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Ultrafiltration, Microfiltration, Nanofiltration and Reverse Osmosis in Integrated Membrane Processes

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1.1 Introduction

Membrane science and technology have known an impressive growth since the early 1960s when Loeb and Sourirajan discovered an effective method for the preparation of asymmetric cellulose acetate membranes with increased permeation flux without significant changes in selectivity. Pressure-driven separation techniques such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have then been extensively studied and developed in industries including desalination and wastewater treatment, biotechnology and pharmaceutics, chemical and food industries. Other membrane processes have been developed and found industrial applications such as gas separation and pervaporation, membrane distillation (MD), electrodialysis (ED), membrane bioreactor (MBRs), and membrane contactors. Membrane technology is usually recognized for the following advantages: operational simplicity, low energetic requirements, good stability under a wide range of operative conditions, high eco-compatibility, easy control and scale-up, large flexibility [1].

With the increasing understanding and development of membrane techniques, it became possible to integrate various membrane operations in the same process with the purpose to improve performance in terms of product quality, plant compactness, environmental impact, and energy use. The concept of integrated membrane processes appears clearly at the end

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of the 1990s [1] when several applications were reported such as hybrid process NF–ED for treatment of pulp bleaching effluents [2], multistages UF, NF and RO for removal of contaminants from wastewater effluents [3] and RO–MD for seawater desalination [4]. In the following years, it became more and more obvious that other combinations could have significant impact [5], such as MBR–RO for wastewater treatment [6], pressure-driven membrane processes–MD for the treatment of wastewaters [7], and multistages pressure-driven membrane processes for high-resolution separations of biomolecules from food and biotechnology feeds [8].

In this chapter, some general backgrounds on membrane processes are first recalled including pressure-driven processes (MF, UF, NF, RO), and MD, ED and MBRs. Examples of membrane integrated processes are then given such as multistages pressure driven membrane processes and pressure-driven membrane processes associated to MD, ED or MBRs. Applications concern seawater desalination, wastewater treatment, separation in biotechnology and food industries and chemical production. These hybrid membrane techniques are further detailed in the following chapters of the book as well as other integrated membrane processes. Integrated membrane processes including gas and vapour separation and catalytic membrane reactors are considered in the second part of this book. Another important aspect of integrated membrane processes concern their association with processes other than membranes. This is also considered in the following chapters.

1.2 Membrane Processes

Various membrane operations are available for a wide range of industrial applications. Pressure-driven membrane processes include MF, UF, NF and RO. Other membrane unit operations include MD, ED and MBRs.

1.2.1 Ultrafiltration, Microfiltration and Nanofiltration

UF is a size exclusion pressure-driven separation process which came into use in the 1960s when Loeb and Sourirajan discovered the preparation of asymmetric cellulose acetate membranes [9]. UF membranes typically have pore sizes in the range of 10–1000 Å and are capable of retaining species in the molecular weight range of 300–1,000,000 Da. Operating pressures are usually in the range of 0.2–4 bar. Typical rejected species include biomolecules, polymers and colloidal particles, as well as emulsions and micelles. UF is found in a very large range of industries such as food, biotechnology and pharmaceutics, chemicals and water production.

MF is a pressure-driven separation process similar to UF with membranes typically having nominal pore sizes on the order of 0.1–1.0 μm [9]. MF applications include concentrating, purifying or separating macromolecules, colloids and suspended particles from solution. MF processing is widely used, for example, in the food industry for applications such as wine, juice and beer clarification, for wastewater treatment, and plasma separation from blood for therapeutic and commercial uses.

NF dates back to the 1970s when RO membranes with a relatively high water flux operating at relatively low pressures were developed [10, 11]. Such low-pressure RO membranes were termed NF membranes. NF is a pressure-driven membrane process, involving pressures between 5 and 20 bar, used to separate ions and molecules in the molecular weight range of 200–2000 g mol^{-1}. NF membranes have relatively high charge and are typically characterized by lower rejection of monovalent ions than that of RO membranes, but maintaining high rejection of divalent ions. Applications include pretreatment before desalination, water treatment, food industry, chemical processing industry, pulp and paper industry, metal and acid recovery, etc.

1.2.2 Reverse Osmosis

RO became commercially viable in the 1960s when Loeb and Sourirajan discovered asymmetric membranes. RO is a pressure-driven process that separated two solutions with different concentrations across a semi-permeable membrane [12]. In RO, the pressure difference Δp between the concentrated side and the dilute side is larger than a certain value that depends upon the difference of the respective concentrations and is called the osmotic pressure difference $\Delta\pi$. The direction of flow is reversed as observed in osmosis and water flows from the concentrate to the dilute side. The rate at which water crosses the membrane is then proportional to the pressure differential that exceeds $\Delta\pi$. In order to overcome the feed side osmotic pressure, fairly high feed pressure is required. In seawater desalination it commonly ranges from 55 to 70 bar. Operating pressures for the purification of brackish water are lower due to the lower osmotic pressure caused by lower feed water salinity. The most commonly used applications of RO are desalination, brackish water and wastewater treatment and concentrating food and biotechnological preparations.

1.2.3 Membrane Distillation

MD is a thermally driven membrane process in which a hydrophobic microporous membrane separates a hot and cold stream of water [13]. The hydrophobic nature of the membrane prevents the passage of liquid water through the pores while allowing the passage of water vapour (Figure 1.1). The temperature difference produces a vapour pressure gradient

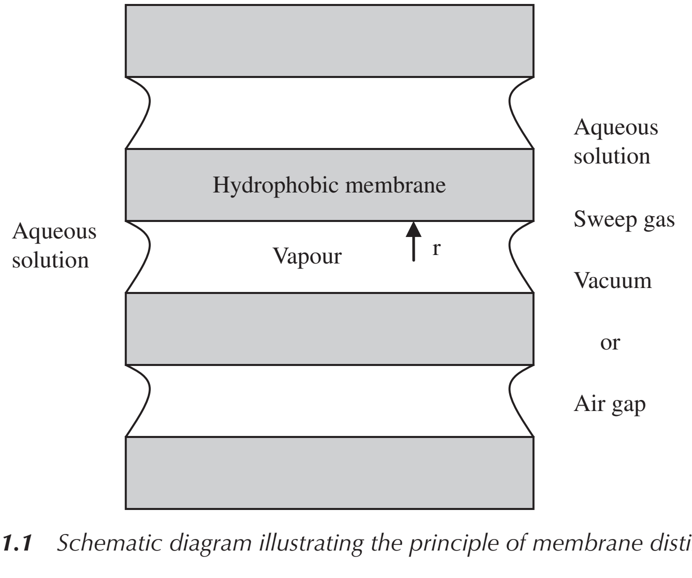

Figure 1.1 Schematic diagram illustrating the principle of membrane distillation.

which causes water vapour to pass through the membrane and condense on the colder surface. The result is a distillate of very high purity. MD has been developed into four different configurations, differing by the method employed to impose the vapour pressure difference across the membrane. The permeate side of the membrane may consist of a condensing fluid in direct contact with the membrane, a condensing surface separated from the membrane by an air gap, a sweeping gas, or a vacuum. MD has been applied for water desalination, waste treatment, and food processing like milk and juice concentration, biomedical applications such as water removal from blood and treatment of protein solutions [14]. In desalination by MD, the heated seawater is in direct contact with one side of the membrane. Salts and organic matter stay in the feed while pure water diffuses through the membrane.

Osmotic distillation (OD) is a variant of MD for which the driving force is a difference in concentration. OD uses the hydrophobic microporous membrane to separate two aqueous solutions having different solute concentrations: a dilute solution on one side and a hypertonic salt solution (concentrated brine stripper) on the opposite side [15]. The hydrophobic nature of the membrane prevents penetration of the pores by aqueous solutions, creating air gaps within the membrane. The water vapour pressure gradient across the membrane determines a transfer of vapour across the pores from the high vapour pressure phase to the low one. This migration of water vapour results in the concentration of the feed and dilution of the osmotic agent solution. OD can proceed at ambient temperature and is an attractive process for the concentration of solutions containing thermo-sensitive compounds such as fruit juices and pharmaceuticals.

Membrane crystallization (MCr) [16] has been proposed as an extension of MD: solutions, concentrated above their saturation limit by solvent evaporation through microporous hydrophobic membranes, reach a supersaturated state in which crystals nucleate and grow. The crystallizing solution flows along the membrane fibres. The driving force of the process is a vapour pressure gradient between both sides of the membrane which may be activated by heating the feed solution. MCr is mainly applied at laboratory scale for the formation of crystals with well-controlled properties and the treatment of brine disposal from RO plants.

1.2.4 Electrodialysis

The general principle of ED is known since the 1940s. The process is based on the movement of charged species in an electrical field: anions move towards the anode, while cations are attracted by the cathode [17]. The movement of the ions is controlled by ion-selective membranes between the anode and cathode. Anion-exchange membranes (AEM) are permeable for anions, while cations are held back. Cation-exchange membranes (CEMs) show the opposite behaviour. The ED stack is divided into several cells by AEM and CEM in an alternating sequence (Figure 1.2). The basic unit of an ED stack consists of a pair of diluted and concentrated compartments. The concentration of ionic species is reduced in the diluted compartments and increased in the concentrated compartments. One major advantage of ED compared to RO is that a higher brine concentration can be achieved because there is no osmotic pressure limitation. Some of the more important large scale industrial applications of conventional ED include brackish water desalination, waste treatment, demineralization of food products and table salt production [17].

Conventional ED can be combined with bipolar membranes in a process termed bipolar membrane electrodialysis (BMED) [17]. Bipolar membranes are composed of

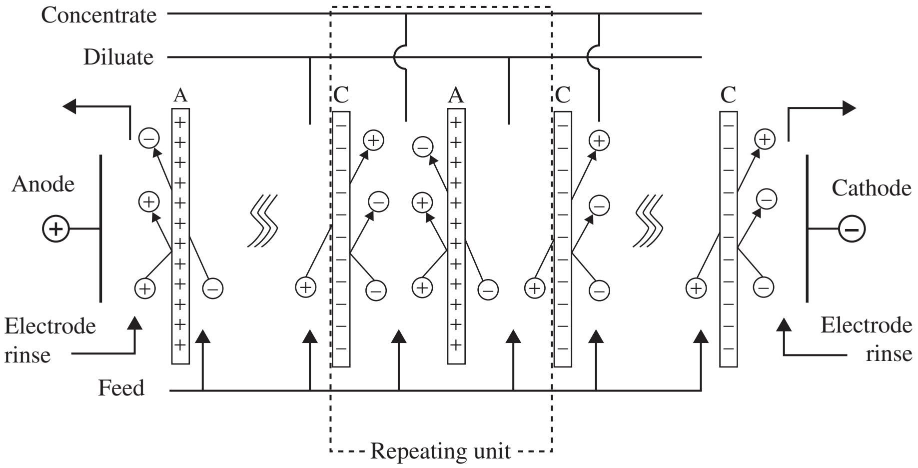

Figure 1.2 *Schematic diagram illustrating the principle of electrodialysis.* Source: *Reproduced from Reference 17 with permission from Elsevier.*

cation- and anion-exchange layers with a 4–5 nm thick transition layer arranged between two electrodes; they are installed in alternating series in an electrodialysis stack. Commercial plants of BMED are utilized to produce acids and bases from the corresponding salts.

1.2.5 Membrane Bioreactors

MBRs have been studied from the 1980s as alternative approaches to classical methods of immobilizing microorganisms, such as enzymes, antibodies and activated sludge. The microorganisms are suspended in solution and compartmentalized by a membrane in a reactor or immobilized within the membrane matrix itself. In the first method, the system consists of a traditional stirred tank reactor combined with a membrane separation unit, such as UF and MF. In the second method, the membrane acts both as a support for the microorganisms and as a separation unit.

Today, membrane bioreactor systems are applied at industrial scale for water treatment such as industrial wastewater, domestic wastewater and specific municipal wastewater [18, 19]. Conventional treatment of wastewater usually consists of a three-stage process: sedimentation of solids in the feed water followed by aerobic degradation of the organic matter using activated sludge and then a second sedimentation process to remove the biomass. An MBR can displace the two physical separation processes by filtering the biomass through an MF or UF membrane. MBRs present several advantages compared to activated sludge plants including their compactness (up to five times more compact than conventional plants), reduced sludge production, and higher product water quality [20]. The two main MBR configurations are immersed and external configurations which are characterized by different operating conditions (membrane material, filtration mode, shear stress, etc.). Membranes are usually flat sheet or hollow fibres (immersed configuration) or multitube (external configuration).

1.3 Combination of Various Membrane Processes

Membrane processes can be associated in the overall purification or production schemes in industrial applications. They often include pressure-driven membrane processes as pre-treatment before other purification steps or as a final treatment. Pressure-driven membrane processes may be associated with other processes such as MD, MBRs and ED. Some examples in the field of wastewater treatment, desalination, food industry and biotechnology and pharmaceutics are given in section 1.3.1.

1.3.1 Pressure-Driven Separation Processes

Due to their different retention properties, pressure-driven membrane processes can be associated in a cascade configuration in a purification scheme. At a first step, setting, flocculation, sand or cartridge filtrations serve to remove very large particles. Then, MF can be used to remove large compounds, such as suspended particles, colloidal materials and bacteria. The obtained suspension can be treated by UF to separate or remove macromolecules, colloids, solutes in the molecular weight range of 300–1,000,000 Da. NF or RO can then be used to remove very small molecules and salts. In a general way, it can be seen that different membrane processes in a cascade are closely linked. The membrane at step n reduces fouling of the membrane at step $n + 1$, thus increasing the permeation flux and reducing the flux decay. At step $n + 1$, the membrane performance depends on steps $<n$. As these integrated processes are used to treat industrial suspensions such as wastewater effluent and food and biological suspensions, it can be foreseen that their behaviour will be very difficult to predict.

1.3.1.1 Pre-treatment in Seawater Desalination

The applicability of membranes in seawater desalination has increased in the last 30 years with more than 2000 RO installations operating worldwide. Many desalination plants have been changed to use membrane processes because they are much more energetically efficient than thermal techniques. In seawater RO desalination, pre-treatment serves to reduce fouling potential, increase membrane life, maintain performance level and minimize scaling on the RO membrane surface [12]. Most RO plants used chemical and physical pre-treatment without membrane technologies. Physical pre-treatment generally uses flocculation, settling, sand filtration and cartridge filtration to obtain feed water with a low silt density index (SDI), where SDI describes the fouling potential of the feed water and is determined in filtration tests with MF membranes. Chemical pre-treatment includes chlorination to disinfect the water and prevent biological growth, coagulation and flocculation agents, pH adjustment, antiscaling agents to reduce precipitation of salts on the RO membrane surface and dechlorination prior to the RO stage to avoid damage of the membrane by oxidation.

The interest in membrane pre-treatment prior to RO has been recognized for many years [21] but has been limited by high cost compared to conventional pre-treatment. With advances in membrane technology and increasing requirements on water quality, the use of membrane pre-treatment prior to RO is now a suitable alternative to conventional pre-treatment [12]. It is generally estimated that membrane pre-treatment will rapidly grow in the coming years. Both UF and MF membranes, used as pre-treatment units, are able to remove suspended particles, colloidal materials, bacteria, virus and pathogenic microorganisms from raw water. They guarantee an SDI of the RO feed water generally below 2.5 even with strong fluctuation of raw water quality, enabling operation with a high and stable permeate flux even in long-term operation. They usually require less chemical addition than conventional pre-treatment, which is characterized by a rather high consumption of chemicals. In addition, membrane systems require significantly less space than conventional pre-treatment.

Membrane pre-treatment prior to RO has been successfully applied at laboratory scale and pilot scale. At laboratory scale, Kumar et al. [22] compared MF and UF membranes using dead-end filtration before RO experiments. Natural seawater was first filtered through a 1 μm prefilter. MF pretreatment was found more effective in reducing RO fouling than conventional filtration. UF pretreatment with the 100 kDa membrane did not decrease fouling compared to the MF membrane. The 20 kDa UF membranes was the most effective in reducing fouling but operated at higher pressures for the same flux as the MF and 100 kDa UF membranes. At three different locations, Vial et al. [23] operated a long-term pilot equipped with 0.1 μm hollow fibre Microza RO membranes for pre-treatment of Mediterranean seawater. Depending on the location, the pilots operated with or without pre-treatment using ferric chloride and with or without daily sodium hypochlorite backwash. The system optimization yielded stable, reproducible permeate flow and permeate SDI below 1.8. Water quality allows RO operation at high recovery, enhancing the total system running cost.

UF was also demonstrated to provide excellent pre-treatment to RO at various desalination sites, for example in Saudi Arabia, Gulf of Mexico, the Red Sea and the Mediterranean [24], and at Qingdao Jiaozhou Bay, the Yellow Sea in China [25]. For example, Pearce et al. [24] operated UF pre-treatment to RO desalination for a 6-month period at Jeddah Port, Saudi Arabia, as an alternative to its conventional pre-treatment facility, which could not meet targeted feed water quality during periods of algal bloom and storms. An average filtrate SDI of 2.2 was obtained, approximately two units better than the existing conventional pre-treatment. Xu et al. [25] utilized UF hollow fibre membranes as pretreatment prior to RO desalination at Qingdao Jiaozhou Bay, the Yellow Sea in China (Figure 1.3).

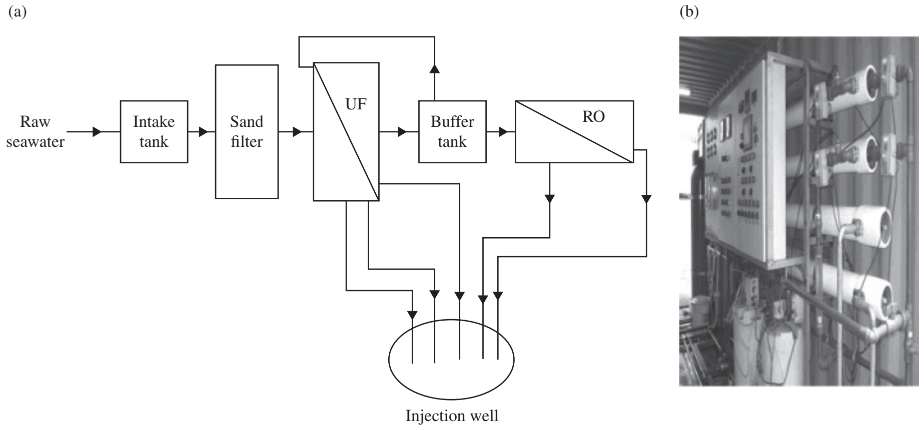

Figure 1.3 *The UF–RO pilot system for seawater desalination. (a) Schematic diagram of the pilot system. (b) Photograph of the pilot system.* Source: *Reproduced from Reference 25 with permission from Elsevier.*

During the experimental periods, the UF–RO system was run stably and successfully, without any chemicals required for disinfection, flocculation, enhanced chemical backwash and cleaning.

The use of NF upstream RO is also a possible alternative as water hardness can thus be strongly reduced, and the most part of multivalent ions can be rejected [26,27]. In addition, monovalent species are retained by 10–50%, depending on their molecular weight and electrostatic interactions with the membrane. As a consequence, the osmotic pressure of RO feed and retentate streams is decreased, thus allowing the system to operate at high water recovery factors with a considerable decrease in scale forming components. For application at industrial scale, the Saline Water Conversion Corporation (Saudi Arabia) has developed NF pretreatment prior to RO. Initial work on a pilot plant scale, resulted in its application in one of the commercial RO plants at Ummlujj in operation since September 2000. Al-Hajouri et al. [28] detailed the long-term operation of the NF–RO plant as well as different research programs which were undertaken and the results obtained.

The comparison of overall costs of membrane pre-treatment and conventional pre-treatment may depend on site-specific factors [12]. Fluctuations in the feed water quality in terms of turbidity and total dissolved solids (TDS) as well as algae bloom can cause problems for conventional pre-treatment, which might result in additional cost. Membrane pre-treatments are less sensitive to fluctuations of feed water quality and supply the RO stage with superior water quality for long-term operation. Membrane pre-treatment therefore might be able to increase RO membrane life and ensure stable operation even under adverse conditions and could thus lead to overall cost reductions.

1.3.1.2 Treatment of Waste Effluents

As industrial effluents are very complex mixtures of contaminants such as suspended solids, molecules and salts, several pressure-driven membrane processes with different properties may be needed to obtain a complete treatment. MF, UF, NF and/or RO in a cascade purification scheme can be adequate alternatives to other processes such as coagulation/flocculation, sand or cartridge filtration, adsorption, etc. The application of membrane processes in the treatment of industrial wastewaters can give a reduction of the environmental impact, a simplification of cleaning procedures of aqueous effluents, an easy re-use of sludge, a decrease of disposal costs and a saving of chemicals, water and energy [5]. These processes have been reported for treatment of several waste effluents from the leather, coke, dairy olive and oil industries.

In the leather industry, traditionally considered as one of the most polluting industries, conventional chrome tanning produces spent liquors containing significant amounts of chromium and other polluting substances, both organic and inorganic. Cassano et al. [29] recovered and concentrated chromium salts through an integrated membrane process at laboratory scale (Figure 1.4). The spent tanning liquors were subjected to a preliminary UF step to remove most suspended solids and fat substances. The permeate obtained from the UF treatment was then subjected to NF in which chromium salts were concentrated to a final value of about 10 g/L. The UF pretreatment reduced fouling of the NF membrane, thus improving the permeation flux and reducing the flux decay.

In coking industries, the treatment of desulphurization wastewater and the recovery of usable substances such as suspended sulphur (SS) and ammonium salts, for example,

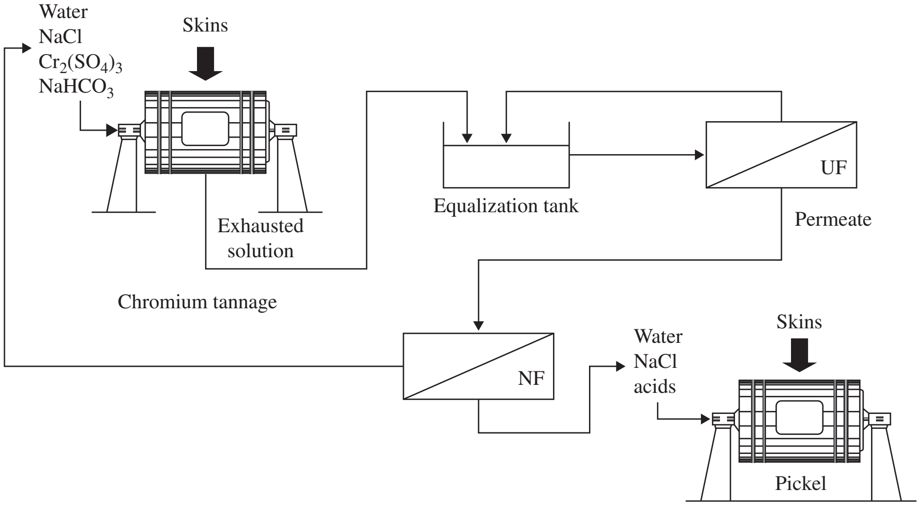

Figure 1.4 *Scheme of the UF/NF process for the recovery of chromium from spent tanning effluents.* Source: *Reproduced with permission from Reference 29. Copyright 2007 American Chemical Society.*

$(NH_4)^2S_2O_3$ and NH_4SCN, is of major concern and can avoid severe environmental problems in the case of improper disposal. Yin et al. [30] proposed an integrated membrane process consisting of UF, NF and RO to treat the wastewater. The permeate resulting from the UF treatment was then introduced to an NF process in which bivalent ammonium salts were separated from monovalent ammonium salts. The final RO process was repeatedly applied to the treatment of the NF permeate to separate monovalent salts and water. Both the NF and RO retentates were circulated in the system for further dialysis to obtain pure salt products.

The dairy industry generates a large amount of wastewater, which contains high levels of suspended solids, ammonia, protein and other nutrients. UF, NF and RO have been proposed for dairy wastewater treatment to produce purified water for water reuse or recover nutrients. A two-stage membrane process with UF + NF was investigated to produce water for discharge and recover the nutrient in wastewater [31]. The recovered nutrient could be used for feed production. UF operation could remove the protein in raw wastewater and decrease the membrane fouling in the NF process. Compared with RO operation, transmembrane pressure was lower and the membrane flux was higher than in NF operation.

A simplified integrated membrane system was also reported to be successful in the treatment of olive mill wastewaters [32]. The integrated membrane process included an initial UF step with 0.02 μm nominal pore size hollow fibre membranes for the removal of suspended solids from olive mill wastewaters. The first UF permeate was treated by a second UF process by using a flat-sheet membrane having a molecular weight cut-off of 1000 Da. Finally, the resulting permeate stream was submitted to an NF process to obtain a concentrated phenolic solution. With this integrated process, different fractions were produced: (1) a concentrated solution containing organic substances at high molecular weight (retentate of both UF processes), (2) a concentrated solution (NF retentate) enriched in polyphenolic compounds suitable for cosmetic, food and pharmaceutical industries and (3) a water stream (NF permeate) which can be reused in the olive oil extraction process as process water or in the integrated membrane system as membrane cleaning solution or in the diafiltration step to increase the yield of polyphenols in UF permeates.

1.3.1.3 Food and Biotechnology Industries

In food and biotechnology industries, feeds are also complex and multicomponent. Membrane process performances for biomolecule fractionation, concentration and purification from these feeds are then much more limited than from simple ones. These last years, a number of solutions have been proposed to achieve high-resolution separations. For example, Zydney and van Reis [33] have exploited a number of different strategies to obtain high performance tangential flow filtration (HPTFF), a complete procedure which includes: (1) proper choice of pH and ionic strength to maximize differences in the hydrodynamic volume of the product and impurity, (2) use of electrically charged membranes to enhance the retention of like charged proteins, (3) operation in the pressure-dependent regime to maximize the selectivity and (4) use of a diafiltration mode to wash impurities through the membrane. Cascade or multistage membrane systems have been proposed from the mid-2000s as an alternative to achieve these high-resolution separations. MF, UF and even NF membranes, with different or similar properties, can be considered at the different stages of the cascade [34]. In such systems, the manner in which the different flows stream within the cascade (e.g. recycling of retentates) contributes towards efficiency of separation and not merely the number of stages [35].

In the biotechnology industry, separation of biomolecules from fermentation broths is a common operation. Zhou et al. [36] investigated the use of a two-stage tangential flow filtration process for the separation of hyaluronic acid from fermentation broth. MF membranes (0.45 and 0.20 μm size) and UF membranes (300 and 100 kDa) were used to achieve the separation in series. The two-stage membrane process was undertaken with two separating schemes: the first using MF followed by UF with pure water as diafiltrate, the second similar to the first except permeate from previous UF stage as diafiltrate for MF stage. The two schemes could effectively separate and purify hyaluronic acid with above 77% overall yield and about 1000 purification factor. The second scheme seemed to be more effective for its higher overall yield (89%) and saving water. A three-stage process (MF, UF, NF) was also designed for the purification of sweeteners from *Stevia rebaudiana* Bertoni [37]. Retentions of the sweeteners for a synthetic mixture and plant extract were measured in combination with flux decline. Starting from an extract purity of 11% with the overall process, a purity of 37% and a yield of 30% could be reached. It was concluded that this process should be seen as a pre-treatment prior to other purification steps, for instance crystallization.

In the dairy industry, there is commercial interest in the production of individual whey proteins with well-characterized functional and biological properties such as α-lactalbumin (α-LA) and β-lactoglobulin (β-LG). A two-stage tangential flow filtration system has been proposed for the purification of both α-LA and β-LG from whey protein isolate [8]. Separation was achieved using 100 and 30 kDa membranes in series. Two purification strategies were examined (Figure 1.5). In Strategy I, the 100 kDa membrane was used in the first stage

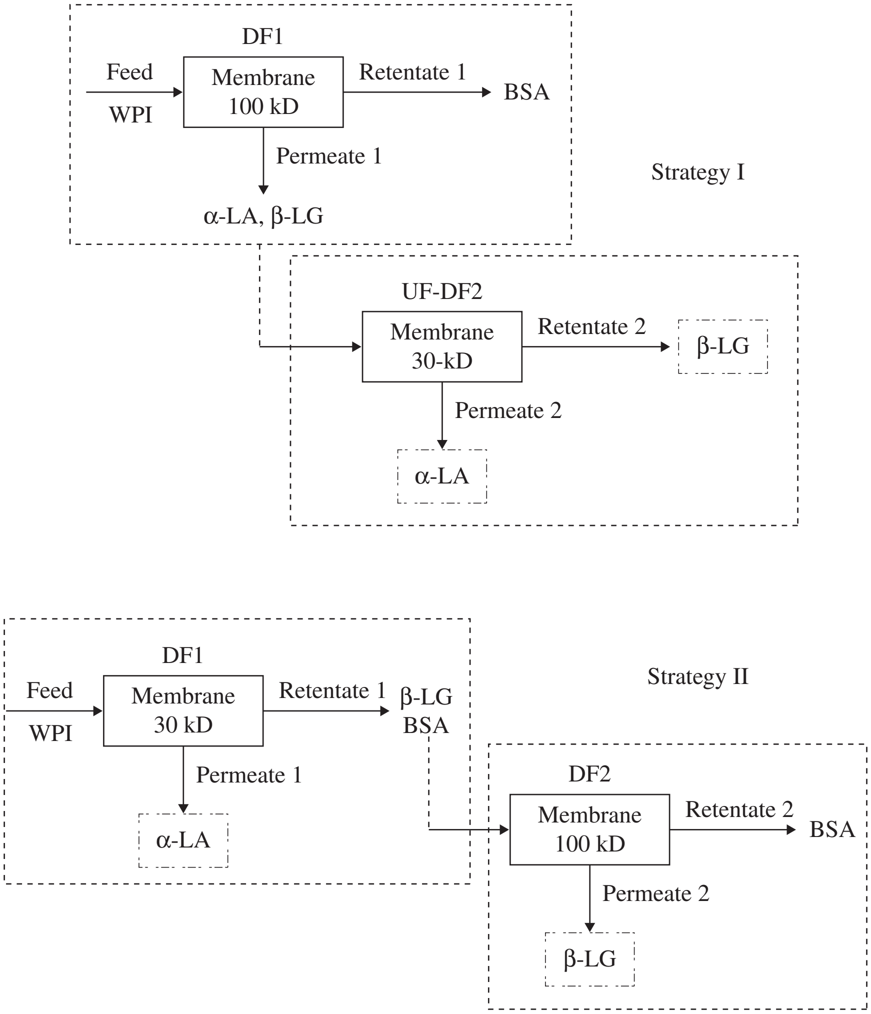

Figure 1.5 *Schematic diagram showing two separation strategies for the purification of α-LA and β-LG from whey protein isolate. Each block represents a separate diafiltration process.* Source: *Reproduced from Reference 8 with permission from Elsevier.*

to remove bovine serum albumin (BSA) while collecting α-LA and β-LG in the permeate solution. The collected permeate was then used as a feed in the second stage where the α-LA and β-LG were separated using a 30 kDa membrane. The membrane combination was reversed in Strategy II, with the 30 kDa membrane used in stage I to obtain purified α-LA in the permeate solution while retaining the β-LG and BSA. The collected retentate was then separated in stage II using a 100 kDa membrane. In order to achieve high degrees of purification and yield during the protein separation, the filtrations in stages I and II were both performed using a diafiltration process to effectively wash the more permeable protein(s) through the membrane. In both cases, the α-LA purification was greater than

10-fold at 90% yield. The recovery of β-LG was more challenging since it was obtained in the permeate from one stage and the retentate from the other. The authors concluded that staged membrane processes for high-resolution separations require further experimental and theoretical investigations to reach optimal performances [8].

1.3.2 Membrane Distillation and Pressure-Driven Membrane Processes

MD can make a significant contribution in increasing the efficiency of the RO process [4]. In RO, the osmotic effect often does not permit reaching values of interest. In MD, concentration polarization phenomena do not have the same limiting effect. Therefore, pure water can be obtained by MD from highly concentrated feeds, with which RO cannot operate. Hybrid pressure-driven membrane processes and MD have been implemented mainly in desalination units, in production of high concentrate solutions in the beverage industry and in treatment of wastewaters.

Seawater desalination by RO is limited by the osmotic pressure; therefore, a high recovery factor is not attainable. Consequently, large volumes of brine are discharged into the sea and the permeate flow rate is limited. From the end of the 1990s [4], MD has been investigated to concentrate RO brine and increase the global recovery of the process. In the following years, a specific attention was paid to optimize operating conditions such as a highly permeable membrane, high feed temperature, low permeate pressure and a turbulent fluid regime. At these operating conditions, Mericq et al. [38] obtained high permeate flow rates even at a very high salt concentration (300 g L^{-1}). At high salt concentrations, scaling occurred (mainly due to calcium precipitation) but had only a limited impact on the permeate flux (24% decrease for a permeate-specific volume of 43 L m^{-2} for the highest concentration of salt). A global recovery factor of 89% was obtained by coupling RO and MD. When MCr unit follows NF and/or RO, the highly concentrated brine does not represent waste but rather the mother liquor in which crystals may nucleate and grow. Like MD, MCr leads to a further increase of the overall water recovery factor. Before the MCr unit, Ca^{2+} ions are precipitated as carbonates by adding Na_2CO_3. This is necessary in order to avoid calcium sulphate precipitation, which causes scale and drastically limits the recovery of magnesium sulphate [26].

The possibility of integrating MD after pressure-driven membrane processes has also been reported in the beverage industry for producing various high concentrated fruit juices (orange, apple, kiwi fruit, passion fruit, etc.) [39, 40]. Separating the suspended solids and pectins from juices by UF or MF decreases viscosity and increases flux of RO and/or OD, maximizing yield and minimizing nutrient and flavour losses. For example, Galaverna et al. [41] reported the production of concentrated blood orange juice according to the following scheme: an initial clarification of freshly squeezed juice by UF; the clarified juice was successively concentrated by RO, used as a pre-concentration technique (up to 25–30 °Brix), then OD, up to a final concentration of about 60 °Brix (Figure 1.6). The integrated membrane process was presented as a valuable alternative to obtain high quality concentrated juice, as the final product showed a very high antioxidant activity and a very high amount of natural bioactive components. An integrated membrane process, which involved UF, RO and OD was also reported to concentrate anthocyanin, a natural red colorant from red radish [42]. The integrated membrane process had the advantages of achieving higher concentration of anthocyanin compared to that of the individual membrane

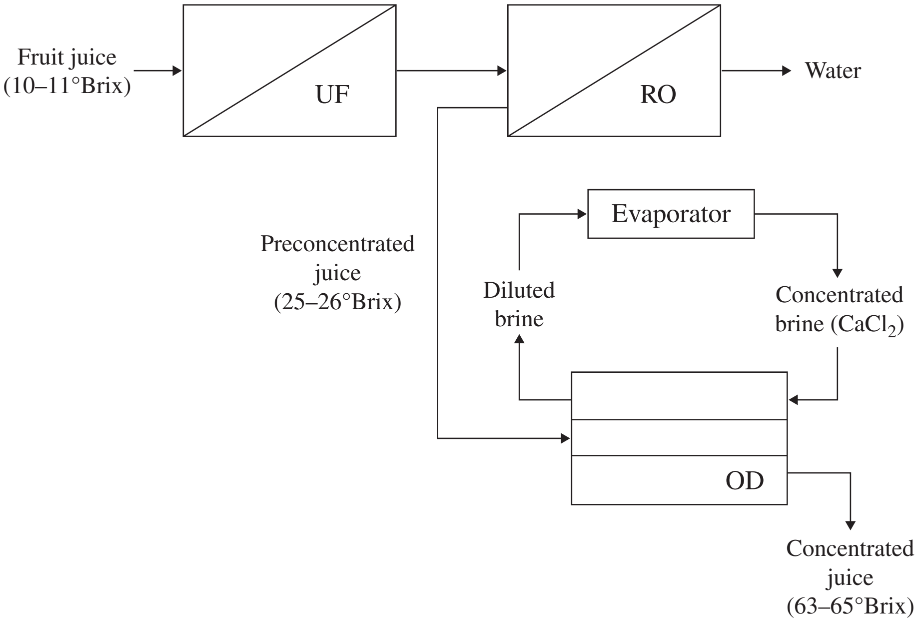

Figure 1.6 *Scheme of the integrated membrane process for the production of concentrated orange juice.* Source: *Reproduced from Reference 41 with permission from Elsevier.*

processes. Final concentration of 26 °Brix (from 1 °Brix) was achieved, with an increase in the concentration of anthocyanin from 40 to 980 mg/100 mL.

Hybrid membrane processes including MF, UF and NF and MD have also been used for treatment of wastewater such as purification of oily wastewater [7], drained wastewater [43], and textile dye bath wastewater [44]. For example, Gryta et al. [7] performed the treatment of oily wastewater collected from a harbour without pre-treatment by a combination of tubular UF and capillary MD as a final purification method. The permeate obtained from the UF process generally contains less than 5 ppm of oil. A further purification of the UF permeate by MD resulted in a complete removal of oil from wastewater and a very high reduction of the total organic carbon (TOC) (99.5%) and TDS (99.9%).

1.3.3 Electrodialysis and Pressure-Driven Membrane Processes

From the 1990s, pressure-driven membrane processes have been proposed as a pre-treatment step prior to ED for treatment of different types of wastewaters. A hybrid process involving NF–ED was designed to recover water from alkaline pulp bleaching effluent having a high content of organic and organochlorinated compounds and salts [2]. NF was selected to remove organic compounds and undertake partial desalination. A higher degree of water purity was further achieved using ED. In another application, ceramic MF membranes were reported as a pre-treatment step prior to ED for removal of colour and contaminants from paper industry wastewaters [45]. The hybrid pilot plant was found more efficient than the single ED process since the ceramic MF membrane eliminated the suspended colloids.

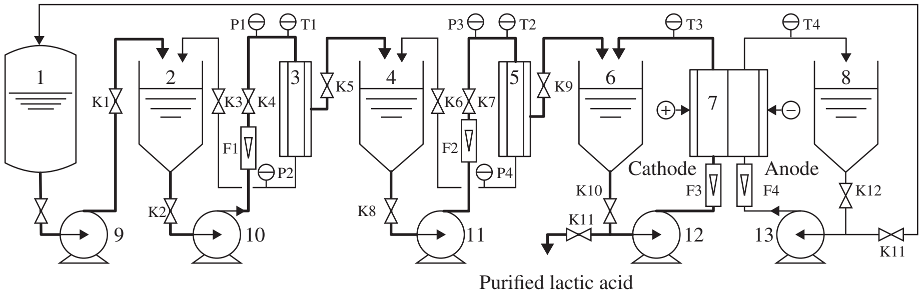

Figure 1.7 *Scheme of the integrated membrane process for the purification of lactic acid from a fermentation broth neutralized with sodium hydroxide: (1) fermentor, (2) UF feed tank, (3) ceramic membrane module, (4) NF feed tank, (5) NF membrane module, (6) acid tank, (7) BMED stack, (8) caustic tank, (9–13) pump, (P1–P4) pressure gauges, (T1–T4) temperature gauges, (F1–F4) flow meters.* Source: *Reproduced with permission from Reference 47. Copyright 2013 American Chemical Society.*

In addition, hybrid pressure-driven processes-ED is a common technique used for the conversion of organic acids such as lactic acid. Lactic acid is a common additive for flavour and preservation in a large number of industries including food and pharmaceuticals [46]. Production is based on an initial biological fermentation step. In order to increase the fermentation yield, the pH is adjusted by addition of a base. The resulting fermentation broth contains the lactic acid as a calcium, ammonium or sodium salt and several organic and inorganic fermentation residues. The largest impurities (i.e. bacterial cells, high molecular weight residues) are eliminated in a first step of clarification that can be done by MF. The fluid is then concentrated by ED. The acid salt is then converted into its free acid form by bipolar electrodialysis (BED) without addition or production of any by-product. In this process, hardness caused by calcium and magnesium cations in the fermentation broth may affect the lifetime of CEMs in the BMED stack. Therefore, Wang et al. [47] proposed a hybrid process using NF as a pre-treatment to remove these ions before BMED (Figure 1.7).

1.3.4 Membrane Bioreactors and Pressure-Driven Separation Processes

MBRs have been extensively implemented these last years for the treatment of wastewaters. With the increasing requirements for water quality, the MBR technique can be complemented by RO or NF. From the early 2000s, MBR–RO has been developed and implemented at municipal wastewater plants. The MBR process can remove above 95% organic carbon and completely remove suspended solids from wastewaters by biodegradation and membrane retention [48]. Subsequently, the RO membrane eliminates dissolved solids, organic compounds, nutrients and pathogens in MBR effluent to produce high quality reclaimed water.

For example, a landfill leachate treatment plant located at Chung-Nam Province in Korea with a capacity of 50 $m^3 d^{-1}$ consisted of an aeration basin equipped with MBR submerged hollow fibre membranes; the effluent was further treated with spiral wound RO elements (Filmtec, USA) [6]. Another MBR–RO system with the capacity of 20 $m^3 d^{-1}$ was reported for the treatment of domestic sewage at Bedok Water Reclamation Plant in Singapore

[49]. The MBR–RO process produced the same or higher water quality (in terms of TOC, NH_4 and NO_3) compared to the conventional activated sludge process, the ASP–MF–RO process. RO membranes in the MBR–RO process could be operated at 22 Lm^{-2} h^{-1} during 5 months, which was 30% higher than that in the ASP–UF–RO process (17 Lm^{-2} h^{-1}).

The MBR–RO technology is limited by membrane fouling, which reduces productivity and increases energy costs, in particular due to membrane fouling in RO systems [48]. The colloidal, organic and inorganic substances in MBR effluents promote organic fouling and scaling of RO membranes. In addition, biofilm development on RO membranes becomes biofouling that decreases RO performance. The soluble polysaccharides and soluble transparent exopolymer particles accumulated on the RO membrane are major factors related to RO fouling. However, the MBR–RO technology was found to reduce fouling compared to filtration–RO [50]. In addition, inline MF pretreatment of the RO feed water can significantly reduce fouling of the RO membranes [48].

1.3.5 Other Processes and Pressure-Driven Separation Processes

A large range of other combinations of membrane processes are possible. Some of them are briefly discussed in sections 1.3.5.1 to 1.3.5.3. Pressure-driven membrane processes may be associated to membrane chromatography for purification of biomolecules, membrane emulsification for beverage and dairy production and membrane extraction for detoxification of biomass hydrolysates.

1.3.5.1 Membrane chromatography and pressure-driven membrane processes

Membrane chromatography is an alternative to bead chromatography for the purification of biological products [51]. Membrane chromatography was developed from the end of the 1990s when Brandt et al. [52] reported Protein A hollow fibre devices for purification of fibronectin from blood plasma and purification of IgG. The benefit of these adsorptive membranes is to maintain high efficiencies at high flow-rates, using large biomolecules with small diffusivities, reducing biomolecule degradation and denaturation. The available interaction modes include affinity interaction, ion exchange, hydrophobic interaction, reversed-phase and multistage chromatography. Membrane chromatography is currently being employed for the purification and polishing of different biomolecular species, including purification of monoclonal antibodies and DNA, and virus capture in biotechnology and food industries.

UF or MF can be implemented before one or several chromatographic steps as a pretreatment of the feed solution. Moreover, UF can be used as a final step for polishing, desalting and buffer exchange. Yu et al. [53] reported the purification of humanized monoclonal antibody expressed in tobacco juice by ion-exchange followed by hydrophobic interaction membrane chromatography. Ion exchange was used for capture and purification, hydrophobic interaction membrane chromatography for high-resolution purification, followed by UF for polishing, desalting and buffer exchange. Using this scheme, both high monoclonal antibody purity and high recovery (77% of monoclonal antibody spiked into the tobacco extract) were achieved. In the dairy industry, membrane chromatography can also be incorporated in integrated purification schemes. Bhattacharjee et al. [54] obtained a relative separation of β-lactoglobulin (β-LG) from whey protein concentrate by fractionation of protein using two-stage UF with 30 and 10 Da membranes followed by ion-exchange membrane chromatography (Figure 1.8). Prior to UF, centrifugation, MF and a four-stage

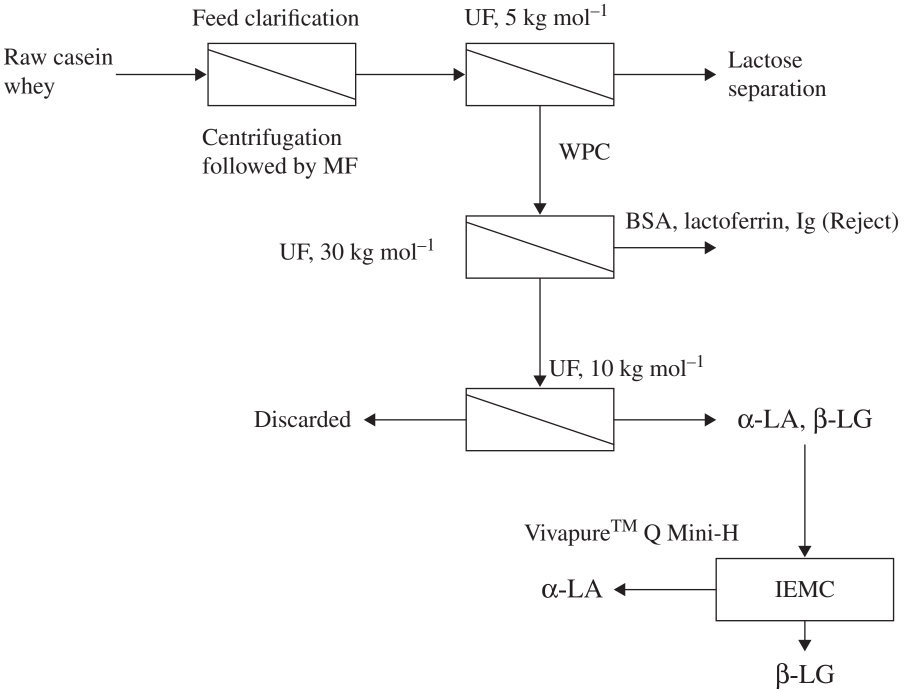

Figure 1.8 *Schematic diagram for the fractionation of* β*-lactoglobulin from casein whey using UF and ion-exchange membrane chromatography (IEMC).* Source: *Reproduced from Reference 54 with permission from Elsevier.*

discontinuous diafiltration were carried out to obtain whey protein concentrate from raw casein whey. At the end of the overall purification scheme, 87.6% purity of β-LG (on total protein basis) was obtained.

1.3.5.2 Membrane Emulsification

Membrane emulsification has been developed from the end of the 1980s as an alternative to other methods of emulsification [55]. The dispersed phase is pressed through the membrane pores, while the continuous phase flows along the membrane surface. Droplets grow at pore openings until they detach. The resulting droplet size is controlled primarily by the choice of the membrane and not by the generation of turbulent droplet break-up. Besides the possibility of using shear-sensitive ingredients, emulsions with narrow droplet size distributions can be produced. A large range of parameters, including flow configurations, membranes, surfactants, pressures, and cross-flow rates, can be varied to modify the dispersed flux and the distribution size. A very large range of colloids can be produced such as simple oil/water and water/oil emulsions to multiple emulsions of different types, solid/oil/water dispersions, coherent solids (silica particles, solid lipid microspheres, solder metal powder), and structured solids (solid lipid microcarriers, gel microbeads, polymeric microspheres, core–shell microcapsules and hollow polymeric microparticles) [56]. Although membrane emulsification has not been integrated so far to other membrane processes, it can be foreseen that such hybrid processes could be attractive in particular in the food and biotechnology industries [57]. For the preparation of beverage emulsions, membrane emulsification can be a suitable alternative to classical homogenization. The flavour products (e.g. orange oils, lemon oils, etc.) can be converted into a water-dispersible emulsion using membrane emulsification with appropriate production conditions. In the dairy industry, the preparation of emulsions with reconstituted milk is usually done by high-pressure homogenization. In such cases, the milk components (casein micelles, whey proteins, and free milk fat globule membranes in buttermilk) may be deteriorated. Membrane emulsification is therefore a suitable alternative to other emulsification processes. It could then be associated to other common membrane operations such as bacteria removal and milk globular fat fractionation using cross-flow MF for the production of drinking milk and cheese milk [58].

1.3.5.3 Membrane Extraction in Biorefinery

The first generation of biofuels, biodiesel, was obtained from plant oil and bioethanol obtained from sugarcane or corn [59]. The second generation is not based on plant products of the food chain but on lignocellulosic biomass. These last 10 years, membrane processes have known an increasing use in biorefinery applications including pervaporation for alcohol recovery and UF of canola oil, as well as new developments such as the UF/NF of lignin in a solvent-based lignocellulose conversion process or the recovery of amino acids via ED. Membrane extraction has also been reported for detoxification of biomass hydrolysates and it can be foreseen that such techniques can be included in integrated membrane processes. A typical biochemical process for biomass conversion includes a thermochemical pretreatment step to improve enzymatic cellulose hydrolysis and to release hemicellulosic sugars from the polymer matrix. Compounds that are toxic to microorganisms in subsequent fermentation steps have to be eliminated and membrane extraction is a possible alternative. For example, Grzenia et al. [60] investigated the use of membrane extraction to detoxify or remove these toxic compounds from corn stover hydrolysates pretreated using dilute sulphuric acid. The organic octanol phase is pumped outside polypropylene hollow fibres while the aqueous hydrolysate is pumped inside the fibres. The organic phase/aqueous phase interface located at the inside surface of the fibres (as the fibres are hydrophobic) is stabilized by maintaining the pressure of the aqueous phase at a value equal to or greater than the organic phase pressure. The hollow fibre membrane immobilizes the organic phase/aqueous phase interface. Octanol and oleyl alcohol were used as organic phase solvents and Alamine 336 as the aliphatic amine extractant. Reactive extraction of sulphuric, acetic, formic and levulinic acid was observed while 5-hydroxymethylfurfural and furfural were extracted due to their distribution in the organic solvent.

1.4 Conclusion

In this chapter, several examples of hybrid membrane processes have been presented, mostly pressure-driven membrane processes in a cascade configuration or associated to other membrane techniques such as MD, MBR and membrane chromatography. A number of these hybrid processes are applied at industrial plants for applications such as reducing fouling of RO for desalination, elimination of contaminants in industrial or municipal wastewater and production of biomolecules with high purities from feeds in food or biotechnology industries. A number of other hybrid systems are expected to be used in industries such as membrane emulsification in the overall production of food, beverage, cosmetic and pharmaceutical preparations, or membrane extraction in biofuels production.

The feeds to be treated are complex and multicomponent suspensions; therefore, the optimization and prediction of these processes is a real challenge. However, very few articles report theoretical modelling with experimental validation. In the following chapters, several examples of hybrid membrane processes will be presented. This will provide a possible basis to better understand and optimize these techniques.

List of Abbreviations

AEM	Anion exchange membrane
ASP	Activated sludge process
BED	Bipolar electrodialysis
BMED	Bipolar membrane electrodialysis
CEM	Cation exchange membrane
ED	Electrodialysis
HPTFF	High performance tangential flow filtration
MBR	Membrane bioreactor
MCr	Membrane crystallization
MD	Membrane distillation
MF	Microfiltration
NF	Nanofiltration
OD	Osmotic distillation
RO	Reverse osmosis
SDI	Silt density index
SS	Suspended sulphur
TDS	Total dissolved solids
TOC	Total organic carbon
UF	Ultrafiltration

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