechanism of the transport of the components of vegetable oils by nonporous membranes. The effect of viscosity is related to temperature, suggesting that the flow through convection exists in these membranes, but its extent is not significant.

However, in porous membranes, which are used in UF, the viscosity factor of the fluid supply, which in turn is related to temperature and solute concentration, represents a major role in determining the permeate flux. According to Kim et al. [21], except for the anomalous behavior of water, all other solvents show a clear correlation between the increase of flow increased and a decrease of viscosity. According to these authors, this indicates that viscosity is the main factor that influences the flow of solvent through UF membranes.

The performance of UF membranes is directly related to the phenomena of interaction between membrane and solvent, which may vary according to changes in solvent properties such as viscosity, molecular size, surface tension (related to polarity), and dielectric constant. Kim et al. [21] analyzed the performance of a UF membrane of PI with 20 kDa molar weight cutoff in the degumming of crude soybean oil. They also performed the filtration of various solvents (water, methanol, ethanol, acetone, and hexane), where the flow was measured, with the aim of evaluating the resistance of the membrane to a specific solvent. Permeability, measured permeate flux as a function of pressure, was higher for the solvent with lower viscosity (hexane, 0.31 cP) while the lowest flow was determined for the solvent of higher viscosity (ethanol, 1.08 cP). Regarding the effect of polarity on the permeate flux, these authors reported that due to the hydrophobicity of the membrane of PI, the lowest flows were recorded in the case of polar solvents such as water and alcohol, while higher flows were found with nonpolar solvents such as acetone and hexane.

An important factor that influences the performance of membrane filtration is its mode of operation. According to Gekas et al. [48], the filtration mode for most unit operations with membranes, among which processes of NF and UF are in cross-flow mode, in which the feed stream is parallel to the membrane surface, while the permeate flux is transverse to it. Thus, the flows of feed and permeate are intertwined, justifying the terminology cross-flow. Moreover, in the conventional mode of filtration, the feed stream is perpendicular to the membrane or filter media and is known as dead end or flow through.

According to Artz et al. [49], who did the deacidification of soybean oil through polymeric membranes of reverse osmosis, the rate of permeate flux was higher at lower transmembrane pressures than at high values, which can be attributed to the polarization concentration and compression of the membrane; as pressure increases on the surface of it, this phenomenon is particularly intense, according to these authors, when using a dead-end filtration design, as used in that experiment.

**23.10.2 Solvent Recovery**

The recovery of a solvent in the processing of vegetable oils is done mainly by evaporation, with vapors recovered from noncondensable gases by absorption in mineral oil. For economic, environmental, and security reasons, make the recovery of a solvent in the most critical steps in the processing of edible oils. The first reverse osmosis membranes
were composed of cellulose acetate and various polymers, which become damaged quickly by exposure to hexane. In the past, these membranes limited its application to aqueous systems and were not suitable for processes such as recovery of hexane from the miscella/oil obtained by solvent extraction [50].

In a process model combining membrane and distillation proposed for solvent recovery from oil miscella in hexane, a unit of reverse osmosis membrane permeates the miscella from the extractor. The section of miscella through the membrane, the permeate resulting in a hexane permeate–rich stream, is recycled back to the extractor, while the retentate, oil-rich stream, is processed by distillation to recover the remaining solvent [50]. The application of membrane technology to separate the oil from the solvent in micelles can be carried out soon after extracting the oil, resulting in crude oil for subsequent refining. Thus, Koseoglu and Engelgau [4] proposed a combined process for hexane recovery, combining the use of membranes with conventional distillation. The use of NF would provide a hexane-rich current, which would be sent to the oil extractor and an oil-rich current, which could be processed by distillation to recover the rest of the hexane. According to the scheme proposed by Raman et al. [30], after filtering the micelle using a compatible NF membrane, permeate, which contains mostly hexane, would be sent for recycling. The retentate could be sent for a second filtration stage, aiming to maximize oil recovery (Figure 23.12).

Alternatively, solvent recovery by membranes could be carried out after degumming the micelle using the UF process so as to obtain hexane-free degummed oil. According to Snape and Nakajima [3], the oil/hexane micelle, previously degummed by UF, could be sent for the NF process in order to maximize solvent recovery, the rest being separated by distillation (Figure 23.13).

The desolventization membrane, however, has some limitations. Results have shown that membranes can be stored in organic solvents for several weeks, which causes no change in their initial flows; however, the combination of organic

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**FIGURE 23.12** Schemes proposed by Koseoglu and Engelgau [4] and Raman et al. [30] for solvent recovery after the extraction process.

**FIGURE 23.13** Oil/solvent separation after degumming by UF, as proposed by Snape and Nakajima [3].
solvents and high pressure leads to considerable changes in membrane performance [3].

Koseoglu et al. [51] reported that in many reverse osmosis membranes used to recover solvent from miscella oil, cotton seed oil in hexane, 25% m m⁻¹, only one membrane was not damaged by hexane but had low flow and low oil retention.

The chemical composition of the membranes has high impact on the transport of organic solvents. Nonpolar solvents have higher flows in the membranes of hydrophobic nature, whose separation mechanisms involve interactions of polymer and solvent, solvent and solute, and solute and polymer [22].

The application of polymeric membranes for organic use requires physical and chemical stability against hexane and temperatures around 50°C–60°C. Materials such as aromatic PA, aromatic PI, PVDF, and polytetrafluoroethylene may be appropriate [52].

Pagliero et al. [53] evaluated the recovery of solvent in miscella degummed sunflower oil/hexane with concentrations of oil between 25% and 45% (w/w). Membranes were synthesized from PVDF, prepared by the process of phase inversion, and evaluated for their flow and selectivity toward the oil. Tests were performed in a 400 mL filtration unit, with an effective area of membrane equal to 31.66.10⁻⁴ m² and agitation of 750 rpm. The best separation was achieved at pressures between 4 and 6 bar, and a temperature of 50°C and 25% oil in miscella (w/w), corresponding to a flow of 30 L m⁻² h⁻¹.

Koseoglu et al. [51] reported the use of NF and UF membranes, aimed at the separation of crude cotton seed oil (25% w/w), in miscella containing hexane, ethanol, and isopropyl alcohol as solvents. Tested membranes were made of PS, fluorinated polymers, PA, and cellulose acetate, with an average MWCO ranging between 150 and 1000 Da. Only PA membranes (OSMO Sepa O, OSMO 192T-89, OSMO 192T-O, Osmonics) were stable in hexane. The best performance was obtained with the membrane OSMO 192T-89, with a molar weight cutoff between 300 and 400 Da, a permeated flux of 7.14 L m⁻² h⁻¹, 21.6% of oil in the permeate, resulting in the retention of oil equalling 13.6%.

Wu and Lee [24] used porous ceramic membranes for the UF of miscella of soybean oil/hexane, based on the different diffusivities between hexane and oil. They used a crude extract of soybean oil/hexane with 33% oil, without any pretreatment. They performed a cross-flow filtration with a membrane disk with a pore diameter of 0.02 μm and a thickness of about 0.1 μm. The best separation conditions were found using a pressure equal to 4 kg cm⁻² and an agitation speed of 120 rpm. The concentration of soybean oil decreased from 33% in the feed to 27% in permeate, representing 20% rejection. The results suggest that smaller pores are essential for an efficient separation. However, the flow becomes even lower with the reduction of pores, implying the need for a large surface area of membrane. It should be noted that the pore size is not considered effective for separating oil/hexane, as is much higher, about 20,000 Da, compared to the molecules in question.

Raman et al. [30] examined NF membranes (provided by Kiryat Weizmann, Israel), resistant to hexane in the recovery of the solvent of miscella (constituted 20% of refined soybean oil dissolved in hexane). In the first stage, at an average flow of 9 L m⁻² h⁻¹, a pressure of 2.76 MPa, and a temperature of 24°C, a retentate with 45% oil was obtained. This was again concentrated through nine successive filtrations on similar membranes, with an average flow of 20 L m⁻² h⁻¹, in the same pressure and temperature. The separation of oil in the combined system was approximately 99%.

Geng et al. [54] investigated the separation of the solvent from a miscella of crude soybean oil/hexane (30% v/v). We used commercial ceramic membranes with different pore sizes (1, 3, and 5 kDa) and a maximum pressure of 6 bar. The membrane pore equal to 1 kDa provided satisfactory results, with the rejection of 70% oil, with low permeate flows. The authors suggest that higher flows can be achieved using the application of higher pressure.

Kuk et al. [55] applied a PA membrane with molar weight cutoff of 1000 Da in a mixture containing ethanol and crude cotton seed oil. The recovery of solvent was 99% with an operational pressure of 2–4 bar, temperature of 25°C, and permeate flow ranging between 1 and 4 L m⁻² h⁻¹. The authors conclude that small pore diameters result in low permeate flows. Typically, low permeate flux can be correlated with fouling consolidation (Figures 23.14 and 23.15), which limits an industrial application of NF processes by polymeric membranes to solvent recovery from micelle (usually ranging between 20% and 40% w/w or v/v of oil in hexane or another organic solvent) in coupled UF/NF processes.

Solute deposition during filtration process, shown in Figure 23.14, is related to phenomena that lead to a typical drop in permeated flux, remarked by a sharp decline on the first 30 min of filtration, when the system enters the operational regime and fouling consolidation occurs, after which the permeated flux remains almost constant. This behavior is more evident in the 1000 Da polymeric NF/UF membrane. According to Ribeiro et al. [47], such statements were
matched by SEM of samples of these membranes that were analyzed after the filtration experiment, as can be seen from Figure 23.15.

23.10.3 Deacidification

The conventional step of deacidification, chemical refining, has a major economic impact in the processing of vegetable oils. This is due to several factors, such as loss of oil due to the hydrolysis of triacylglycerols by the alkali and the soap itself having a low commercial value. However, since fatty acids have many applications, the soap is usually treated with concentrated sulfuric acid, which resulted in the generation of highly polluting effluents; the water used to wash the oil after treatment with alkali needs to be treated before being released into the environment. In theory, the membrane technology would solve most of these problems. The ideal process would use hydrophobic membranes. Appropriate NF membranes allow a partial separation of fatty acids [6].

In an experiment simulating refining crude soybean and canola oils, without the addition of organic solvents and using polymeric membranes, Subramanian et al. [56] reported that a filtration process in a single step is able to remove phospholipids, pigments, and oxidation products, as well as increased from 12% to 26%, this range was depending on the type of oil and the content of tocopherols in the permeate compared with the original levels of tocopherols in crude oils, due to the preferential permeation (negative rejection) of these compounds, in relation to triglycerides. However, the process did not separate free fatty acids from crude oils, and also, the permeate flux was low. These authors concluded that this single-step process using membranes was suitable as an alternative to chemical refining only for degumming and clarification processes, not for deacidification.

In another study, Snape and Nakajima [3], using membrane separation for lipids classes in hydrolyzed sunflower oil, observed that free fatty acids permeated the membrane and preferentially concentrated in the permeate, while triglycerides were retained. Mono- and diglycerides showed intermediate behavior; that is, they were equally distributed between permeate and retentate.

Koike et al. [57] using a commercial dense reverse osmosis membrane, consisting of cellulose acetate and silicone-polyimide, could efficiently separate free fatty acids, monoacylglycerols, diacylglycerols, and triacylglycerols of high oleic sunflower oil, hydrolyzed by lipases and diluted with solvents (ethanol and hexane).

Lai et al. [58], in a combined process of permeation of soybean oil with reverse osmosis NF membranes in combination with extraction by subcritical liquid pressurized carbon dioxide, obtained a preferential permeation of oleic acid in relation to triglycerides. From a system model of 40% of oleic acid and 60% of triglycerides (soybean oil), the permeation through the reverse osmosis membrane (BW 30) resulted in a permeate above 80% w/w of oleic acid, while the permeation through the membrane for NF (NF 90, MWCO = 200 Da) resulted in a permeate with approximately 50% w/w of oleic acid. However, the last membrane showed a significantly high permeate flux compared with that obtained with the BW 30.

23.10.4 Removal of Pigments (Bleaching)

Vegetable oils contain various pigments, including chlorophyll, carotenoids, xanthophylls, and its derivatives, which need to be removed to obtain oil color acceptable to the consumer. Additionally, the oxidation of vegetable oils is favored by the presence of some pigments, and chlorophyll has been implicated in the poisoning of nickel used as a catalyst in hydrogenation reactions. The high cost of land clarifier, oil losses, and subsequent problems associated with the disposal of waste generated has led to interest in the application of membrane technology to replace the traditional process of removal of pigments [3].

Koseoglu et al. [51] examined 15 different UF membranes in the removal capacity of pigments in various vegetable oils, including soybean, canola, cotton seed oil, and peanuts. Only five membranes were resistant to hexane; however, their identifications were not disclosed. Chlorophyll and β-carotene were retained by membranes, but efficiency varied between membranes and oils. In general, color readings in permeated oils were on the order of one-tenth of those obtained in crude oils.

Reddy et al., cited by Snape and Nakajima [3], investigated the use of a polyimide ultrafiltration membrane with the skin layer of cross-linked silicone (NTGS 2100), for the removal of chlorophyll and β-carotene from crude sunflower oil and the content of tocopherols in the permeate compared from 12% to 26%, this range was depending on the type of oil and the content of tocopherols in crude oils, due to the preferential permeation (negative rejection) of these compounds, in relation to triglycerides. However, the process did not separate free fatty acids from crude oils, and also, the permeate flux was low. These authors concluded that this single-step process using membranes was suitable as an alternative to chemical refining only for degumming and clarification processes, not for deacidification.

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oil, getting above 95% rejection to chlorophyll; however, the flow of permeate was extremely low, 0.1–0.2 kg m⁻² h⁻¹. The addition of hexane mixed to the crude oil, up 50%, increased the permeate flux but reduced the rejection of chlorophyll around 70%.

### 23.10.5 Removal of Waxes

Waxes can be defined as a mixture of long-chain nonpolar compounds and comprise a variety of different chemical groups, including hydrocarbons, esters, aldehydes, ketones, sterol esters, fatty alcohols, fatty acids, and sterols [59].

The total amount of waxes present in oils depends on the type of oil, temperature, type of extraction, and solvent used. Wax content in vegetable oils can cause turbidity when the oil is stored at low temperature. In this condition, the waxes present will crystallize, causing oil turbidity or forming a precipitate. Due to this reason, oils need to submit to a process called winterization, which keeps the oil at low temperature to crystallize the waxes content and remove them by filtration or centrifugation [60].

Waxes content in crude vegetable oils is extremely variable. Sunflower, rice, and corn oils have waxes in their composition, and crude sunflower oil can have 1.0% w/w of wax [61].

The waxes must be entirely removed by refining processes, since refined oil containing up to 8 mg kg⁻¹ of these compounds can promote turbidity in 48 h, at low temperatures [62].

Removal of wax is critical in sunflower oil, since the oil, after refining processes, contains around 6 mg kg⁻¹ [63].

Waxes present in vegetable oils can be removed by MF membranes with an average pore diameter of 0.05–1 μm. Depending on the type of oil, its temperature is adjusted to −10°C to 20°C to crystallize the wax before the MF process. Most waxes are retained with a minimal amount in permeate. For example, sunflower oil containing 2600 mg kg⁻¹ wax can be cooled to 5°C and processed through a membrane made of polyethylene, in hollow-fiber configuration with an average pore diameter of 0.12 μm. At a pressure of 2 bar and a temperature of the fluid supply of 10°C, the average permeate flow was 10 L h⁻¹ m⁻². The content of wax in permeate was 30 mg kg⁻¹, and during the cold test, it showed no turbidity. Fouling in the membrane caused by the wax was offset by backflushing procedure with nitrogen under high pressure [64].

Removal of waxes from sunflower oil by MF membranes has been carried out on an industrial scale for several years by a company in Japan [3].

In permeation, the effect of wax in the formation of fouling can be minimized or canceled by the temperature of the feed. In experiments with the UF of miscella of crude sunflower and soybean oils, Pagliero et al. [65] reported that high temperatures (50°C) led to a complete dissolution of waxes present in crude sunflower oil, equaling the fouling obtained in this oil to the crude soybean oil and, consequently, leading to similar permeated flows in both sunflower and soybean oils.

### 23.10.6 Degumming

The process of degumming is usually carried out after the separation of oil from the miscella. The gum is phospholipids that can be removed by the addition of water to crude oil, causing them to be hydrated and removed. In contrast, degumming by membranes can be done directly with the miscella. Being amphoteric molecules, phospholipids form reverse micelles in the miscella, with molecular weight above 20 kDa and molecular size from 20 to 200 nm. In UF, degumming by membranes can be used to separate micelles from the oil–hexane mixture (miscella). The permeate consists of hexane, triglycerides, free fatty acids, and other small molecules, while almost all the phospholipids are retained by the membrane. Membranes suitable for this application should be resistant to hexane made, for example, in PA, polyethersulfone (PES), PVDF, PI, PAN, or inorganic [6].

Reversed micelles, to be formed, absorbing pigments in their structure, some amount of free fatty acids and other compounds, and then were removed in the retentate fraction with most of the phospholipids [66].

Both UF polymeric membranes and polymeric membranes for NF may be suitable for the degumming of vegetable oils. While in UF membranes the rejection mechanism of phospholipids is mediated by the molecular size exclusion, in nonporous membranes, rejection occurs also by the solution–diffusion effect, which is related to the interactions between these solutes and the membrane active layer. Additionally, membranes retain hydratable and nonhydratable phospholipids, resulting in almost the total rejection of these compounds [67].

Membrane degumming can be performed either with the miscella, generally 20%–30% of crude oil in hexane, m/m, and with the crude oil without the addition or removal of solvent.

In the case of miscella degumming, the greatest difficulty has been the low stability of the membranes to organic solvents, whereas in the degumming of crude oils, the main problem is the low permeate flow as a result of high oil viscosity, resulting in sharp fouling, dropping this technology for an application in industrial large scale [68].

According to Subramanian et al. [56], in a study of degumming of crude sunflower oil extracted by cold pressing, using polymeric composite membranes, obtained not only the retention of phospholipids by 100%, depending on the type of membrane, but also that of pigments and oxidation products. However, the permeate flux needs to be increased for an industrial application.

In a study of the degumming of crude sunflower and soybean oils, with no added solvent, using polymeric UF membrane with a molar weight cutoff of 15 kDa. Koris and Vatai [69] obtained at an operational pressure of 5 bar, a temperature of 60°C, and a flow rate of 0.3 m³ h⁻¹, 77%, and 73.5% of the retention of phospholipids in sunflower and soybean oils, respectively.

Permeate flows of both oils were not compared. With the addition of 1% water to sunflower oil, the retention of
phospholipids increased to 97%, probably, according to these authors, due to the increased formation of reverse micelles.

In an experiment with miscella degumming of soybean oil in hexane, 25% m⁻¹, using UF membranes made from PVDF, PES, and PS, Ochoa et al. [70] found that the stability of membranes in organic liquids is influenced by both the type of polymer and the average pore size. Small-pore membranes become more stable, while that for the type of polymer, the results showed that PVDF is more stable in hexane than PES and PS membranes.

During the degumming, the authors reported a sharp decline in the permeate flux at the beginning of the process of permeation and attributed this behavior to the concentration polarization and to membrane fouling, and this initial sharp drop in the flow was more intense in PES and PS membranes. The decline in the permeate flux was much less pronounced in the long term, 250 min, that initially, 50 min; this trend implies that a system of consolidation of fouling caused by the cake may have affected the membrane after the initial filtration. Additionally, PVDF membranes achieved the highest retention of phospholipids, up to 98%.

In miscella degumming of sunflower and soybean oils in hexane, 25% m⁻¹, using UF membranes made of PVDF with polyvinylpyrrolidone (PVP) as an additive, Pagliero et al. [53], under the experimental conditions of 2–6 bar and 30°C–50°C, reported that the permeate flux versus time indicates that the degumming of sunflower oil produced more fouling in the membrane than soybean oil degumming and attributed this phenomenon to the presence of waxes in the sunflower oil and the effect of these waxes on the formation of greater fouling in the lower temperature of filtration. However, the retention of phospholipids was slightly higher in sunflower oil, up 100% in some cases. The process of degumming also resulted in the reduction of red color in both oils, but only yellow color was reduced in the sunflower oil.

On the effect of pressure and temperature parameters on permeate flux during degumming, Pagliero et al. [66], in an experiment with degumming of crude soybean oil miscella in hexane, 25% m⁻¹, found that under high pressure, 6 bar, the phenomenon of the concentration polarization begins to exert a significant influence on the process of permeation, making the permeate flux less sensitive to the transmembrane pressure applied. At high pressure, a layer of rejected molecules, gel-polarized layer, was deposited on the membrane surface and permeate flux was highly dependent on the consolidation of this layer, being little affected by pressure. As temperature increases, the permeate flux increases in direct proportion, because the increase in the temperature of the feed reduces its viscosity.

23.10.7 Separation of Minor Components: Tocopherols and Carotenoids

23.10.7.1 Separation of Tocopherols

Tocopherols are natural antioxidants present in vegetable oils, with a beneficial effect on their quality. Therefore, recent studies have focused on the application of membrane technology in the preservation or concentration of these compounds [29].

The preferential permeation of tocopherols in relation to triacylglycerols in membrane processes was first observed by Subramanian et al. [56]. They performed a filtration of peanut oil and crude sunflower oil, which produced permeates with high levels of tocopherols. They used polymeric membrane prepared in laboratory, with silicon as active layer and PS and PI as support layers, without the description of the characteristics of pore. Experiments were conducted at 30 bar, 40°C, and 400 rpm. Peanut and sunflower oils showed negative retentions of tocopherols of −60% and −96%, respectively. According to the authors, tocopherols do not seem to have affinity with the micelles of phospholipids and low molecular weight of these compounds, together with possible interactions with the membrane material, resulting in a higher permeation or, similarly, in negative values of retention.

Subramanian et al. [56] showed negative retention of tocopherols (~18% to ~24%) for crude soybean oil through filtration in commercial membranes containing silicon as the active layer and PS and PI as support layers (no description of pore size), operational conditions of 30 bar, 40°C, and 800 rpm. This resulted in an increase of 12%–15% of these compounds in permeate. Experiments with canola oil performed under the same conditions increased the content of tocopherols in permeate at 25%.

Subramanian et al. [29] reported the application of dense membranes (not porous) in the study of permeation of different tocopherols. A membrane was used with an active layer of silicon and PI as a support layer (NTGS-2200, Nitto Denko, Japan). Experiments were carried out with high oleic sunflower oil with enriched tocopherol acid, with pressure and temperature ranging from 20 to 50 bar and 20°C to 50°C, respectively. Tocopherols showed preferential permeation when compared with triacylglycerols, corresponding to negative values of rejection (~30% to ~52%). However, the concentration of tocopherols in the feed led to reduction in the rate of permeation of the same, but without significant effect on the total flow. The authors do not mention the characteristics of the membrane pore.

Nagesha et al. [71] evaluated the selectivity of membranes with dense silica and PI as the active layer and support, respectively, on the permeation of tocopherols. They used samples of deodorized distillate of soybean oil (DDOS), diluted or not in hexane and DLOS oil ester, without dilution. For comparison, model systems consisting of mixtures of oleic acid and tocopherols in different proportions (80:20 and 50:50), diluted or not in hexane, were selected. In a standard model, (free of hexane) was added to a mixture of fatty acids methyl esters (FAMES) from soybean oil and tocopherol (90:10). Experiments were conducted on a pressurized filtration unit with nitrogen at 30 bar, 30°C, and 800 rpm. The study revealed that preferential permeation of tocopherols in relation to other constituents of low molecular weight (fatty acids and FAMES) occurs. The selectivity of the membrane to tocopherols increased with the esterified DDOS.
The presence of hexane positively influenced the permeation of tocopherols, by providing greater solubility of these compounds in relation to other constituents of the feed. The authors conclude that the membrane processes have good prospects in the enrichment or concentration of tocopherols of DDOS. However, pilot-scale experiments would be needed for the complete development of the process.

23.10.7.2 Separation of Carotenoids

Carotenoids are generally tetraterpenoids of 40 carbon atoms, consisting of color pigments of red, yellow, or orange present in fruits and vegetables, and are classified as carotenes or xanthophylls. Carotenoids are polyene hydrocarbons with varying degrees of unsaturation, and xanthophylls are synthesized from carotenes, by reactions of hydroxylation and epoxidation. β-carotene and lycopene are examples of carotenones, whereas lutein and zeaxanthin are xanthophylls. Carotenoids are composed of eight isoprene units and methyl groups and have a central long carbon chain with conjugated double bonds. These molecules are removed during the process of refining oils and fats. More than 600 types of carotenoids have been isolated from natural sources. Of these, approximately 50 are precursors of vitamin A. The carotenoid precursor has at least one ring of β-ionone not replaced by side chain polyenic with a minimum of 11 carbon atoms. Among the carotenoids, β-carotene is the most abundant in foods and has the highest activity of vitamin A.

According to Darnoko and Cheryan [73], palm oil contains high concentrations of carotenoids and tocopherols and can be removed in its conversion to methyl esters and subsequent application of membrane technology to separate carotenoids and tocopherols. Several solvent-stable NF membranes were studied for this application. The flow, with a standard solution of methyl ester of crude palm oil, was in the range of 0.5–10 L m⁻² h⁻¹, and the retention of β-carotene was 60%–80% at a pressure of 2.76 MPa at 40°C. A process of multistage membrane is designed for the continuous production of methyl esters of concentrated carotenoids of crude palm oil. With a feed rate of 10 ton per hour of methyl esters of palm oil containing 0.5 g L⁻¹ of β-carotene, the process might produce 3611 L h⁻¹ of concentrate of carotenoids containing 1.19 g L⁻¹ of carotene and 7500 L h⁻¹ of bleached methyl esters containing less than 0.1 g L⁻¹ of β-carotene. In conclusion, the authors claim that the economy of this process is promising.

Chiu et al. [74] performed the concentration of carotenoids from crude palm oil using membrane technology. They used a flat sheet polymeric NF membrane (NP10), composed by polyethersulfone (PES), with a molar weight cutoff of 200 Da. In this experiment, the red palm oil ethyl esters flux was 7.5 L m⁻² h⁻¹ and the rejection of β-carotene was 75%, at an operational pressure of 2.5 MPa and a temperature of 40°C. According to these authors, the results of this study showed that the separation using membranes is effective in the recovery of carotenoids from red palm oil, presenting a high potential regarding the use of this technology for industrial application in the near future.

23.10.8 Separations of Emulsions

Emulsions are heterogeneous systems consisting of one immiscible liquid completely diffused in another liquid in droplets of 0.1 μm diameter or greater [75].

According to Kocherginsky et al. [76], polymeric membranes have been shown to be an effective means of separation in the breakage of water-in-oil emulsions. The separation of emulsions is only possible using hydrophilic membranes with a pore size smaller than the diameter of the droplets in the emulsion. In general, the smaller the mean pore size, the better the efficiency of the separation of components in the emulsion. The use of low pressure favors this separation. According to these authors, membranes act by facilitating the coalescence of droplets present in the dispersed phase simultaneously with permeation through the pores of the membrane or even through nonporous membranes.

According to Coutinho et al. [77], ceramic membranes can also be used to efficiently separate emulsions. Fontes et al. [78], using a composite inorganic microporous membrane made of alumina and silica as support and with a tubular structure, sintered in the laboratory at a final temperature of 1450°C and with a mean pore size of 0.3–20 μm, suitable to separate emulsions of 2% v/v of oil (sunflower and soybean) in water. They demulsified this emulsion efficiently by the cross-flow MF mode in a turbulent regime (Re > 10,000) with transmembrane pressures of 1.5–3.0 bar and obtained a carbon retention over 90%. In another study, Del Colle et al. [70] performed a de-emulsification of a mixture of sunflower oil and water (1% v/v) at 25°C with MF by tubular alumina membranes sintered in laboratory at 1450°C and with 0.5 μm of pore diameter. These tubular ceramic membranes were impregnated with a zirconium citrate solution and submitted to 600°C and 900°C. The membrane that was treated at 600°C showed better separation performance, achieving 99% retention of the oily phase. However, the membrane submitted to 900°C had a low permeate carbon concentration, presenting, additionally, a better flow rate. According to these authors, these differences in the flow rate showed that the heat treatment (600°C or 900°C) used after the impregnation of the ceramic ultrastructure of the membrane was the component that interfered with the behavior of the two membranes studied, probably due to changes in the microcrystalline structure of the zirconium nanoparticles after the heat treatment.

23.10.9 Study of the Membrane Cleaning Processes

Due to the limiting effects imposed by fouling on the permeate flux, it is necessary to adopt efficient methods of cleaning of the membranes in order to bring the values of flow to baseline and thus prolong the life of the membranes.

Basso et al. [79] performed an efficient cleaning process for alumina ceramic membrane, used in degumming by the UF of crude soybean oil on a pilot scale in order to restore the levels of permeate flux. In this cleaning method, which used only hexane, the best results were obtained by...
the combination of high tangential velocity of the feed fluid (5.0 m s⁻¹) and at low transmembrane pressure (0.45 bar).

Smith et al. [80] studies the effect of backwash in maintaining the flow in membrane systems and concluded that the performance of this procedure, during the process of membrane filtration, can effectively remove most of the compounds responsible for the reversible fouling of the membrane, reducing the pressure of work and increasing the permeate flux.

Cakl et al. [81] analyzed the effects of backflushing on the restoration of the permeate flux in the MF process of oil emulsions, performed in a ceramic membrane. The results showed that backflushing can maintain the permeate flux close to an appropriate value for a long time. It was observed that the effect of backflushing was more significant when associated with a short time procedure of backpulsing and a higher speed of permeation. The magnitude of the effect of transmembrane pressure difference in the reverse flow caused no significant effect.

In the study of the optimization of the cleaning process in ceramic membranes used previously in the filtration of beer, now with the fouling out, the cleaning experiments were performed at a transmembrane pressure of 0.2 bar and a flow rate of 2 m s⁻¹. Backwashing, and also periodical backpulsing, has achieved a substantial increase in flow after 8 min by rinsing, suggesting a partial removal of membrane material. The increase in temperature had a significant impact on the cleaning of the membrane as well as the recuperation of the initial flow of it, and the value of restoring the stream to a temperature of 80°C was 20% higher than to a temperature of 22°C, while increasing the temperature of 40°C to 80°C led to a reduction in the cleaning time of 26 to 11 min.

The influence of the rinse on the removal of protein waste from the ceramic membrane fouling has been established by Cabero et al. [82]. They compared the process with and without rinsing water recycling and obtained a more efficient removal of waste to the process carried out without the water circulation, a fact explained by the redeposition of particles in the water recirculated. The efficiency of the rinsing performed at 50°C was higher than in the 20°C because water has a higher power of solubilization at higher temperatures. By varying the transmembrane pressure of 0.05–0.3 MPa and keeping the temperature constant and the speed, it was found that the higher efficiency of rinsing occurred at a pressure of 0.15 MPa, whereas the lowest efficiencies were obtained for the extreme pressure values.

REFERENCES

A Critical View on Separation Processes by Membrane Technology Applied in Vegetable Oil Refining


