

Chapter 2

Recovery Technologies for Water-Soluble Bioactives: Advances in Membrane-Based Processes

Alfredo Cassano

Abstract In this chapter, an overview of membrane separation systems in the food industry is provided. Basic principles of pressure-driven membrane operations are described, together with some key advantages and shortcomings compared to conventional technologies. Selected applications of membrane unit operations and integrated membrane systems in specific areas of agro-food production (dairy, soybean, fish processing, olive oil) are also reviewed and discussed, highlighting their potential with respect to the separation, concentration and purification of high-added-value compounds, improvement in food quality and the reduction of environmental pollution.

Keywords Food processing • Pressure-driven membrane operations • Microfiltration (MF) • Ultrafiltration (UF) • Nanofiltration (NF) • Reverse osmosis (RO)

Nomenclature

a	Constant ([-])
b	Constant ([-])
c	Constant ([-])
C	Concentration ($[\text{mol m}^{-3}, \text{mol L}^{-1}]$)
d	Constant ([-])
d_h	Hydraulic diameter ([m])
D	Diffusion coefficient ($[\text{m}^2 \text{s}^{-1}]$)
J_s	Solute flux ($[\text{mol m}^{-2} \text{s}^{-1}]$)
J_v	Volume flux ($[\text{m s}^{-1}]$)
k	Mass transfer coefficient ($[\text{m s}^{-1}]$)
l	Membrane thickness ([m])
L	Length ([m])
P	Permeability ($[\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}]$)
p	Pressure ([Pa or bar])

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<i>R</i>	Rejection ([-])
<i>R</i>	Resistance ($[m^{-1}]$)
<i>Re</i>	Reynolds number ([-])
<i>Sc</i>	Schmidt number ([-])
<i>Sh</i>	Sherwood number ([-])
<i>t</i>	Time ([s])
<i>u</i>	Velocity ($[m\ s^{-1}]$)
<i>V</i>	Volume ($[m^3]$)
VCR	Volume concentration ratio ([-])
WCR	Weight concentration ratio ([-])
<i>Y</i>	Yield ([-])

Greek Letters

δ	Boundary layer thickness ([m])
Δ	Difference ([-])
μ	Viscosity ([Pa s or $m^2\ s^{-1}$])

Abbreviations

BOD	Biological oxygen demand
CA	Cellulose acetate
COD	Chemical oxygen demand
DF	Diafiltration
Igs	Immunoglobulins
MF	Microfiltration
MPCs	Milk protein concentrates
MWCO	Molecular weight cut-off
NF	Nanofiltration
OMW	Olive mill wastewater
PA	Polyamide
PAN	Polyacrylonitrile
PE	Polyethylene
PES	Polyethersulphone
PP	Polypropylene
PS	Polysulphone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
RSM	Response surface methodology
RO	Reverse osmosis
TOC	Total organic carbon
TAA	Total antioxidant activity
UF	Ultrafiltration
WPCs	Whey protein concentrates

Subscripts

- b Bulk
- c Cake
- g Membrane wall (gel)
- i Inlet
- m Membrane
- o Outlet
- p Permeate
- r Retentate
- s Solute
- v Volume
- 0 Initial value

2.1 Introduction

The global demand for membrane modules in water treatment and industrial applications was valued at approximately USD 15.6 billion in 2012. With growth in subsequent years estimated at 8 % annually, the market is forecast to increase to USD 21.2 billion in 2016 and to approach USD 25.0 billion in 2018 (Market Report 2013). In the food industry, the current market for membranes constitutes about 20–30 % of the overall manufacturing industry worldwide, with growth of around 7.5 % per year (Daufin et al. 2001).

Membrane separation processes have special importance in food processing and food wastewater treatments. They can contribute to the simplification of traditional processing steps for the manufacture of food ingredients and to the formulation of novel foods with improved sensory and nutritional characteristics.

Membrane processes offer several advantages over conventional separation techniques such as decantation, centrifugation, filtration, solvent extraction and evaporation (thermal/vacuum concentration). One of the most important advantages in the field of food processing is the ability to operate at room temperature, thus preserving heat-sensitive compounds that can be deactivated or denatured at higher temperature (e.g. proteins). In addition, membrane separation does not involve the use of chemical substances or phase changes, so it is characterized by low energy consumption and reduced environmental impact. Another attractive feature of membrane processes is the simplicity of their layout and their modular design that allows for easy scale-up and increased production capacity.

The membrane market today offers a full range of membranes and systems to maximize the economic use of water and the recovery of valuable compounds from food processing streams in order to meet the special needs of both food processors and environmental discharge standards.

In this chapter, the potential for pressure-driven membrane operations in areas of agro-food production is analyzed and discussed. The first part of the chapter will focus on basic principles of the technology, including typical membrane types and modules

used in different membrane-based operations, and on membrane fouling, which represents a key disadvantage of membrane filtration. The second part of the chapter will provide an outlook on specific applications of pressure-driven membrane operations in different areas of agro-food production (dairy, fish, olive oil, and other foods and beverages), highlighting their potential for the recovery of water and high-added-value compounds from the original solutions, and for reducing the environmental burden of food processing wastewater. The integration of different membrane unit operations at both the laboratory and industrial scale is also considered. This appears to be an attractive way to redesign the conventional production cycles of the agro-food industry within the context of a process intensification strategy, enabling dramatic improvements in manufacturing and processing, and reducing the equipment size/production capacity ratio, energy consumption and waste production.

2.2 Basic Principles of Pressure-Driven Membrane Operations

2.2.1 Membrane Types and Modules

In general, a membrane can be defined as a selective barrier separating two adjacent phases that allows the selective transport of particular species between the two phases in a specific or non-specific manner. Synthetic membranes can be produced from organic materials (polymers) as well as inorganic materials (ceramics, zeolites, metals and their alloys). Membrane chemistry determines important properties such as hydrophilicity or hydrophobicity, the presence or absence of ionic charges, chemical and thermal resistance, binding affinity for solutes or particles, and biocompatibility (Strathmann et al. 2006). Polymeric membranes dominate the industrial membrane technology market because they are highly competitive in performance and affordability. The most common polymeric membranes are manufactured from cellulose acetate (CA), polysulphone (PS), polyethersulphone (PES), polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) and polyamide (PA). Many membrane polymers are grafted, custom-modified or produced as copolymers to improve their properties. Indeed, many studies have sought to enhance the performance of hydrophobic membranes (i.e. PVDF membranes) by introducing hydrophilic functional groups such as $-\text{SO}_3\text{H}$ or $-\text{COOH}$ to the surface by chemical modification or by adding water-soluble polymers such as poly(vinylpyrrolidone) or poly(vinyl methyl ether) to the membrane casting solutions (Baker 2000).

Ceramic membranes are manufactured from inorganic materials (e.g. alumina, zirconia, titania and silica). They exhibit high resistance to aggressive media (acids, alkalis, strong solvents) and high mechanical and thermal stability. Although their production costs are higher than those of polymeric membranes, they are ecologically friendly and durable, and have a longer lifetime.

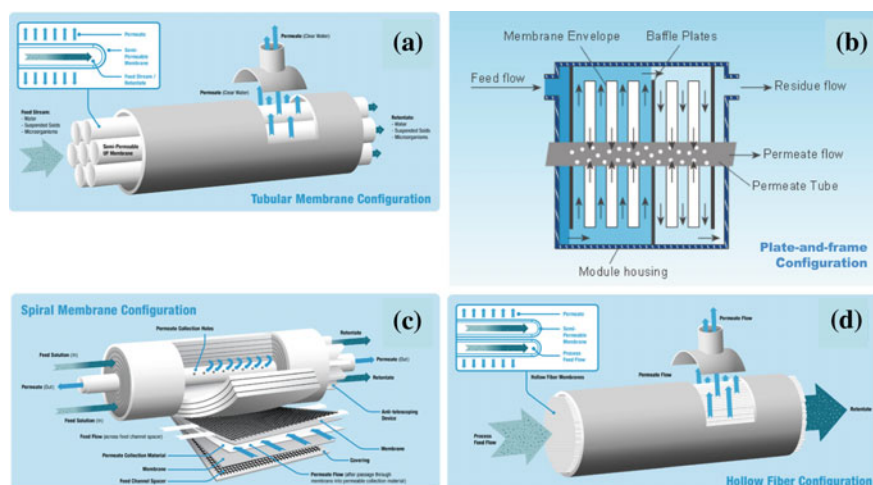


Fig. 2.1 Schematic representation of **a** tubular, **b** plate-and-frame, **c** spiral-wound and **d** hollow fiber membrane module (adapted from Koch Membrane Systems)

On the basis of their structure, synthetic membranes can be classified as porous membranes, homogeneous membranes, solid membranes carrying electrical charges, and liquid or solid films containing selective carriers (Strathmann et al. 2006).

Porous membranes consist of a solid matrix with defined pores having diameters ranging from less than 1 nm to more than 10 μm . They can be classified as follows: macroporous, with average pore diameters larger than 50 nm (i.e. microfiltration and ultrafiltration membranes); mesoporous, with average pore diameters ranging from 2 to 50 nm (i.e. nanofiltration membranes); and microporous, with average pore diameters of between 0.1 and 2 nm. Dense membranes, such as those used in reverse osmosis, have no discrete permanent pores, but separation occurs through fluctuating free volumes.

In addition, the structure of membranes may be symmetric, asymmetric or composite. Symmetric membranes are characterized by identical structure and transport properties over the whole cross-section. They range in thickness from 100 to 200 μm . A decrease in membrane thickness results in an increased permeate flux. Asymmetric membranes consist of a dense ‘skin’ layer supported by a porous layer providing mechanical strength. The skin layer is characterized by pores with small diameters and thickness of 0.1–1 μm . Separation characteristics are determined by the nature of the membrane material or by the pore size of the skin layer. Composite membranes also have a dense skin layer, but the top and the sub-layer originate from different polymeric materials with different structures. Generally, the top layer is formed by a dense polymer supported by a microporous substrate (Ramakrishna et al. 2011).

Synthetic membranes used at the industrial level are installed in devices called *membrane modules*. On a large industrial scale, membrane modules are generally available in four basic designs: tubular, hollow fiber, spiral-wound and plate-and-frame.

They are quite different in their design, mode of operation, production costs and energy requirements for pumping the feed solution through the module.

Tubular membrane modules (Fig. 2.1a) consist of several polymeric membranes cast on porous paper or plastic tubular inserts. Membrane tubes are assembled in a housing according to a shell-and-tube configuration. The feed solution is pressurized inside the tubes and the permeate is collected in the shell side of the housing. Tube diameters are typically 10–25 mm.

Tubular designs are suitable for feed solutions with high solids content and large suspended particulate, affording easy control of concentration polarization and membrane fouling phenomena. The membrane area, however, is typically small in comparison with that of other configurations.

Plate-and-frame membrane modules (Fig. 2.1b) are mainly used for products with high viscosity and high solids content. Membranes, feed flow spacers and porous permeate support plates are layered between two endplates and placed in a housing. The feed stream is pressurized in the system and passed over the membrane surface. The permeate passes through the membrane into the permeate channel and is then collected into a central permeate collection manifold. Plate-and-frame modules are quite expensive; they are used in a small number of specific applications for separation of components of highly fouling feeds.

Spiral-wound membrane modules (Fig. 2.1c) consist of a sandwich of flat-sheet membranes, spacers and porous permeate flow material wrapped around a central permeate collecting tube. The feed solution is pumped into the spacer channel tangentially to the membrane surface; the permeate passes through the membrane into a porous permeate channel reaching the permeate collecting tube. Due to their compact layout and high membrane surface-to-volume ratio, spiral-wound elements offer cost-effective solutions for treating large feed volumes. However, the treatment of viscous materials or materials with high solids content is difficult, and feed pretreatment is required (Schwinge et al. 2004). Commercial systems are about 1 m in length, with diameters between 10 and 60 cm. Membrane area can range from 3 to 60 m².

Hollow fiber membrane modules (Fig. 2.1d) have a design similar to that of tubular systems but with a smaller membrane diameter (the inside diameter of fibers may range from 0.5 to 1.2 mm). These modules offer high packing density and can withstand relatively high pressure. They can also be used for small volume filtration, and the feed can be supplied either inside or outside the fibers. However, the treatment of viscous feeds and solutions containing particulate matter is difficult. Consequently, extensive pretreatment of the solution is needed in order to remove particles, macromolecules or other materials that can precipitate at the membrane surface. Due to the self-supporting nature of the membranes, hollow fiber systems can be backwashed to aid in cleaning; in this case, the permeate flow is reversed to dislodge the fouling material from the membrane surface, allowing easier control of concentration polarization and fouling phenomena.

The selection of a specific membrane system depends on several aspects including cost, packing density, risk of membrane plugging and ease of cleaning. Feed and membrane properties, as well as operating conditions such as applied pressure, tangential flow velocity and temperature, are all parameters affecting

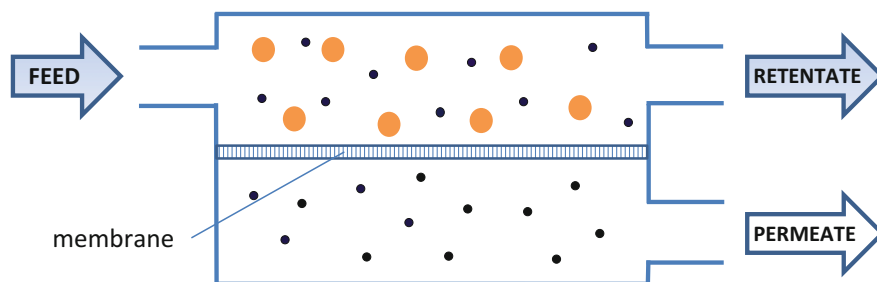


Fig. 2.2 Mechanism of membrane separation

membrane performance. As mentioned above, one of the main limitations of membrane operations lies in membrane fouling, which is associated with the deposition of particles onto the membrane surface and within membrane pores.

2.2.2 Pressure-Driven Membrane Operations

In pressure-driven membrane processes, the membrane acts as a selective barrier through which solvent fluids with permeable solutes are selectively transported under a hydrostatic pressure applied on the feed side. As a result, the feed solution is divided into a permeate fraction containing all components that have permeated the membrane and a retentate fraction containing all compounds rejected by the membrane, within some of the solvent (Fig. 2.2). The separation is based mainly on molecular size, but to a lesser extent on molecular shape, charge and hydrophobicity.

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are typical pressure-driven membrane operation classifications, and represent the key membrane technologies in the food industry.

Microfiltration is used to separate particles with diameters of 0.1–10 μm from a solvent or from low molecular weight compounds. These particles are generally larger than those separated by UF or RO. Consequently, the osmotic pressure for MF is negligible, and hydrostatic pressure differences in MF are relatively small (0.5–4 bar).

Ultrafiltration is a membrane process similar to MF in the mode of separation, based on the use of asymmetric membranes with pore sizes in the skin layer of 2–10 nm. Dissolved molecules or small particles larger than the pore size are retained, though this technique is generally not used for separating particles larger than 0.1 μm in diameter. UF membranes are typically characterized by their molecular weight cut-off (MWCO), defined as the equivalent molecular weight of the smallest species that exhibit 90 % rejection. The MWCO of UF membranes is between 10^3 and 10^6 Da. Hydrostatic pressure of 2–10 bar is typically used.

Nanofiltration membranes are classified between UF and RO membranes in terms of their ability to reject molecular or ionic species, and operate at pressures intermediate between those of UF and RO (generally 3–30 bar). These membranes

are usually characterized by a charged surface with pore diameters of 1–3 nm and MWCO of 200–1000 Da; therefore, components of a fluid are fractionated primarily according to their molecular size and charge. Typically, small uncharged organic molecules and inorganic salts are rejected, especially if multivalent ions are involved. This may lead to significant osmotic pressure across the membrane, which reduces the driving force for the mass transport. Therefore, the use of membranes with high affinity for the solvent ensures high solvent flux and high solute rejection.

Reverse osmosis membranes are typically used to separate low molecular weight compounds from water. Particle sizes for RO applications range from 0.1 to 1 nm, and solutes with molecular weight of approximately 150 Da or less are separated. Since the osmotic pressure of a solution containing low molecular weight solutes can be rather high, hydrostatic pressure on the order of 10–100 bar is applied as driving force in RO to obtain significant transmembrane flux.

The separation capacity of pressure-driven membrane operations is illustrated in Fig. 2.3, which shows that the dimensions of the components involved in these separations range from less than 10^{-3} μm to over 1 μm .

The separation characteristics of membranes can be expressed in terms of membrane rejection (or retention) according to the following equation:

$$R = \left(1 - \frac{C_p}{C_r} \right) \cdot 100 \tag{2.1}$$

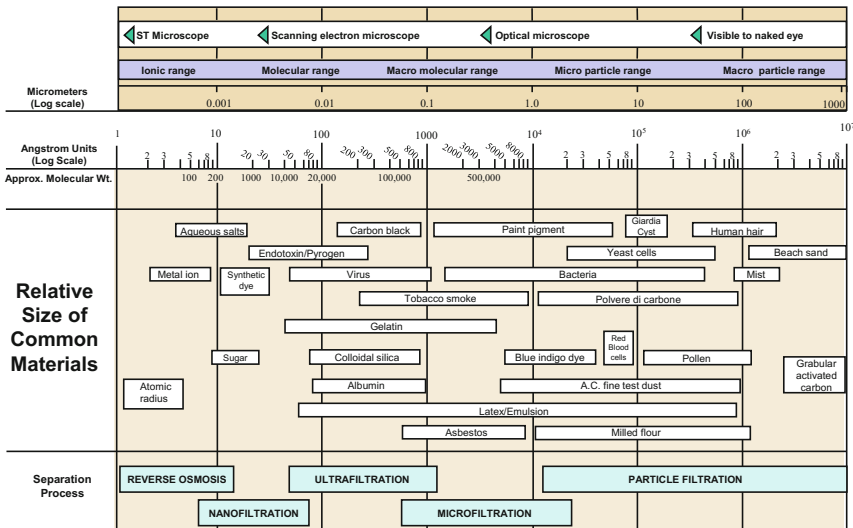


Fig. 2.3 Separation capability of pressure-driven membrane operations (adapted from Osmonics, Inc.)

where R is the membrane rejection for a given component in defined conditions of hydrostatic pressure and feed solution concentration, while C_p and C_r are the concentrations of the component in the permeate and retentate streams, respectively. However, the concentration in these streams depends not only on membrane rejection, but also on the volume concentration ratio (VCR), which for a batch process is defined as:

$$VCR = \frac{V_o}{V_r(t)} = \frac{V_o}{V_o - V_p(t)} \quad (2.2)$$

where V_o is the initial feed volume (L) of the feed, $V_r(t)$ is the final volume (L) of the retentate at particular time (t), and $V_p(t)$ is the volume collected on the permeate side at a particular time (Singh et al. 2013).

Another important parameter is the yield (Y) of a component, which is the fraction of a specific component in the original feed recovered in the final retentate. It is given by:

$$Y = \frac{C_r V_r}{C_o V_o} \quad (2.3)$$

where C_o is the initial feed concentration.

For a batch process, the yield of a particular component is an exponential function of the decreasing volume of the feed in the system, according to the following equation:

$$Y = (VCR)^{R-1} \quad (2.4)$$

In a continuous single- or multistage process, the steady state is achieved at higher levels of concentration. For such a process, the yield is given by:

$$Y = \frac{1}{VCR - R(VCR - 1)} \quad (2.5)$$

and the concentration of a component in the final retentate can be calculated from the following equation:

$$C_r = C_o Y (VCR) \quad (2.6)$$

In MF and UF processes, the retention is affected mainly by the pore size due to the sieving effect; in NF and RO, the membrane retention is affected mainly by electrostatic forces, as well as by other interactions between membrane and solutes. Therefore, membrane retention is also affected by factors such as polarity and solute-membrane interactions, and the MWCO provides only an initial prediction of the membrane's capacity for removing specific compounds (Guizard and Amblard 2009).

The permeate flux through the filter medium is affected by the applied pressure difference across the membrane (between the filtrate and permeate sides of the membrane), the resistance of the membrane and of the cake layer and the viscosity of the fluid being filtered.

The volumetric flux (J_v) is expressed using Darcy's law and a resistance-in-series model:

$$J_v = \frac{\Delta p}{\mu(R_m + R_c)} \quad (2.7)$$

where Δp is the transmembrane pressure (Pa), μ is the permeate viscosity (Pas), R_m is the membrane resistance (m^{-1}) and R_c is the cake resistance (m^{-1}).

Δp is generally calculated as follows:

$$\Delta p = \frac{p_i + p_o}{2} - p_p \quad (2.8)$$

where p_i is the pressure at the inlet of the membrane module, p_o is the pressure at the outlet of the membrane module and p_p is the permeate pressure.

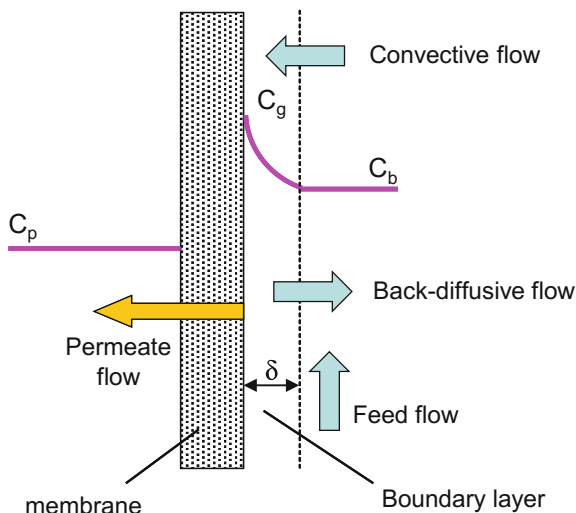
Pressure-driven membrane operations can be performed in either dead-end or tangential-flow configurations. In the dead-end mode, the feed is forced perpendicularly to the membrane surface, and the retained particles tend to form a cake layer on the membrane surface, the thickness of which increases with the filtration time. Therefore, the permeation rate decreases with increasing cake layer thickness. In the tangential-flow mode, the feed solution flows tangentially to the membrane surface and the permeate passes through the membrane due to the imposed transmembrane pressure difference. Unlike in dead-end filtration, the cake layer formed by rejected particles on the membrane surface does not build up indefinitely, but quickly reaches a steady state. The cake layer remains relatively thin due to the high shear exerted by the solution flowing tangential to the membrane surface, clearing the deposited particles towards the retentate exit.

2.2.3 Concentration Polarization and Membrane Fouling

In membrane separation processes, the separation takes place in a very small region close to the membrane, called the *boundary layer*, as well as over the membrane itself (Fig. 2.4). This results in a higher local concentration of the rejected species at the membrane surface compared to the bulk, enhanced by the depletion of the permeating components in the boundary layer adjacent to the membrane surface. This local solute concentration build-up is known as *concentration polarization*, and is chiefly responsible for the marked deviation in flux from that of pure water.

In RO, small solutes are separated from a solvent through a dense membrane. The feed solutions are characterized by high osmotic pressures, and concentration

Fig. 2.4 Concentration profile during membrane processing of partially or completely rejected solutes (c_p = permeate concentration; c_g = membrane wall (gel) concentration; c_b = bulk concentration; δ = boundary layer thickness)



polarization leads to an increase in osmotic pressure that is proportional to the solute concentration at the membrane surface. As a consequence, a decrease in permeate flux is observed at a constant applied Δp in both batch and continuous processes. In MF and UF, only macromolecules are retained by the membrane, and the osmotic pressure difference between the feed and the permeate solution is relatively low. Consequently, in these processes, the pressure difference required for operation is also low, but the diffusion of macromolecules from the membrane surface back into the bulk solution is slow. Under these conditions, the retained components can precipitate on the membrane surface, leading to the formation of a solid layer, which affects membrane performance by reducing the transmembrane flux and modifying the selectivity of the membrane.

According to another view, the flux decay can be explained by assuming that the solute accumulated on the membrane surface creates hydrodynamic resistance to the solvent flow in addition to membrane resistance. A dense particle layer is formed by small particles, while large macromolecules form a 'gel' layer. The formation of this gel layer on the membrane surface affects membrane separation characteristics by changing the rejection selectivity towards low molecular weight compounds. In addition, concentration polarization is responsible for the existence of a limiting flux when a feed solution is filtered through a semipermeable membrane. At low pressures, the relationship between permeate flux and applied pressure is linear, and is similar to that of pure solvents. As the pressure is increased, the flux deviates from linear flux–pressure behaviour to a point at which it becomes independent of pressure. The gel layer is assumed to be dynamic; therefore, increasing the tangential flow velocity or decreasing operating pressure or feed solute concentration can cause the system to revert back to a higher and more pressure-responsive permeation rate.

According to the *film model* theory, mass transport resistance is due to a film of liquid near the membrane; a steady state is established by the convective transport of solutes to the membrane surface and the diffusive flux of retained material back into the bulk solution. This is expressed by the following balance equation (Bhattacharya and Hwang, 1997):

$$J_s = J_v C_b + D \frac{dC}{dx} = 0 \quad (2.9)$$

where J_s is the solute flux, J_v is the membrane volume flux, C_b the bulk concentration of the rejected solute, D the diffusion coefficient, and dC/dx the concentration gradient of the solute in the boundary layer (see Fig. 2.4).

Integration over the boundary layer of thickness δ gives:

$$J_v = \frac{D}{\delta} \ln \frac{(C_m - C_p)}{(C_b - C_p)} \quad (2.10)$$

where C_m is the solute concentration at the membrane surface, C_p is the solute concentration in the permeate, and C_b , the solute concentration in the bulk.

Introducing the solute mass transfer coefficient $k = D/\delta$ into Eq. (2.10) leads to:

$$J_v = k \ln \frac{(C_m - C_p)}{(C_b - C_p)} \quad (2.11)$$

which is the general form of the equation for any component.

When the solute concentration at the membrane surface reaches a value at which a ‘gel’ is formed ($C_m = C_g$), the equation is reduced to the form:

$$J_v = k \ln \left(\frac{C_g}{C_b} \right) \quad (2.12)$$

The term C_g/C_b refers to the membrane polarization ratio.

Empirical equations correlate the mass transfer coefficient to the channel geometry and flow regimes. This correlation can be expressed in a general form as (Sherwood et al. 1975):

$$Sh = a Re^b Sc^c \left(\frac{d_h}{L} \right)^d \quad (2.13)$$

where Sh , Re and Sc are the Sherwood, Reynolds and Schmidt numbers, respectively; L is the length of the feed flow channel (or tube); d_h is the hydraulic diameter of the feed channel; and a , b , c and d are characteristic constants for different geometries to be experimentally determined.

The Sherwood number is given by:

$$Sh = k \frac{d_h}{D} \quad (2.14)$$

The Schmidt number is given by:

$$Sc = \frac{\mu}{D} \quad (2.15)$$

where μ is the viscosity.

The Reynolds number in a channel (or in a tube) is given by:

$$Re = \frac{d_h u}{\mu} \quad (2.16)$$

where u is the fluid velocity. In general, Re values less than 1800 are considered to indicate laminar flow and Re greater than 4000 indicates turbulent flow.

Methods for reducing concentration polarization include (i) reduction of the applied pressure; (ii) reduction of solids concentration in the feed solution; (iii) hydrodynamic modifications and the use of turbulent promoters to improve mass transfer; (iv) the use of rotating cylinders or vibratory shear-enhanced units; (v) chemical modification of the membrane surface; and (vi) application of an external body force such as an electric field to influence the charge on macromolecules, the use of ultrasound to induce cavitation at the surface, or the injection of inert gas to induce turbulence.

Membrane fouling is a major problem in pressure-driven membrane operations. It can be considered a long-term flux decline caused by the interaction of chemical species and their deposition on the membrane surface or within the membrane pores. This phenomenon can be induced by several mechanisms, including increased interfacial concentration due to concentration polarization, the adsorption of solutes within the pores, partial or complete pore blocking, the formation of a cake from excluded solutes, and the precipitation or gelation of inorganic and organic particulate at the membrane surface. The general effect is an overall increase in resistance to mass transport, reduction in the membrane surface and change in separation properties of the membrane. Indeed, the presence of foulants at the membrane surface or within the pores affects the passage of solutes through the membrane due to the lower porosity and the difference in charge properties of the fouled membrane in comparison with the clean membrane (Schäfer et al. 2000).

The degree of membrane fouling determines the frequency of cleaning required and the lifetime of the membrane; therefore, it has a significant effect on the cost, design and operation of membrane plants (Boerlage et al. 2004).

Different substances can contribute to fouling phenomena, including organic materials (e.g. proteins, polysaccharides and humic acids), colloidal or particulate matter, inorganic compounds (poorly soluble salts and metal hydroxides), chemical reactants and biological components (microorganisms, products of their metabolism, and cell debris).

In addition, the fouling propensity of a membrane is strongly influenced by the membrane material: for example, proteins may bind to the membrane by hydrophobic effects, hydrogen bonding or electrostatic interactions, depending on the membrane material and protein type. Some functional groups of fat substances are similar to those of PVDF and PS membranes, resulting in considerable fouling phenomena.

The ionic strength, pH and electric charge of the feed material are also significant, since they affect the charge of both membrane surface and particles, the conformation and stability of molecules, and the effective size of the cake layer (Vyas et al. 2000).

Several factors can be considered for controlling and minimizing fouling phenomena, including the selection of appropriate feed-stream pretreatment methods, membrane materials and module configurations, modification of membrane properties, and optimization of cleaning procedures.

Feed-stream pretreatment methods, including adsorption onto active carbon, pH adjustment, heat treatment, the addition of complexing agents, and chlorination, aim to remove or to stabilize foulants by changing the properties of the feed solution.

As reported above, the use of tubular and plate-and-frame designs is preferred for feed solutions containing high solids content and large suspended particulate matter.

The use of turbulence promoters, ultrasonic vibrations, or rotating modules aimed at increasing the convective transport of solutes back to the bulk solution is also effective for reducing membrane fouling.

Operating parameters such as flow rate, transmembrane pressure, temperature and feed concentration have great influence on membrane fouling. Generally, an increase in temperature results in a reduction in viscosity and an increase in the diffusion coefficients of molecules, resulting in higher permeation fluxes, although protein denaturation may be a limiting factor.

Higher rates of tangential flow tend to reduce the aggregation of the feed solids in the gel layer, increasing their diffusion back towards the bulk. This leads to an overall reduction in the effect of concentration polarization. However, in some cases the increase in tangential flow velocity effects the removal of larger particles from the membrane surface, but stratification of smaller particles on the membrane surface, with consequent pore plugging.

Generally, an increase in the feed concentration results in a faster decline in the permeate flux with time, due to higher fouling of the membrane in the presence of higher concentrations of foulants.

As reported previously, when a feed solution is treated by MF or UF, a typical flux plateau is observed where an increase in Δp yields no flux increase; the permeate flux approached at a specific Δp limit value is defined as *limiting flux*. This phenomenon is due to a combination of concentration polarization and membrane fouling (Wu et al. 1999). Below a certain flux, known as the *critical flux*, the relationship between the applied pressure and flux may be linear. Therefore, operating below the critical flux can afford greater control of the fouling phenomenon.

Procedures for cleaning to reduce membrane fouling are based on hydraulic, mechanical, electrical and chemical methodologies. The selection of a system depends on the module configuration, the chemical resistance of the membrane and the type of fouling.

Hydraulic cleaning is typically achieved by *in situ* methods such as back-flushing and back-pulsing. Back-flushing consists in periodically reversing the transmembrane flow to remove foulants from the membrane surface and pores. With this approach, the direction of the permeate flow is reversed at regular intervals (i.e. 5–30 s once every 30 min to several hours). The back-flushing medium can be the permeate, another liquid or a gas. The procedure is carried out with tubular and hollow fiber membranes, which can withstand the reversal in pressure difference.

In back-pulsing, high speeds and pressure fluctuations are employed to dislodge particles accumulated on the membrane surface. Typically, high-pressure pulses (up to 10 bar) are applied for very short intervals (typically <1 s) (Sondhi and Bhawe 2001).

The injection of gas bubbles at high velocities through tubular membrane systems is a mechanical method that can be used to create turbulence at the membrane surface in order to dislodge fouling materials. The use of electrical pulses to produce a movement of charged species away from the surface can be also applied for metallic membranes.

Chemical cleaning is generally realized by cleaning-in-place (CIP) methodologies in order to partially or completely restore the permeate flux. The composition of the cleaning solution is strongly dependent on the nature of fouling agents and the properties of the membrane. Alkaline solutions such as NaOH and KOH up to pH 12 are used to solubilize and break down organics and proteins. Acid cleaning solutions at pH 1.5–2.8 are mainly used to remove inorganic foulants.

Cleaning solutions should be pumped through the system at high velocity and low operating pressure in order to avoid the penetration of foulants into membrane pores. Most chemical cleaning solutions complete their action in 30–60 min; enzymatic cleaning agents may require longer times. The temperature of cleaning solutions should be as high as possible, complying with the temperature limitation of the membrane module.

2.3 Milk and Dairy Industry

The food sector of greatest significance for pressure-driven membrane operations is the dairy industry. Most relevant applications cover the treatment of milk, whey and waste streams, and they are well established at the industrial level. Membrane processes are used in the standardization of milk, whey and milk protein concentrations, fractionation of protein hydrolysates, removal of bacteria and fat from milk, concentration of milk for cheese production, demineralization of whey and cheese brine treatments. For some applications, the integration of pressure-driven membrane processes has been integrated into existing installations, resulting in particular benefits in terms of improved quality, development of new products such as functional and health-promoting foods, enhanced process efficiency and better control of the environmental impact (Rosenberg 1995).

2.3.1 Milk Processing

The protein and total solids content of milk can be standardized using UF membranes to overcome variations in composition. These membranes retain proteins, fats, and insoluble and bound salts, allowing the permeation of water, lactose and soluble salts.

The combination of MF and UF membranes is of interest for the fractionation of caseins. The use of MF membranes with a pore size of 0.2 μm enables the production of a permeate fraction containing mostly whey proteins and a retentate enriched in native caseins that can be used for cheese making. The MF permeate can be further treated by UF to produce high-quality whey protein concentrates (WPCs).

Karasau et al. (2010) compared the performance of ceramic and polymeric membranes in the treatment of skim milk for the manufacture of casein; PVDF and ceramic membranes with a pore size of 0.2 μm provided comparable results when operated at comparable values of applied pressure, tangential flow velocity and temperature.

Milk protein concentrates (MPCs) containing 50–85 % proteins can be obtained through a combination of MF and UF processes with diafiltration (DF) and an appropriate adjustment of pH and temperature. These concentrates find application in the manufacture of cheese products, dietary supplements, cultured products and dairy-based beverages.

The Tetra Pak UF technology is an elegant application of membrane technology in semi-hard cheese production, with significant advantages, especially in terms of higher product yield, when compared with traditional methods. In this approach, which is used to produce fresh white and Mediterranean cheese varieties such as feta and queso fresco, the cheese is packed as a liquid and is coagulated inside the final packaging. The process line for semi-automatic production of microbially acidified feta cheese, the Tetra Tebel Casofill® BAF (bacteriologically acidified feta), consists of a UF step in which milk is concentrated about 5.5 times to a final total solids content of 36–39 %. The UF retentate is then pasteurized and homogenized at 75–80 °C. After cooling, it is pumped to the fermentation tank, and finally is subjected to the filling step (Kiers 2001; Tamime et al. 2006).

2.3.2 Whey Processing

Whey is a liquid co-product of the cheese and casein industries. It has a low solids content (up to 5–6 %), and as a waste, it has high biological oxygen demand (BOD = 30–50 g/L for 1000 L of whey), making whey disposal difficult, costly and environmentally detrimental. Whey solids constitute mainly lactose (~ 50 g/L), whey proteins (~ 6 g/L) such as α -lactalbumin, β -lactoglobulin, bovine serum

albumin, lactoferrin and immunoglobulins, and minerals (~ 6 g/L) and fat (0.3 g/L).

Whey protein concentrates (WPCs) can be produced using UF membranes with MWCO of ~ 10 kDa. These membranes allow the separation of lactose and minerals from the proteins, producing a retentate stream, which can be further processed by evaporation and spray drying. The protein content of the final product may be controlled by the degree of concentration during UF. WPCs with protein content of 35–60 % can be obtained at a VCR ranging from 4.5 to 20, respectively.

The lactose and mineral content in WPC can be further reduced using a DF step in which deionized water is continually added to the retentate while lactose and minerals are continuously recovered in the permeate stream. Selecting a proper combination of UF and DF can lead to an improvement in the purity of WPCs of up to 75–80 %. WPCs are important sources of protein for a large variety of food products, including beverages, processed meats, baby foods, yogurt and cottage cheese (Zidney 1998).

Yorgun et al. (2008) investigated the recovery of proteins from white and curd cheese whey using spiral-wound UF, NF and RO membranes. Among the studied membranes, the highest protein recovery and greatest reduction in chemical oxygen demand (COD) were obtained using a PS NF membrane module with an MWCO of 200 Da. The module exhibited an initial permeate flux of 24 L/m²/h when cheese whey was treated at a Δp of 8 bar and a recirculation flow rate of 2500 L/h. A permeate with a COD of 2787 mg/L (COD removal 97.4 %) was produced, while the protein rejection was 88 %. Further COD removal from the NF permeate required an additional RO stage as a polishing step. This combination allowed the recovery of protein in the NF retentate (first step), while lactose was recovered in the RO retentate (second step), with simultaneous production of clean RO-water as the last permeate.

PVDF UF membranes with MWCO of 6–8 kDa effected protein rejection of between 92 and 98 % in the treatment of milk and whey, with an acceptable permeate flux (30 L/m²/h) at low pressures (3 bar). A temperature of about 50 °C was considered a limit value for achieving good performance, avoiding denaturation of proteins and damage to membrane materials. The use of PA NF membranes (MWCO 400 Da) enabled the recovery of lactose from milk and whey UF permeates. Through the selection of proper operating conditions (i.e. VCR of 5, Δp of 20 bar and 30 °C), a concentrated solution containing 20–25 % lactose was obtained with a lactose yield higher than 90 %. This solution could be reused in the confectionery industry, while the permeate stream depleted from lactose could be reused for cleaning or irrigation, or as a last resort, discharged as sewage (Atra et al. 2005), with no adverse environmental impact.

MF and UF processes can also be used to isolate immunoglobulins (Igs) from colostrum whey. The MF of colostrum with membranes of 0.1 μm pore size produces a clear permeate, free from fat globules and casein micelles, containing 80 % of the initial Igs. The MF permeate, or serocolostrum, is then concentrated by UF membranes with MWCO of 100 kDa (Piot et al. 2004).

Korhonen et al. (1998) investigated the use of MF, UF and RO membranes in combination with cation-exchange resins for the concentration of Igs. The Ig level of the final freeze-dried concentrates varied from 45 to 75 %.

NF membranes can be used to demineralize whey before evaporation and drying. These membranes retain proteins and multivalent ions (i.e. Ca^{2+}), removing monovalent ions such as Cl^- , Na^+ and K^+ . When sweet whey is treated (pH 6.0–6.6) using negatively charged membranes, the retention of proteins (negatively charged at neutral pH) and polyvalent anions results in the accumulation of negative charges in the retentate stream. This leads to increased transmission of Cl^- and OH^- and to partial transmission of Na^+ and K^+ in order to maintain the electroneutrality in the permeate fraction. In the case of acid whey (pH 4.5–5), the membrane is positively charged, and the retention of proteins (positively charged at acidic pH) and polyvalent cations results in increased transmission of Na^+ , K^+ and H^+ , and partial removal of Cl^- (Gernigon et al. 2011). Desalination of up to 40 % can be achieved through a combination of NF and DF.

Lactic acid is one of the major food preservatives used in the food industry. Conventional fermentative processes for producing lactic acid are characterized by high costs due to the separations steps needed to meet the quality requirements of food grade. NF and RO processes are useful approaches for the removal of lactic acid from fermentation broths in the cell separation step. The transport of lactic acid through NF membranes (AFC80, PCI Membrane and DK2540C, Filtration Engineering) in the treatment of whey ultrafiltrate fermentation broths was investigated by González et al. (2008). The rejection selectivity of both membranes towards lactate increased by increasing the pH, due to the electrostatic repulsion between the ions and the membrane surface: as the pH increased from 2.7 to 6, the lactate rejection increased from 45 to 82 % for the AFC80 membrane and from 10 to 91 % for the DK2540C membrane.

2.4 Fish-Processing Wastewater Treatment

Fish industry wastewater contains potentially valuable molecules for the food sector, such as proteins, flavors and aroma compounds, and the recovery of these materials can lead to significant productivity gains (Massé et al. 2008).

Afonso and Bórquez (2002) evaluated the performance of an integrated process based on a combination of MF and UF membranes for the recovery of proteins from the effluents of a fishmeal plant. The MF pretreatment drastically reduced the oil, grease and suspended matter content in the original effluent. A UF ceramic membrane (Carbosep M2, tubular, 15 kDa MWCO) reduced the organic load of the MF permeate and allowed the recovery of valuable raw materials, including proteins. Protein rejection ranged from 49 to 62 %, depending on the operating conditions. The highest protein rejection was achieved at a Δp of 4 bar and a crossflow velocity of 4 m/s. A conceptual process for the treatment of 10 m³/h of fishmeal effluent was designed. The plant generated 1 m³/h of concentrate containing 170 g/L of solids

and 112 g/L of proteins. An economic assessment of the integrated MF-UF process for production of 544 tons/year of fishmeal (66 % protein content) yielded a net present worth of US \$160,000, a 17 % rate of return, and an 8-year return on investment, indicating the feasibility of the process for protein recovery and pollution reduction (Afonso et al. 2004).

Mameri et al. (1996) also investigated the use of UF for the recovery and concentration of proteins from fishery washing wastewater. A tubular PS membrane with MWCO of 20 kDa and a multichannel ceramic membrane with 0.1- μm pore size produced similar apparent rejection (70–80 %) of proteins, despite their different pore diameters. The UF process allowed an increase in the protein concentration in the feed solution from 5 to 35 g/dm³, while simultaneously reducing the biochemical oxygen demand (BOD) by 80 %.

2.5 Recovery of Bioactive Compounds from Vegetable Extracts

The last few decades have seen rapidly growing interest in the utilization of phytochemicals in functional foods, given their beneficial effect on human health, lack of toxicity and low cost. Indeed, epidemiological studies have shown a significant positive association between the intake of fruits and vegetables and a reduced risk of chronic diseases such as cancer, cardiovascular disease, diabetes, osteoporosis, Alzheimer's disease and immune disorders (Kaur and Kapoor 2001).

Conventional extraction techniques for the purification of natural products include solvent extraction, ultrasound-assisted extraction, pressurized liquid extraction, enzyme-aided extraction, supercritical fluid extraction, resin-based extraction and alkaline extraction. These methods have some inherent drawbacks, including the degradation of the target compounds due to high temperatures and long extraction times (as in solvent extractions) and health-related risks.

With a number of advantages including high separation efficiency, low energy requirements, mild operating conditions, no additives, simple equipment and easy scale-up, membrane-based technologies can provide interesting alternatives to conventional systems (Li and Chase 2010).

The purification and concentration of phenolic compounds from aqueous vegetable extracts using membrane operations or integrated membrane systems is a topic that is attracting increasing attention. Prodanov et al. (2008) employed UF membranes with MWCO of 10, 30 and 50 kDa for the separation of phenolics in almond skin extracts according to their molecular weight. Low molecular weight phenolic compounds were recovered in the UF permeate, while proanthocyanidin oligomers were obtained from the retentate.

The use of a PES UF membrane with an MWCO of 30 kDa allowed concentration of R-phycoerythrin from a crude extract of the macro-algae *Grateloupia turuturu* without denaturation or accumulation of undesirable molecules. A VCR of

5 was effective for R-phycoerythrin concentration and pre-purification: 100 % of R-phycoerythrin was recovered, while 32.9 % of other proteins and 64.6 % of sugars passed through the membrane (Denis et al. 2009).

UF membranes also proved successful for concentration of phenolic compounds extracted from grape seeds (Nawaz et al. 2006). The maximum amount of polyphenols (about 11 % of the total weight of the seeds) was recovered by combining a solid-to-liquid ratio of 0.2 g/mL with a 50/50 mixture of water and ethanol as extracting liquid, a two-stage extraction, and a UF membrane with a pore size of 0.22 μm . The procedure provided high extraction rates and extraction selectivity, short extraction times and significant labor savings.

The aqueous extraction of *Castanea sativa* leaves combined with a UF process for the concentration and selective recovery of phenolic compounds was investigated by Diaz-Reinoso et al. (2011). A combination of two membranes of 5 and 10 kDa was proposed for producing a retentate with 40 % active compounds. The use of membranes increased the phenolic content by 18 %, whereas the application of an additional precipitation with ethanol resulted in an increase of 36 %. Diaz-Reinoso et al. (2009) also investigated the use of commercial UF and NF membranes for processing aqueous extracts from grape pomace in order to obtain fractions enriched in antioxidant compounds. All selected membranes with MWCO between 250 and 1000 Da exhibited similar rejection of phenols and sugars, and were suitable for concentration purposes.

Reversible and irreversible fouling phenomena contribute to overall deterioration in the performance of UF membranes in the treatment of aqueous solutions containing polyphenolic compounds. Adsorption onto membrane surfaces and pore walls followed by either pore blocking or narrowing appear to be the main fouling mechanisms when PES membranes are used. In addition, membranes with larger pore sizes (MWCO 100 kDa) were found to exhibit less fouling than membranes with smaller pore sizes (MWCO 10 kDa) (Susanto et al. 2009). Filtration studies of phenolic compounds (such as 2-nitrophenol and 2-chlorophenol) through thin-film composite polyamide NF and RO membranes suggested the formation of a fouling monolayer on the membrane surface. Such fouling led to increased hydrophobicity and diminished roughness of the membrane surface. As expected, solute rejection was higher for the RO membrane than the NF membrane. (Sotto et al. 2013).

Mello et al. (2010) evaluated the performance of an NF membrane composed of PA and PS (NF90, GE Osmonics, Minnetonka, MN, USA) for the concentration of flavonoids and phenolic compounds from aqueous and ethanolic propolis extracts. No loss of compounds was detected in the permeate solution produced from the aqueous extract (the NF membrane retained around 94 % of the phenolic compounds and 99 % of the flavonoids). As a consequence of the higher amount of compounds extracted by alcohol, lower retention of phenolic compounds was measured when the ethanolic extract was nanofiltered.

Polyimide NF membranes resistant to organic solvents (StarMem 122 and DuraMem 200, Evonik Industries, Essen, Germany) were also shown to be very efficient for the concentration of phenolic substances from ethanol–water propolis extracts (Tylkowski et al. 2010). DuraMem 200 with an MWCO of 200 Da

exhibited rejection higher than 95 % for all investigated compounds, including flavones, flavonols, flavanones, dihydroflavonols and other phenolics. At applied pressure of 30 and 50 bar, stable permeate fluxes of 2.66 and 4.05 L/m²/h were measured. The performance of the membranes was also evaluated for concentration of biologically active compounds extracted with ethanol from *Sideritis scardica* Griseb, a plant of the Balkan Peninsula recognized for its high antioxidant activity due to the presence of flavonoids and polyphenols (Tylkowski et al. 2011). Experimental results indicated that membrane rejection was strongly related to the MWCO of the membrane, and that separation of flavonoids from low molecular weight polyphenols occurred at MWCO higher than 400 Da.

The concentration of phenolic compounds from aqueous mate (*Ilex paraguayensis* St. Hil.) extracts with a spiral-wound NF membrane (HL2521TF, Osmonics, Minnetonka, MN, USA) of 150–300 Da was investigated by Aguiar Prudêncio et al. (2012). Chlorogenic acid and epigallocatechin gallate were the main antioxidant compounds detected in concentrates obtained at VCR 4 and 6. The concentration of phenolic compounds and antioxidant activity increased by increasing the VCR (Negrão Murakami et al. 2011).

The recovery of phenolic compounds from citrus by-products by membrane-based operations has been also investigated. Bergamot is the common name of a natural citrus fruit (*Citrus bergamia* Risso) produced in southern Italy. The essential oil, which is obtained from the peel by wash-scraping the fruit, is widely used in the cosmetic industry despite the presence of synthetic surrogates on the market. However, the juice has not found a real use in the food industry due to its bitter taste, even though it contains natural phenols with marked anticholesteremic activity (Di Donna et al. 2009). Tubular ceramic NF membranes with MWCO of 450–1000 Da were evaluated for their selectivity towards sugars, organic acid and flavonoids in the treatment of ultrafiltered bergamot juice. Suspended solids were removed in the preliminary UF step, reducing fouling phenomena in the subsequent NF step. The best separation of polyphenols from sugars occurred with the NF 450-Da membrane, which exhibited the highest rejection selectivity towards flavonoids (95.4 %) and the lowest rejection of sugar compounds (48.7 %) (Conidi et al. 2011).

The same authors evaluated the performance of different polymeric spiral-wound NF membranes (with MWCO of 250–1000 Da) in the treatment of pressed liquors obtained from pigmented orange peels for the separation of phenolic compounds from sugars. The results indicated that the average rejection selectivity towards sugars was reduced by increasing the MWCO of the selected membranes, while rejection of anthocyanins remained higher than 89 % for all the NF membranes investigated (Conidi et al. 2012).

The concentration of anthocyanins from roselle extract (*Hibiscus sabdariffa* L.) using flat-sheet UF and NF membranes with MWCO of 2–150 kDa was investigated by Cissé et al. (2011). The authors suggested that all membranes with nominal MWCO equal to or less than 20 kDa could be used for concentrating anthocyanins. Higher retention of anthocyanins was observed for the NF

membranes. In addition, at average transmembrane pressures, these membranes exhibited similar permeate fluxes when compared with UF membranes.

NF has also been found to be effective for the concentration of anthocyanins from ultrafiltered aqueous extract of aronia berries (Gilewica-Lukasik et al. 2007). The retention of anthocyanins was almost complete in the presence of sodium sulfate (IV) (rejection higher than 99 %), while the filtration of pure aronia solution or that containing sulfate (VI) was not as effective (rejection of 91–95 %).

The fractionation of phenolic compounds with membrane-based separation processes is another topic of interest. Santamaria et al. (2002) proposed sequential filtration with polymeric NF and UF membranes to fractionate proanthocyanidins from winery waste extracts on the basis of their molecular weight. The proposed process, depicted in Fig. 2.5, allowed the production of proanthocyanic fractions with different degrees of polymerization.

Grape anthocyanins were fractionated using flat-sheet PVDF UF membranes with MWCO of 10 to 1000 kDa. Polymeric forms were retained by membranes with MWCO of less than 100 kDa, while monomers were recovered in the permeate fractions (Kalbasi and Cisneros-Zevallos 2007). UF membranes with MWCO of 10 kDa also allowed separation of low molecular weight tannins from

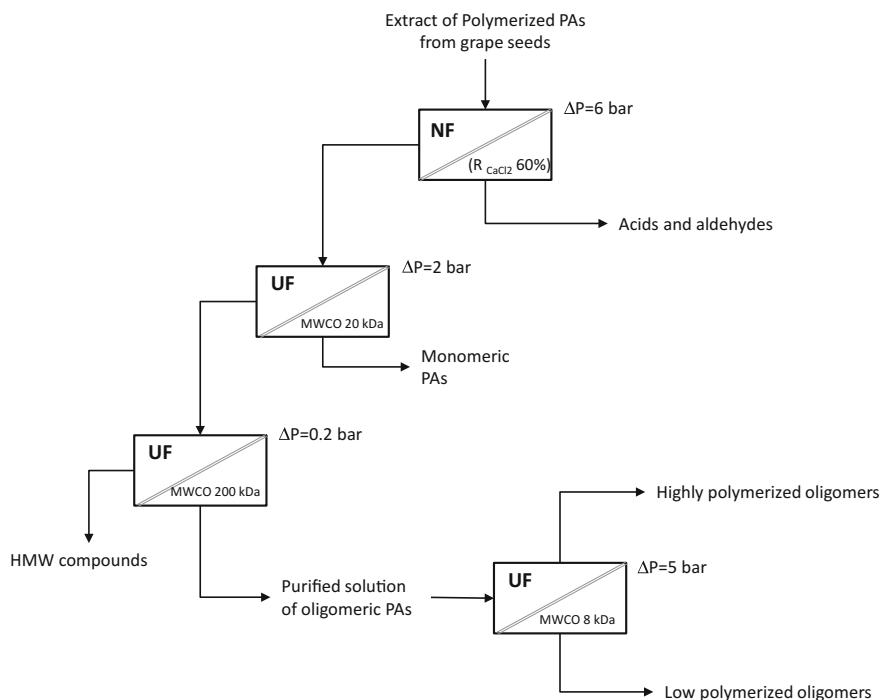


Fig. 2.5 Fractionation of proanthocyanidins (PAs) by integrated membrane operations (*HMW* High molecular weight; *MWCO* Molecular weight cut-off; *R* Rejection) (adapted from Santamaria et al. 2002)

high molecular weight phenolic compounds in the treatment of crude extract of persimmon (a plant belonging to the Ebenaceae family that is widespread in China, Japan and Korea) (Gu et al. 2008).

MF and UF membranes are also an effective tool for the separation of oligosaccharides and low molecular weight impurities from high molecular weight compounds (Li and Chase 2010). Fructo-oligosaccharides, which are widely recognized as functional food ingredients, can be purified and concentrated using NF membranes (Li et al. 2004) or low-MWCO UF membranes. Thin-film polymeric membranes with MWCO of 1 to 8 kDa were used to purify xylo-oligosaccharides from an almond shell hydrolysate (Nabarlatz et al. 2007). Selectivity was maximized by operating at low pressures, and was increased by reducing the MWCO of the membrane.

Tubular polymeric UF membranes (ESP04, PCI Membranes, Poland) and ceramic monolithic NF membranes (Kerasep Nano, Novasep, France) with MWCO of 4 and 1 kDa, respectively, were found to be effective for the purification of xylo-oligosaccharides from monosaccharides and salts from rice husk xylan (Vegas et al. 2008). NF membranes with MWCO of 150 to 300 Da were also proven to be efficient for the recovery of xylose from hemicellulose hydrolysates. Considerable xylose purification was achieved in short-term filtrations, which produced permeate streams containing 78–82 % xylose as total dry solids (Sjöman et al. 2008).

The purification of fructo-oligosaccharides from a mixture of sugars with different NF membranes was investigated by Kuhn et al. (2011). Specifically, the authors evaluated the performance of PA and PES flat-sheet membranes with MWCO over a range of 150 to 1000 Da in both dead-end and tangential-flow configurations. The best results were obtained with the NP030 membrane (Microdyn-Nadir, Germany) with an MWCO of 400 Da, which showed 66 % retention selectivity towards fructo-oligosaccharides, while retention selectivity towards glucose, fructose and sucrose was 18, 15 and 24 %, respectively. DF tests with this membrane produced a concentrate containing 80 % fructo-oligosaccharides.

2.5.1 Soy Protein Extracts

UF represents a valid alternative to the use of isoelectric precipitation for the production of soy protein isolates or concentrates from soy protein extracts. The use of UF allows the recovery of all solubilized proteins, avoiding the formation of whey-like products and resulting in increased protein recovery (Nichols and Cheryan 1981). In addition, undesirable compounds such as oligosaccharides (sucrose, raffinose and stachyose) and phytic acid can be selectively separated from the proteins through selection of optimal operating parameters and membrane types (Kumar et al. 2003).

The combination of UF and DF results in high phytic acid removal and high levels of protein purification. Phytic acid removal is affected by pH: high removal percentages have been observed within a pH range of 5–6.7 (Ali et al. 2010). UF

membranes with MWCO of 50 kDa represent the best option for obtaining high values of permeate fluxes, high protein rejection and high removal of oligosaccharides (Skorepova and Moresoli 2007). In addition, the use of UF membranes with MWCO of 5–30 kDa enables the retention of isoflavones, widely recognized for their anticarcinogenic properties due to their complexation with proteins (Singh 2007). In contrast, in the conventional isoelectric precipitation processes, most of the isoflavones remain soluble after the precipitation step.

The main functional properties of protein isolates (solubility, ability to emulsify, ability to bind water or fat and ability to form foams or gels) obtained by a combination of UF and DF were higher than those obtained with traditional isoelectric precipitation processes (Manak et al. 1980).

Soy protein isolates can also be used as a source of peptides of interest for nutraceutical applications. UF membranes compete with other technologies such as chromatography and ion-exchange resins for use in the fractionation and purification of specific peptides. In particular, soy protein hydrolysates can be subjected to a sequential treatment with UF membranes of increasing MWCO values (i.e. from 5 to 100 kDa) in order to produce different soy peptide fractions (Deeslie and Cheryan 1991).

Wastewater from the manufacture of soybeans contains valuable compounds such as proteins and sugars; their recovery appears to hold great potential for reducing the pollution load of produced effluents while simultaneously utilizing valuable resources.

The integration of pressure-driven membrane operations can be exploited for the extraction of proteins, oligosaccharides and isoflavones from yellow bean product wastewater (Jiang and Wang 2013). UF membranes retain soybean proteins, and the concentrated solution can be spray-dried to obtain a pure soybean protein powder. Soy isoflavones in the UF permeate are adsorbed on weak polar macroporous resins and then eluted with ethanol. Soybean oligosaccharides in the resin effluent liquid can be concentrated using NF membranes, and the concentrated liquid can be used for preparing oligosaccharide powders. The final treatment of the NF permeate by RO produces pure water through the removal of inorganic salts.

Soybean soaking water contains on average of 0.08 % (w/w) crude proteins and 0.02 % (w/w) carbohydrates. Their COD (typically higher than 10 g/L) must be properly reduced for purposes of reuse. The performance of a combined NF-RO membrane system for separating and recovering soluble materials from soybean soaking water was investigated by Guu et al. (1997). The pretreated water (after sedimentation and centrifugation) was nanofiltered through a spiral-wound membrane module (NF40-2514A, FilmTec/DOW Chemical Co.) up to a weight concentration ratio (WCR) of 7. The NF permeate was then subjected to an RO process using a spiral-wound membrane (BW30-2514, FilmTec/DOW Chemical Co.) up to a WCR of 6. Both processes were operated at 30 °C and a Δp of 25 bar. NF and RO retentates were inoculated with probiotic cultures of *Lactobacillus acidophilus* CCRC 10695 and *Bifidobacterium longum* CCRC 11847 in order to assess the possibility of producing lactic acid by fermenting soluble materials (Fig. 2.6). The combination of the two selected cultures produced up to 7.5 g/L of organic acids,

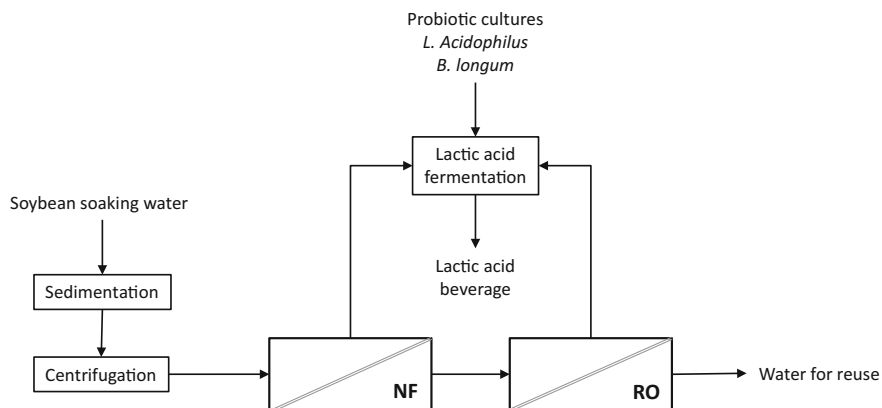


Fig. 2.6 Recovery of soluble compounds and water from soybean soaking water (adapted from Guu et al. 1997)

represented mainly by lactic acid, after 48 h of fermentation at pH 5.5 and a temperature of 37 °C. With this process, the fermentation broth after centrifugation and pasteurization is able to be used for the formulation of lactic acid beverages, while the RO permeate can be reused within the factory for cleaning and soaking purposes.

Spiral-wound NF and RO membranes have also been used for concentration of oligosaccharides (mainly sucrose, raffinose and stachyose) from steamed soybean wastewater after the removal of high molecular weight proteins by UF (Matsubara et al. 1996). Operating in a batch concentration mode, concentrated solutions containing 22 % (w/v) and 10 % (w/v) of oligosaccharides were obtained by RO and NF processes, respectively. The COD of the treated effluent (8400–8700 mg/L) was reduced by 99.6 and 98.1 %, respectively.

2.5.2 Olive Mill Wastewater

The procedures for extraction of olive oil from olives (press extraction, two-phase and three-phase centrifugation systems) produce large amounts of polluted liquid waste, known as olive mill wastewater (OMW) or vegetation water. It is a dark acidic liquid containing organic substances (sugars, tannins, organic acids, nitrogen-containing substances, and phenolic compounds including polyphenols, polyalcohols, pectins and lipids) and minerals. COD and BOD are found in a range of 40–220 and 35–110 g/L, respectively (Niaounakis and Halvadakis 2006). Several physicochemical, biological and combined processes, including centrifugation, membrane filtration, flocculation, adsorption, oxidation, and aerobic and anaerobic treatments, have been proposed for reducing the pollution load of these wastes. If properly managed, however, OMW represents an inexpensive and

convenient source of polyphenols, water-soluble compounds widely recognized for their anti-inflammatory, antimicrobial and antioxidant activity (Obied et al. 2005). These properties are reflected in the high market price and great demand for OMW in pharmaceutical, cosmetic and nutrition applications. According to the 'olive tree biorefinery' concept recently proposed by Federici et al. (2009), the recovery of phenolic compounds from OMW represents an efficient tool for valorization of the olive oil extraction residues.

Several methods have been proposed for the recovery of polyphenols from OMW, including liquid–liquid extraction (Kalogerakis et al. 2013), adsorption onto resins (Scoma et al. 2011), supercritical fluid extraction (Lafka et al. 2011) and fungal enzyme-aided extraction (Garcia Garcia et al. 2000). Most of these methods are expensive and present some drawbacks, such as the presence of residual solvents in the extract and the co-extraction of undesirable compounds.

Pressure-driven membrane operations, mostly in sequential form, meet the requirements for the recovery, purification and concentration of polyphenols from OMW, providing several advantages (low energy requirement, no additives, mild operating conditions, efficient separation and easy scale-up) over conventional technologies (Takaç and Karakaya 2009; Garcia-Castello et al. 2010; Mudimu et al. 2012).

Paraskeva et al. (2007) proposed a combination of UF and NF or RO membranes for a complete fractionation of OMW. In order to improve the performance of the UF membranes (multichannel ceramic membranes with 100 nm pores) and reduce their fouling, OMW was pre-filtered with an 80 μm PP screen. The UF process separated high molecular weight constituents including fats, lipids and suspended solid particles. A drastic reduction in turbidity was also observed independently of the applied Δp . At Δp values higher than 1.75 bar, the permeate fluxes were independent of the applied pressure. The NF treatment of the UF permeate with spiral-wound polymeric membranes (MWCO 200 Da) yielded a concentrated stream containing more than 95 % of the initial phenolic compounds. Better efficiency of the OMW treatment was achieved by applying RO (spiral-wound membrane modules 100 MWCO) after UF. Permeate fractions (75–80 % of the initial volume) from NF and RO treatments exhibited quality characteristics suitable for discharging in aquatic systems, according to EU regulations, or for irrigation.

An integrated membrane process for the selective separation of polyphenols from OMW was patented by ENEA in 2005 (Pizzichini and Russo 2005). In the proposed approach, depicted in Fig. 2.7, OMW was acidified at pH 3–4.5 in order to prevent oxidation of polyphenols, and was then subjected to enzymatic treatment with pectinase to hydrolyze cellulose, hemicellulose and pectin. The degradation products were separated by centrifugation to obtain a partially clarified liquid fraction, which was then subjected to a first MF step carried out with ceramic membranes (pore size of 0.1–1.4 μm). The MF permeate was fed to a UF unit equipped with spiral-wound polymeric membranes (PS, PES, PA or CA) with MWCO ranging from 1 to 20 kDa. The DF process, which consists of the addition of water to MF and UF concentrates, can increase the recovery of phenolic compounds in the permeate fractions. Solid residues from the centrifugation step can be

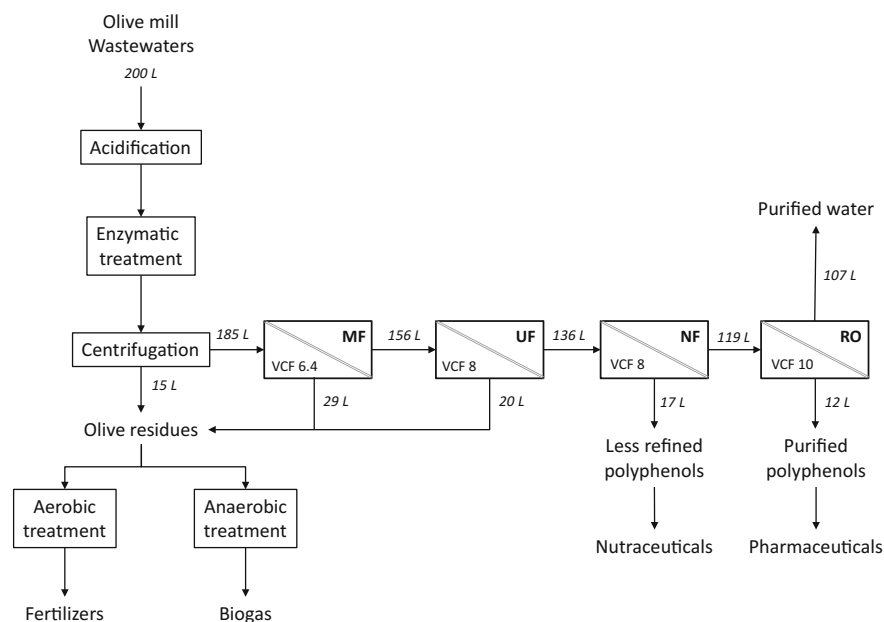


Fig. 2.7 Proposed process scheme for the recovery of water and phenolic compounds from OMW (adapted from Pizzichini and Russo 2005)

added to MF and UF retentates and used as a basis for compost production or subjected to aerobic or anaerobic treatment. The UF permeate is subjected to an NF treatment with spiral-wound polymeric membranes (PA or nylon, MWCO 150–250 Da), producing a permeate containing the maximum amount of hydroxytyrosol and other polyphenols of biomedical interest, and a retentate containing various phenolic compounds (including tyrosol, coumaric acid, hydroxytyrosol and caffeic acid), which can be used for the production of functional foods or cosmetics. The NF permeate is subjected to a final RO treatment using spiral-wound polymeric membranes made of composite PA, producing a concentrated liquid enriched in purified polyphenols of interest for pharmaceutical applications and ultrapure water suitable for beverage formulations.

The combination of UF and NF polymeric membranes for the recovery of phenolic compounds from OMW was recently investigated at the laboratory level by Cassano et al. (2013). OMW, produced according to a three-phase centrifugation process, was pretreated with hollow fiber UF membranes (PVDF, pore size 0.02 μm , Toray) in order to remove most of suspended solids. The UF permeate was then subjected to a second UF step performed with 1000-Da flat-sheet membranes (Etna 01PP composite fluoropolymer, MWCO 1 kDa, Alfa Laval, Sweden). A concentrated phenolic solution was obtained by treating the UF permeate with a spiral-wound NF membrane (NF90, Filmtec/Dow, USA). Analyses of phenolic compounds, total antioxidant activity (TAA) and total organic carbon (TOC) in feed

and permeate fractions for each process are summarized in Table 2.1. The rejection selectivity of the UF and NF membranes towards these compounds is also included. Phenolic compounds were recovered in the UF permeate of the first UF step; most of the organic substances were separated from phenolic compounds in the second UF step, as shown by the high rejection selectivity of the Etna 01PP membrane towards TOC.

Table 2.1 Analyses of polyphenols, total antioxidant activity (TAA) and total organic compounds (TOC) in samples of olive mill wastewaters treated by UF and NF membranes (adapted from Cassano et al. 2013)

Membrane type	Parameter	Feed	Permeate	Rejection (%)
UF (PVDF, 0.02 mm)	Polyphenols (mg GAE/L)	1409	1033	26.7
	TAA (mM Trolox)	3000	2750	8.3
	TOC (mg/L)	13,436	8898	33.7
UF (composite fluoro-polymer, 1 kDa)	Polyphenols (mg GAE/L)	960.8	654.6	31.8
	TAA (mM Trolox)	2695	1750	35.0
	TOC (mg/L)	9000	2500	72.1
NF (polyamide, 150 Da)	Polyphenols (mg GAE/L)	624.7	43.3	93.0
	TAA (mM Trolox)	1825	125	93.0
	TOC (mg/L)	2800	95	96.4

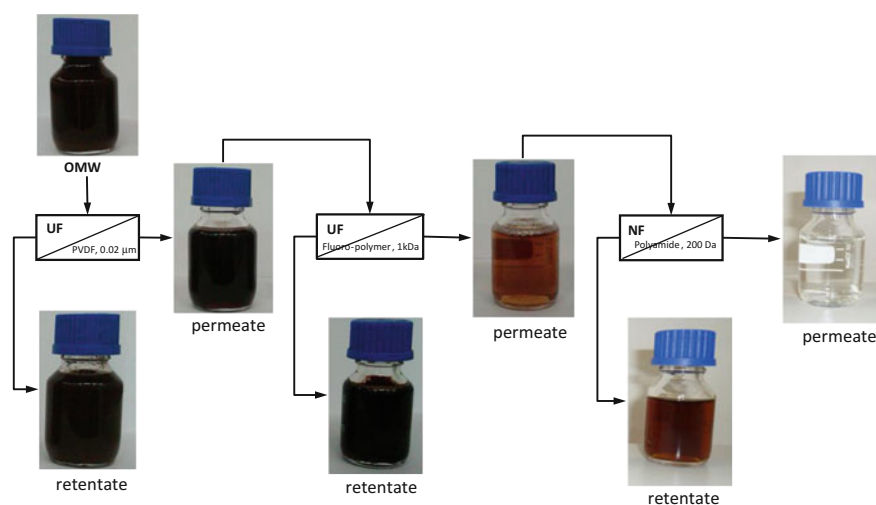


Fig. 2.8 Permeate and retentate fractions from an integrated membrane process for the recovery of polyphenols from OMW (Cassano et al. 2013) (with permission of Elsevier)

Permeate and retentate samples from the fractionation of OMW with the selected membranes are shown in Fig. 2.8.

According to the proposed process, three main fractions are produced: (i) a concentrated solution (retentate of both UF processes) containing high molecular weight organic substances, which can be subjected to anaerobic digestion for the production of biogas; (ii) a concentrated solution (NF retentate) rich in polyphenolic compounds suitable for cosmetic, food and pharmaceutical industries as liquid, frozen, dried or lyophilized formulations; and (iii) a water stream (NF permeate), which can be reused as processing water, membrane cleaning solution, or in the DF step to increase the yield of polyphenols in UF permeates.

2.6 Conclusions and Future Trends

Pressure-driven membrane operations offer a wide range of advantages over conventional technologies for the separation, purification and concentration of high-added-value compounds from food products and food processing wastewater. A high degree of selectivity, better control of the production process, water savings and low energy costs are additional advantages.

The demand for products with greater nutritional value, the development of environmentally friendly processing procedures and the increasingly urgent need to reduce water consumption are all factors that will contribute to the continued growth of the membrane market. In addition, the possibility of combining different membrane operation units within integrated membrane systems or with conventional separation technologies offers interesting new perspectives for redesigning traditional flow sheets of the agro-food industry within the context of process intensification strategies.

The optimization of procedures for reducing membrane fouling, including the development of new membranes and membrane modules less prone to fouling, appears to be a promising area for future investigations aimed at improving the productivity, selectivity and durability of membrane systems. Additional challenges concern the development of functional membranes with specific functional groups grafted onto their surface, conferring high selectivity for target substances and low fouling.

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